Chapter 7: Couplings Between Changes in the Climate System and Biogeochemistry

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Table of Contents

Executive Summary

Biogeochemical cycles interact with the climate system over a variety of temporal and spatial scales. Nonlinear interactions involving physical, chemical and biological processes within or between the different compartments of the Earth system could amplify (positive feedbacks) or attenuate (negative feedbacks) the disturbances produced by human activities. The response of the climate system to anthropogenic perturbations is therefore expected to be more complex and more chaotic than a simple cause-effect relationship; it involves reciprocal interactions with the land surface, the carbon cycle, reactive gases and aerosol particles.

The Land Surface and Climate

- Changes in temperature, moisture, and solar irradiance as well as atmospheric composition will affect the distribution and functioning of terrestrial ecosystems. The ecosystem response, in turn, will alter the momentum, energy, and water balance of the atmosphere, as well as the cycling of carbon, methane, dust and other atmospheric trace constituents.
- Changes in land vegetation, soils, and water cycle resulting from human activities can affect regional climate through shifts in cloudiness, surface temperatures, and radiation.
- Land use changes have contributed ~35% of the buildup of atmospheric CO_2 since preindustrial times – indicating that future scenarios and model projections must account for land use change.
- Many modelling studies demonstrate that changing land cover can have local and regional climate impacts that are comparable in magnitude with temperature and precipitation changes observed over the last several decades as reported in Chapter 3.
- New developments in dynamic vegetation schemes and coupled climate-carbon models have shown that the physiological forcing of stomatal closure can contribute 20% to the rainfall reduction in the Amazon associated with rising atmospheric CO_2 levels.

The Carbon Cycle and Climate

- The average increase in atmospheric CO_2, determined from the global CMDL network, was 1.88 ppm yr^{-1}, or 3.99 Pg-C yr^{-1} for 2000–2004.
- The land was a large source of CO_2 to the atmosphere in 1988 because of fires, and appeared to be a smaller sink for 1998–2003 because of the severe droughts.
- The airborne fraction of fossil fuel CO_2 appears to have increased in the last decade, and the partitioning of carbon sink between ocean and land appears to have shifted. However, it is premature to conclude if this is indicative of a long-term trend.
- New estimates, based on estimates of deforested areas from satellite images, yield a CO_2 source from land use modification of ~0.95+/–0.4 Pg-C yr^{-1} for the decade of the 1990's. The satellite-based estimate represents approximately 50% of the previous estimates based on FAO statistics. This reduction of tropical land source implies a concomitant reduction in the tropical land sink to balance the global carbon budget.
- Interannual variability (~2–4 years) in atmospheric CO_2 concentrations results primarily from changes in net land uptake, not ocean uptake (from inverse analyses).
- Inverse analyses of observations show ocean uptake of CO_2 greater in Northern than Southern extratropics, while the tropics are outgassing (0–1.5 Pg-C yr^{-1})
- There is a net terrestrial sink of CO_2 in the Northern Hemisphere, with NH fluxes better constrained than those in the tropics.
- Interannual variability in global terrestrial CO_2 uptake is greater than ocean uptake; variability in terrestrial uptake is greater in the tropics that in temperate or boreal regions.
- Increasing CO_2 concentrations in the ocean are lowering the pH (increasing the acidity) with expected but poorly known consequences for marine ecosystems and sediments.
- Decreasing surface ocean buffer capacity for CO_2, due to lowering pH and rising surface temperatures, reduces the rate at which the ocean can take up excess atmospheric CO_2.
- The recent model intercomparison project (C^4MIP) shows that, when the carbon cycle is coupled to a climate model, the atmospheric CO_2 buildup (scenario A2) is enhanced by ~20–180 ppm in year 2100 and temperature by 0–1.5°C relative to model predictions for which this coupling is ignored. Even

though all models exhibit a positive carbon-climate feedback, the magnitude of this feedback varies considerably between models.

- Differences in ocean uptake between models are due to differences in the removal rate of CO_2 from the surface ocean to greater depths due both to physical and biogeochemical processes.
- Uncertainties in terrestrial uptake and release of CO_2 are due to the magnitude of the fertilization effect, the land use legacy, limits on the growth and size of the terrestrial biosphere, and the turnover time of soil carbon.
- Terrestrial carbon storage depends on both temperature and moisture. Changes in temperature and moisture tend to co-vary, albeit with signs and magnitudes that depend on region and time scale.
- Overall, climate change will increase the fraction of anthropogenic CO_2 that remains in the atmosphere. Increasing CO_2 will increase the uptake by both the land and the ocean; climate change will cause reduced uptake by both the land and the ocean.

Reactive Gases and Climate

- The atmospheric burden of methane has not increased significantly during the period 2000–2005. Emissions of methane from energy use and from northern wetlands appear to have decreased, while emissions from lower latitudes have probably been increasing. This offset may explain the temporary slow down of the methane growth rate.
- Climate change could affect substantially the sources of methane, particularly those associated with wetlands and rice agriculture. Emissions are expected to increase in warmer and wetter climate and to decrease in warmer and dryer climate. The growing use of hydrogen-based energy should not affect stratospheric temperature and ozone in a substantial way. However, the use of hydrogen-powered vehicles should lead to a significant decrease in NOx emissions, and therefore in the concentration of tropospheric ozone and OH in urban areas.
- New model estimates of the global tropospheric ozone budget suggest that the transport of ozone from the stratosphere (approximately 500 Tg yr^{-1}) is smaller than estimated in the TAR (770 Tg yr^{-1}), while the photochemical production and destruction rates (5000 and 4500 Tg yr^{-1}, respectively) are higher than estimated by TAR (approx. 3000 and 3500 Tg yr^{-1}).
- Climate change affects air quality by modifying the dispersion rate of pollutants, the chemical environment for ozone and aerosol generation, and the strength of emissions from the biosphere, fires, and dust. Although the sign and magnitude of these effects are highly uncertain. and may vary greatly depending on region, there is the potential for significant air quality degradation.
- Long-term trends in the tropospheric concentration of OH, and hence in the oxidizing capacity of the atmosphere are determined by changes in the concentrations of methane, carbon monoxide and nitrogen oxides, and potentially by climate change. There are still large uncertainties in the model estimates and in the observation-derived values of the trends and inter-annual variability of the mean OH concentration. These changes have an important impact on the variability of the methane growth rate.
- Model calculations suggest that the effect on the OH burden of increasing concentrations of methane and carbon monoxide together with climate warming (which produces an increase in the methane oxidation rate) could be partly offset by increasing concentrations of NOx and water, so that future methane lifetime should remain relatively unchanged during the next decades.
- Model calculations suggest that past ozone depletion has induced surface cooling, which approximately balanced the greenhouse warming produced by increasing atmospheric abundances of ozone depleting substances and their substitutes.
- Since the pre-industrial era (circa 1750), the positive radiative forcing estimated from changes in tropospheric ozone has been larger than the negative forcing resulting from stratospheric ozone depletion. However, over the 1970–2000 period, these two forcings were of approximately equal importance, but opposite in sign.
- The changes in the stratospheric climate associated with the projected increase in the concentration of greenhouse gases could affect the recovery of polar ozone resulting from the phase-out of chlorofluorocarbons. This climate feedback should be more prominent in the Arctic than in the Antarctic.

Aerosol Particles and Climate

- An increasing aerosol load due to human activities decreases regional air quality and the amount of solar radiation reaching the earth's surface ("solar dimming"). In some areas such as eastern Europe, the "solar dimming" trend has been reversed since the collapse of the East Bloc.
- Increased light absorbing aerosol particles aloft, e.g., black carbon, lead to increasing atmospheric stability and a reduction in cloud amount, especially in polluted regions of the Northern Hemisphere.
- Increases in aerosol particles/clouds from human activities are causing a reduced daily range in surface temperature, with some evidence of a "weekend" effect due to differences in human activities on weekends and during the work week.
- Models suggest that global mean evaporation and precipitation have decreased in response to the increased aerosol load between pre-industrial times and the present, but projections indicate that both may increase with climate change over the next century.
- The magnitude of the overall indirect aerosol effect on clouds remains uncertain, because it comprises interactions with the climate system and feeds back on cloud and large-scale dynamics and the hydrological cycle.

7.1 Introduction

The Earth system is complex. Nonlinear interactions involving physical, chemical and biological processes (Figure 7.1.1) occur either within specific compartments of the Earth system (atmosphere, ocean, land) or between them. Feedbacks can either be negative or positive. Negative feedbacks damp forcing applied to the system; in this case, they provide a stabilizing mechanism and tend to keep the Earth system close to its present equilibrium state. Positive feedbacks amplify applied perturbations, and potentially produce transitions towards a new equilibrium state. Thus, in the presence of positive feedbacks, minute actions could trigger abrupt, sometimes large and perhaps unmanageable changes in the Earth system.

[INSERT FIGURE 7.1.1 HERE]

An important aspect of climate research is to identify potential feedbacks, and determine if these tend to stabilize or destabilize the current climate system. In particular, it is important to assess if such feedbacks could produce large and undesired responses to perturbations applied as a result of human activities. Studies of past climate evolution on different timescales (including paleo-periods) can shed some light on the mechanisms that could trigger nonlinear responses to external forcing. The purpose of this chapter is to investigate some of the feedbacks of potential importance for the Earth system. Specifically, it will examine how terrestrial ecosystems, the carbon cycle, reactive gases and aerosol particles could affect the climate system. Large uncertainties remain in many issues discussed in this chapter, so that quantitative estimates of the importance of the coupling mechanisms discussed in the following sections are not always available. In addition, the regional disparity in the role of some cycles and the complex interactions between them limits our ability at present to provide a simple quantitative description of the interactions between biogeochemical processes and climate change.

7.1.1 Terrestrial Ecosystems and the Climate System

Far from being a passive recipient of changes in a coupled ocean-atmosphere system, the terrestrial biosphere interacts strongly with the climate, providing both positive and negative feedbacks due to biogeophysical and biogeochemical processes. Some of these feedbacks, at least on a regional basis, can be of the same order of magnitude as greenhouse gas forcing.

7.1.4. Biogeophysical feedbacks

Changes in the structure or functioning of terrestrial ecosystems can feed back to climate via changes in evapotranspiration, albedo or roughness (which affects momentum transfer between the surface and the atmosphere). The evapotranspiration feedback is well-known. For example, half or more of the precipitation that falls on the Amazon Basin is recycled back to the atmosphere via evapotranspiration, affecting the climate both through cloud formation and through the partitioning of sensible and latent heat at the land surface; and the growing season is characterized by a small diurnal temperature range (Schwartz and Karl, 1990; Collatz et al., 2000; Durre and Wallace, 2001; Bonfils et al., 2004, 2005). Thus, changing the nature of terrestrial ecosystems through land-use change could feed back strongly on climate. Betts (2001) has estimated that past deforestation has led to decreases in near surface air temperature of up to 1^{o}C over large areas of central North America and central Eurasia. This is about the same magnitude as the observed increase in surface temperature over the last century.

Terrestrial ecosystems are also coupled to climate via albedo feedbacks. The classic example is the so-called taiga (boreal forest) - tundra feedback system. The albedo of snow-covered vegetation is much lower for boreal forest than for tundra, as the snow lies underneath the dark canopy of the forest but over the top of the much lower tundra vegetation. The measured winter albedo differs sharply for the two vegetation types - about 0.75 for snow-covered tundra and 0.2 to 0.4 for boreal forest. The darker forest therefore absorbs more radiation than the bright, snow-covered tundra, warming the soil under the forest, which in turns favours the growth and expansion of the forest. This gives rise to the positive feedback effect. The taiga-tundra feedback effect has been shown to be important in the functioning of the Earth System in the past. The early to mid-Holocene climate in the northern high latitudes cannot be simulated correctly by considering orbital forcing and ocean-atmosphere dynamics only; the taiga-tundra feedback must be included (Berger, 2001).

7.1.4.2 Biogeochemical feedbacks

These operate primarily through the carbon cycle, and there is a range of processes in terrestrial ecosystems that influence the flux of carbon between land and the atmosphere. Although there are many carbon compounds (e.g., CH_4, VOCs) that terrestrial ecosystems exchange with the atmosphere, this brief summary will focus on processes that control the exchange of CO_2:

The CO_2 fertilization effect. As atmospheric CO_2 concentration increases, photosynthetic rates of plants also increase. In general, this leads to higher carbon uptake by terrestrial vegetation but the relationship is nonlinear and is modified by several important interactions - with the hydrological and nutrient cycles, for example. The interreaction with the hydrological cycle is especially important through increases in water use efficiency due to increasing atmospheric CO_2 concentration, which further stimulates growth and uptake of carbon from the atmosphere. Also, different types of plants (e.g., those with C3 and C4 photosynthetic pathways) have intrinsically different responses to changing atmospheric CO_2 concentration. The CO_2 fertilisation effect is a negative feedback on increasing atmospheric CO_2 concentration and thus on a warming climate.

Nutrient mineralisation. Increasing temperature and changing moisture regimes have impacts on the mineralisation of nutrients in the soil, most notably on nitrogen compounds. This has the effect of releasing plant-available nitrogen compounds which act as a stimulant to growth, thus increasing the uptake by vegetation of carbon from the atmosphere. This is also a negative feedback on climate.

Heterotrophic respiration. Organic carbon compounds in the soil, originally derived from plant material, are slowly oxidised by bacteria and returned to the atmosphere as CO_2. A variety of organic compounds are respired at different rates depending on the nature of the compound and on the communities of mycorrhizal fungi (Treseder et al., 2003). Both temperature and soil moisture can significantly affect rates of heterotrophic respiration, which generally increases with increasing soil temperature. Differences in the magnitude of this rate increase (or the lag between photosynthesis and respiration) were largely responsible for the spread in results of coupled carbon cycle-climate models, and the temperature-heterotrophic respiration relationship is an active area of research in terrestrial ecology. Changes in heterotrophic respiration with climate constitute a positive feedback.

Biome shifts. A shift of ecosystem structure can affect climate by changing the partitioning of carbon between the atmosphere and the land surface. These feedbacks can be either positive or negative, depending on the nature of the shift. For example, migration of boreal forest northward into tundra would initially lead to an increase in carbon storage in the ecosystem due to the larger biomass of trees than of herbs and shrubs. This would be a negative feedback. In the longer time frame (e.g., centuries), the changes in soil carbon would need to be considered to determine the overall effect. A shift in tropical rainforest to savanna, on the other hand (as simulated in the Cox et al., 2000 study), would result in a net flux of carbon from the land surface to the atmosphere and thus would be a positive feedback.

Disturbances. Fire is probably the most important disturbance in terms of the carbon cycle. Fire is a natural component of the dynamics of several biomes - for example, boreal forests and savannas. If averaged over a long period of time with no underlying change in frequency or extent, fires are neutral in terms of the carbon cycle; carbon lost to the atmosphere rapidly during a fire is regained slowly during the subsequent regrowth. However, if fires become more frequent or cover larger areas of land, such as appears to be happening in the Canadian boreal forests over the last several decades, such fire-affected biomes could become net sources of carbon to the atmosphere during the fire regime shift. This would be a positive feedback to climate, given that a warming climate increases the probability of fires.

Details on feedbacks between climate and the land surface are provided in Section 7.2.

7.1.2. The Carbon Cycle and the Climate System

During the last decade, the scientific community has realized that interactions between biogeochemical processes and the physical climate system could generate additional feedback processes, and hence affect the future evolution of the Earth's climate. An important example is provided by the climate carbon interactions. In the past, models treated the changes in the atmospheric CO_2 concentration as an external forcing factor,

and derived the corresponding response of temperature. Recently, however, it was recognized that the level of atmospheric CO_2, which increases with the intensity of fossil fuel emissions, also depends on the rate of carbon uptake by the ocean and by the land, and that these uptake fluxes are themselves dependent on the atmospheric CO_2 level and on climate.

The dynamics of carbon cycle-climate interactions through this century have been simulated using coupled global carbon-climate models (Friedlingstein et al., submitted). These models suggest that the overall effect of carbon cycle-climate interaction is a positive feedback; by 2100 the atmospheric CO_2 concentration is higher and the climate is consequently warmer in all coupled model runs than for the uncoupled runs. Differences in the magnitudes of the feedbacks among the models, which remain substantial, are due to different underlying sensitivity associated with the representation of both climate and carbon cycle processes in the models. More details on this issue are provided in Section 7.3.

7.1.3. Reactive Gases and the Climate System

Interactions between climate and atmospheric oxidants, including ozone, provide other important coupling mechanisms in the Earth system. The concentration of ozone has increased substantially in the troposphere since the pre-industrial era, and has contributed to radiative forcing, especially in polluted areas of the world. Below the tropopause, ozone is produced by photo-oxidation of carbon monoxide (CO), methane (CH_4) and nonmethane hydrocarbons in the presence of sufficiently high levels of nitrogen oxides (NO_x). The emissions of ozone precursors have increased as a result of larger use of fossil fuel, more frequent biomass burning and more intense agricultural practices. The level of pre-industrial ozone is not accurately known, so that the resulting radiative forcing cannot be accurately determined, and must rely on model estimates.

What are even less well quantified are the changes in the atmospheric composition that could result from climate changes, and could involve different processes. The photochemical production of the hydroxyl (OH) radical, which occurs in the presence of ozone and water vapour, should be enhanced in a wetter atmosphere. Since OH destroys ozone, this climate chemistry feedback should be negative, and should limit the future increase in tropospheric ozone that will result from enhanced anthropogenic emissions of the precursors. At the same time, the atmospheric concentration of methane, a greenhouse gas whose main loss is due to the reaction with OH, should also be reduced, so that here again, the feedback is negative.

Other chemistry-related processes could provide an amplification of the initial effect. For example, if the frequency of lightning flashes increases in response of climate warming, the nitrogen oxides released by thunderstorms would lead to additional ozone production, and hence to enhanced greenhouse warming. The effect on ozone of a simultaneous increase in NO_x and water vapor is complex because hydroxyl radicals produced by water modify the partitioning between nitrogen compounds. The scavenging mechanisms affecting several chemical species will also be modified in response to climate-driven perturbations in the hydrological cycle. Changes in the natural emissions of chemical compounds (e.g., biogenic hydrocarbons by the vegetation, nitrous and nitric oxide by soils, ocean exchanges of chemical compounds) in response to climate change provide the potential for additional feedback mechanisms. The importance of these effects is not yet well quantified. Several of them depend on the expected evolution in the land vegetation as climate evolves. These issues are further discussed in Section 7.4.

Finally, the recovery of stratospheric ozone in the future decades could also be affected by future climate changes. Significant amounts of ozone are destroyed by chlorine compounds, which are released in the stratosphere by industrially manufactured chlorofluorocarbons. In particular, the chemical destruction of ozone at high latitudes requires the presence of polar stratospheric cloud (PSC) particles, on which chlorine is activated by heterogeneous chemical processes. The formation of these clouds is a strong function of temperature and of the water vapour concentration. A cooling of the lower polar stratosphere, caused by enhanced radiative cooling by CO_2, could facilitate the formation of PSCs, produce more ozone destruction, and delay the ozone recovery. If this process is accompanied by an intensification of the Brewer-Dobson meridional circulation, a warming of the polar region could occur, with a reduction in the chemical ozone destruction, and probably an acceleration of the ozone recovery. This question is also discussed in Section 7.4.

7.1.4 Aerosol Particles and the Climate System

The presence of tiny sulphate aerosol (SO_4) particles in the atmosphere tends to cool the Earth's surface by scattering some of the incoming solar radiation back to space. In addition, by acting as condensation nuclei (CCN), these particles tend to modify the radiative properties of the clouds (Twomey effect) or their lifetime (Albrecht effect), which contribute to additional surface cooling. As the major natural source of sulphate is provided by dimethyl sulphate (DMS), an organic compound whose production in the ocean and release to the atmosphere depends on climatic factors, and specifically on the temperature of the upper ocean, Charlson et al. (1987) suggested that the sulphur cycle could generate a feedback loop whose sign and amplitude remain uncertain. In many areas of the Earth, however, the importance of this potential feedback loop has been considerably reduced by the presence of large amounts of SO_4 particles produced as a result of human activities (e.g., coal burning). With an elevated atmospheric aerosol load, principally in the Northern hemisphere, it is likely that the temperature increase during the last decade has been smaller than the increase that would have resulted from the climate forcing by greenhouse gases alone. Other indirect effects of aerosols on climate have been suggested, including the evaporation of cloud particles through absorption of solar radiation by soot, which in this case, provides a positive warming effect. These questions are discussed in Section 7.5.

Aerosols deriving from human activity are also delivering more nitrogen and iron to the surface ocean (e.g., Tegen et al., 2004). These nutrients are 'new' to the ocean (Meshkhidze et al., 2003), therefore having the potential to increase the export of biogenic carbon to the ocean interior, and they also have the potential to act as ballast, also increasing the sinking of biogenic carbon to the ocean interior (e.g., Klaas and Archer, 2002). Both effects represent a negative feedback to atmospheric CO_2 concentrations.

7.2 The Changing Land Surface and Climate

7.2.1 Introduction to Land Climate Response from Human Activities

Land surface as a dynamical component of the climate system (illustrated in Figure 7.2.1) responds to inputs from the atmosphere, including radiation, precipitation, and other meteorological variables of the overlying boundary layer. How it responds to these inputs is controlled by its structure, i.e., all the details of its governing processes. Its structure may involve how it exchanges moisture and heat with the atmosphere or what is its vegetation state and how that is determined by slow biological processes. There is a large variety in the processes included in land models and in the concepts that are used to express them mathematically. Furthermore, this structure is modified by both climate change and land use change. Thus, the outputs from a land model depend on a wide variety of factors and so are not easily evaluated in terms of their reality.

[INSERT FIGURE 7.2.1 HERE]

Humans influence the physical land climate through modifications of atmospheric greenhouse gas and aerosol concentrations and by land use change. The consequent changes in land climate over long time scales can modify the land cover state with similar consequences as anthropogenic land use change. The natural and anthropogenic land cover changes also affect the exchange of carbon between the land and the atmosphere. Changes in the physical land climate can also modify land-atmosphere carbon exchanges. What is most important depends on the question being addressed: e.g., what is the a) change of surface land climate in response to changing global radiative balances from greenhouse gases; b) feedbacks between land and atmospheric variability; c) bias in simulation of current climate; d) responses of surface land climate to changing land use? Although a) may be the primary focus of AR4, all these questions have been addressed in recent literature and collectively are important for determining the interactions between land climate changes and human activities.

7.2.2 How Does Land Surface Mediate Climate Change?

7.2.2.1 Why does land have a larger effect on regional than global climate?

On a global spatial scale and longer time scales, climate change is largely controlled by processes of global radiation balance. Land is only about 30% of the globe, and its ability alone to affect global radiation balance is largely through its ice and snow cover, and the shading of the latter by vegetation. Processes such as desertification that make the surface reflect more radiation (i.e., increase its albedo) generally occur over

relatively small areas and are judged to collectively have a relatively small effect. However, on a regional scale and at the surface, many additional more localized and shorter time scale processes can affect climate in other ways, and possibly be of comparable or greater importance. Variability in tropical ocean temperatures, e.g., connected to ENSO, determines major changes in the patterns of precipitation and drought over continents

Shifts in cloudiness can occur and atmospheric circulation systems can redistribute energy to maintain overall balances. Because low clouds are normally closely coupled to the surface, those over land can be significantly changed by changes of land properties. Land has a strong control on the vertical distribution of atmospheric heating, through its Bowen ratio and radiative exchanges (e.g., Betts, 2004). The Bowen ratio determines how much of the radiation delivered to land goes into the near surface boundary layer versus how much is delivered as latent heat at higher levels. Land is more sensitive to changes in its energy balance under cold stable conditions than under warm unstable ones because of the dependence on stability of surface exchange coefficients. Consequently, a change in the diurnal amplitude of surface radiative heating can have a substantial impact on night-time and hence average temperatures. If applied locally, compensating effects may be expected elsewhere. Effects that modify local or regional temperatures may also influence distributions of precipitation, but this possibility is difficult to assess because of model differences and an inadequacy of quantitative studies.

Changes over land that modify the Bowen ratio can cause large changes of surface temperature, both locally and regionally. These changes will produce adjustments elsewhere to maintain global energy balance. Attempts have been made to find such remote adjustments (Avissar and Werth, 2005). Such adjustments occur in multiple ways, and are part of the dynamics of climate models. For example, the locally warmer temperatures can lead to more rapid vertical decreases of atmospheric temperature so that at some level overlying temperature is lower and radiates less. The net effect of such compensations is that averages over larger areas will give much smaller estimates of change.

Thus such regional changes are better described by local and regional metrics or on larger scales by measures of change in spatial and temporal variability rather than simply in terms of a mean global quantity. The large amount of such details involved is best addressed by assessments at a local and regional scale. However, the IPCC with its global perspective should provide overall guidance regarding these issues and how well they can currently be quantified and how they couple to global climate change.

7.2.2.2 What has been learned regarding forcing terms important for land climate?

Local precipitation intensities are increasingly considered in some ways to be as important as precipitation amounts. However, it is difficult for climate models to quantify such intensities. A related dimension is the amplitude and phase of the diurnal cycle in precipitation, which is simulated by climate models but apparently not yet very well (e.g., Collier and Bowman, 2004). Betts (2004) reviews how the diurnal cycle of tropical continental precipitation is linked to land surface fluxes and argues that errors in a model can feed back on model dynamics with global impacts.

7.2.2.3 How is land structure characterized?

Because of its complexity, there are no uniformly accepted approaches to including land structure in a climate model. It has been treated with a wide variety of approaches. Table 7.2.1 shows a possible breakdown into various structural components and an assessment of their relative importance and understanding from the viewpoint of inclusion in a climate model. This is derived from consideration of the literature since TAR (reviewed here) as well as earlier work.

Simulation of annual runoff is reported by Milly and Shmakin (2002a) to be primarily sensitive to values assumed for aerodynamic roughness and the leaf stomatal resistance. They identified a major bias in regions of seasonal dryness that they attributed to their lack of accounting for two-way coupling between their root-zone and deeper aquifer water storage. They found a dry bias in modelled evapotranspiration, which they attributed to several factors but in particular, their neglect of leaf water evaporation. Milly and Shmakin (2002b) found, as might be expected, a substantial improvement in their modelled runoff from use of a vegetation type-based stomatal conductance varying geographically rather than a global value. Some features such as treatment of leaf water evaporation may have little effect on the determination of monthly evapotranspiration (e.g., as found in the analysis of Desborough, 1999) but still produce important changes

of temperature and precipitation. Much of the model structure is intended to address short time scale and diurnal variability and its potential coupling to the atmosphere. For example, Wang and Eltahir (2000) compare model results (their Figure 1) for realistic versus uniform precipitation intensities. Both cases have about the same evapotranspiration, but evidently, for the latter case, the feedback on precipitation is so strong that their runoff drops from 700 mm y^{-1} to nearly zero. Other recent studies such as reviewed here also suggest that identical scenarios for global warming or land-use change introduced into models with different structures may give significantly different outputs of land climate. On the other hand, Pitman et al. (2005) in a coupled study with land configurations of different complexity and forced by AMIPII SST's were unable to find any impacts on atmospheric variability.

Table 7.2.1. Preliminary assessment of structural factors important for the land response to global climate change and land use change. Current literature addressing these questions is fragmented and conclusions are likely to be dependent on both land and atmospheric models used.

Structural Factor	How Important?	Certainty of its Modelling
Roughness	***	***
Bowen ratio (depends on collective effect of several other structural factors)	***	**
Soil moisture Profile	**	**
Root representation	*?	*
Complex micrometeorology	x??	x
albedo	**	**
Canopy/stomatal conductance	*?	*
Partitioning of radiation	*?	*

Notes:
*** = high
** = moderate
* = low
x = very low
? = not enough evidence but could add another *

Much of the current literature addressing the issue of the appropriate structure to use for land processes in climate models has been asking what is the impact of additions to or observational improvements of vegetation complexity. When this additional complexity incorporates general knowledge or new observational constraints, it might be thought of as an improvement to a model. Whether it is useful enough to be adopted by others then depends on the answer to the question "what difference does it make?" There has been a considerable body of literature reporting on the consequences for various climate models of improvements in their land models of their descriptions of leaf cover and descriptions of types of vegetation cover. Henderson-Sellers (2003) in comparing the surface fluxes among 19 models submitted to the AMIPII intercomparison, reports for controlled conditions, over an order of magnitude difference between sensible fluxes of different models. However, more recently developed models cluster much more tightly.

Many modelling studies have been able to demonstrate that changing land cover can have local and regional climate impacts that are comparable in magnitude to temperature and precipitation changes observed over the last several decades as reported in Chapter 3. Current literature demonstrates large disparities in conclusions. For example, Snyder et al., (2004) show that removal of temperate forests can give a summer (JJA) warming of 1.3°C and a reduction in precipitation of –1.5 mm day^{-1}. Oleson et al., (2004) on the other hand, conclude that removal of temperate forests in the US would cool JJA by 0.4 to 1.5°C and probably increase precipitation depending on details of the model and prescription of vegetation.

The discrepancy between these two studies published in the same edition of the same journal, may in this case be largely an artifact of visibly different assumptions as to the endpoint model structure. The first study assumes conversion of forest to desert and the second to crops. However, the large number of such studies that demonstrate a potentially important impact of human activities on climate through land use modification suggest that IPCC should incorporate in its assessments of regional climate change the possible contributions of land use and land cover change.

7.2.3 What Has Been Learned About Land Model Structures Since the TAR?

7.2.3.1 Properties affecting radiation

Albedo and emissivity have long been recognized as a land contribution to radiative balance.
Surfaces that have more or taller vegetation are commonly darker than those with short or sparse vegetation. With sparse vegetation, the net surface albedo also depends on albedo of the underlying surfaces, especially if a light soil or snow. For models that separately balance canopy and surface energy budgets, the partitioning of radiative fluxes between these components also becomes important.

New satellite data show the importance of radiation heterogeneities on the plot scale for the determination of albedo and PAR, and appropriate modelling concepts are being advanced (e.g., Yang and Friedl (2003) and Niu and Yang, 2004; Pinty et al., 2005). The inclusion of reasonably accurate values of emissivity in models has been addressed by Zhou et al. (2003a,b) and Ogawa and Schmugge (2004).

7.2.3.2 Properties affecting Bowen ratio

Soil moisture control of the partitioning of that energy between sensible and latent flux has been demonstrated to be very important for local and regional temperatures, and their coupling to precipitation. Oglesby et al. (2002) carried out an initially dry soil anomaly study where the dryness of the soil over the US Great Plains for at least the first several summer months of their integration produces a warming of about 10–20°C. The simulated mass flux from moist convection has been demonstrated important for surface fluxes. In particular Williamson et al. (2005), using data from the ARM study site, have shown that flaws in model parameterizations of convection can cause perturbations in evapotranspiration that lower temperatures by more than 1°C from excessive evapotranspiration.

How can vegetation modify the Bowen ratio? The most important factors for Bowen ratio (e.g., Table 7.2.1) are surface roughness, leaf area, and availability of water from the soil for use of vegetation. The height of the vegetation is the most important determinant of surface roughness that determines the production of mechanical turbulence. Whether water has been intercepted on the surface of the leaves or its loss is only from the leaf interior as controlled by stomates makes a large difference. Vegetation that is shorter and with more leaves has the most latent flux and the least sensible flux. A replacement of forests with shorter vegetation together with the normally assumed higher albedo should then cool the surface. However, if the replacement vegetation has much less foliage or cannot access soil water as successfully, a warming may occur. Thus deforestation can modify surface temperatures by up to several degrees in either direction depending on the details of what type of vegetation replaces the forest and the climate regime assumed. Drier air can act to increase evapotranspiration but leaves may have negative feedbacks through their conductance to reduce this effect. In absence of leaves, forests in early spring appear as especially dry surfaces with consequent large sensible fluxes and high boundary layer (e.g., Betts et al., 2001)

Representation of leaf phenology in models has advanced from specified constant leaf cover or simple phenology rules to prescribed leaf cover (e.g., van den Hurk et al., 2003; Buermann et al., 2001) that is constrained by observational estimates (e.g., Tian et al., 2004a-c) and to prognostic approaches that estimate leaf cover on the basis of physiological processes (e.g., Arora and Boer, 2005a). Arora (2005) gives a brief overview of the issues in modelling stomatal conductance for climate simulations. Levis and Bonan (2004) discuss how in middle latitude forests the springtime leaf emergence when it is interactively modelled provides a negative feedback on the rapid increases of temperature by their increased transpiration.

Addressing the dynamics of leaf carbon uptake as coupled to evapotranspiration may require consideration of the controls by nitrogen and the nutrient cycling (e.g., Dickinson et al., 2002). The difference in temperature of leaves in sun or shade has a significant effect on canopy transpiration (Dai et al., 2004). Dynamic vegetation models have advanced and explicitly simulate competition between plant functional types (PFTs) (Sitch et al., 2003; Bonan et al., 2002a, b, 2003), e.g., Arora and Boer (2005b) suggest a generalized form of competition-colonization equations that permit equilibrium coexistence of different PFTs .

Surface fluxes interact with the boundary layer and lead to various additional model feedbacks (depending on details of other modelling components) involving changes of humidity, boundary-layer heights, cloud-

fraction and precipitation, e.g., Ek and Holtslag (2004) discuss conditions under which reduced evapotranspiration can increase boundary layer cloudiness.

7.2.3.3 Detailed vertical layering

The importance of simulating resolved vertical profiles of soil moisture and temperature (Rosnay, 2003; Dai, 2003) and hydrological effects of horizontal heterogeneity of topography (Koster et al., 2000) has been emphasized in recent work. The parameterization of water uptake by roots contributes to the computed soil water profile (Feddes et al., 2001; Barlage and Zeng, 2004), and efforts are being made to make the roots interactive, e.g. Arora and Boer (2003). Wu and Dickinson (2004), and Wu et al. (2002a, b) characterize the coupling of layered soil water to ET and climate variability. Models have also moved from single slab to multilayer snow models (Stieglitz et al., 2001; Dai et al., 2003).

7.2.3.4 Recognizing spatial complexities

Various heterogeneities of snow distributions have been shown to be important for determining the melting of snow and other aspects of surface energy balances, but these are not yet considered in global climate models. Approaches to use of a subgrid distribution of snow properties have been addressed by Roesch et al. (2001) and Liston (2004); and snow depth modelling by Strack et al. (2004). Sturm et al. (2001) describe how Arctic shrubs promote snow depth and how warming would increase snow depths.

Energy exchanges between surface and canopy are important for overall surface temperature determination (e.g., Dickinson et al., 2005; Zeng et al., 2005) and its remote sensing (Friedl, 2001). Modelling of turbulence of complex canopies has been advancing in directions that can provide improved formulations (e.g., Katul et al., 2004; Poggi et al., 2004).

7.2.3.5 Can increased complexity make any difference?

Many details such as described above may be nearly invisible in comparisons with the more standard meteorological measurements. Thus they may be of little interest for models whose only metric is a matching to such measurements. In some cases, they may be simply a response to speculation that such further details will turn out in some way to be beneficial to a model. However, they are mostly driven by important modelling questions that cannot be answered without inclusion of such complexity or by the data and important questions of other communities at smaller spatial scales. For example, there is considerable literature advancing the hypothesis that the presence of vegetation will provide a positive feedback on the melting of snow through its lower albedo. This hypothesis has been supported by models that assumed that energy absorbed by the vegetation would be delivered to the snow. This is not obvious and its demonstration by a climate model requires the inclusion of more complex micrometeorology and radiative transfer than implemented in current models.

Greater complexity in hydrological structures of climate models is commonly suggested by advances in understanding of surface hydrology and of plot level soil and vegetation descriptions by ecological measurements. For example, the need for detailed layering in snow was discovered by soil temperature and respiration measurements made in the BOREAS field program. The previous single slab snow models generated soil temperatures tens of degrees too cold, although this error had little direct effect on surface air temperatures. Climate models are expected by various communities to provide relevant information for other parts of the system than simply the atmosphere, which can only be achieved if the models include adequate complexity to describe the processes of interest.

It is always possible that improvements expected from adding structure to land models may be masked by remaining errors common to several or all models in their atmospheric simulations. Gutowski et al. (2003) analyze such a dry bias common to several models in looking at precipitation in the South Central US.

7.2.4 How Can We Quantitatively Relate Land Climate Changes to Atmospheric Inputs and Structural Change?

7.2.4.1 Assessing quantitative sensitivity is complicated

Temperature change on a global scale is largely related to changes of global radiative forcing at the top of the atmosphere. However, changes of near surface temperatures on regional or smaller scales may be locally of equal significance and occur for reasons other than global radiative forcing. Structural changes from land

use change or changes in precipitation or in radiative exchanges between surface and atmosphere may drive important land climate change without any connection to global radiative forcing.

Such changes, however, are more poorly understood than those forced by global radiation. Sensitivity should be considered as a multivariate issue. It includes the question as to how near-surface temperature (which more directly affects human activities) can change independently of the "global temperature" and how "wetness" can change. A difference between atmosphere and surface temperature can result from a thermal-radiative decoupling (e.g., Betts et al., 2004).

"Wetness" describes the strong Bowen ratio controls on surface fluxes. The presence of vegetation complicates the concept of surface wetness in ways not yet accounted for in all global models. Wetness in the presence of vegetation involves water stores on leaves, in shallow soil and in deep soil. The latter has received most attention in discussion of evapotranspiration. It represents the bulk of the water stored and imposes the longest time scale. However, it is the rapidity of evaporation of the near surface stores that allows them to be of comparable importance for surface water and energy balances. (Dickinson et al, 2003 discuss the significance of these disparate timescales.) On longer time scales, evaporation from the fast reservoirs acts primarily as a surface energy removal mechanism, and from the water viewpoint, largely to cancel some of the incident precipitation. Another complication, currently not included very well in climate models, is that over some fraction of moist soils, water tables can be high enough to be hydrologically connected to the rooting zone, or even to the near surface store as in wetlands (e.g., Koster et al. (2000), Marani et al., 2001; Milly and Shmakin, 2002a; Liang et al., 2003; Gedney and Cox, 2003).

The study by Scanlon et al. (2005) provides a nice example of how the dynamics of wetness, expressed as soil moisture, can depend on vegetation. She monitored soil moisture in the Nevada desert with lysimeters either including or excluding vegetation and for a multiyear period that included times of anomalously strong precipitation. Without vegetation, much of the moisture penetrated deeply, had a long lifetime and became available for recharge of deep groundwater, whereas for the vegetated plot, the soil moisture was all extracted by the plants for transpiration.

Climate model simulations of the climate change deriving from greenhouse gases include significant feedbacks between the land surface and atmospheric precipitation. Some observational evidence for such feedback has been noted by D'Odorico and Porporato (2004) in support of a low-dimensional model of such feedbacks. Analysis of such feedbacks in full climate models is difficult: only recently have efforts been initiated to examine this issue (Koster et al., 2004). Unfortunately, the initial conclusion is that from a statistical viewpoint, this feedback is poorly constrained, with some models having strong coupling from soil moisture back to precipitation, and some almost none. Such a coupling may be an important component of the description of regional climate change resulting from global warming or land use change, and it determines the potential predictability of precipitation from modelling of soil moisture.

7.2.4.2 Mechanisms for forcing the diurnal temperature cycle

The diurnal cycle of temperature over land is maintained by daytime solar heating and nighttime radiative cooling. Daytime warm season heating produces a thick convective boundary layer with substantial heat capacity which is consequently insensitive to perturbations in the amplitude of the diurnal radiative forcing. Thus, daytime warm season temperatures are most readily changed by changing the Bowen ratio. Such changes may occur from changes of land structure such as vegetation cover, e.g., Bonan (2001), or by changes in precipitation. Nighttime and high latitude winter surface temperatures, on the other hand, are most readily altered by changes in atmospheric downward thermal radiation.

Qian and Giorgi (2000) discussed how the rapid growth of SO_2 emission in China since 1979 should be producing regional aerosol effects, and noted a reduction of the day-night temperature range of –0.26°C/decade over Sichuan. For reasons mentioned above this is difficult to attribute directly to reduction of solar heating. Bonan (2001) and Oleson et al. (2004) indicate that conversion of forests to agriculture could give such a daytime cooling. However, changes of land use of the magnitude required to give such a result seem unlikely. Huang et al. (2005) have modelled the growth of sulphate aerosols and their interactions with clouds in the context of a regional climate model, and find over Southern China a decrease in the day-night temperature range that is comparable with that observed by Zhou et al.(2004) and Qian and

Giorgi. The analysis of Huang et al. shows the nighttime temperature to be a result of increased nighttime cloudiness connected to the increase of aerosols.

7.2.4.3 Mechanisms for forcing climate change from spatial heterogeneity

Clark et al. (2004) show an example of a squall-line simulation where variation of soil-moisture on the scale of the convection substantially modifies the rainfall pattern. Pielke (2001), Weaver et al. (2002), and Roy et al. (2003) have also addressed various aspects of convective scale precipitation coupling to land surface heterogeneity. If deforestation occurs in patches rather than uniformly, the consequences for precipitation could be quite different. Avissar et al. (2002) suggest that there may be an increase in precipitation resulting from partial deforestation as a consequence of the mesoscale circulations triggered by the deforestation, as in Silva Dias et al. (2002b). Such studies have indicated mechanisms by which small scale inhomogeneities may modify precipitation. However, characterizations of how land has changed globally to force such modifications are not yet available.

7.2.4.4 Sensitivity to vegetation change

Maynard and Royer (2004a) address the sensitivity to different parameter changes in African deforestation experiments and find that changes of roughness, soil depth, vegetation cover, stomatal resistance, albedo, and leaf area index all could make significant contributions. Voldoire and Royer (2004) find that such changes may impact temperature and precipitation extremes more than means, in particular the daytime maximum temperature and the drying and temperature responses associated with El Niño events. Snyder et al. (2004a,b) also address the response to vegetation removal and African deforestation.

Several studies have linked changes of land use to the climate change expected from increasing greenhouse gases. Maynard and Royer (2004b) find that anticipated changes in land cover modify the response of African climate to that of the greenhouse warming, in particular by further increasing the temperatures.

Guillevic et al. (2004) address the issue of the importance of interannual variability of leaf area as inferred from AVHRR satellite data, and conclude that substantial sensitivity exists. In contrast, Lawrence and Slingo (2004) find very little difference in climate simulations between use of annual mean value of vegetation characteristics versus a prescribed seasonal cycle. They indicate some scepticism as to the realism of their result and suggest some model modifications that would give a much larger sensitivity.

Osborne et al. (2004) examine effects of changing tropical soils and vegetation: variations in vegetation produce variability in surface fluxes and their coupling to precipitation. Thus, interactive vegetation can promote additional surface and atmospheric variability as analysed by Crucifix et al. (2005).

7.2.4.5 How can regional scale changes of vegetation modify precipitation regimes?

Marengo and Nobre (2001) found that removal of vegetation led to a decrease in precipitation and evapotranspiration and a decrease in moisture convergence in central and northern Amazonia. Oyama and Nobre (2004) show how removal of vegetation in notheastern Brazil would substantially decrease precipitation.

New developments in dynamic vegetation schemes and coupled climate-carbon models (Cox et al., 2000; Betts et al., 2003; Huntingford et al., 2004) have demonstrated the possibility of large feedbacks between further climate change and vegetation change. In particular, they found a large die-back in the Amazon vegetation and large reductions in Amazon precipitation. They also showed that the physiological forcing of stomatal closure from the rising CO_2 levels could contribute 20% to that rainfall reduction . Their simulated forest die-back also exerts two positive feedbacks on the precipitation reduction: (1) a biogeophysical feedback through reduced forest cover suppression of local evaporative water recycling, and (2) a biogeochemical feedback through the release of CO_2 contributing to an accelerated global warming (Betts et al., 2003). Levis et al., (2004) demonstrate a dynamic coupling between changes of African rainfall and vegetation.

How land cover and its change help structure rainfall transitions has been considered by Fu and Li (2004) and DeFries et al. (2002b). Grimm (2003) has examined a possible feedback between soil moisture and the monsoon activity over tropical South America

7.2.4.6 How can changes of land properties change boundary layer properties to modify occurrence of clouds and their radiative effects?

Ek and Holtzlag (2004) discuss soil moisture cloud feedbacks as already mentioned. Chagnon et al. (2004) present strong observational evidence of a large increase in boundary layer clouds in the Amazon in areas of partial deforestation.

The triggering of the annual South American Monsoon System may be connected to (1) a loading of aerosols due to biomass burning and (2) consequent modification of solar radiation (Artaxo et al., 1990) and atmospheric thermodynamic stability. Recent model and observational results have indicated that the aerosol plume produced by biomass burning at the end of the dry season is transported to the south and may interact with frontal systems, thus indicating a possible feedback to the precipitation regime (Freitas et al., 2005) through the radiative of cloud microphysical processes (Silva Dias et al., 2002).

7.2.4.7 How can the presence of aerosols and clouds modify land properties such as their carbon storage?

Aerosols and clouds reduce the availability of visible light needed by plants for photosynthesis. However, the leaves in full sun may be light-saturated, i.e. they do not develop sufficient enzymes to utilize that level of light. Leaves that are shaded, however, are generally light limited. They are only illuminated by diffuse light scattered by overlying leaves, or by atmospheric constituents. Thus, an increase of diffuse light at the expense of direct light will promote leaf carbon assimilation and transpiration. Because of the observational uncertainties as to whether or not the additional diffuse light can overcompensate for the greater loss of direct light, this topic is controversial. It has been addressed by Gu (2002, 2003); Roderick et al., 2001; Cohan et al., (2002).That the aerosol-induced increase in diffuse radiation by the Mt. Pinatubo eruption could provide an enhanced terrestrial carbon sink has been suggested as an explanation of the temporary decline in the growth rate of atmospheric CO_2 that followed the eruption (Roderick et al., 2001; Gu et al., 2003).

7.2.4.8 How can vegetation structure be changed by changing climate?

Analyses of satellite sensed vegetation greenness and meteorological station data suggest an enhanced plant growth and lengthened growing season duration in northern high latitudes since the 1980s (Zhou et al., 2001, 2003c). This effect is further supported by modelling linked to observed climate data (Lucht et al., 2002). Nemani et al. (2002, 2003) suggest that increased rainfall and humidity spurred plant growth in the United States and changes in climate have eased several critical climatic constraints to plant growth and thus increased global terrestrial net primary production.

7.2.5 Functioning of System Models - Improving Their Basis for Quantitative Evaluation of Impacts of Land Changes

7.2.5.1 Lower complexity model characterizations

Because full realistic coupled climate models are so complex, analyses of the various potential feedbacks have been rather limited. Thus, potentially important mechanisms are better initially described in low or intermediate complexity models. Lower complexity models have been developed of interactive vegetation with multiple equilibria (Zeng et al., 2002; Foley et al., 2003; Wang et al., 2004; Zeng et al., 2004). Such models demonstrate how assumed feedbacks between precipitation and surface fluxes generated by dynamic vegetation may lead to the possibility of flip-flops between two soil moisture and precipitation regimes. The Sahel margin appears to most readily generate alternating precipitation regimes.

7.2.5.2 Model feedback intercomparisons

Because of the complicated nature of couplings between land and the atmospheric hydrological cycle, their presence in a model gives no assurance of their correctness. Observational validation however, can be difficult to achieve. An alternate likely more limited, but potentially more quantitative evaluation approach, is the intercomparison of models from multiple groups. Land fluxes alone have been so intercompared for a number of years under the auspices of Project for Intercomparison of Land Surface Schemes (PILPS). The important question of how models differ in their coupling to the atmosphere has been less thoroughly addressed. Irannejad et al. (2003) have developed a statistical methodology to fit monthly fluxes from AMIP II climate models to a simple linear statistical model, depending on such factors as monthly net radiation, and surface relative humidity. With this fitting, they are able to run any such model with the forcing from any other model and in this way are able to characterize contributions to flux differences from the

atmospheric forcing versus the surface model. Apparently both are major source of variability; they find that the coupled models are more in agreement because of offsetting differences in the atmospheric and land models.

It has long been reported in individual modelling studies that soil moisture can have a significant influence on precipitation. Only recently however have there been attempts to quantify this coupling, from a statistical viewpoint (Dirmeyer, 2001; Koster et al., 2001, 2002; Reale and Dirmeyer, 2002; Reale et al., 2002; Koster et al., 2003. Koster and Suarez (2004) analyse statistically records of precipitation over the US and find positive "memory" in the data for at least 3 months into the future. As previously mentioned, Koster et al (2004) report on a new model intercomparison activity, the Global Land Atmosphere Coupling Experiment (GLACE), that compares differences in the variability of precipitation among a large number of major climate models that is caused by interaction with soil moisture. They do this by an experimental protocol where they generate ensembles of simulations with and without soil moisture prescribed from a single simulation. They report a wide range of differences between models - apparently we can yet have no confidence in this important feedback component of a climate model and therefore its possible contribution to global warming simulations.

7.2.5.3 Improved global and regional data

Specification of land surface properties in climate models has been increasingly improved through new more accurate global satellite observations. They have provided in particular albedos of soils in non-vegetated regions (e.g., Tsvetsinskaya et al., 2002), (Wang et al., 2004), and emissivities (Zhou et al., 2003a,b), and constrain model calculated albedos in the presence of vegetation (Zhou et al., 2003d; Oleson et al., 2003), vegetation underlain by snow (Jin et al., 2002), and the role of leaf area (Tian et al., 2004a-c). Radiative temperatures are a key constraint (recent analyses include Oku and Ishikawa, 2004). Precipitation data sets combining rain gauge and satellite (Clem et al., 2002; Adler et al., 2003) are providing important diagnostic constraints for climate modelling, as are observations of runoff (Dai and Trenberth, 2002; Fekete, 2002).

7.2.5.4 Field observational programs

New and improved local site observational constraints collectively describe the land processes that need to be modelled. The largest recent such activity has been the LBA project in the Amazon (Malki et al., 2002). LBA studies have included physical climate on all scales, carbon dynamics, nutrient dynamics, and trace gas fluxes. The first of these is reviewed here. Goncalves et al. (2005) have discussed the importance of incorporating land cover heterogeneity in weather prediction models for South America. Rocha et al. (2005) and Quesada et al. (2005) have quantified water and energy budgets for a forested and a savanna site respectively. They find large differences in the water budgets between the *campo sujo* savanna at the IBGE Reserve and the dense forest at the Tapajós National Forest. Dry season evapotranspiration for the savannah averaged 1.6 mm day^{-1} versus 4.9 mm day^{-1} for the forest. Both ecosystems depend on deep rooting to sustain evapotranspiration during the dry season. Rocha et al. (2005) also observed that hydraulic lift recharged the forest upper soil profiles each night. At Tapajós, the forest showed no signs of drought stress allowing uniformly high carbon uptake throughout the dry season (July – December 2000) (Rocha et al.2005, and Goulden et al., 2005).

Tibet as another key region continues to be better characterized from observational studies (e.g., Gao et al., 2004). With its high elevation, hence low air densities, land drives a much higher boundary layer than elsewhere. However, the water vapour mixing ratio is found to strongly drop off within the boundary layer (Yang et al., 2004).

7.3 The Carbon Cycle and the Climate System

7.3.1 Contemporary Carbon Budget

7.3.1.1 Global budget of atmospheric CO_2

Concentrations of atmospheric CO_2 have increased each year since measurements started in 1959 (Figure 7.3.1a; Keeling et al., 2004; Conway and Tans, 2004), roughly parallel to emission rates. The average CO_2 increase for 2000–2004, based on the CMDL network, is 1.88 ppm yr^{-1} or 3.99 Pg-C yr^{-1} (with an uncertainty of ±0.3% or 0.3 ppm for the total change over 5 years). The *airborne fraction* (the proportion of fossil fuel emissions appearing as annual increment) averaged 0.55 from 1959 to 2000 (Figure 7.3.1b). Year-to-year

fluctuations in the airborne fraction occur associated with ENSO events, volcanic eruptions, and other major climatic events (Bacastow et al., 1980; Lintner, 2002; Lucht et al., 2002; Reichenau and Esser, 2003; Rödenbeck et al., 2003; Angert et al., 2004, 2005). However there is remarkably little variation in the 5-year mean values (horizontal lines in Figure 7.3.1b), with the important exception of the early 1990s. The annual increase in 1998, 2.5 ppm, was the highest ever observed, although the airborne fraction that year (0.82) was no higher than peak values observed in prior decades. On average, the terrestrial biosphere and the oceans together have consistently removed ~45% of the CO_2 emitted from fossil sources since 1959.

[INSERT FIGURE 7.3.1 HERE]

The concentration of CO_2 is currently higher in the Northern Hemisphere than in the South. The excess, ΔCO_2^{N-S}, has increased with emission rates of fossil fuel by about 0.5 ppm (Pg-C yr^{-1}) $^{-1}$ (Figure 7.3.1*c*), giving a clear signature of the global impact of fossil fuel CO_2. The intercept of the best-fit line is –0.8 ppm, indicating that, without anthropogenic emissions, CO_2 would be slightly higher in the Southern Hemisphere than in the North, presumably due to transport of CO_2 by the ocean circulation. The relationship between ΔCO_2^{N-S} and fossil fuel emissions has been generally consistent over the 45 years of record, but with inter-annual fluctuations as large as ±0.4 ppm (Figure 7.3.1*d*). At least some of this variability may be attributed to changes in atmospheric circulation (Dargaville et al., 2003).

7.3.1.2 Carbon cycle variability from 1990 to 2003

The early 1990s featured anomalously strong global sinks for atmospheric CO_2. The airborne fraction dropped to 0.4, and values of ΔCO_2^{N-S} were rather low (Fig. 7.3.1). Manning and Keeling, (2005; Figure 7.3.2) observed low rates of decline of atmospheric O_2, and Miller et al. (2005) report a comparable shift in values for $\delta^{13}CO_2$, suggesting that uptake of atmospheric CO_2 by terrestrial ecosystems was largely responsible for increased efficiency of removing fossil fuel CO_2 from the atmosphere.

[INSERT FIGURE 7.3.2 HERE]

Enhanced uptake of atmospheric CO_2 in the early 1990s has been attributed to the combined effects of the Mt. Pinatubo eruption and ENSO events (Reichenau and Esser, 2003; Rödenbeck et al., 2003), raising speculation that that negative feedback on rising CO_2 might lower projections of future increases. During this period, aerosols from the eruption of Mt. Pinatubo scattered sunlight and lowered atmospheric temperatures; there was a strong El Niño event, and the greenness index (NDVI) may have been lower globally. Lower temperatures are expected to reduce rates for respiration of labile pools in terrestrial ecosystems, and the ENSO may have simultaneously induced additional uptake of CO_2 by the ocean (Angert et al., 2005). Diffuse sunlight is used more efficiently that direct light by terrestrial ecosystems (Gu et al., 2003), offsetting reduced solar fluxes from the haze layer. Thus many influences of the eruption appeared to enhance uptake of CO_2 by terrestrial ecosystems. However, similar effects were not observed after the eruption of El Chíchon, which was almost as large as the Mt. Pinatubo eruption and which also was associated with an El Niño event. Hence the explanation for this huge anomaly remains speculative.

After 1995 the airborne fraction returned to values consistent with previous decades (Figure 7.3.1b). The decadal analysis of Manning and Keeling (2005) also indicates lower uptake by the terrestrial biosphere in 1993–2003, as compared with 1990–2000 (Table 7.3.1). The remarkably high CO_2 growth in 1998 coincided with a global increase in CO concentrations attributable to wildfires. Achard et al. (2004) estimated 0.88 ± 0.07 Pg-C emitted from the burning of 2.4×10^6 ha of peatland in the Indonesian forest fires in 1997–1998 (Page et al., 2002), which would account for 0.4 ppm of CO_2 added to the atmosphere. There were also unusually large forest fires in the boreal zone that year (Yurganov et al., 2004). From 1998–2003, extensive droughts in mid-latitudes of the northern hemisphere (Hoerling and Kumar, 2003) may have led to decreased photosynthesis and carbon uptake (Lotch et al., 2005; Angert et al., 2005; Ciais et al., 2005), helping to push up the airborne fraction towards historical values.

Table 7.3.1. Decadal Global CO_2 budgets. The **bold** numerals show the **total amounts** in **Pg-C** for each decade. The *italics* give the *mean annual flux* for emissions and sinks, and the *change* in *ppm* as derived from atmospheric CO_2 and O_2 measurements (Manning and Keeling, 2005; also see Figure 2.2).

Fossil Emissions	Land Sink	Ocean Sink	Atmos. Rise	Time Period
63.5 *(3.00)*	**14.2** *(0.67)*	**17.1** *(0.81)*	**32.2** *(1.52)*	01/01/1990 to 01/01/2000
64.8 *(3.05)*	**5.1** (*0.24)*	**22.4** *(1.05)*	**37.3** *(1.76)*	01/01/1993 to 01/01/2003

We cannot infer trends in net uptake by land or ocean ecosystems over periods shorter than 5–10 years. Inter-annual variations in the ventilation of the ocean mixed layer (Manning and Keeling, 2005) can produce significant changes of the O_2:N_2 ratio on a yearly basis. The N-S gradient in CO_2 is influenced by changes in atmospheric circulation, changes in rates of fossil fuel emissions and in the time derivative of emissions (due to the lag inherent in inter-hemispheric exchange) (Rödenbeck et al., 2003; Dragaville et al., 2003). The long-term stability of uptake rates suggests the absence of vast changes in the carbon cycle globally over the last 45 years, but unfortunately the diverse sources of variability can mask quite significant trends. Hence consistent, very carefully calibrated studies of atmospheric CO_2 are needed over long time periods to determine if, as suggested by data from recent year, CO_2 growth rates and/or airborne fractions are increasing, or if there has been a shift in the land/ocean balance.

7.3.2 Carbon Cycle Processes

7.3.2.0 Understanding the global CO_2 budget

On average, 30–50% of the net removal of CO_2 from the atmosphere, and a larger fraction of the inter-annual variation, may be attributed to uptake by the terrestrial biosphere, and the balance is taken up by the oceans (e.g., Bousquet et al., 2000; Battle et al., 2000; Manning and Keeling, 2005; Table 7.3.1). The loci of uptake and release, and the underlying processes, must be understood if we are to predict the future trends of CO_2 concentrations in atmosphere. We summarize below current knowledge of the processes that regulate the carbon cycle on land (7.3.2.1) and in the oceans (7.3.2.2). We then summarize large-scale net CO_2 exchange and associated spatiotemporal variations inferred from data using bottom-up and top-down (inverse) models (7.3.3). Finally we examine the results of initial model studies that attempt to simulate interactions between climate change, large scale carbon fluxes, and atmosphere CO_2 concentrations, and we place these studies in context (7.3.4).

7.3.2.1 Terrestrial vegetation and the global CO_2 budget

Factors affecting the carbon cycle in terrestrial ecosystems include: (1) *direct climate effects* (changes in precipitation, temperature, aerosol scattering), (2) *intrinsic ecosystem effects* (land use including deforestation, reforestation, afforestation and historical legacies), and (3) *atmospheric composition effects* (fertilization by rising CO_2 or inputs of nutrients, damage by pollution).

7.3.2.1.1 Where is C being stored, where emitted, in the terrestrial biosphere

Carbon uptake and storage in the terrestrial biosphere is the net sum of uptake due to growth, reforestation, and sequestration and emission due to deforestation, forest damage by pollution, and disturbance of soils. Forests (live and dead trees, soils) and peatlands contain the largest stocks of organic matter globally, and have the greatest potential to influence the global carbon cycle. Battle et al. (2001) argued, on the basis of changes in $^{13}CO_2$:$^{12}CO_2$ and O_2:N_2 that forest re-growth at middle latitudes roughly balanced deforestation in the tropics during the 1980s. Then, in the early 1990s, uptake of CO_2 and storage as organic matter by the terrestrial biosphere accelerated, and sinks exceeded sources due to deforestation since that time. Increasing forest uptake after 1990 could reflect slower rates of deforestation, or greater uptake by forests (see below), stimulated by changes in atmospheric composition, climate, and/or historical (land use) factors. The apparent return to values typical of earlier decades (noted above) suggests a transient global phenomenon rather than some kind of long-term stimulation ("greening", *cf.* Idso et al., 1994) of the biosphere.

7.3.2.1.2 Effects of land use change and exploitation of forest resources on global CO_2

CO_2 sources from tropical deforestation: During the past 25 years, large-scale clearing of forests has been essentially a tropical phenomenon. Agriculture and exploitation of forest resources have reached into formerly remote areas of old-growth forest in the tropics, in contrast to mid-latitudes where exploitation previously eliminated old-growth. DeFries et al. (2002a) and Achard et al (2004) estimated net release of CO_2 from tropical deforestation and regrowth in the range 0.6 (0.3– 0.8) and 0.9 (0.5–1.4) Pg-C yr^{-1} for the 1980s and 1990s, respectively (DeFries), and 0.98 ± 30 Pg-C yr^{-1} in the 1990s (Achard), using satellite data and terrestrial carbon models (see Table 7.3.2). Changes in forest area were found to be lower than given by

the United Nations Food and Agriculture Organization Forest Resource Assessment (FRA), 1.9 (0.6–2.5) Pg-C yr^{-1} (Houghton et al., 2003). The Defries and Achard estimates are broadly consistent with the global budget for terrestrial systems, but it is harder to accommodate the large source estimated by Houghton.

Table 7.3.2. Estimated carbon emissions from tropical deforestation in the 1990s (Pg-C yr^{-1}).

Author	Tropical Americas	Tropical Africa	Tropical Asia	Pan-Tropical
Houghton	0.75 ± 0.3	0.35 ± 0.2	1.09 ± 0.5	2.20 ± 0.6
De Fries	0.43 (0.21–0.62)	0.12 (0.08–0.14)	0.35 (0.19–0.59)	0.91 (0.50–1.36)
Achard	0.44 (0.35–0.52)	0.16 (0.13–0.19)	0.39 (0.32–0.56)	0.98 (0.81–0.12)

Note:
Differences mainly reflect estimates of deforested areas, higher for Houghton (FAO deforestation statistics) than for de Fries et al and Achard et al. (independently analyzed satellite data with wall-to-wall coverage).

7.3.2.1.3 Forest re-growth in middle and high latitudes

In contrast to the tropics, forest areas generally increased during the 20th century at middle and high latitudes. This surprising trend reflects the intensification of agriculture and forestry. More food is being grown on less land, reflecting mechanization of agriculture, increased fertilizer use, and adoption of high-yield cultivars. Likewise intensive forest management and agroforestry produce more fiber on less land; improved forest management favors more rapid regrowth of forests after harvest. These trends have clearly led to carbon sequestration by re-growing forests, with beneficial effects on global concentrations of CO_2. It should be noted however that industrialized agriculture and forestry require high inputs of fossil energy, so it is difficult to assess the net global effects of agricultural intensification on the atmosphere.

Regional studies have confirmed the plausibility of strong mid-latitude sinks due to forest re-growth. Networks of eddy flux towers have been developed where the exchange fluxes of CO_2 are measured directly, every hour, for a decade or longer (Baldocchi et al., 2003). These observations show that forests on long-abandoned former agricultural lands (Curtis et al., 2002; Valentini et al., 2004) and in industrial managed forests (Hollinger et al., 2002) take up significant amounts of carbon every year. Analysis of forest inventory data shows that, in aggregate, current forest lands are significant sinks for atmospheric CO_2 (Pacala et al., 2001). There are very few old-growth forests at mid-latitudes (most are less than 70 years old), and these forests are accumulating biomass simply because of their ages and stages of succession. The uptake rates inferred from flux towers are generally consistent with those inferred from inverse studies (e.g., Hurtt et al., 2003). Stocks of soil carbon are also likely increasing due to replenishment of soil organic matter and necromass depleted during the agricultural phase, and changes in soil microclimate associated with reforestation; these effects might add 30–50% to the quantity of CO_2 sequestered in biomass (e.g., Barford et al., 2001).

The carbon balance of high latitude forests is less clear. Significant regrowth of forests appears to be taking place across Scandinavia and Russia (*citations*). But fire disturbance in North American and Eurasian boreal forests was higher in the 1980s than in any previous decade on record (Kurz and Apps, 1999; Kurz et al., 1995, citation needed for Eurasia), and significant soil organic matter appears to be released in these fires. Permafrost in many areas (e.g., Alaska: Osterkamp and Romanovsky, 1999) is also currently warming. These processes are both likely to lead to release of important quantities of CO_2 (Harden et al., 2000; Goulden et al., 1998). Increased fire frequency and thawing of frozen soils may both be linked to climatic variations and trends (Zuang et al., 2003; Hess et al., 2001; Flannigan et al., 2000; Kurz and Apps,1999), which feature notable warming in the latter part of the 20th century (Osterkamp and Romanovsky, 1999).

7.3.2.1.4 Effects of climate variations and trends and changes in atmospheric composition on forest uptake or emission of CO_2

A CO_2 sink in undisturbed tropical forests? Despite expanding areas of deforestation and degradation, there are still large areas of tropical forests that are among the world's great wilderness areas, with fairly light human impact, especially in Amazônia. Old growth tropical forests contain huge stores of organic matter, and they account for a major fraction of global net primary productivity (40% of global biomass, >60% of global NPP, Brown and Lugo, 1982). Changes in the carbon balance of these regions could have significant effects on global CO_2.

The net carbon balance of an area of forest may be measured by net primary production (input of organic matter) and heterotrophic respiration (output), or alternatively, ecosystem photosynthesis (input) and respiration (output). In many ecosystems, fire must be added on the output side, and in managed systems, harvesting must be taken into account. On long time scales, input and output must approximately balance, and changes in inputs eventually produce corresponding changes in outputs. Variations of inputs of organic matter, or of effective rates of mineralization, can result in a net flux of carbon to or from the forest system if they occur on a timescale shorter than the carbon residence times, even where basic ecosystem function is unchanged. For example, variations in cloudiness, precipitation and temperature might result in significant interannual variations in forest carbon balance. Bigger perturbations, such as episodes of mortality, or land management practices such as suppression of fires, can result in net fluxes that persist for decades at landscape or even continental scale (Pacala et al., 2001; Koerner, 2004).

Data do not yet exist to compile a systematic forest inventory and carbon budget across the whole landscape in tropical regions. Recent investigations of the carbon balance of tropical forests have focused on long-term plots in mature, undisturbed ecosystems. These might be expected, on average, to be in carbon balance, and imbalances could indicate ecological responses to global atmospheric change. Indeed, Phillips et al. (1998) and Baker et al. (2004) reported that their forest plots appeared to be accumulating carbon at a mean rate of 0.7 ± 0.2 t-C ha^{-1} yr^{-1}, implying net carbon uptake into live biomass of 0.6 ± 0.3 Pg-C yr^{-1}, although they noted large variability between plots, due to the natural dynamics of tree death and regrowth..

The rise in mean atmospheric CO_2 from a preindustrial value of 280 ppm to more than 375 ppm (in 2004) might cause net uptake of CO_2 simply by stimulating plant photosynthesis, since the respiration response will lag behind. The CO_2 concentration of the atmosphere has increased on average by ~1.5 ppm yr^{-1}, 0.4% of the background concentration. The incremental stimulation of photosynthesis each year (estimated from biochemical studies) might average about 0.25% (e.g. next year's photosynthesis should be 1.0025 times this year's) (Berry references). Using of ~10 years for the mean turnover rate for organic matter in tropical forests (Taylor and Lloyd, 1996), one might expect a present imbalance between uptake of CO_2 and respiration of 2.5% (1.0025^{10}), consistent with rate of live biomass increase (~3%) inferred from plot studies by Philips et al. (1998).

Other factors affecting these forests could be the pan-tropical rise in air temperatures by 0.26°C per decade in recent decades (Malhi and Wright, 2004), which could enhance nutrient mineralization, but alternatively this warming might increase water stress and respiration rates. Forest response to CO_2 might not be limited by light or by CO_2, as assumed above, but by other factors such as low nutrient availability (Lewis, Malhi and Phillips, 2004; Koerner, 2004; Chambers and Silver, 2004), architectural constraints on how much biomass a forest can hold, ecosystem level constraints such as light competition, or differential responses that might favour shorter lived trees or agents of disturbance (insects, lianas) (Koerner, 2004). Indeed, Baker et al. (2004) reported higher mortality rates and increased prevalence of lianas in their plots. If these changes in forest dynamism occurred in the last 10 years, it is possible that even the *sign* of the imbalance inferred from plot measurements could be incorrect. Necromass was not determined, and areas with recent increases in dynamism, rates of decay of dead wood more than offset the increases in live biomass that occurred in response to mortality events (release of the subcanopy) (Rice et al., 2004).

Another outstanding uncertainty is any methodological bias associated with sub-sampling of a natural disturbance and recovery matrix of the forest (with mature forests undergoing occasional local disturbance (e.g. storm blowdowns) followed by sustained periods of recovery. Subsampling of this matrix may leads to an artefactual apparent increase in biomass, depending on the size-frequency distribution of disturbances, and the recovery time of forests from such disturbances (Koerner, 2004). By far the biggest biomass increases were estimated for floodplain forests, where forests pass through a successional sequence starting at river-deposited gravel; the plots on these floodplains could involve forests in mid-succession, and thus be unrepresentative of the large-scale forest.

In this context, it is noteworthy that studies involving large-area plots (9–50 ha) have indicated either no net long-term change or a long-term net decline in estimated above ground live biomass [*1. BDFFP site, Manaus, Brazil*, 18 1-ha plots in the PDBFF site, monitored 15 yr, Laurance et al., 2004; *2. Barro Colorado I., Panama*, 50 ha plot, 15 yr, Chave et al., 2003; *3. La Selva, Costa Rica*, 18 0.5-ha plots, 4 (-6) yr, Clark

2004a; *4. JACARANDA plots, Manaus, Brazil*, two long-transect 5-ha plots, 6 yr, biomass data in Baker et al., 2004), and the 20 ha plot in Tapajos (5 years) showed increasing live biomass offset by decaying necromass (Saleska et al., 2003; Fearnside, 2000)]. Indeed, Körner (2004) argued that accurate assessment of trends in forest carbon balance requires long-term monitoring of many replicate plots or very large plots at each site in order to capture the localized and/or sporadic biomass changes associated with the natural forest disturbance regime.

One of the key discoveries from the plot network has been that western Amazonian forests are 2–3 times more productive than eastern forests (Malhi et al., 2004), but similar or lower in biomass. Hence the residence times for live biomass carbon in western Amazonian forests is less than in eastern forests. This finding has implications for wider considerations of ecosystem response to stimulations of productivity (whether by CO_2 or N deposition or anything else), suggesting the long-term response to increased productivity in a mature forest ecosystem may not be a large increase in biomass, but an increase in turnover rate. Dynamism of tropical forests may be much more responsive than biomass, and system-level response (decrease in lifetime) is very different from the plant-level response (increase in productivity) (Koerner, 2004).

If the results from the plots could in fact be extrapolated, the mean above ground carbon sink would be 0.61 ± 0.22 Pg-C ha^{-1} yr^{-1} (Baker et al., 2004), or 0.89 ± 0.32 Mg-C ha^{-1} yr^{-1} including corrections for small trees, lianas, and below-ground biomass. Multiplying by the FAO estimate of Neotropical moist forest area (5,987,000 km^2) gives a Neotropical moist forest biomass sink of 0.54 ± 0.19 Pg-C yr^{-1} (Malhi and Phillips 2004) Scaling-up taking into account soil type would increase this value to about 0.62 ± 0.18 Pg-C yr^{-1}. Finally, if the as yet uncompiled data from the African and Asia tropics (which account for 50% of global moist forest area) were to show a similar trend to Amazonia, the global moist tropical live biomass sink would be about 1.2 ± 0.4 Pg-C yr^{-1}. This value is close to the net source inferred by DeFries and Achard (Table 7.3.2). Taken at face value, the combined net exchange of CO_2 between the atmosphere and tropical land ecosystems would be ~0, which is intriguingly consistent with inferences from inverse studies of little net flux from low latitudes.

Atmospheric composition effects: Free Air CO_2 Enrichment (FACE) studies have been used to examine the response of ecosystems to a large (usually about 50%) step increase in CO_2 concentration. The results of these have been quite variable (Nowak et al., 2004). In some instances, the expected stimulation was not observed or decreased to near zero after a few years (Oren et al., 2001) or there was even an inhibition of growth by elevated CO_2 (Shaw et al., 2002). Nevertheless, on average some stimulation has been observed in FACE experiments—but not as much as predicted from the kinetics of photosynthesis. These results clearly demonstrate other factors (nutrients for example) can limit plant growth, and throttle the CO_2 fertilization effect. However, the CO_2 perturbation used in FACE experiments is roughly 100 fold larger than the annual rate of CO_2 increase imposed annually in nature. Therefore, one might expect stronger constraints on the CO_2 fertilization effect in the FACE experiments than might occur in nature. Overall, we do not presently have an accurate measure of the magnitude of the CO_2 fertilization effect, and it may be quite difficult to determine by direct measurement due to the strong influence of other factors such as succession, disturbance, etc.

Nutrient and pollutant deposition are considered in sections 7.4.2 and 7.5.1.

7.3.2.1.7 Direct effects of land cover on climate

Land cover demonstrably affects both surface and regional climate. In the past several centuries, large-scale land-cover change occurred primarily in temperate latitudes through conversion of forests and grassland to agriculture; and then reversion to forests. Both the surface and regional climate, and global energy balance, have been affected. The dominant effect of forest regrowth in midlatitudes on the surface climate record has likely been cooling during summer, due to increased conversion of incoming radiation to latent heat and increases in boundary-layer cloudiness (DeFries et al., 2002b; Freedman et al., 2001); the effect was cooling 0.3–0.6 C between 1910 and 1990, according to Roy et al. (2003). A particularly strong effect is noted in late spring when leaves emerge on trees (Collatz et al., 2000; Durre and Wallace, 2001; Bonfils et al., 2004, 2005), with long-term trends associated with replacement of sparsely-vegetated croplands by forests (Fitzjarrald et al., 2001). Modelling studies (e.g., Snyder et al., 2004; Oyama and Nobre, 2004) and analysis of historical data appear to agree on these effects. Trends have likely been the opposite in the tropics due to

deforestation there. Freedman et al. (2001) pointed out that there is a feedback between forest cover and CO_2 uptake. Analyzing data for New England, they showed that forest cover increases boundary-layer cloudiness in late spring and early summer, and that CO_2 uptake was enhanced by the resulting increase in diffuse light.

More uncertain is the influence of land cover on global climate. DeFries et al. (2002b) argued that future deforestation would warm the near-surface atmosphere by up to 2°C and lead to drier hydrologic conditions in the tropics. Warming appears likely over reforested land areas due to lower albedo, and cooling over deforested land areas (Brovkin et al., 1999, 2004). Overall, global effects appear to be rather small. Nevertheless the influence of land cover change on climate *data*, and thus on trends inferred from those data, may be more significant. Thus the most likely effects of changes in forest cover on climate have been to mask regional warming trends at surface stations in midlatitudes, and enhance warming trends in the tropics.

7.3.2.2 Ocean carbon-cycle processes

So far, the oceans have taken up 48% of the anthropogenic CO_2 emissions from fossil fuel burning and cement manufacturing (Sabine et al., 2994). Changes in climate will affect the ocean carbon cycle (for observations, see Chapter 5, Sections 5.4.2 and 5.4.3), which itself will feed back onto climate change. So far, a series of marine carbon cycle climate feedbacks were identified. The as yet missing explanation of the glacial-interglacial CO_2 drawdown in the atmosphere indicates a gap in our knowledge with respect to marine processes, which are significant for biogeochemical forcing of climate (see paleo-climate carbon Box 6.2 in Chapter 6). It is possible that a series of smaller feedbacks add up to an overall important feedback. Future impacts of the marine carbon cycle onto the climate system are not only triggered by climatic forcing alone, but also depend on further other anthropogenic forcings such as land use, water treatment, and building of freshwater reservoirs. One of the most important forcings, namely the emissions of fossil fuel CO_2, depends on human behaviour and not on climate itself, although climate change may influence human behaviour. Moreover, marine carbon cycle feedbacks work on a variety of time scales. Long-time scale processes would persist for several tens of thousands of years, even when anthropogenic CO_2 emissions would stop immediately. Marine biogeochemical feedbacks of climatic relevance are summarised in Figure 7.3.3 and Table 7.3.3.

[INSERT FIGURE 7.3.3 HERE]

[INSERT TABLE 7.3.3 HERE]

In Table 7.3.3, we discriminate the feedbacks by their respective original forcing. Some of the feedbacks have wider implications than just a direct influence on the climate system. These implications are mentioned, if they seem to be of relevance for the climate change context. Table 7.3.3 reflects that only a few ocean climate biogeochemical feedbacks are well established. These are the feedbacks involving the inorganic carbon cycle. Organic carbon cycle feedbacks – including destabilisation of gas hydrates and purposeful CO_2 storage – are not well known due to the extreme complexity of processes involved and the difficulty of observing these processes. This does not mean that the organic carbon cycle may be not important for climate. We simply do not know at present. The basics of marine carbon chemistry and ocean acidification are explained in Box 7.1.

[START OF BOX 7.1]

Box 7.1: Marine Carbon Chemistry and Ocean Acidification

In the atmosphere, CO_2 is fairly inert and stays there mainly as molecular CO_2. In contrast, any CO_2 which enters the ocean through air-sea gas exchange is hydrated to carbonic acid H_2CO_3 and dissociated into "free CO_2" (CO_2 plus H_2CO_3), HCO_3^- (bicarbonate), CO_3^{2-} (carbonate), and protons H^+. The ratio of the respective concentrations [CO_2 plus H_2CO_3], [HCO_3^-] and [CO_3^{2-}] is roughly 1:100:10 but varies considerably. Their sum is called total dissolved inorganic carbon, [TCO_2]. The ability of seawater to dissociate carbonic acid is quantified through the variable "alkalinity" (TAlk) which couples the marine carbon cycle to all other chemically active substances in seawater including water itself. The alkalinity is mainly determined by the cycles of calcium carbonate and borate. Thus the alkalinity inventory of the oceans as a whole varies usually on geological time scales only. In equilibrium, the CO_2 partial pressures (pCO_2) in the atmosphere and the underlying seawater are equal. The higher this equilibrium CO_2 partial pressure is, the more carbonic acid is

dissociated in the ocean, and the higher is the proton concentration. A higher proton concentration means more acid conditions, i.e., a decrease in pH value ($pH=-\log_{10}([H^+])$. In parallel to increasing seawater pCO_2, the concentrations [CO_2 plus H_2CO_3], [HCO_3^-], and [H^+] increase while [CO_3^{2-}] decreases. The relative amount of CO_2 additions to the ocean, which can be buffered through dissociation of carbonic acid, decreases with rising pCO_2: the "buffer factor" (see Figure 7.3.5) decreases, i.e. the seawater becomes less efficient for additional further CO_2 uptake. At a given equilibrium pCO_2, alkalinity, temperature, and salinity, the concentrations [HCO_3^-], [CO_3^{2-}], and [H^+] are uniquely determined (see Box 7.1, Figure 1) through the mass action law, and one cannot change one component without adjusting also the others.

[INSERT BOX 7.1, FIGURE 1 HERE]

The ocean acidification through uptake of anthropogenic CO_2 leads to more corrosive conditions for calcium carbonate ($CaCO_3$) in the ocean ("coffee machine analog"), i.e. towards an increase of areas which are undersaturated with respect to $CaCO_3$. The dissolution or preservation of $CaCO_3$ in seawater is set by the solubility product: $K_{sp} = [Ca^{2+}] \times [CO_3^{2-}]$. At lower [$CO_3^{2-}$] in the water column during increasing acidification, two primary effects are expected: (1) the dissolution of $CaCO_3$ at the ocean floor (available corals, available $CaCO_3$ sediments) will be increasingly furthered, and (2) the biocalcification within the water column may be inhibited or slowed down (less biological production of corals as well as calcifying phytoplankton and zooplankton) (Royal Society, 2005). The metastable $CaCO_3$ form aragonite (corals, pteropods) will be particularly susceptible to a pH lowering. The dissolution of $CaCO_3$ sediments will occur on a very long time scale involving ten thousands of years and slowly increasing the alkalinity including the concentration of the carbonate ion CO_3^{2-}. On very long time scales this alkalinity compensation will be quantitatively significant for the neutralization of the anthropogenic CO_2. Or vice versa, the anthropogenic CO_2 invasion will impact on the deep sea $CaCO_3$ sediment for tens of thousands of years, even if anthropogenic CO_2 emissions would be halted immediately (Archer, 2005). For the carbon cycle, the hampering of biocalcification at the sea surface will probably not be quantitatively as important as the $CaCO_3$ dissolution on the sea floor but will occur immediately with decreasing surface ocean pH. A decrease in biocalification alone will act as a small negative feedback (less alkalinity or CO_3^{2-} consumption) to atmospheric CO_2, but the effect of the marine particle flux (decreasing particle sinking velocities) may act as a positive feedback. Potential ecological changes due to ocean acidification may be severe, especially for corals in tropical, stably stratified waters, but also for cold water corals, and may influence the marine food chain up to higher trophical levels. These ecological changes therefore also have a considerable socio-economic impact. Apart from the absolute magnitude of a pH lowering, the expected fast rate of pH change at the sea surface can cause difficulties for marine ecosystems to adjust accordingly. Since the beginning of the industrial revolution, the sea surface pH dropped by about 0.1 pH units (corresponding to a 30% increase of the hydrogen ion concentration). Assuming a realistic emission scenario for anthropogenic CO_2 such as the A1B scenario, biocalcification will become difficult in particular within the Southern Ocean realm by year 2100. Further details are found in Royal Society (2005). It is important to state that ocean acidification is not per se a consequence of climate change but a consequence of fossil fuel CO_2 emissions, which are themselves the main driver of the anticipated climate change. Therefore, the issue needs to be addressed by both climate change communities and global change scientists in a broader approach.

[END OF BOX 7.1]

7.3.2.2.1 Warming of the ocean surface water

The warming of the surface ocean as expected under a further accumulation of greenhouse gases in the troposphere has effects on the inorganic as well as the organic carbon cycles.

The solubility of CO_2 gas in seawater as well as the two dissociation constants of carbon acid in seawater depend on temperature and salinity (and also pressure) (Weiss, 1974; Millero et al., 2002). Warming of the water reduces the solubility and dissociation of CO_2 and acts towards higher pCO_2. For a 1ºC increase of the sea surface temperature, a change of 4.9–7.0 μatm in atmospheric pCO_2 results after 100–1000 yr taking into account the solubility effect only, and 6.9–10.2 μatm for a combined effect of the temperature increase on solubility and dissociation constants after 100–1000 yr (use of the model of Heinze et al., 2003; see also Plattner et al., 2001; Broecker and Peng, 1986). The effect of rising seawater temperatures may be partially compensated by increasing fresh water releases to the ocean due to melting of ice sheets (see 7.3.2.2.2). Detailed changes in hydrographic conditions in the ocean surface layer can lead to further adjustments of the

solubility feedback. The solubility and dissociation feedback on a warming climate is positive, potentially in the order of few tens of µatm in atmospheric pCO_2 increase and associated with uncertainties due to the difficulty in to predicting hydrographic surface ocean conditions. The feedback starts to build up immediately but depends on the turnover time of the ocean surface waters and their overall warming.

Photosynthesis in the surface ocean is by far the largest contribution to biological primary production in the world ocean. On a yearly average (averaged over one seasonal cycle), the export of biologically bound carbon out of the surface ocean is the critical variable for potential changes of the atmospheric pCO_2 due to biological process. Species composition and rain ratio changes (rain ratio = ratio of C atoms which are fixed to particulate organic carbon POC to those which are fixed to particulate inorganic carbon PIC, namely $CaCO_3$, by biota) are discussed under 7.3.2.2.3 and 7.3.2.2.7. As long as the ocean circulation and nutrient as well as carbon supply remain constant, without any further feedback, the biological cycling of carbon would have only a small influence on the atmospheric pCO_2 due to the non-linearity of the carbon chemistry (see 7.3.2.2.7). It is difficult to quantify the direct effect of temperature on the uptake kinetics of marine biota for carbon and nutrients. According to the model of Michaelis-Menten kinetics, the uptake velocity of marine phytoplankton for nutrients and carbon approaches a maximum value (V_{max}) at sufficiently large nutrient availability and decreases at low nutrient availability. The indicator is the half saturation constant K_s, i.e. the value of the ambient nutrient concentration where the uptake velocity is $V_{max}/2$. Though it may be expected that higher temperatures favor an acceleration of chemical reactions there is no conclusive formulation for V_{max} at hand. Behrenfeld and Falkowski (1997, see their Figure 4) summarise a set of available $V_{max}(T)$ relationships in the form of maximum chlorophyll specific carbon fixation rates from different models, which implies that a pure temperature dependency may be difficult to deduce. The sign and magnitude of the biological productivity feedback to warming of the surface water are not yet known. Given a strong increase in V_{max} with increasing surface water temperature, potentially a negative feedback with a change of several tens of atmospheric pCO_2 is possible (e.g. Heinze et al., 1991).

Dissolved organic carbon (DOC) is considered to be stored in the ocean as a refractory pool with a very low turnover rate (Bauer et al., 1992) and a more semi-labile fraction (Carlson et al., 1994; Børsheim and Myklestad, 1997; Loh et al., 2004). The oceanic inventory of the semi-labile DOC fraction is estimated to be of about the same order as the atmospheric CO_2 inventory (Mopper and Degens, 1979; Hedges, 1992). The composition of dissolved organic matter in the ocean is still widely unknown (Loh et al., 2004). Both DOC fractions may react to an increase in the ambient seawater temperature, e.g., due to increased bacterial activity at higher temperatures. This feedback is expected to be positive, i.e., enhancing a climatic warming.

7.3.2.2.2 Freshening of the ocean surface

A freshening of the seawater due to additional inputs from melt water (sea ice, ice sheets, shelf ice) under a warmer climate will lead on the average to a negative feedback concerning the atmospheric pCO_2. Of course, the net effect depends on the vertical redistribution of the respective salinity anomaly. The effect would be larger if a melt water lid would cover the ocean rather than the additional freshwater being well mixed with the seawater. For a 0.5 psu decrease of the sea surface salinity, a change of –0.48 to –0.59 µatm in atmospheric pCO_2 results after 100–1000 yr taking into account the solubility effect only, and –2.1 to –3.1 µatm for a combined effect of the temperature increase on solubility and dissociation constants after 100–1000 yr (use of the model of Heinze et al., 2003; see also Plattner et al., 2001; Broecker and Peng, 1986). The expected negative feedback thus is small.

7.3.2.2.3 Rising CO_2 and acidification (pH lowering)

The uptake of anthropogenic CO_2 by the ocean leads to shift in the dissociation of free carbon dioxide to bi-carbonate and carbonate and induces a respective acidification or pH value decrease in seawater (see Box 7.3, but also, e.g., Harvey, 1969; Caldeira and Wickett, 2003) (Figure 7.3.4). This shift in the inorganic carbon equilibrium has consequences for both the inorganic carbon cycle and biological feedback processes.

[INSERT FIGURE 7.3.4 HERE]

For a quantification of the uptake of anthropogenic of CO_2 by the ocean two different issues must be considered: the kinetics of the uptake (how quick or slow is excess CO_2 taken up from the atmosphere) and the ultimate uptake capacity (how much can be stored in the ocean at final equilibrium). For a quick look, one can consider an ocean surface layer of a given thickness and determine how much excess CO_2 from the

atmosphere will be taken up by this layer. This approach has been pursued by Bolin and Eriksson (1959). The simultaneous change in pCO_2 (or $[CO_2]$, i.e., the CO_2 concentration in water, if the solubility is known) and the change in total dissolved inorganic carbon concentration [DIC] in a water parcel of arbitrary volume equilibrating with the atmosphere can be expressed as a ratio called buffer factor or Revelle factor (e.g. Zeebe and Wolf-Gladrow, 2001; after Roger Revelle 1909–1991, TA = const. indicates that the alkalinity of the water – i.e. its ability to dissociate acids such as H_2CO_3 – is assumed to be constant):

$$RF_0 = \{ d[CO_2]/[CO_2] / d[DIC]/[DIC] \}_{TA=const.}$$

For a preindustrial pCO_2 value of 280 μatm this buffer factor amounts to about 8.4. This means that for a 1% change in the ocean storage of DIC the pCO_2 in the water changes by 8.4%. The buffer factor depends on temperature (see also 7.3.2.2.1), salinity (see also 7.3.2.2.2), and the pCO_2 (or pH value, as pH sinks with increasing pCO_2). The buffer factor increases quasi-linearly with rising pCO_2 and reaches a value of about 10.2 at 500 μatm pCO_2 (Figure 7.3.5). This means, that the increase in ultimate buffer capacity of a seawater parcel slows down as pCO_2 rises. This positive feedback of the inorganic oceanic carbon system on climate warming forcing is very well known. Details of its realisation depend on the kinetics for the CO_2 uptake, mainly on the renewal of surface waters by waters which have not yet equilibrated with the atmospheric CO_2. Given that the present ocean circulation would remain constant with further rising atmospheric pCO_2, the stably stratified mid and low latitude oceans will get increasingly less efficient as sinks for atmospheric CO_2 and the high latitude oceans – where deep water production occurs – will relatively gain in importance as "bottleneck" regions for downward CO_2 transport. The fact that the area of stably stratified ocean waters by far exceeds the hydrostatically less stable polar regions, and the anticipated slowing down of meridional overturning circulation, make this feedback quantitatively even more significant.

[INSERT FIGURE 7.3.5 HERE]

The impact of anthropogenic ocean acidification on the ocean saturation state with respect to $CaCO_3$ is already detectable (Feely et al., 2004; Orr et al., 2005). This acidification of seawater may have a significant impact on the biocalcification of marine organisms, corals and calcifying plankton organisms (coccolithophoridae, pteropods, foraminifera) in all surface ocean provinces, (Royal Society, 2005), as well as other bottom dwelling calcifyers in shallow waters (the effect on deep $CaCO_3$ sediments is discussed in a following paragraph). In laboratory experiments with the coccolithophore species *Emiliana huxleyi* and *Gephyrocapsa oceanica*, a significant reduction in $CaCO_3$ (PIC) production and a stimulation of particulate organic carbon (POC) production resulted under high ambient CO_2 partial pressure (Zondervan et al., 2001; Riebesell et al., 2000). Respective studies are being repeated at present, and there are indications that other species also may show different reactions, even with a reversal in the sign of the change (Tortell et al., 2002). Under nitrogen limiting conditions, even a decrease in both $CaCO_3$ production and POC production was detected in a laboratory experiment at high CO_2 partial pressures, so that no conclusive quantification of the $CaCO_3$ feedback is possible at this stage (Sciandra et al., 2003). The relative small negative feedback on a reduced $CaCO_3$ production on atmospheric pCO_2 may be compensated for by a change of the ballast for settling biogenic particles (Heinze, 2004; see also 7.3.2.2.7) and the associated shallowing of remineralization depth levels in the water column for organic carbon. The potential reduction in biocalcification provides probably only a minor feedback, but may have a major ecological impact, such as shifts in species composition. So far an increase of harmful algae blooming is observed, which so far, however, is mainly associated with a warming of the sea surface layer (Mudie et al., 2002; Van Dolah, 2000). Rising pCO_2 leads also to a reduction of coral reefs, which are particularly susceptible to an acidification as they consist on the less stable $CaCO_3$ mineral aragonite (Kleypas et al., 1999; Hughes et al., 2003). Likewise, shallow benthic calcifying organisms such as benthic foraminifera would be affected by the lowering in ocean pH. The feedback on atmospheric CO_2 due to the $CaCO_3$ dissolution would be negative (because the alkalinity changes twice as much as the dissolved organic carbon concentration during $CaCO_3$ dissolution).

While the corrosion of shallow water carbonate depositions and corals due to acidification occurs on a relatively short time scale, increased carbon storage in the ocean leads also to the dissolution of calcareous sediments in the deep sea (Broecker and Takahashi, 1978). This process is well known from sediment core analysis for the past climatic cycles (e.g., Balsam, 1983; Farrell and Prell, 1989). The feedback of $CaCO_3$ sediment dissolution on atmospheric pCO_2 is negative and quantitatively significant on a 10^3–10^5 yr time

scale, where $CaCO_3$ dissolution will account for a 60–70% compensation of the anthropogenic CO_2 emissions, while the ocean water column will account for 22–33% on a time scale of 10^2–10^3 yr and the remaining 7–8% may be in addition compensated by long-term terrestrial weathering cycles involving silicate carbonates (Archer et al., 1998) (Figure 7.3.6). The ultimate extreme long-term overall buffering of the ocean including the $CaCO_3$ sediment feedback amounts to approximately 11/12 of the atmospheric perturbation, leaving 1/11 airborne (Bolin and Eriksson, 1959). Due to the slow $CaCO_3$ buffering mechanism, the mean atmospheric lifetime of anthropogenic CO_2 is estimated to be 30,000-35,000 years (Archer, 2005).

[INSERT FIGURE 7.3.6 HERE]

A potential risk associated with the neutralization of anthropogenic CO_2 through $CaCO_3$ sediment dissolution is the destruction of wide areas of bottom and sediment fauna with so far not assessed impacts on the global biosphere, food chain, geochemical cycling and biodiversity. Potential feedbacks resulting from these potential changes are not known. Even with an immediate stop of excess CO_2 emissions, the anthropogenic CO_2 evasion to the atmosphere would leave its imprint on the marine sediment for the next several ten thousands of years.

Elevated ambient CO_2 levels appear also have an influence on the production rate of POC by marine calcifying plankton organisms (Zondervan et al., 2001). This increased carbon binding under higher CO_2 levels was also observed at three diatom species (diatoms are silicifying phytoplankton organisms) (Riebesell et al., 1993). For regulating the atmospheric pCO_2 it is critical to know, whether these increased carbon fixation rates (which are also observed in terrestrial ecosystems) translate also into increased export production rates. This question so far could not be answered from laboratory experiments. Potentially dedicated in situ CO_2 release experiments may address this question. Studies on the nutrient to carbon ratio in marine phytoplankton have not yet resulted in significant changes of the C:N:P ratio ("Redfield ratio") in organic tissue (Burkhardt et al., 1999) with CO_2 concentration. This insensitivity indicates that the CO_2 fertilisation effect may only be quantitatively significant in areas, were nutrients are not fully used up (such as the HNLC (high-nutrient-low-chlorophyll) areas of the Southern Ocean and few other selected regions). In these areas, however, other limiting factors may inhibit an increased POC production due to other factors such as lack of micronutrients (e.g., iron, zinc, Franck et al., 2003). Overall, a change of net carbon fixation with rising pCO_2 is neither confirmed nor can it be ruled out. Magnitude and sign of the feedback under real world conditions are yet unknown (difficulties due to regional and species dependent conditions; experiments so far very selective; higher growth rates potentially could lead to more pulse like plankton blooms and a net increase in particle export from the euphotic zone).

A lower pH of seawater influences all pH dependent chemical reactions where seawater is involved. Among others, the solubility of iron depends on pH. Measurements on Fe(III) hydroxides revealed a strong pH dependency between pH 2–7, but near constant solubilities in the pH range relevant for seawater (pH 7–8.5) (Byrne and Kester, 1976; Kuma et al., 1996; Liu and Millero, 2002). Therefore, a respective feedback of increased iron availability and stimulation of biological production under higher CO_2 concentrations is unlikely to be significant.

7.3.2.2.4 Changes in cloud cover, sea ice cover, and incoming solar radiation

Climate change will be associated with regional changes in cloud cover, sea ice cover, and hence incoming solar radiation into the surface ocean. Plankton production in the surface ocean depends on light availability and spectral composition (e.g., Jassby and Platt, 1976) and thus changes in the carbon fixation (changes in both the $CaCO_3$ and POC production) are possible due to this shift in light availability. It is not known how the biologically controlled part of the carbon system in the polar oceans will change after a significant retreat of sea ice coverage. The absorption of incoming solar radiation by phytoplankton can regionally be important to feedback on ocean surface temperatures (Wetzel et al., under revision in *2005*; Wetzel at al., 2004). Changes in incoming solar radiation will also be modulated by this feedback into potential temperature changes (see also 7.3.2.2.7). The climate feedback of this process is so far not accurately quantifiable.

7.3.2.2.5 Increasing stratification and reduction in large scale meridional overturning, shift of shelf regimes

The ocean circulation is one of the "governing parameters" for the marine carbon cycle. Changes in the vertical overturning and stratification of the ocean change the supply for nutrients for biological carbon fixation, the alkalinity and dissolved inorganic carbon transport into the surface layer and away from it, and regulate the vertical redistribution of dissolved substances.

In a simplified view one may assume that with a reduction of ocean circulation the rates of biological production may remain identical, because the slowing down of ocean circulation is compensated by a nutrient concentration increase (see Broecker and Peng, 1982; usually the nutrient concentration is an indicator for the age of open ocean waters). However, during the last glacial, a partial decoupling between shallow and deep large scale ocean circulation may have led to a vertical fractionation of nutrient as well as carbon concentrations and an efficient deep ocean storage of atmospherically derived carbon (Boyle, 1988). A respective storage of additional excess anthropogenic CO_2 in the deep-sea by a more sluggish ocean circulation under climatic warming may thus provide a negative feedback to atmospheric CO_2 on millennial time scales (reduced outgassing of already stored carbon). This negative feedback could be enhanced by an acceleration of $CaCO_3$ sediment dissolution in order to compensate for the excess CO_2. In view of the different physical forcing conditions of the late glacial and future ocean circulations, an analog conclusion from the glacial ocean conditions may be misleading here (Crowley, 1990). The magnitude and sign of the feedback are not yet known for future conditions.

A more sluggish ocean circulation and more pronounced density stratification would slow down the vertical transport of carbon and the replenishment of the ocean surface with water which has not yet been in contact with anthropogenic CO_2. This narrowing of the "bottleneck" for anthropogenic CO_2 invasion into the ocean would provide kinetically a significant positive feedback on atmospheric greenhouse gas concentrations (also due to potential increases in N_2O release from the ocean, see 7.3.2.2.7) (Bolin and Eriksson, 1959; see also the coupled climate model simulations by Cox et al., 2000; Friedlingstein et al., 2001). The efficiency of the buffer factor feedback (see 7.3.2.2.3) would be increased by the circulation feedback into a positive climate forcing feedback enhancing warming.

Changes in ocean circulation in the course of a climatic shift can regionally affect shelf sea circulation systems. Different types of shelf sea systems have been identified (Walsh, 1991) that can result in either nutrients plus carbon export from the shallow seas into the open ocean or vice versa a lift of nutrients plus carbon onto the shelf and towards coastal areas. The North Sea may provide regionally a net sink for atmospheric CO_2 (Thomas et al., 2004), but this export will presumably be compensated by a net source in shelf sea systems of different type (Smith and Hollibaugh, 1993, i.e., the extrapolation to all shelf seas worldwide accounting for up to 20% of anthropogenic CO_2 uptake as made by Thomas et al., 2004, is not valid).

In an equilibrium climate including steady state biogeochemical forcing, export and new production would be equal when globally integrated. During shifts of ocean circulation, transient mismatches may occur between global export production of biologically bound carbon plus carbon on one side and new production plus outgassing of carbon in upwelling areas respectively on the other side. Due to the regionally varying conditions and complexity of governing processes respective transient net CO_2 release or uptake events are likely to occur but are difficult to predict in detail.

7.3.2.2.6 Biogeochemical forcing (river loads, aeolian deposition, dust, micronutrients)

Biogeochemical cycling in the ocean is ultimately fuelled by input of matter from the continents through aeolian deposition and river runoff loads (and to some degree also through ground water seeping and inputs from the earth's interior). The ocean water column and top sediment act then as an interface between input of matter and output of matter back to the lithosphere.

Input of carbon (DIC, DOC), alkalinity (ability of seawater to dissociate weak acids; approximated by $[TA] = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]$), phosphate, nitrate (and ammonium), and silicic acid to the ocean takes place mainly through river runoff. The composition of river loads is both influenced by climate and anthropogenic activities. Rising CO_2 levels in the atmosphere and land use may lead to increased chemical and physical weathering resulting in increased carbon and alkalinity loads in rivers (for alkalinity

see Raymond and Cole, 2003; for dissolved organic carbon see Freeman et al., 2004; Hejzlar et al., 2003; Clair et al., 1999). Depending on the lithology and soil composition of the catchment areas, increased levels of alkalinity, DIC, or DOC can lead to local positive or negative feedbacks. Mobilisation of $CaCO_3$ and silicate carbonates from soils and transfer to the ocean will lead to a negative feedback on atmospheric CO_2 (Dupre et al., 2003). Input of DOC and DIC from soils will lead to a positive feedback. Variations in nutrient supply, as induced by anthropogenic activities, can lead to local deviations from the large scale average P:N:C:Si ratios ("Redfield ratios") in marine waters, especially near coasts, and change the biolimiting factors. Nutrient supply to the ocean has been changed through retention of silicic acid in freshwater systems due to the building of water reservoirs (e.g. Humborg et al., 2000) and increased nitrate release from land due to fertilizer use as well as nitrogen deposition from the atmosphere in highly polluted areas (Green et al., 2004; De Leeuw et al., 2001). These supply changes can lead to a species shift, biological production changes, anoxia, and methanogenesis in coastal waters. Nitrogen release through rivers has probably doubled from the beginning of the industrial revolution up to now (Green et al., 2004). Possibly the growth of calcifying organisms relative to silicifying plankton could be stimulated and result in a local positive feedback to atmospheric CO_2.

Deposition of continentally derived matter from the atmosphere to the ocean surface provides an important source of micronutrients and ballast material to the ocean. Iron (also zinc and others, e.g., Frew et al., 2001) is a biolimiting micronutrient. Areas where iron is not supplied by aeolian transport in sufficient amounts tend to be iron limited resulting in elevated surface ocean concentrations of nutrients (HNLC regions). The aeolian supply of these micronutrients in a warmer climate depends on wind patterns, soil humidity, and lithology of land areas. A warmer climate may result on the average in a decrease of dust mobilisation and transport (Mahowald and Luo, 2003; Werner et al., 2002; though land use may result also in increased dust loads, Tegen et al., 2004). See paragraph 7.5.1.1 in this chapter for a detailed discussion on dust to climatically active aerosol. A decrease of dust loads would transfer less soluble or bioavailable iron to the oceans. It thus would lead to net positive feedback towards further increasing CO_2 by a weakening of marine biological production. Reaction of dust particles with anthropogenic SO_2 in the atmosphere, in contrast, may lead to a further mobilization of iron in mineral dust (Meshkhidze et al., 2003) and hence to a net fertilization of ocean waters, thus providing a negative climate feedback. Apart from chemical consequences of atmospheric dust deposition variations, a weakening of dust supply to the ocean surface can lead to a further positive feedback: Less clay ballast material may lead to smaller marine particle aggregates (biogenic matter produced within the ocean plus clay material brought in form the atmosphere) and to slower settling velocities of particles through the water column (Ittekkot, 1993; Haake and Ittekkot, 1990) (Figure 7.3.7). The consequence would be shallower remineralization depth levels and release of DIC higher up in the water column favouring increased outgassing of CO_2 to the atmosphere (see also 7.3.2.2.7).

[INSERT FIGURE 7.3.7 HERE]

7.3.2.2.7 Secondary feedbacks involving marine biological productivity (from changes in species composition and particle flux mode, N_2O cycle, DOC storage, TEP, DMS)

Reactions of the marine carbon cycle to different climatic and anthropogenic boundary conditions can induce a series of further feedbacks to the climate system, which cannot straightforwardly be traced back to one single forcing. Quantifications of these feedback processes in an integrated way are still difficult. Nevertheless these feedback processes have to be addressed. Lack of detailed evidence does not rule out potential surprises within this complex system.

The non-linearity of the marine carbon chemistry can provide a weak negative feedback in absolute terms of atmospheric pCO_2 change. As the partial pressure in seawater increases non-linearly with increasing DIC, the same amount of carbon extracted from the surface ocean by marine biota will lead to a somewhat larger pCO_2 reduction at higher ambient pCO_2. Of course, remineralization of POC compensates for this reduction, so that this negative feedback would only be active at an increase of biogenic particle export production, and would turn into a positive feedback in case of a decrease in export production. The feedback would work instantaneously and is accurately quantifiable at the process level but difficult to quantify for the ocean as a whole.

Changes in plankton species composition and regional shift of high production zones can lead to a series of further feedbacks. Light absorption due to these shifts by oceanic organisms may change and affect the

respective feedback on heating up the ocean surface water (Wetzel et al., *submitted in 2004*; Wetzel at al., 2004). An albedo change can be induced leading to either a negative or positive feedback to climate warming. The increased amount of blooms involving calcifying organisms as indicated for the high northern latitudes (Broerse et al., 2003; Smyth et al., 2004) can lead to a temporarily increased surface ocean albedo, though the effect on the radiation budget is quantitatively small (Tyrell et al., 1999). A positive or negative albedo feedback may also result from an areal reduction of coral reef systems or bleaching of corals, as the sediment composition in shallow water systems in principle influences the reflectance (Werdell and Roesler, 2003) and hence the seawater temperature.

Any ecological changes in the upper ocean may lead to a change in the vertical particle flux mode, in particular concerning the size as well as sinking speed of particle aggregates and the associated remineralization depth horizon. A deepening of this horizon would have the net effect of a surface ocean pCO_2 drawdown, a shallowing would result in an increase of surface ocean pCO_2 (see also 7.3.2.2.6 and 7.3.2.2.3). There exists evidence for $CaCO_3$ to have an important ballast role in marine particle aggregates (Armstrong et al., 2002; Klaas and Archer, 2002). Therefore, any weakening of $CaCO_3$ export production may lead to a decrease in particle settling velocities potentially compensating (Heinze, 2004) or even overriding the negative feedback effect of increased alkalinity levels with less $CaCO_3$ production. Changes in the supply of iron for biological production can influence the thickness of biogenic silica shells of diatoms. Under lower iron availability, these opaline shells would be thicker and hence would increase particle settling velocities (Hutchins and Bruland, 1998). This negative feedback, however, may be overridden by the weaker biological production itself at iron stress plus the favouring of $CaCO_3$ shell material production if silicon is used up quicker as in a reference state. It is possible, that a surface nutrient depletion under global warming conditions leads to a weakening of biogenic silica production and a reduction of the ballast effect also due to less diatoms in marine particle rain. The corresponding favoring of small particles may lead to a positive feedback on atmospheric pCO_2 (Bopp et al., submitted in 2005). The marine inventory and distribution of DOC (dissolved organic carbon) may be susceptible to species shifts, warming, and CO_2 partial pressure, though no conclusive quantification of respective feedbacks can be provided at present (Engel et al., 2004). Potentially increased production of TEP (transparent exopolymer particles; Alldredge et al., 1993; Passow, 2002) during the build-up of biogenic particulate can accelerate the particle sinking through aggregate formation (Alldredge et al., 1993; Kiørboe et al., 1996; Passow et al., 2001).

Ecological changes in conjunction with circulation changes can lead to either increases or decreases of low oxygen or even anoxic zones in the world ocean. Under oxygen depletion, denitrifying organisms can use the oxygen in nitrate for remineralization of organic matter. During the conversion of nitrate to molecular nitrogen, N_2O also is produced which shows up as maxima below and above the O_2 minimum zones (Zehr and Ward, 2002). Outgassing of this N_2O would contribute to a further increase of greenhouse gas concentrations in the atmosphere. Associated with anoxic marine conditions are further enhanced mobilizations of methane (Fuhrmann and Capone, 1991). On the other hand, nitrification at the sea surface can occur through biological N_2 fixation in coastal areas (Herbert, 1999) as well as in the open ocean (here in particular through the cyanobacterium *Trichodesmium*, Capone et al., 1997; Orcutt et al., 2001). N_2 fixation in principle would provide a means of strengthening biological carbon fixation; however, during N_2 fixation N_2O also is produced which at least may partially compensate for such a negative feedback. For a lowering of pH values in seawaters, a reduction of N_2 fixation has been indicated (Huesemann et al., 2002). An increase of iron would stimulate N_2 fixation, so this process also depends on the iron supply (Raven and Falkowski, 1999) which may increase due to mobilisation in a more acid environment or decrease with less dust supply in a warmer and more humid climate.

Dimethylsulphide (DMS) and its precursor DMSP are produced by a few classes of phytoplankton including specifically coccolithophores ($CaCO_3$ producing phytoplankton) (Matrai and Keller, 1993). DMS can be of climatic relevance as it can provide the basis for cloud condensation nuclei once it enters the atmosphere as marine aerosol (Shaw, 1983; Charlson et al., 1987; see also section 7.5.1.4 in this report. The “CLAW” (an acronym formed from the initials of the authors of Charlson et al., 1987) hypothesis suggests the following negative feedback loop: An increase in temperature and solar forcing would lead to an increase in biological production, which would induce a cooling effect due to production of DMS (and hence sulphate aerosol) and an associated cloud albedo (and possibly a reduction of atmospheric CO_2 through increased biological production in the ocean). So far, modelling studies on DMS production in a future warmer climate indicate

an increase of DMS production by 3% for a doubling (Bopp et al., 2004) and 14% for a tripling (Gabric et al., 2004) of the preindustrial pCO_2 in the atmosphere. The largest changes occur at high latitudes (specifically in the Southern Ocean) with only small changes in the tropics and sub-tropics. The expected negative feedback on radiative climate forcing is expected to be globally relatively small (–0.05 W m^{-2} for $2\times CO_2$, Bopp et al., 2004), but may locally become significant.

7.3.2.2.8 Destabilization of methane gas hydrates

Marine gas hydrates consist mostly of methane (CH_4) and occur in sediment pore space under specific conditions of low temperatures, high pressure, and sufficient CH_4 availability, in particular at continental margins (Kvenvolden, 1993). If the state variables pressure and temperature are changed, CH_4 gas can potentially be set free in large quantities, an event which may have contributed to the latest Paleocene thermal maximum 55 million years before present (Dickens, 2001). The significance of gas hydrates for global change is not yet clarified (Kvenvolden, 2000, 2002). Potentially, larger amounts of CH_4 hydrate can be set free from the oceans also due to statically unstable continental margins and technical seabed installations (Beauchamp, 2004). It is possible that CH_4 from hydrates – once it is set free – is oxidized to CO_2 before entering the atmosphere (and thus have a less large impact than CH_4 itself on a further greenhouse gas increase) and may lead to massive microbial blooms in the world ocean (Valentine et al., 2001; Elvert et al., 2001). Potential destabilisation of gas hydrates would provide a positive feedback to global warming. Recently, the existing reservoir size CH_4 of gas hydrates was correct down with respect to previous estimates (ca. 500–2500 Pg-C) (Milkov, 2004). The potential use of these hydrates as a fossil fuel resource will have to be taken into account in emission scenarios.

7.3.2.2.9 Purposeful CO_2 storage in the ocean as an anthropogenic feedback to rising atmospheric pCO_2

Next to storage of anthropogenic CO_2 in terrestrial geological reservoirs, two options for purposeful oceanic CO_2 storage have been discussed: deep injection of CO_2 into the water column (e.g., Brewer et al., 2000) and large scale ocean surface fertilisation (e.g., Benemann, 1992). Purposeful storage of CO_2 would possibly provide a temporary negative feedback to climate change, while the long-term gross feedback would be zero or could potentially even turn into a positive one, e.g. if humans do not favour an energy saving strategy, but use the sequestration option to burn even more fossil fuel. Direct injection of anthropogenic CO_2 after its capture in the deep North Pacific Ocean appears to be the most efficient method (Orr, 2002), especially when the CO_2 is stored as liquid CO_2 lakes in isolated bathymetric features. The mitigation option of direct CO_2 injection into the water column is discussed in detail in the IPCC Special Report on Carbon Dioxide Storage and Capture, Chapter 6 (Caldeira et al., 2005.) The negative side effect on the local deep-sea ecosystems and unknown feedbacks of the bottom biogeochemical systems has to be taken into account. The impact of local changes of the chemical environment near CO_2 injection sites and liquid CO_2 pools over entire biomes and larger timescales is unclear (Caldeira et al., 2005). Fertilisation of the ocean in HNLC regions (especially the Southern Ocean) through addition of micronutrients, in particular iron, has been tested in several field experiments (e.g., Bakker et al., 2005; De Baar et al., 2005; Bishop et al., 2004). The poor efficiency of purposeful fertilisation has been documented over more than 10 years of research (De Baar, 1992; Watson et al., 1994; Cicerone et al., 2004; Zeebe and Archer, 2005). Therefore, and in view of its negative ecological and climatic side effects (Chisholm et al., 2004; Fuhrmann and Capone, 1991), artificial ocean fertilisation can practically be ruled out as a useful mitigation option. In any case, once it has re-entered the oceanic water column, the artificially stored carbon will reappear at the ocean surface – except for a small fraction within in each mixing cycle that becomes neutralized by $CaCO_3$ sediment dissolution – on a timescale of 300-1000 years (Caldeira et al., 2005). Any deliberate ocean CO_2 storage, therefore, would remain a temporary anthropogenic feedback to rising atmospheric CO_2 concentrations.

7.3.2.3 Feedbacks at the glacial-interglacial scale

From ice core measurements, it has been shown that the global atmospheric concentrations of the greenhouse gases CO_2 and CH_4 have changed with glacial-interglacial temperature and climate variations (see paleo climate carbon Box 6.23 and Sections 6.3.3. and 6.5.3 in Chapter 6; Monnin *et al.*, 2001). The changes were in a direction towards an amplification of the cooling from interglacial to glacial values starting at about 280 ppm and 700 ppb decreasing to 190 ppm and 450 ppb respectively. The negative trend in CH_4 values with temperature is attributed mainly to changes in the terrestrial vegetation with a reduction of wetlands and an increase in permafrost areas. The lower glacial CO_2 values must be caused by marine processes as the reduction of terrestrial vegetation under colder and dryer conditions would have caused a relative increase of atmospheric CO_2 (Kaplan *et al.*, 2002). In order to compensate for this terrestrial carbon release, even a

somewhat larger drawdown of atmospheric CO_2 than 90 ppm must be explained by oceanic processes. These have not yet been conclusively identified. Therefore, a significant gap in our knowledge of ocean carbon cycle climate feedbacks still remains (Archer *et al.*, 2000; Sigman and Boyle, 2000). As in the glacial ocean, we expect a slowing down of oceanic overturning during a future climate change. The mode of ocean circulation, e.g. differences in shallow and deep circulation, may be considerably different from the glacial situation. Also the ca. 120 m interglacial-glacial sea level lowering may have led to a considerably different biogeochemical forcing of the open ocean than today. For these reasons, the paleo-record may not be an overall reliable analog for the future evolution of carbon cycle feedback processes.

7.3.3 Interannual and Regional Variation in Carbon Fluxes Inferred from Observations

7.3.3.1 Global budget - interannual fluctuations

The observed rate of atmospheric CO_2 increase exhibits large variations every 2-4 years (see Figure 2.4), which cannot be accounted for by the small year-to-year variability (IAV) in global fossil CO_2 emissions. This implies the existence of year-to-year fluctuations in the CO_2 uptake by land and ocean regions. Over the past two decades, low CO_2 uptake rates (i.e., high atmospheric growth rates) occurred in 1987, 1994–1995, 1997–1998, and in 2002–2003. The record lowest uptake of 0.1 Pg-C only (highest atmospheric growth rate of 2.7 ppm) occurred in 1998 during the strongest El Niño of the 20th century. The yearly increase in atmospheric CO_2 in 2002 and 2003 exceeded for the first time 2 ppm yr^{-1} in two consecutive years, while there was only a rather weak El Niño. Conversely, high CO_2 uptake (low growth rates) occurred in 1981, 1992–1993 and 1996–1997. Generally, the high and low CO_2 uptake periods correspond to the succession of La Niña and El Niño episodes, as has long been recognized (Bacastow, 1976), although the relationship between CO_2 growth and the Southern Oscillation Index is evolving with time (Lintner, 2002). There are at least two remarkable exceptions to this, the 1992–1993 high uptake period popularly called the "post Pinatubo" period, and 2002–2003 low uptake period where for the first time since observations began, low uptake did not coincide with any developing El Niño.

[INSERT FIGURE 7.3.8 HERE]

Since the TAR, a consensus has emerged from top-down inversion studies that the CO_2 fluxes IAV is mostly due to land fluxes, and that the Tropical lands contribute strongly to the global terrestrial IAV (Figure 7.3.8). Such a predominant terrestrial IAV forcing is indicated from: (1) CO_2 concentrations observed at different stations and used in atmospheric inversions by Bousquet et al. (2000), Rödenbeck et al. (2003) and Baker et al. (2004); (2) consistent relationships between $\delta^{13}C$ and CO_2 globally (Francey et al., 2001) or zonally, and (3) direct measurement of O_2 and CO_2 since 1991 (see Figure 2.2; Manning, 2001; Manning and Keeling, 2005).

7.3.3.2 Bottom-up estimates of ocean atmosphere carbon fluxes from observations

Due to the high variability of air-sea CO_2 fluxes, the still scarce direct measurements of sea surface pCO_2 and the varying wind speeds, it is difficult to firmly assess changes in the carbon flux between ocean and atmosphere over the past decades (see Chapter 5, Section 5.4.2.2). Takahashi et al. (2002) normalize all available sea surface pCO_2 measurements between 1956 and 2000 for the reference year 1995 to come up with an annual oceanic net uptake of about 2.2 (±0.5) Pg C yr^{-1}. This number may be biased due to special wind speed conditions in 1995 and errors in the height of the wind speed data applied. Sabine et al. (2004) estimate the total oceanic uptake of anthropogenic CO_2 to be 118(±19) Pg C for the period 18001994 from inorganic carbon measurements and a tracer-based technique for separation of anthropogenic carbon from natural carbon in the ocean water column. This indirect method can lead to an overestimate of the carbon uptake which can be corrected to 111(±25) Pg C for the period 1800–1994 (Keeling, 2005). Forward model simulations with a biogeochemical ocean general circulation model forced by daily NCEP/NCAR reanalysis data from 1948–2003 yield an oceanic net CO_2 uptake of 1.49 Pg C yr^{-1} for the years 1980–1989 and 1.74 Pg C yr^{-1} for 1990–1999 (Wetzel et al., 2005). From the beginning of the industrial revolution up to now, the Southern Ocean turned from a source to a net sink of atmospheric CO_2 (Hoppema, 2004). The North Atlantic CO_2 sink strength is weakening in recent years (Lefèvre et al., 2004). ENSO events and decadal variability have a strong impact on the net marine CO_2 uptake in the Pacific Ocean (Takahashi et al., 2003; Wetzel et al., 2005).

7.3.3.4 Regional carbon fluxes inferred from bottom-up approaches

7.3.3.4.1 Terrestrial observations

Locally, stand-level biometric measurements can be used to estimate the carbon balance of land ecosystems (Net Biome Productivity or NBP) but they are difficult to upscale since one must account for soil carbon changes and for the impact of disturbances in controlling the long term averaged carbon balance (Schulze et al., 2000; Korner, 2003). In boreal forests for example, carbon losses caused by disturbances and consumption of forest products comprises about 20% of NPP and can exceed the ecosystem carbon sink (Shvidenko and Nilsson, 2003). One cannot simply scale NBP from limited duration (less than 10 years) eddy-covariance NEE data (Baldocchi et al., 2001) because most eddy flux towers are located in young or middle-aged stands and do not sample the effect of disturbances, and because the length of those records is too short to average out the large fluctuations in NEE generally observed from one year to the next. The alternative to measure stand NBP is to use chronosequences (e.g., Mund et al., 2002).

Regionally, extensive forest biomass inventory measurements estimate the measured volume growth of stem wood and changes in forest area, the modelled fine litter and coarse debris production, corrected for harvest and slash production in managed forests using bookkeeping type of models and other information for upscaling. The advantage here is covering and understanding spatial variability, at the expense of detailed knowledge of component processes. Systematic forest biomass inventories have been developed in temperate and boreal forests in North America, Western Europe, Russia, China to measure the commercial value of wood. In the tropics where there is no commercial forest inventory, stem growth measurements have been carried out as part of research networks (Malhi et al., 2004; Phillips et al., 1998).

7.3.3.4.2 Terrestrial models

Many spatially explicit models of terrestrial ecosystems have been developed to analyze and predict the response of terrestrial carbon pools and fluxes to changing climate and atmospheric composition, and more recently to land use and management practices (e.g., McGuire et al., 2001). These models, similar to those used in the TAR, encapsulate biogeochemical processes responsible for biomass production as driven by climate and radiation, and calculate NPP as the difference between photosynthesis and autotrophic respiration components. After mortality, litter and soil organic matter decomposition is calculated, allowing estimates of the ecosystem carbon balance. The development of more realistic process-driven models enables the handling of diverse resolutions and scales, and the use of assimilation methods to allow the efficient processing of large amounts of data, particularly when using remote sensing observations (e.g. Wang and McGregor, 2003). The current generation of global terrestrial models are generally very crude in their description of 1) forest growth and management, 2) carbon cycling over cultivated lands and wetland, 3) soil organic matter decomposition, 4) frozen soil carbon dynamics, 5) the effects of land-use change and fire, 6) coupling between carbon and nutrients cycling, 7) absorption of radiation by canopies, 8) effects of biodiversity.

7.3.3.4.3 Attribution of bottom-up regional carbon fluxes to processes

It is fair to say that there are problems of quantifying NBP at various scales, and attributing it to the controlling processes. Firstly, at the spatial scale of stands, NBP can only be defined from the in situ carbon balance and thus does not include the fluxes of “displaced” carbon such as the losses to streams and rivers, or the fate of wood products in harvested forests. A second issue deals with temporal scales, because NBP contains “background” fluxes such as the formation of charcoal in fire-disturbed forests, the inclusion of carbon into mineral soil horizons, or the entrainment of rock-weathered DIC to the ocean. Those fluxes are part of the “background” natural carbon cycle and evolve on long time scales, whereas we are interested in NBP as the anomalous terrestrial uptake occurring on decadal time scales in response to the current perturbation of the carbon cycle. It is virtually impossible to separate “background natural” from “anthropogenic” NBP In field studies, except maybe when using the bomb-radiocarbon signal to determine the soil component of ecosystem carbon storage (e.g., Trumbore et al., 1996). Ranges of NBP estimates for three distinct biomes are presented in Figure 7.3.9.

[INSERT FIGURE 7.3.9 HERE]

7.3.3.5 Regional carbon fluxes inferred from atmospheric CO_2 observations and inverse modelling

7.3.3.5.1 Background

The atmosphere mixes and integrates surface fluxes that vary spatially and temporally. The distribution and temporal evolution of CO_2 in the atmosphere can be used to quantify surface fluxes, using numerical models of atmospheric transport combined with a representation of surface exchange fluxes. Typically the sub-model defining surface flux is adjusted to provide the best match to observed concentrations. This approach ("inverse modelling") may be adapted to the specific circumstances at the scale of continents or large ocean gyres, where the precision and representativeness of the measurements should match that of the relevant major source and sink processes. Because of the long atmospheric life time of CO_2, the horizontal gradients of concentrations which carry the information on the magnitude and spatial distribution of sources and sinks are quite small, and remain difficult to define with the present network of stations. In addition, atmospheric transport models are imperfect, to a largely unknown extent, and the inverted fluxes consequently depend on the model used.

7.3.3.5.2 Atmospheric measurements

Atmospheric transport mixes air on the global scale on time scales of roughly a year. Therefore, the gradients in atmospheric CO_2 concentrations associated with regional fluxes are small compared to the background value of CO_2. The global network of atmospheric CO_2 concentration measurement sites is shown in Chapter 2 (see also WMO/GAW, 2000). Most of these sites are discrete sampling sites, where flasks are collected approximately once a week, and there are a small number of in situ continuous stations. The network consists of different national networks and programs, with the US NOAA/CMDL contributing the largest dataset. The atmospheric network is much denser over the oceans than over the continents, and much denser in the Northern mid-to-high latitudes than in the Tropics, or in the Southern high latitudes. Fluxes upwind of areas with denser coverage of stations are better constrained by the data.

7.3.3.5.3 Atmospheric inversion models

Using as an input the atmospheric CO_2 data described above, the atmospheric inverse models determine a global distribution of surface CO_2 sources and sinks which minimize a mismatch between modelled and observed gradients of concentrations, accounting for measurements errors. Bayesian synthesis inversions, the most widely used method pioneered by (Enting et al., 1995) are required simultaneously to fit optimally the available data while simultaneously preserving information present in an *a priori* flux model. When doing so, a number of modes of variability of the fluxes are explicitly solved for utilizing the information contained in the atmospheric observations, while a number of other modes are constrained by the *a priori* settings. One can explicitly propagate errors on atmospheric measurements and errors on the prior fluxes onto the sought fluxes, thus delivering a very useful set of uncertainty estimates. Generally, Gaussian random errors are assumed for the measurements and for the a priori fluxes, translating into Gaussian errors on the inverted fluxes. We report this *random uncertainty* as colored bars in the inversion fluxes of Figure 7.3.10.

[INSERT FIGURE 7.3.10 HERE]

In addition, inverse model results are biased by a certain choice of arbitrary settings. Those biases are difficult to quantify, and even harder to relate to the unknown truth. Arbitrary settings which can bias inverted fluxes include 1) the choice of a particular atmospheric transport model, 2) the assumed ability for this model to match a point observation with a grid-box model simulation (representation error), 3) the choice of fixed *a priori* temporal flux variations (e.g., as in Gurney et al., 2002; Gurney et al., 2003) or spatial flux variation within a given region (see discussion in Kaminski et al., 2001). There is also a bias arising from the fact that fossil fuel emissions are generally considered to be of perfectly known magnitude and patterns, so that their effect can be easily modelled and subtracted from atmospheric CO_2 data to solve for "residual" land and ocean fluxes. These various biases translate into a spread in the inverted fluxes. A lower limit to the magnitude of these biases can be obtained by performing an ensemble of inversions where the arbitrary settings are varied (e.g., using different transport models through the same inversion procedure, as done by the TRANSCOM-3 project ref). We report the *spread of mean fluxes* deduced from inversion ensembles with different settings as a grey bar in Figure 7.3.10.

The fluxes inferred from inverse models also depend critically on how the atmospheric observations are treated. Inhomogeneities and gaps in the data are inevitable, and the increasing number of sites in the network generates spurious changing estimates of regional fluxes as an artefact of adding stations downwind

of regions previously not well constrained. Further, network inhomogeneities, coverage denser over oceans (Patra et al., 2005), and calibration are also sources of bias on regional fluxes inferred from inversions. Several studies showed that the network is not dense enough for stations to be redundant. That means that in some cases, adding or removing sites (Bousquet et al., 1999; Law et al., 2003), or varying errors on the data (Krakauer et al., 2004) have strong implications for the inverted fluxes.

7.3.3.5.4 Atmospheric inversion results: mean regional fluxes

In general, confidence in the long-term mean fluxes is lower than confidence in the year-to-year variations of the fluxes. Many inversion ensembles, each with different settings, have been produced since the TAR (Baker et al., 2004; Gurney et al., 2002; Gurney et al., 2003; Peylin et al., 2002, 2005a; Rödenbeck et al., 2003). An updated breakdown of oceans and land fluxes for large latitude bands is given in Figure 7.3.10. Inversion results are reported with their random estimation errors and a necessarily imperfect estimate of the (range of) bias implied by various settings in each ensemble. In the TRANSCOM-3 project 16 different transport models were compared through the same inverse procedure (Gurney et al., 2002, 2003). The results showed that differences between transport models cause uncertainties of smaller (or similar) magnitude than the random estimation error. This means that, for most regions, adding new measurements would be most beneficial for inversions. Over northern land regions, (e.g., boreal Asia), the models differ strongly in the way they respond to the seasonal cycle of the terrestrial CO_2 exchange, so that improving models is needed. Tropical regions, in particular tropical landmasses, could not be adequately constrained because of insufficient data, a general feature of all current inversions.

All possible inversion settings were certainly not explored in the TRANSCOM-3 ensembles. In particular there was no assessment of the effect of the 'a priori aggregation' bias resulting from setting a fixed spatial pattern to the fluxes within each region. Inverting the fluxes at a much higher spatial resolution, up to the model grid itself (Kaminski et al., 1999; Rödenbeck et al., 2003). Peylin et al., 2005b) overcomes that limitation, but it implies nevertheless that the a priori flux model still influences the inversion result. Figure 7.3.10 shows differences above their 1-σ errors between TRANSCOM-3 and Rödenbeck et al. (2003) ensembles over tropical and northern continents for the period 1992–1996. Part of these differences can be explained by different methodologies, in particular a different network of 35 stations (monthly flask data) in Rödenbeck et al., (2003) vs. 76 stations (smoothed flask data) in TRANSCOM-3. Figure 7.3.11 gives a range of 0.4–2.3 Pg-C y^{-1} for uptake in Northern continents, and a range of 0.4 Pg-C y^{-1} sink to 1.8 Pg-C y^{-1} source over tropical continents during 1992–1996. Compensation effects obviously exist between the inversion results in the North and in the Tropics. Note that the inverse results for the 1992-1996 time period appear to confirm the anomalously strong uptake of CO_2 by terrestrial systems, although in some cases information on O_2 or $\delta^{13}CO_2$ was used in the inversion.

[INSERT FIGURE 7.3.11 HERE]

Figure 7.3.11 gives the breakdown of inversion fluxes for five large regions of the Northern Hemisphere: North America, North Atlantic, Europe, North Asia, and North Pacific. There are important differences in the mean of different ensembles, except over North America where all inversion fluxes generally agree within their errors to a mean sink ranging between 0.6 and 1.1 Pg-C y^{-1}, although large uncertainties still pertain to that estimate (full range 0 to 1.6 Pg-C y^{-1}). Larger differences between the inversion ensembles are found over Europe (range –0.9 to +0.2 Pg-C y^{-1}) and over North Asia (range -1.2 to +0.3 Pg-C y^{-1}), a latter region where inversions are sensitive to transport model choices, as seen from the large grey error in Figure 7.3.11.

What is robust? i.e., inversion ensembles agree within their errors

- The ocean uptake deduced from all inversions is higher in the Northern Extratropics than in the Southern Extratropics.
- The tropical oceans are outgassing CO_2 to the atmosphere (range 0 to 1.5 Pg-C y^{-1}), as expected from upwelling of CO_2-rich waters (Feely et al., 1999).
- The global land vs. ocean flux partitioning from inversions is within the uncertainty of the O_2 derived global budgets. This result cannot serve as an independent verification since some inversions precisely use that constraint.
- The Northern Hemisphere land fluxes are better constrained than the tropical land fluxes.

- There is a mean terrestrial sink in the Northern Hemisphere, with a fraction in North America, in Europe and Northern Asia. Very large uncertainties pertain to individual regional flux estimates, but the smallest spread is found over North America.
- The North American carbon sink estimated by recent inversions is large, but on average lower than an earlier, widely cited study (Fan et al., 1998). Nevertheless the estimate by Fan et al. (1998) remains within the inversion range of uncertainty.

What is not robust? i.e., inversion ensembles disagree within their errors

- The partition of terrestrial fluxes between northern and tropical lands.
- The sink function of tropical lands: if tropical lands inverted fluxes give a CO_2 source of similar magnitude than tropical deforestation in Table 7.3.2, then tropical undisturbed terrestrial ecosystems are about carbon neutral; if tropical lands inverted fluxes are a net sink of CO_2, then undisturbed tropical ecosystems are a huge sink of CO_2.
- The mean flux estimate of most individual regions is not robust through inversions.

7.3.3.5.5 Mean regional fluxes, bottom-up estimates and inversions

Bottom up estimates of regional carbon fluxes have been summarized in Section 7.3.1.4.4. Comparing inversion estimates of large-scale sources and sinks with bottom up estimates is not an easy task because 1) inversion fluxes may already contain a certain amount of *a priori* knowledge of bottom-up fluxes, especially of air-sea fluxes, so that the two approaches are not fully independent 2) the time period for which inversion models and bottom-up estimates are available is often not consistent, in the presence of fluxes that can vary substantially from one year to the next (see 7.3.1.4.5), 3) the distribution of CO_2 fluxes given by inversions does not match the distribution of carbon storage generally given by bottom up , in the presence of lateral fluxes. Lateral fluxes act to transport carbon away from where CO_2 is exchanged to or from the atmosphere, in such a manner that the regional changes in *carbon storage* have a geographically distinct distribution than the CO_2 fluxes (Tans et al., 1995; Sarmiento and Sundquist, 1993). Bottom up methods are measuring carbon storage changes, and inversions CO_2 fluxes. Lateral fluxes include the emissions of reduced carbon compounds (VOCs, CO, CH_4) by ecosystems and anthropogenic combustion processes, transported and oxidized by OH chemistry (Enting and Mansbridge, 1991: Folberth et al., 2005: Suntharalingam et al., 2005), trade of wood and food products harvested from ecosystems (Ciais et al., 2005; Imhoff et al., 2004), and riverine transport of dissolved inorganic and organic carbon to the ocean (Aumont et al., 2001; Meybeck, 1987). The main results from comparison of bottom-up with inversion mean fluxes are:

- Inversions determine a higher ocean sink in the Northern extratropics than in the Southern extratropics, in contrast with oceanographic estimates (Takahashi et al., 2002; Takahashi et al., 1999), although new measurements of ΔpCO_2 in winter over the Southern Ocean may reconcile both estimates (Metzl et al., 1999).
- Inversions tend to estimate higher terrestrial carbon uptake over Northern Hemisphere lands than bottom up estimates (Nabuurs et al., 1997; Goodale et al., 2002; Pacala et al., 2001; Janssens et al., 2003; Shvidenko and Nilsson, 2003) (see Figure 7.3.11), but part of this discrepancy can be explained by laterally-transported carbon via reduced carbon compounds, rivers and food and wood trade.
- Inversions determine that tropical land regions are either close to neutral, or a sink of CO_2, qualitatively in agreement with limited forest biomass changes measurements in the Amazon (Phillips et al., 1998; Malhi and Grace, 2000).

7.3.3.5.6 Atmospheric inversion results: interannual changes in regional fluxes

Three inversion ensembles calculated the changes in monthly regional fluxes over the last two decades (Bousquet et al., 2000; Rödenbeck et al., 2003). As for mean regional fluxes, these studies report a random error and the error range of sensitivity inversions with different settings (set of atmospheric stations, atmospheric measurement errors, transport model, the choice, a priori flux constraints, spatial or temporal scales at which the fluxes are solved for).

Bousquet et al., (2000) used large regions and varied different inversion settings for the period 1980–1998. They found that the year-to-year regional flux changes could be more robustly inverted than their mean values.

Rödenbeck et al. (2003) used one transport model and an inversion at the resolution of model grid for the period 1982–2002, and changed different inversion settings. In particular, different stations from the CMDL network (see Figure 2.3) were used, from 11 sites up 35 sites, showing an impact on the inversion mean fluxes but less on broad regions variability. The effect of using interannually varying winds was concluded to have a relatively small impact on the fluxes variations.

Baker et al. () used large regions but 13 different transport models for the period 1988–2002. Their results suggest that the spread of transport models has a lesser impact on the year-to-year regional flux anomalies than on the mean fluxes (see 7.3.1.3.3). In other words, the changes of regional fluxes owe more to errors in atmospheric data, a priori constraints, than to inter-model differences.

What is robust? i.e., inversion ensembles agree within their errors

- At the scale of the globe, the IAV of land fluxes is larger than the one of ocean fluxes.
- At the scale of large latitude bands the IAV of land fluxes is larger than the one of ocean fluxes
- Tropical land fluxes exhibit on average a larger variability than temperate and boreal land fluxes, and their variability suggests unambiguously an El Niño forcing, with anomalous sources during El Niño episodes in 1982–1983, 1986–1987 and 1997–1998, and anomalous sinks during La Niña episodes.
- The 1997–1998 high CO_2 growth rate episode is attributed to an abnormal source in the Tropics, with a significant fraction of it in South East Asia, in good agreement with bottom up estimates (fires in Indonesian moist forests)
- The Tropical Pacific ocean is a region where the significance of the inversion results for year-to-year changes is high, in good agreement with bottom up estimates (ΔpCO_2 observations)

What is not robust? i.e., inversion ensembles disagree within their errors

- The 1992–1993 low CO_2 growth rate episode during the post Pinatubo climate disturbance is attributed either to the Northern mid latitudes by Bousquet et al. and to the Tropical lands by the two other ensembles
- At the scale of continents or ocean basins in the Northern Hemisphere, the errors increase and the significance of the inverted flux inter-annual changes is quickly lost.

7.3.3.5.7 Year to year changes in regional fluxes, inversion and bottom-up

- Globally, inversion results agree with independent ocean carbon model calculations on the rather small variability of air sea fluxes (±0.5 Pg-C y^{-1} between extremes), and conversely on to large variability of land fluxes (±4 Pg-C y^{-1} between extremes). Yet, inversions and ocean models differ on the geographic contributions to the year-to-year variability.
- In the Northern Extratropics (Figure 7.3.11), Baker et al. (year?) and Bousquet et al. (year?) obtain a significant variability in air sea fluxes, in contrast to Rödenbeck et al. (2003). On the one hand, over the North Atlantic ocean, Gruber et al. extrapolated a large variability comparable to Bousquet et al. (year?) (extremes of ± 0.3 Pg-C y^{-1}) using data from the Bermuda station during 1984–2000. On the other hand, for that region McKinley et al. (2004) modelled a small variability (extremes of ±0.1 Pg-C y^{-1}) comparable to the one of Rödenbeck et al. (2003), and suggested that a larger variability could be an effect of the large region settings (ref). Note that all inversions are not strictly independent from bottom-up studies, as they include a priori information to constrain the air-sea flux variations, which may in turn influence their results.
- El Niño and La Niña episodes force respectively a large release and uptake of CO_2 over the tropical continents, in particular over the Amazon. Flux anomalies are large (2 -3 Pg-C y^{-1}) and in general good agreement with many bottom-up biospheric model calculations. In the Equatorial Pacific ocean, all inversions obtain a flux variability which compares well in magnitude and timing with ocean models results (Le Quere et al., 2000, 2003; McKinley et al., 2003, 2004) and with ΔpCO_2 observations (Feely et al., 2002). The flux variability in that region is paced by El Niño, with a smaller net CO_2 source to the when upwelling of CO_2-rich waters diminishes.
- The 1992–1993 low CO_2 growth rate episode during the post Pinatubo climate disturbance is not a robust result of inversions. Bousquet et al. (2000) find an enhanced terrestrial uptake in the Northern Hemisphere, while Baker et al. (year?) and Rödenbeck et al. (year?) place it in the Tropics. Analysis

of remotely-sensed vegetation activity and a terrestrial carbon model calculation by Lucht et al. (2002) produces good agreement with Bousquet et al. Apart from higher NPP, lower respiration or a combination of both conventionally expected from the cooling, an overall increase in photosynthesis may have occurred via the increased fraction of diffuse sunlight (Roderick and Farquhar, 2001). However, this increase is not supported by the changes in the NDVI or the seasonal cycle of CO_2 post-Pinatubo (Angert et al., 2004).

- The 1997–1998 high CO_2 growth rate period can be consistently explained by abnormally high and intense fire emissions. For Indonesia alone, a source of +0.8 to +2.6 Pg-C from peat forest fires was estimated by Page et al. (2002). For the globe, approximately 2/3 of the 1997–1998 growth rate excess was attributed to fire emission anomalies, with main contributors South East Asia (60%), South America (30%) and a small Siberian contribution (van der Werf et al., 2004). Similarly, Langenfelds et al. (2002) analyzed the correlations in the interannual growth rate of CO_2 and other species at 10 stations and linked the 1997–1998 (and the 1994–1995) anomalies and to high fires emissions as a single process. The relationship between El Niño and CO_2 emissions from fires is however not uniform, with for instance in Africa drier conditions determining less fire emissions due to less biomass. In addition, co-varying processes such as reduced NPP caused by the dry conditions over tropical forests during El Niño episodes may be superimposed on fire emissions.

7.3.4 Coupled Climate-Carbon Cycle Projections

7.3.4.1 Introduction

The majority of model simulations of future climate prescribe future scenarios for global CO_2 concentrations using relatively simple offline carbon cycle models. Hence model projections do not account for two-way coupling between climate change and the carbon cycle. But we know that reservoirs of carbon on land and in the ocean respond to changes in climate. Global concentrations of atmospheric CO_2 have been observed to respond to the El Niño Southern Oscillation and Arctic Oscillation (Jones et al., 2001; Bousquet et al., 2000; Rayner et al., 1999; Lintner, 2002; Russell and Wallace, 2004) and to the perturbation of climate and aerosol scatter from the Pinatubo volcanic eruption (Hansen et al., 1996; Jones and Cox, 2001; Lucht et al., 2002; Angert et al., 2004).

The TAR reported two initial climate projections using AOGCMs with interactive carbon cycles. Both indicated positive feedback due largely to impacts of climate warming on land carbon storage (Cox et al., 2000; Friedlingstein et al., 2001), but the magnitude of the feedback varied markedly between the models (Friedlingstein et al., 2003). Since the TAR a number of other climate modelling groups have completed climate-carbon cycle projections (Thompson et al., 2004; Matthews et al., 2004a, b; Zeng et al., 2004, Brovkin et al., 2004; Raddatz et al., 2005; Fung et al., 2005; Kawamiya et al., 2005; Sitch et al., 2005), as part of the Coupled Climate-Carbon Cycle Model Intercomparison Project (C^4MIP). The models involved in C^4MIP differ in the complexity of their components (Table 7.3.4).

Table 7.3.4. Models involved in the coupled climate-carbon cycle intercomparison project (C^4MIP).

Model	Atmosphere	Ocean	Land Carbon	DGVM	Ocean Carbon	Reference
HadCM3LC	HADCM3 $2.5^o \times 3.75^o$,L19	$2.5^o \times 3.75^o$, L20 flux-adjusted	MOSES/ TRIFFID	Yes	HadOCC	Cox et al., 2000
IPSL-CM2C	LMD5 5.6^o x 3.6^o, L19	OPA,	SLAVE	No	NPZD	Dufresne et al., 2002
NCAR CSM-1	CCM3 T31, L18	NCOM 3.6° long, 0.8–1.8° lat	LSM, CASA	No	OCMIP-biotic	Doney et al., 2005; Fung et al., 2005
MPI	ECHAM5, T63, L19	MPI-OM, 1.5°, L40,	JSBACH	Yes	HAMOCC5	Raddatz et al., 2005
LLNL	CCM3, 2.8° × 2.8°, L18	POP 0.6° x 0.6°, L40	IBIS	Yes	OCMIP	Thompson et al., 2004
FRCGC	CCSR/NIES/FRCGC T42L20(~2.8° ×	COCO No flux adjustment,	Sim-CYCLE	No	NPZD	Kawamiya et al.. 2005:

	2.8°)	3-hour coupling, (0.5–1.4°) × 1.4°, L20				Hasumi & Emori, 2004
UMD	QTCM	One-box	VEGAS	Yes	Abiotic tracer	Zeng et al., 2004
UVic-2.7	EMBM 1.8° × 3.6°	MOM 2.2, 1.8° × 3.6°, L19, no flux adjustment	MOSES/ TRIFFID	Yes	OCMIP Abiotic	Meissner et al., 2003; Matthews et al., 2005
CLIMBER2-LPJ	2.5-D statistical-dynamical, 10° × 5.1°	Zonally-averaged; 2.5°lat, 3 basins	LPJ	Yes	NPZD	Brovkin et al., 2004; Sitch et al., 2005
BERN-CC	EBM 2.5° × 3.75°	HILDA box-diffusion model	LPJ	Yes	Perturbation approach	Joos et al., 2001; Gerber et al., 2003

The models were forced by historical and SRES A2 anthropogenic emissions of CO_2 for the 1850–2100 time period. Each modelling group carried out at least two simulations, one "coupled" in which climate change affects the carbon cycle, and one "uncoupled" in which CO_2 is treated as a non-radiatively active gas (so that the carbon cycle experiences no CO_2-induced climate change). The difference between these runs defines the climate-carbon cycle feedback.

7.3.4.2 Carbon budget changes

Table 7.3.5 shows the change in the carbon budgets over the course of the uncoupled and coupled runs, including of the fractions of the total CO_2 emissions which end up in the atmosphere, land and ocean in 2100.

Table 7.3.5. Simulated air, land, and ocean -borne fractions in 2100 of the cumulative anthropogenic CO_2 emissions over the entire period of the model runs. Columns 2–4 show reservoir inventory fractions as: coupled (uncoupled).

Model	Air-borne Fraction	Land-borne Fraction	Ocean-borne Fraction	Feedback Factor (*F*)	Atmospheric CO_2: Coupled – Uncoupled (ppm)
HadCM3LC	0.72 (0.49)	0.05 (0.30)	0.24 (0.20)	1.47	225
IPSL-CM2C	0.47 (0.40)	0.22 (0.30)	0.32 (0.30)	1.17	75
NCAR-CSM1	0.54 (0.52)	0.25 (0.26)	0.21 (0.22)	1.04	20
MPI	0.54 (0.46)	0.22 (0.30)	0.24 (0.24)	1.17	82
LLNL	0.41 (0.36)	0.44 (0.49)	0.15 (0.15)	1.14	54
FRCGC	0.63 (0.60)	0.10 (0.10)	0.27 (0.30)	1.05	25
UMD	0.64 (0.55)	0.01 (0.06)	0.35 (0.39)	1.16	87
UVic-2.7	0.59 (0.48)	0.17 (0.28)	0.23 (0.26)	1.23	127
CLIMBER	0.58 (0.52)	0.22 (0.27)	0.20 (0.21)	1.12	53
BERN-CC	0.48 (0.42)	0.26 (0.32)	0.26 (0.26)	1.14	75

The uncoupled models all take-up fairly similar fraction of emissions (airborne fraction 56±7 (1σ) %), but this is achieved through different contributions from the land and the ocean. The fraction of emissions taken-up by the land is 27±12% owing primarily to differences in how CO_2-effects on photosynthesis are modelled. The change in oceanic inventory is 25±7% of the total emission, mostly due to differences in the transport of CO_2 to depth. In the models, there are compensating variations between land and ocean uptake, so the range in the atmosphere is relatively smaller than those in the land and ocean reservoirs.

The effect of climate change on the rate of increase of atmospheric CO_2 can be quantified by the feedback factor: $F = \Delta C_A^c / \Delta C_A^u$, where ΔC_A^c is the change in CO_2 in the coupled run, and ΔC_A^u is the change in CO_2 in the uncoupled run. All models show positive climate-carbon cycle feedbacks (Table 7.3.5), with $F \approx 1.17 \pm 0.12$ but with widely varying magnitudes.

7.3.4.3 Feedback analysis

In order to understand model behaviour and identify key uncertainties, model experiments are compared in terms of the responses of the land and ocean carbon uptake to changing climate and CO_2 (Friedlingstein et al., 2003):

$$\Delta C_L = \beta_L \Delta C_A + \gamma_L \Delta T$$

$$\Delta C_O = \beta_O \Delta C_A + \gamma_O \Delta T$$

where ΔC_L and ΔC_O are the change in land and ocean carbon storage (both in Pg-C) arising from an increase in atmospheric CO_2 concentration of ΔC_A (ppmv) and a temperature increase of ΔT (ºC). The gain of the climate-carbon cycle feedback loop, *g*, can be defined in terms of the feedback factor, *F*:

$$F = 1 / (1 - g) = \Delta C_A^c / \Delta C_A^u$$

The effect of changing CO_2 on global mean temperature can be approximated as $\Delta T \approx \alpha \Delta C_A$ where α is the linearized transient climate sensitivity factor for rising CO_2 (units: ºC ppm^{-1}), leading to an expression for gain in terms of the sensitivity coefficients (Friedlingstein et al., 2003):

$$g = -\alpha (\gamma_L + \gamma_O) / (1 + \beta_L + \beta_O)$$

Note that the gain of the carbon cycle is larger for higher effective climate sensitivities α (Jones et al., 2003a; Govindasamy et al., 2005) and for more negative values of γ_L and γ_O. However, the climate-carbon cycle feedback is weaker if ocean and land uptake respond very positively to increasing CO_2 (i.e., large β_L and β_O).

Although this analysis neglects some of the non-linear aspects of the climate-carbon cycle feedback, it provides a valuable way to begin characterising the different model responses. Table 7.36 compares the α, β and γ coefficients from each of the C^4MIP models.

Table 7.3.6. Carbon cycle gain (*g*) along with component sensitivities of climate to CO_2 (α), and land and ocean carbon storage to CO_2 (β_L, β_O) and climate (γ_L, γ_O).

Model	α (ºC ppm^{-1})	β_L (Pg-C ppm^{-1})	β_O (Pg-C ppm^{-1})	γ_L (Pg-C ºC^{-1})	γ_O (Pg-C ºC^{-1})	Gain *g*
HadCM3LC	0.0054	1.3	0.9	–175	–24	0.31
IPSL-CM2C	0.0064	1.6	1.6	–98	–30	0.15
NCAR-CSM1	0.0033	1.1	0.9	–22	–16	0.04
MPI	0.0069	1.4	1.1	–63	–22	0.20
LLNL	0.0077	2.8	0.9	–85	–14	0.10
FRCGC	0.0063	0.3	1.1	0	–23	0.04
UMD	0.0050	0.2	1.5	–40	–67	0.14
UVic-2.7	0.0059	1.2	1.1	–100	–42	0.20
CLIMBER	0.0053	1.1	0.9	–57	–22	0.10
BERN-CC	0.0046	1.6	1.3	–104	–38	0.13

(1) *Increase in ocean carbon uptake with atmospheric CO_2*. The ocean will take up CO_2 at a rate which depends on the difference between the partial pressures of CO_2 in the atmosphere and the surface ocean.

Model estimates of uptake differ primarily because of differences in the rate at which carbon is exported from the surface ocean to depth by both the large-scale circulation (Doney et al., 2004) and the biological pump (Sarmiento et al. 2004). The coefficient $\beta_O \approx 1.14 \pm 0.26$ Pg-C ppmv^{-1} gives the rate of change of ocean carbon storage with CO_2 alone.

(2) *Increase in land carbon uptake with atmospheric CO_2.* Although the experimental evidence of CO_2 fertilisation at the patch-scale is equivocal (Oren et al., 2001; Luo et al., 2004) most climate-carbon cycle models represent the current land-carbon sink by this mechanism (Cramer et al., 2001). Figure 7.3.12a shows the change in land carbon storage against atmospheric CO_2 concentration from each of the uncoupled C^{4}MIP runs. The mean gradient of the line defines β_L , $\approx 1.24 \pm 0.73$ Pg-C ppmv^{-1}. Table 7.3.6 shows the range of β_L. Experiments with the LLNL model, in which the CO_2-fertilisation effect was capped at current day show the extent to which a large β_L can reduce the atmospheric CO_2 levels and consequently the magnitude of the carbon cycle feedback (Thompson et al. 2004).

[INSERT FIGURE 7.3.12 HERE]

(3) *Dependence of ocean carbon uptake on climate.* Climate change can affect ocean carbon uptake by influencing the transport of carbon to depth by the large-scale circulation (e.g., by slowing down the thermohaline circulation), the solubility pump and the biological pump. In particular, increases in thermal stratification as the upper ocean warms may suppress vertical transport. The γ factor for the ocean is defined as: $\gamma_O = (\Delta C_O - \beta_O \Delta C_A) / \Delta T$, where β_o is defined from the uncoupled run as discussed above. Table 7.3.6 shows the values of $\gamma_O \approx -31 \pm 15$ Pg-C $^oC^{-1}$, with all models showing a suppression of ocean uptake with climate change.

(4) *Dependence of land carbon storage on climate*. Land carbon storage depends on the balance between the input of carbon as Net Primary Productivity (NPP), and the loss of carbon as heterotrophic (soil) respiration (R_h). Both of these terms are strongly climate dependent. Plant productivity depends on, inter alia, water availability and ambient temperatures. Changes in water availability depend critically upon uncertain regional aspects of climate change projections and are therefore likely to be a dominant source of uncertainty (see Chapter 11).

The overall sensitivity of land carbon storage to climate (Figure 7.3.12b) is quantified in terms of $\gamma_L \approx -73 \pm 50$ Pg-C $^oC^{-1}$. Seven of the ten models have γ_L in the range –40 to –104 Pg-C $^oC^{-1}$, even though γ_L ranges from 0 (FRCGC) to –175 Pg-C $^oC^{-1}$ (Hadley). The models all simulate a reduction in land carbon storage due to climate change alone, primarily due to a reduction in photosynthesis as water stress increases, and an accelerating breakdown of soil organic matter as the land warms.

Representation of photosynthesis in the models varies greatly in complexity, with some models including climate and biogeochemical control on stomatal conductance and hence canopy photosynthesis, transpiration, and leaf area; while others include highly simplified treatment of the dependence of canopy photosynthesis on climate. The wide range in photosynthesis response is also tied to the very different representation of hydrologic cycle in the models (physical climate model or carbon model). The well-documented range in modelled temperature and precipitation changes (see Chapter 10) thus present very different degrees of water stress for photosynthesis.

The C^{4}MIP models utilise different representations of soil carbon turnover, ranging from single-pool models (Hadley) to nine-pool models (NCAR- CSM1). However, all of the models assume a similar acceleration of decay with temperature, approximately equivalent to a doubling of the specific respiration rate for every 10 °C warming (i.e. $q_{10} = 2$). There is also a wide range of soil moisture sensitivity which, when coupled with the range of modelled soil moisture changes, contributes to the divergent results.

The temperature sensitivity is broadly consistent with a long history of lab and field measurements (Raich and Schlesinger, 1992), although there is an ongoing debate about the extent of acclimation of R_h to higher temperatures. The expected dependence on temperature was not found at the whole-ecosystem level for decadal time scales, in forest soils (Giardina and Ryan, 2000, Melillo et al., 2002) grasslands (Luo et al., 2001), or boreal forests (Dunn et al., 2005). However, these discrepancies in part reflect the rapid acclimatization of labile pools of organic matter through changes in the pool size. Strong temperature

responses can still occur on much longer time scales so long as litter inputs to the soil are maintained (Knorr et al., 2005), *although this is a theoretical result yet to be demonstrated in the field.*

The strong negative impact of climate change on land carbon storage in the Hadley model is the primary reason for its large positive climate-carbon cycle feedback (Friedlingstein et al., 2003). A number of studies have looked at aspects of this, including the marked drying under climate change in the Amazon basin (Cox et al., 2004), the choice of $q_{10} = 2$ for soil respiration (Jones et al., 2003b), the use of a single-pool soil carbon model (Jones et al., 2005b), and the parameterisation of plant respiration (Huntingford et al., 2004). In each case the characteristics of the Hadley Centre model appear to encourage a larger γ_L, but no single assumption accounts completely for the large sensitivity, or has been unequivocally falsified. For example, the use of a single soil carbon pool has been suggested as the predominant reason for the large feedback strength in the Hadley model (Zeng et al., 2004), but recent tests with a multi-pool soil model indicate that this explains only a small fraction of the discrepancy (Jones et al., 2005b).

The relatively small positive feedback in the NCAR CSM-1 model (small magnitude of γ_L) reflects a trade-off between CO_2 sources from degraded tropical ecosystems and CO_2 uptake in higher latitudes (Fung et al. 2005). The model indicates negative covariance between soil moisture and temperature (warmer, drier) in the tropics but positive correlation (warmer, wetter) at high latitudes (Doney et al., 2005 fig. 2; or Fung et al. (2005), Figure 7.3.13). Since evapotranspiration and vegetation demand for water increase in a warmer climate, tropical ecosystems degrade and high latitude systems agrade. All the models tend to show increasing aridity at low latitudes but give divergent results at high latitudes (e.g. Cox, Betts, Bertelot, Matthews, Fung), indicating that the response of the global system may need to be disaggregated in order to elucidate the driving factors in each model. The large magnitude for γ_L in the Hadley model reflects negative covariance in both low and high latitudes, as a result of the large climate sensitivity (α).

[INSERT FIGURE 7.3.13 HERE]

Summary: Importance of carbon cycle-climate feedback - The coupled climate-carbon cycle models participating in the C^4MIP project all support the following qualitative statements:

- Climate change will increase the fraction of anthropogenic CO_2 emissions which remain airborne (see Table 7.3.5), producing a positive feedback on climate change.
- CO_2 increase alone will tend to enhance uptake by both the land and the ocean ($\beta_O > 0$, $\beta_L > 0$).
- Climate change alone will tend to suppress land and ocean carbon uptake ($\gamma_O < 0$, $\gamma_L < 0$).

However, there is much less agreement over the magnitude of these various effects. Seven out of the ten models produce a feedback factor in the range 1.11 to 1.24, but they do this for very different reasons. Furthermore, it is not currently possible to rule out the large feedback (F=1.44) in the Hadley Centre model, or the very small feedback in the NCAR-CSM1 model (F=1.03). At this stage it is safest to assume that an amplification of CO_2 increase by 2100 in the range 10–25% is most likely, but with larger positive feedbacks possible (as a high-impact, low probability case). All models point towards declines of tropical ecosystems, a potentially major impact on world biotic and economic resources. But model validation is at an early stage, and issues of the first order remain unresolved. Thus the potentially important results from this very first C^4MIP should be regarded as preliminary indicators of matters needing intensive study.

7.3.4.4 Missing processes and critical uncertainties

The model intercomparison was designed as a benchmark study, rather than a simulation or prediction. While the results for the 19th and 20th centuries resemble those observed, they cannot be directly compared with the real world, as critical mechanisms (e.g. solar variability, other anthropogenic radiative forcing, legacies of prior land use, macro- and micro-nutrient limitation on terrestrial and marine productivity) were excluded from the experimental protocol. The results from this intercomparison highlight a number of critical outstanding issues for understanding climate-carbon cycle feedback.

Differences in model estimates of oceanic uptake also arise because of the differences in land uptake, with the oceans steadily absorbing carbon not absorbed by the land. Models with the most efficient export to the deep tend to have less negative γ_O and larger β_O—viz. oceanic sequestration is relatively efficient and is only slightly slowed down by climate warming; g is consequently reduced. These factors are discussed in 7.3.2.2.

On land, major uncertainties in the projections are the following:

(1) *Dependence of carbon storage on temperature and soil moisture.* The global inventory of fossil fuel carbon that ends up on land is the result of local competition between temperature and moisture effects on photosynthesis and respiration, and the regional competition between regions of carbon accumulation and loss. Spring warming would lengthen growing season, especially at middle to high latitudes (e.g., Keeling et al., 1996; Myneni et al., 1997), while summer drying or tropical droughts would decrease net carbon uptake (Angert et al., 2005). Thus the wide range and hence uncertainties in projections of land carbon storage are intimately tied not only to the sensitivity of these processes to climate change, but also to uncertainties in the modelled projections of climate change itself. Separating moisture dependence from temperature dependence of photosynthesis and decomposition is critical but not straightforward, because the co-variance of temperature and moisture anomalies varies spatially and temporally. Furthermore, as recognized early by Jenny (1941), rates of mineralization of the large pools of soil organic matter depend at least as much on soil moisture as on temperature. However, experimental evidence is equivocal at best at the whole-ecosystem level for decadal time scales. These anomalies suggest that climate models may underestimate positive feedback of climate on photosynthesis, and overestimate positive feedback of climate on mineralization of soil carbon for the year 2100.

(2) *CO_2 fertilization and land use legacy.* The C^4MIP climate-carbon cycle models represent the current land-carbon sink as stimulated carbon assimilation and sequestration in response to rising CO_2. Experimental evidence for this "CO_2 fertilization" is also equivocal at best (Cramer et al., 2001; Oren et al., 2001; Luo et al., 2004; DeLucia et al., 2005). The models exclude, by design, the effects of legacies of prior land use, in contrast to current hypothesis/observation that the contemporary forest landscape, with mostly young ages, plays a major role in current net carbon sequestration (e.g., Pacala et al., 2001; Schimel et al., 2001; Hurtt et al., 2002). Thus the present models might overestimate β_L and underestimate positive feedback by confounding legacies of land use, which do not increase with rising CO_2, with fertilization, which does respond to CO_2.

(3) *Soil carbon turnover*. The C^4MIP models specify, for each of the different soil carbon pools, "standard" turnover rates for a specified temperature and soil moisture, with the rates modulated by variations in temperature and moisture. Recent ^{14}C measurements in temperate ecosystems (check) show that over half of the photosynthetic flux is returned to the atmosphere within 5 years via heterotrophic respiration, so that the flux-weighted turnover time of soil carbon is shorter than the mass-weighted turnover time (Trumbore and Gaudinski, 2003). A shorter turnover time would decrease carbon storage and increase the positive feedback on climate. On the other hand, manipulation experiments have also shown changes in the microbial population at high CO_2 levels, so as to slow soil carbon turnover (Treseder et al., 2003), increase carbon storage and reduce positive feedback on climate.

(4) *Limits to growth*. Nitrogen and other resources are known to limit photosynthesis. Other limitations include structural limitations and genetic longevity (Zavaleta et al., 2003a, b), which are not yet included in this generation of models. These limits would mostly likely decrease the unrestrained carbon uptake and storage in the C^4MIP models and increase $|\gamma_L|$, thus magnifying the carbon-climate feedback.

(5) *Other ecosystem processes.* Conversion of biomass and soil organic matter to CO_2 also depends on combustibility of ecosystems and organic soils (Kasischke et al., 2005; Cochrane, 2003; Nepstad et al., 2004; Randerson et al., 2002a-d, 2005; Jones and Cox, 2005), not just on respiration. The correlation between temperature and soil moisture shown in Figure 7.3.13 suggests disturbance regimes not included in the C4MIP models would likely further magnify carbon-climate feedbacks.

(6) Evolution of the landscape. Changes in the distribution of ecosystems would occur with changes in climate and atmospheric CO_2 levels, at the same time that humans are expected to alter the landscape. Yet the 21st century climate and atmospheric conditions have no analogue in past climates. It is difficult to assess the full suite of carbon-climate consequences of these changes, other than to assert that conversion from high to low biomass would tend to increase the positive carbon-climate feedback, and vice versa.

In order to reduce the uncertainties in climate-carbon cycle projections, it is critically important to constrain carbon cycle models by observations. This requires long-term measurements of natural ecosystems, ecosystem manipulations covering climatically relevant time scales, and more sophisticated models which

can more easily utilise this data. The current simplistic representations of ecosystem processes run the risk of misidentifying the causes of contemporary carbon exchanges, and therefore of poorly predicting future carbon cycle feedbacks.

There is at the same time an urgent need to improve process representation and expand the suite of processes in the models, including forest regrowth and recovery effects (Sitch et al., 2005), ecosystem demography (e.g. Moorcroft), carbon-nitrogen interactions (e.g., Nadelhofer et al., 2004) and the effects of temperature-precipitation covariance (Bonfils et al., 2005; Angert et al., 2005; Hutyra et al., 2005) on the land, and more complete treatments of ocean ecosystems (e.g., resolving more than one phytoplankton functional type), including iron and other micronutrient limitations (see 7.3.2.2).

[START OF QUESTION 7.1]

Question 7.1: Are the Increases in Atmospheric Carbon Dioxide and Other Greenhouse Gases During the Industrial Era Caused by Human Activities?

Yes, the increases in atmospheric carbon dioxide and other greenhouse gases in the industrial era are caused by human activities. For carbon dioxide, human activity, including burning fossil fuels and land use change, have released more carbon dioxide to the atmosphere than can be accounted for by greater atmospheric carbon dioxide concentrations. For methane, another important greenhouse gas, human activities contributed almost half of the annual emissions over the last 20 years. For nitrous oxide, human activity contributes about one third to one half of the total nitrous oxide emitted to the atmosphere each year. Most of the halogen containing gases are manufactured by humans, and were not present in the atmosphere before the industrial era.

Human activities are an important, and often dominant source, of the increase in atmospheric concentration of carbon dioxide and greenhouse gases.

Carbon Dioxide (Panel a)
Fossil fuel combustion, together with cement manufacture, has released about three quarters of the total carbon dioxide released to atmosphere during the last twenty years. The remainder of the carbon dioxide emitted to the atmosphere is by land use change, much of which occurs in the tropics.

The total quantity of carbon dioxide is exchanged between the land and atmosphere each year is estimated to be 120 Pg C and between the ocean and atmosphere is estimated to be 90 Pg C. These numbers are generally in balance, or at steady state for the global carbon cycle, and thus are not the cause of the rise in atmospheric carbon dioxide. The increase in atmospheric concentration is about 1.5% of the total exchange. A variety of techniques, including the oxygen to nitrogen ratio, use of the isotopes of carbon for tracers, and model estimates have been used to determine that human activity is causing the increase in atmospheric carbon dioxide. These techniques all provide further evidence and support for the partitioning of human driven emissions, into land, ocean and atmospheric reservoirs as shown in Panel a.

[INSERT QUESTION 7.1, FIGURE 1 HERE]

Halogen-Containing Gases (Question 7.1, Figure 1, Panel b)
The halogen-containing gases include chlorofluorocarbons, CFCs, hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) and halons. Before industrialization, there were only a few naturally occurring halogen-containing gases, e.g., methyl bromide and methyl chloride. The atmospheric abundances of key halogen-containing gases produced by humans are shown in Panel b. The development of new techniques for chemical synthesis resulted in a proliferation of chemically manufactured halogen containing gases during the last 50 years of the 20th century. As a result of the Montreal Protocol, and its adjustments and amendments, the concentration of many halogen-containing species, including CFCs is no longer increasing at the Earth's surface. The abundance of gases not covered by the Montreal Protocol, HCFCs, continues to increase.

Methane (Question 7.1, Figure 1, Panel c)

Human activities are responsible for almost half of the methane emitted to the atmosphere. The natural sources of methane to the atmosphere include wetlands, termites, oceans, and methane hydrates. The human activities that produce methane include energy production, land fills, raising ruminant animals, rice agriculture and biomass burning. The sinks for methane include chemical oxidation in the troposphere, and the much smaller soil uptake and eventual destruction in the stratosphere. The atmospheric increase and the atmospheric abundance of methane are determined by the balance between emissions and destruction.

Nitrous Oxide (Question 7.1, Figure 1, Panel d))
Human activities are responsible for about one-third to one-half of the total emissions of nitrous oxide. The natural sources of nitrous oxide include oceans, chemical oxidation of ammonia in the atmosphere, and soils. Tropical soils are a particularly important source of nitrous oxide to the atmosphere. The human activities that emit nitrous oxide include transformation of fertilizer N into N_2O and its subsequent emission from agricultural soils, biomass burning, emissions from cattle and feedlots, and some industrial sources, including nylon manufacture. Most of the nitrous oxide emitted to the atmosphere is eventually removed by destruction in the stratosphere. The atmospheric increase and the atmospheric abundance of nitrous oxide are determined by the balance between emissions and destruction.

[END OF QUESTION 7.1]

7.4 Reactive Gases and the Climate System

The atmospheric concentration of many reactive gases has increased substantially during the industrial era as a result of human activities. Some of these compounds (methane, nitrous oxide, halocarbons, ozone, etc.) interact with longwave (infrared) solar radiation and, as a result, contribute to 'greenhouse warming'. Ozone also absorbs efficiently shortwave (ultraviolet and visible) solar energy, so that it protects the biosphere (including humans) from harmful radiation and plays a key role for the energy budget of the middle atmosphere. Many atmospheric chemical species are emitted at the surface as a result of biological processes (soils, vegetation, oceans) or anthropogenic activities (fossil fuel consumption, land-use changes) before being photochemically destroyed in the atmosphere, and converted to compounds that are eventually removed by wet and dry deposition. The oxidizing power (or capacity) of the atmosphere is determined primarily by the atmospheric concentration of the hydroxyl (OH) radical (daytime) and to a lesser extent of NO_3 (night time), ozone and H_2O_2. The coupling between chemical processes in the atmosphere and the climate system are complex because they involve a large number of physical, chemical and biological processes that are not always very well quantified. An important issue is to determine to what extent predicted climate change could affect air quality. The goal of this Section is assess recent progress made in the understanding of the two-way interactions between reactive gases and the climate system.

7.4.1 Methane (CH_4)

7.4.1.1 Biogeochemistry and present-day budgets of CH_4
Atmospheric CH_4 originates from both non-biogenic and biogenic sources. Non-biogenic CH_4 includes emissions from fossil fuel (natural gas, petroleum and coal) burning, biomass burning, and geological sources (fossil CH_4 of geothermal and volcanic origin). However, emissions from biogenic sources account for more than 70% of the global total. These sources include wetlands, rice agriculture, livestock, landfill and termites. CH_4 emission from these sources is an ecosystem process that results from a complex sequence of events beginning with primary fermentation of organic macromolecules to acetic acid (CH_3COOH), other carboxylic acids, alcohols, CO_2 and H_2, followed by secondary fermentation of the alcohols and carboxylic acids to acetate, H_2 and CO_2, which are the ultimate precursors of CH_4 ($CH_3COOH \rightarrow CH_4+CO_2$ and $CO_2+4H_2 \rightarrow CH_4+2H_2O$). Methane-producing archaea (methanogens) are the only known organisms capable of these substrate conversions. CH_4 production from these sources is generally limited by availability of substrates and anaerobiosis conditions. Not all of the CH_4 produced is emitted to the atmosphere. Most of it (50-90%) is oxidized (i.e. in the presence of molecular oxygen) before emission to the atmosphere, by methanotrophs or methane oxidizing bacteria, which convert CH_4 into CO_2, water and microbial biomass. CH_4 consumption in this case is limited by both O_2 and CH_4 availability and regulated largely by meteorological variables such as moisture and temperature. Although anaerobic CH_4 oxidation (no molecular O_2 present) exists in some environments (Orphan et al., 2002; Hallam et al., 2004), its role in contributing to the global CH_4 budget is highly uncertain. The net rate of CH_4 emissions from sources depends on an

imbalance between production and oxidation, which is strongly influenced by climatic and edaphic factors (temperature, water table, substrates and pH (Conrad, 1996)).

Estimating emissions from CH_4 sources is based on three approaches: extrapolation from on-site direct flux measurements, a process-based modelling approach that represents the actual physical and biological processes of CH_4 production and emission (bottom-up approach), and inverse modelling that relies on observations in the atmosphere (top-down approach). Direct flux measurements provide the initial estimates of upper and lower emission ranges, under the assumption that point measurements represent all locations that share similar characteristics such as soil or ecosystem type, which is not necessarily true. Therefore, extrapolation of direct flux measurements to larger scales contains considerable uncertainty. The process-based modelling approach requires sufficient understanding of local parameters and processes, and assumes that such characteristics apply to other sites (e.g., Cao et al., 1998; Walter et al., 2000, 2001a, 2001b). Currently, only a few such locations exist where parameters are investigated to sufficient detail for modelling. Extrapolation from results of a few sites to regional or global scales thus is still associated with uncertainties. On the other hand, the top-down approach helps overcome the weak points in bottom-up methods by bypassing limitations in our understanding of methanogenic-methanotrophic and their interactions with environmental factors. Inadequate observations and uncertainties in modelled circulation patterns are the main obstacles for its extensive application (Chen and Prinn, 2005a; Dentener et al., 2003; Mikaloff Fletcher et al., 2004a, 2004b). Measurements of the isotopes of CH_4 (^{13}C and ^{14}C) can provide additional constraints on CH_4 budgets and specific sources. However, such data are even more limited (Mikaloff Fletcher et al., 2004a, 2004b; Lassey et al., 2000).

Table 7.4.1. Sources, sinks, and atmospheric budgets of CH_4 ($Tg\text{-}CH_4\ yr^{-1}$)

Reference	Base Year	Methane Sources							Total
		Biogenic Sources					Non-Biogenic Sources		
		Wetlands	Rice Agriculture	Livestock	Landfill & Waste	Termite	Biomass Burning	Energy	
Wuebbles and Hayhoe, 2002	-	123[a]	60	81	61	20	52[b]	106	503
Bogner and Matthews, 2003	1996	-	-	-	16–57	-	-	-	-
Mikaloff Fletcher et al., 2004a, b	1999	221	54	91	35	29	88	82[c]	610
Wang et al., 2004	1994	176	57	83	49	20	41	81[c]	507
Chen and Prinn, 2005[d]	1996–2001	145	112	189[e]	-	23	43	84	596
TAR	1998	-	-	-	-	-	-	-	598

Reference	Base Year	Methane Sinks			
		Oxidation by OH in Troposphere	Oxidation in Terrestrial Ecosystem	Loss to Stratosphere	
Wuebbles and Hayhoe, 2002	-	445	30	40	515
Wang et al., 2004	1994	428	-	30	492
Ridgewell et al., 1999	-	-	38	-	-
TAR	1998	506	30	40	576

Notes:

(a) Comprises of emission from natural wetland of 100 Tg, oceans 4 Tg, marine sediments 5 Tg and geological sources 14 Tg
(b) Includes wild fires emission of 2 Tg
(c) Includes hydrate emission of 4 Tg
(d) Inverse result of control scenario in Chen and Prinn, 2005.
(e) Includes emission from landfill and waste

Partly due to differences in methodologies used and the nature of data employed, there are currently large uncertainties in CH_4 emission estimates of individual sources and how they have varied over the past. The currently available range of total annual emissions is 500 to 600 Tg-CH_4 yr^{-1} (Table 7.4.1), similar to those given in TAR. Although estimates have not changed much since the time reported in TAR, advances have been made in constraining individual source strengths. A recent estimate, which optimized emission sources based on the previous bottom-up and top-down reported values in combination with the worldwide observation results in a 3-D atmospheric transport and chemical model (ATCM) simulation, gives global emissions of 596 Tg-CH_4 yr^{-1} (Chen and Prinn, 2005a, 2005b). This estimate has significantly reduced the uncertainty in global source strength through employing high quality datasets and rigorous inter-laboratory calibrations (from 13 high-frequency stations that measured methane concentration between 24 and 36 times per day, and flask samples collected periodically between 1966 and 2001 (once per week) from locations situated worldwide). Uncertainty in estimates of northern wetland emission has been greatly reduced (<25% of means) due to the existence of numerous high-frequency monitoring stations. Results from this study indicate that southern and tropical regions account for >70% of total global wetland emissions. During 1996-2001, significantly reduced emissions are suggested from energy use (coal and natural gas) and slightly for wetlands while significantly increased emissions are found from animals and wastes, wetland rice agriculture (20% increase, mostly between 0-30ºN) and tropical biomass burning (30-80% since 1996). In other studies that included both observation results and $^{13}C/^{12}C$ ratios of CH_4, an increase in emissions from tropical wetlands is also suggested (Mikaloff Fletcher et al., 2004a; Wang et al., 2004). Such increased emissions probably result from temporary wetlands that are flooded for only part of the year (during the rainy season, Kaplan, 2001), and thus are not accounted for in bottom-up estimates. Recently, advances have been also made on mapping global distribution of methane by using space-born near-infrared absorption spectroscopy (Frankenberg et al., 2005). The results from such observations suggest high emission from tropical rainforest, supporting the findings from top-down inversion results of Mikaloff Fletcher et al. (2004a) and Chen and Prinn (2005). It seems, therefore, that the reduced emissions, notably in energy use and northern wetland lands, are compensated by increased emission from lower latitudes. Such offsetting changes in sources and sinks may be one of the reasons for the temporary slow down in the current growth rate (Chapter 2). However, an increase in CH_4 emissions from certain wetlands was observed in 2001 (Table 7.4.2), suggesting that the current slowdown of CH_4 growth may be temporary (Chen and Prinn, 2005a).

Table. 7.4.2. Control Case annual anomalies of emission trend during 1996–2001 compared to the deviation from mean during the same period. The values are expressed in Tg-CH_4 yr^{-1} (Chen and Prinn, 2005b).

Region	1996	1997	1998	1999	2000	2001
Wetland-Northeast[a]	2.7	1.9	1.5	–2.8	–2.0	2.5
Wetland-Northwest[b]	–1.9	1.5	2.2	0.2	–1.6	–0.4
Wetland-South[c]	2.5	3.2	5.3	–3.2	-10.7	2.8
Rice agricultured	–7.5	–4.8	22.3	–1.4	1.9	–10.4
Biomass burning (Africa)	0.8	1.1	0.5	0.5	–0.6	–2.3
Biomass burning (America)	1.6	1.4	0.5	0.5	–3.7	–0.4
Biomass burning (Asia)	–0.1	–1.2	0.8	–0.3	0.9	–0.2
Wetland Total	1.7	1.8	13.7	–6.1	–13.8	2.7
Rice Total	–5.9	-3.8	17.6	–1.1	1.5	–8.2
Biomass Total	2.3	1.3	1.8	0.8	–3.4	–2.8
Overall Total	–1.9	–0.7	33.1	–6.5	–15.7	–8.3

Notes:
(a) North America and Canada
(b) Europe and Russia
(c) Below 30°S
(d) 21% of area is overlapped with wetlands

Results from both a process-based model for 1984–1999 (Dlugokencky et al., 2001) and an inverse model for 1996–2001 (Chen and Prinn, 2005) indicate that the largest contributors to global inter-annual variation in emissions during 1996–2001 are emissions from rice agriculture and wetlands. Contributions from biomass burning are relatively small. However, errors may arise in estimates of biomass burning due to lack of data (mainly undersampling of the total amount of burning). CH_4 emissions from biomass burning also depend on fire type, which could be highly variable resulting in a large uncertainty.

Wetland emissions were suggested to account for the large increase in emissions in 1998 (Dlugokencky et al., 2001; Mikaloff Fletcher et al., 2004; Chen and Prinn, 2005b). The ENSO event that occurred in late 1997 and early 1998 associated with enhanced precipitation at low latitudes likely stimulated methanogenesis in low latitude wetlands (Bell et al., 1999). Chen and Prinn (2005) partitioned this wetland contribution into northern wetlands (5–12 Tg), tropical wetlands (8–13 Tg) and rice agriculture (10 Tg) (Table 7.4.2). Unusually warm and dry conditions in the northern hemisphere during the ENSO period also increased biomass burning. CH_4 releases of 3–5 Tg in 1998 were attributed to boreal forest fires in Eastern Siberia due to these unusual warm and dry conditions (Kasischke et al., 2002).

For rice agriculture, there has been a downward trend over the past few decades in estimates of CH_4 emissions using bottom-up methods. This trend is largely due to results from the increasing number of in-situ flux measurements used for emission extrapolation, which collectively indicate lower overall emissions from rice agriculture. However, emission estimates still vary greatly in both space and time. The non-homogeneous nature of paddy-field soils and different cultivation practices mainly account for such variations (Aulakh et al., 2001; Li et al., 2002). Sass et al. (2002) measured emissions at a single site in the U.S. over nine years and observed a year-to-year flux variability of approximately ±50% of the annual mean over the entire period. Using the standard deviation of mean CH_4 flux as a measure of variability, they found that accounting for rice plant height and grain yield reduced spatial variability from 25.2 to 17.7% of the mean. Temporal variability over the entire 9-year data set was 49% of the mean, 71% of which was explained by variations in average rice plant height and total nitrogen fertilizer application. This highlights the finding that even with a consistent measurement approach, there remains a year-to-year variation in emissions, and that emissions are highly sensitive to local factors. Global estimates of emissions from this source will still likely contain a certain level of variation due to such factors.

For landfills, estimates of CH_4 emissions are normally based on measured or estimated national solid waste generation, the fraction landfilled, the fraction landfilled that is expected to biodegrade anaerobically, the degradable organic carbon content of that fraction, and the CH_4 content of the biogas product. For some developed countries, subtractions are made for methanotrophic CH_4 oxidation in cover soils and CH_4 recovery via pumped system. In general, estimates still contain greater uncertainty when compared with emissions from wetland and rice agriculture, since solid waste data are lacking for many countries, reliability of existing data is questionable, no internal variability is available, there is a wide range in magnitude (7 order difference, Bogner and Mathews, 2003), and there are no international networks/campaigns to measure landfill CH_4 emissions. Bogner and Mathews (2003) developed a methodology for estimating CH_4 emission from landfills during 1980–1996, based on per capita energy generation to estimate the amount of solid waste generation. Their best estimate ranged between 16 and 57 Tg, which is within the ranges reported for other studies (e.g., in TAR).

Once in the atmosphere, CH_4 is destroyed through two main mechanisms: oxidation by OH in the troposphere and by methanotrophs in terrestrial ecosystems. Some CH_4 is also lost to the stratosphere. Current estimates for these sinks combined span 492–576 Tg-CH_4 yr^{-1}. The abundance of OH (Section 7.4.2) and its chemistry determine CH_4 sink strength, the lifetime of CH_4 and its growth rate in the atmosphere. Current observations indicate a stabilized growth rate (Chapter 2) which may result from changes in such OH chemistry. However, observed trends in the seasonal cycle of CH_4 and OH concentrations inferred from methylchloroform measurements (a strong positive trend of 15±22% during 1979–1989, followed by a strong decrease the following decade, Prinn et al., 2001) do not support a continued decrease in CH_4 growth rate. It appears, then, that changes in emissions rather than increasing sink strengths are responsible for the major part of the observed slowing.

Consumption of atmospheric CH_4 in terrestrial ecosystem ranges between 20 and 51 Tg-CH_4 yr^{-1}, with the best estimates around 30–38 Tg (TAR, 1998; Ridgwell et al., 1999). Over recent decades, this sink strength has probably decreased due to intensification of agriculture that alters the methanotrophic community and activity (Knief et al., 2005). Changes in land use, especially cultivation of formerly undisturbed soils, reduce the sink strength for atmospheric methane by 60–90% (Whalen and Reeburgh, 1990; Steinkamp et al., 2001; Knief et al., 2005). The impact is most pronounced in the dry tropical forest where sink strength accounts for a third of the total global sink and where rapid deforestation is occurring (Keller and Reiners, 1994). An estimate for the effect of land use change and agricultural intensification is a 3 Tg yr^{-1} reduction in sink strength (Ridgwell et al., 1999).

Assuming a combined sink of ~576 and a combined source of ~596 Tg-CH_4 yr^{-1} yields an imbalance of 20 Tg-CH_4 yr^{-1} in source emissions over sink removals.

7.4.1.2 Effects of climate

We learn about the effects of climate on CH_4 biogeochemistry mainly from examining records of the past and from model simulations under various climate change scenarios. The Vostock ice core record back to 420,000 years BP (Petit et al., 1999) reveals that atmospheric concentration is closely tied to atmospheric temperature records, decreasing and rising in phase with temperature at the inception and termination of glacial episodes (Wuebbles and Hayhoe, 2002). Another study showed that following each transition, temperature increased more rapidly than CH_4 concentration (Brook et al., 2000). Since biogenic CH_4 production and emission from major sources (wetland, landfill, rice agriculture) are temperature-dependent, climate change scenarios with a warmer atmosphere, suggest enhanced emissions from these sources.

Wetlands are the largest CH_4 emitter globally (25–40% of total global emission, Table 7.4.1). Several studies have demonstrated a high sensitivity of wetlands CH_4 emission to temperature and water table. Before the 1990s global CH_4 emissions increased steadily, due both to an increase in generic sources, and to elevated surface temperature leading to an increased emission from wetlands (Walter et al., 2001a, 2001b; Christensen et al., 2003; Zhuang et al., 2004). The sensitivity of wetland emissions to climate varies depending on regional and local factors. Earlier estimates of the effect of warming on CH_4 emission were given by Chapman and Thurlow (1996). From the relationship between emission and temperature at two sites in Scotland, they predicted that CH_4 emission would increase by 17, 30 and 60% for warmings of 1.5, 2.5 and 4.5 °C (warming above the site's mean temperature during 1951–1980). A model simulation by Cao et al. (1998) yielded a 19% emission increase under a uniform 2°C warming. The combined effects of 2°C warming and 10% increase in precipitation yielded an increase of 21% in emissions. In most cases, the net emission depends on how an increase in temperature affects net ecosystem production (NEP), as this is the source of methanogenic substrates (Christensen et al., 2003), and on the moisture regime of wetlands, which determines its aerobiosis/anaerobisis. Emissions are enhanced under a scenario where an increase in temperature is associated with increases in precipitation and NEP. On the other hand, emission decreases if elevated temperature results in either reduced precipitation or NEP.

Walter and Heimann (2000) assessed how changes in water table and temperature would affect emission in several northern wetlands. When the water table is above the soil surface, CH_4 emission follows soil temperature. If the water table is below the soil surface, the pattern of emission is mainly driven by changes in soil temperature but the amplitude is influenced by the water table depth. An increase in temperature of 1°C results in 20% increase in simulated CH_4 emission while a water table increase of 10 cm would increase emission 0–25%, depending on initial wetness and dryness of wetlands. Under dry conditions, an increase in the water table enhances CH_4 emission significantly while under wet conditions water table changes have only a small effect.

A standard benchmark for climate change studies is a doubling in CO_2 concentration. Shindell et al. (2004) have applied a GCM to simulate a 3.4°C due to this doubling in CO_2 and found that CH_4 emission increases by 78% above current emissions from wetlands. Zhuang et al. (2004) use a terrestrial ecosystem model (TCM) to study how rates of CH_4 emission and consumption in high-latitude soils of the Northern Hemisphere (north of 45ºN) have changed over the past century (1900–2000) in response to observed change in the region's climate, based on the emission data for the 1990s. They estimate that net emissions of CH_4 have increased by an average 0.08 Tg-CH_4 yr^{-1} during 20th century. The decadal net CH_4 emission rate correlates with soil temperature, water table depth and NPP. Estimates of emission from northern wetlands

also depend largely on the formulation of the active layer (for methanogenesis): increasing the active layer a mere 10 cm could increase net CH_4 emission as much as 38% (Zhuang et al., 2004). In summary, although sensitivity to climate change differs among wetlands, most studies point towards increasing emission trends under warmer temperature and enhanced precipitation scenarios.

In rice agriculture**,** climate factors that will likely influence CH_4 emission are those associated with plant growth. Plant growth determines how much substrate will be available for either methanogenesis or methanotrophy and thus the net emission (Matthews and Wassmann, 2003). As mentioned above, plant growth (height) strongly correlates with CH_4 emission in a Texas rice field (Sass et al., 2002). Any climate change scenario that results in an increase in plant biomass is likely to increase CH_4 emission from rice agriculture (Xu et al., 2004). However, the magnitude of increased emission depends largely on field management. For instance, field drainage could significantly reduce emission due to the introduction of aerobiosis in the soil (i.e. influx of air into anaerobic zone which subsequently suppresses methanogenesis).

Climate also affects CH_4 sinks. Several model studies indicate that CH_4 oxidation in soil is relatively insensitive to temperature increase (Ridgwell at al., 1999; Zhuang et al., 2004). A doubling of CO_2 would likely change the sink strength only marginally (in the range of –1 to +3 Tg yr^{-1}, Ridgwell et al., 1999). However, any change in climate that leads to altering the amount and pattern of precipitation may significantly affect the CH_4 oxidation capacity of soils. A process-based model simulation indicated that CH_4 oxidation strongly depends on soil gas diffusivity, which is a function of soil bulk density and field capacity (Bogner et al., 2000; Del Grosso et al., 2000).

In summary, since TAR advances have been made in constraining estimates of CH_4 source strengths and in understanding of emission variations. These improvements are attributed mainly to increasing availability of measurement data worldwide and improved modelling tools (e.g., Chen and Prinn 2005a, 2005b; Mikaloff Fletcher, 2004a, 2004b). An understanding of climate effects on CH_4 sinks and sources has evolved, and such effects have been quantified. As a result, wetlands and rice agriculture are identified as the CH_4 sources that are most sensitive to climate change and thus will likely contribute most to changes in global CH_4 budgets in the future. A warm and wet climate would likely enhance emission from these sources while a warm but dry climate would likely reduce emission. Since these sources are located in the tropics where measurements are lacking, uncertainty in future emission estimates could be reduced by an increase in measurement coverage in such regions.

7.4.2. Nitrogen Compounds

The nitrogen cycle is important to the functioning of the earth system and to climate (Figure 7.4.1, Holland et al., 2005). Nitrogen is a major limiting nutrient in terrestrial and aquatic ecosystems and an important catalyst in tropospheric photochemistry. Over the last century human activities have dramatically increased inputs of reactive nitrogen to the global atmosphere by as much as three to five fold. Reactive nitrogen is the combination of oxidized, reduced and organically bound nitrogen but not the atmospherically abundant N_2 gas. The impact of the change in the N cycle has led to problems such as compromised air quality and human health, acidification of ecosystems, degradation of coastal estuaries, and acceleration of the eutrophication of lakes (Vitousek et al., 1997; Rabalais, 2002; Townsend et al., 2003; Galloway et al., 2004).

[INSERT FIGURE 7.4.1 HERE]

Perturbations of the nitrogen cycle impact the atmosphere climate system through production of three key N containing trace gases: nitrous oxide (N_2O), ammonia (NH_3) and nitrogen oxides (NO_x=NO+NO_2).

7.4.2.1 Nitrous Oxide (N_2O), Nitrogen Oxides (NOx=NO+NO_2), and Ammonia (NH_3)

Nitrous oxide is the nitrogen trace gas with the longest atmospheric lifetime, 120 years (range 97–137) (Prather et al., 1998). Nitrous oxide concentrations serve as a tracer for human manipulation of the global nitrogen cycle. The exponential rise in tropospheric N_2O concentrations shown in Figure 7.4.2.a confirms the profound modification of the global nitrogen cycle. Tropospheric abundances of N_2O have increased from pre-industrial values of about 270 ppb (TAR) to between 315 and 319 ppbv (CMDL, ALE-GAGE). Estimates of the global N_2O budgets have changed little since the TAR. The sources and sinks remain out of balance, thus generating a continuing increase in atmospheric concentrations of N_2O. Much of the imbalance

globally can be attributed to the intensification of human activity, particularly agriculture, (Galloway et al. 2005). The average annual growth rate for 1999–2000 was 0.85–1.1 ppbv yr^{-1} (WMO Ozone Assessment 2002). The emissions of N_2O from soils, natural plus agricultural, remain the dominant source of N_2O to the atmosphere (Bouwman et al., 2002b, c). Since the TAR, much of the focus has been on refining the estimates of N_2O from agricultural sources, the single biggest anthropogenic source of N_2O (Del Grosso, 2005; Smith and Conen, 2004). The long lifetime of atmospheric N_2O also means that it plays an important role in stratospheric ozone depletion. Nitrous oxide is likely to become increasingly important as the emissions of atmospheric halogens decline in compliance with the Montreal Protocol.

[INSERT FIGURE 7.4.2 HERE]

Measurements of changes in atmospheric concentrations of NO_x and NH_x ($NH_3 + NH_4^+$) are challenging to establish because the atmospheric lifetimes of these chemical species are days to weeks instead of years. The short atmospheric lifetimes of NO_x and NH_x generate pronounced spatial and temporal variations in their distribution. Their atmospheric concentrations are much more variable regionally and through time than are measurements of N_2O. Figure 7.4.2a depicts the exponential increase in fossil fuel NO_x emissions. Total global NO_x emissions have increased from an estimated 11 Tg-N y^{-1} pre-industrially (Holland et al., 1999; Galloway et al., 2004) to between 35 and 50 Tg-N y^{-1} for 2000 and are forecast to be 105–131 Tg-N y^{-1} by 2100 (Lamarque et al., 2005). The estimates of contemporary and future NO_x emissions were based on 29 simulations by 6 tropospheric chemistry models using the A2 scenario projections for 2100 (Lamarque et al., 2005). Land use change continues to have a significant impact on both NO and N_2O emissions. Land use change impacts NO: recent estimates show that logging increases N_2O and NO emissions by 30–350% depending on conditions. Interactions between soil emissions and scavenging by plant canopies have a significant impact on soil NO_x emissions to the free troposphere; the impact may be greatest in regions where fossil fuel emissions are rising, in subtropical and tropical regions (Ganzeveld et al., 2002).

Since pre-industrial times, there has been an exponential increase in all the available indices of the intensity of agricultural nitrogen cycling, the primary source for NH_3 emissions (Bouwman et al., 2002a, b & c; Figure 7.4.2b and Table 7.4.3). Total global NH_3 emissions have increased from an estimated 11 Tg-N y^{-1} pre-industrially to 54 Tg-N y^{-1} for 2000, and are projected to increase to 116 Tg-N y^{-1} for 2050 (Holland et al., 1999; Galloway et al., 2004).

Table 7.4.3. Global sources (in Tg-N yr^{-1}) of NO_x, NH_3, and N_2O. (From Bouwman et al., 2002a, b, c).

Source	NO_x	NH_3	N_2O
Anthropogenic sources			
Fossil fuel	21.9	0.1	0.2
Industrial processes	1.7	0.2	0.3
Animal husbandry	0.7	21.6	3.4
Fertilizer and crops	0.4	12.6	2.2
Biomass burning	7.7	5.9	0.7
Human excreta	–	2.6	0.2
Coastal water	–	–	1.9
Atmospheric deposition	0.3	–	0.6
Natural sources			
Soils under natural vegetation	13.0	2.4	6.6
Oceans	–	8.2	3.6
Lightning	12.2	–	–
Tropospheric chemistry	0.9	–	0.6
Stratospheric chemistry	0.7	–	–
Total source	59.5	53.6	20.3

Because the atmospheric lifetimes of NO_x and NH_x are relatively short, 1 day-2 weeks, quantification of changes in atmospheric concentrations over time are harder to establish than for nitrous oxide or carbon

dioxide. The short atmospheric lifetime also means that the deposition of NH_x and NO_x and their reactions products, including aerosols, is the primary mechanism for removing these chemical species from the atmosphere. Estimates of the rate of removal of both NH_x and NO_x are provided by measurements of atmospheric deposition that have been conducted over the US and Western Europe to quantify acid rain inputs (Holland et al., 2004). Evaluation of these data for the 25 years of available measurements suggests that there is substantial seasonal and interannual variability in the wet deposition of NH_x and of NO_3—the primary removal product(s) for NH_3 and NO_x emissions respectively. However, no clear trend in the deposition of either compound, or in precipitation, emerges over the last 25 years. Chemical transport models represent the deposition removal of NO_x and NO_x reaction products and NH_x and NH_x reaction products. A recent intercomparison of 29 simulations and 6 different tropospheric chemistry models focusing on present-day and 2100 conditions for NO_x and its removal products forecasts that average N deposition over land will increase by a factor of 2.5 in 2100, mostly due to increases in NO_x emissions (Lamarque et al., 2005). Climate contributions to the changes in oxidized N deposition are limited. In Brazil, changes in land use can change the amount of N deposited by as much as fourfold (Lara et al., 2005).

7.4.2.2. Carbon nitrogen interactions

Estimated and projected terrestrial carbon storage requires nutrient inputs, especially nitrogen (Hungate et al., 2003). Nitrogen is a primary limiting nutrient throughout mid and high latitude terrestrial ecosystems, and an important limiting nutrient for plant growth throughout for subtropical and tropical terrestrial ecosystems (Vitousek et al., 1998). Additional nitrogen supply through fertilization and deposition increases plant growth (Vitousek, 2004). When labelled nitrogen (^{15}N) is added to soil and litter layers, much of the additional nitrogen remains there and does not translate into increased carbon storage in wood after 7 years of N addition (Nadelhoffer et al., 2004). Studies of canopy uptake of atmospheric nitrogen suggest that this may be an important mechanism for nitrogen uptake and potentially for carbon storage (Sievering et al. 2000). Nitrogen deposition is spatially correlated with increased atmospheric ozone. Because ozone has a detrimental effect on plant growth, the combined net effect of N deposition and high atmospheric ozone concentrations on ecosystem carbon storage requires further examination (Holland and Carroll, 2003, Ollinger and Aber, 2002). Inclusion of the nitrogen cycle into global carbon cycle models (Figure 7.4.3) can cause a significant reduction in global carbon uptake in response to a 2°C warming because of carbon and nitrogen feedbacks within the plant and microbial system.

[INSERT FIGURE 7.4.3 HERE]

7.4.3. Molecular Hydrogen

Atmospheric H_2 has recently received increased attention, because of its potential role as an indirect greenhouse gas and the expected perturbations of its budget in a prospective *hydrogen economy* (Tromp et al., 2003; Schultz et al., 2003; Warwick et al., 2004). Potential consequences of drastically increased H_2 emissions include a reduction of the global oxidizing capacity (presently H_2 constitutes 5–10% of the global average OH sink, Schultz et al., 2003), and increased formation of water vapour, which could lead to increased cirrus formation in the troposphere and additional cooling in the stratosphere, thereby leading to more efficient ozone depletion (Tromp et al., 2003).

There have been several studies of the global tropospheric H_2 budget (see Table 7.4.4), and they generally agree on a total source strength between 70 and 90 $TgH_2\,yr^{-1}$, which is approximately balanced by a sink of equal magnitude. About half of the H_2 is produced in the atmosphere via photolysis of formaldehyde (CH_2O), which itself originates from the oxidation of CH_4 and other volatile organic compounds. The other half stems mostly from the combustion of fossil fuels (e.g., car exhaust) and biomass burning. About 10% of the global H_2 source is due to ocean biochemistry and nitrogen fixation in soils. Presently, about 50 $TgH_2\,yr^{-1}$ are produced in the industrial sector, mostly for use in the petrochemical industry (e.g., refineries) (Lovins, 2003). Evaporative losses from industrial hydrogen are generally assumed to be negligible (Zittel and Altmann, 1996). The dominant sink process of atmospheric H_2 is deposition with catalytic destruction by soil micro-organisms and possibly enzymes (Conrad and Seiler, 1981). The seasonal cycle of the observed H_2 concentrations implies an atmospheric lifetime of about 2 years (Novelli et al., 1999; Simmonds et al., 2000; Hauglustaine and Ehhalt, 2002), whereas the lifetime with respect to OH oxidation is 9–10 years. This implies that the deposition sink is about 3 to 4 times as large as the oxidation. Loss of H_2 to the stratosphere and the subsequent escape to space is negligible for the tropospheric H_2 budget, because there is no

significant gradient between tropospheric and stratospheric H_2 mixing ratios, and the budgets of the troposphere and stratosphere are largely decoupled (Warneck, 1988).

Table 7.4.4. Summary of global budget studies of atmospheric H_2 (Tg-H yr^{-1}).

	Sanderson et al. (2003a)	Hauglustaine and Ehhalt (2002)	Novelli et al. (1999)	Ehhalt (1999)	Warneck (1988)	Seiler and Conrad (1987)
Sources						
Oxidation of CH_4 and VOC	30.2	31	40 ± 16	35 ± 15	50	40 ± 15
Fossil fuel combustion	20	16	15 ± 10	15 ± 10	17	20 ± 10
Biomass burning	20	13	16 ± 11	16 ± 5	15	20 ± 10
N_2 fixation	4	5	3 ± 1	3 ± 2	3	3 ± 2
Ocean release	4	5	3 ± 2	3 ± 2	4	4 ± 2
Volcanoes	–	–	–	–	0.2	–
Total	78.2	70	77 ± 16	71 ± 20	89	87
Sinks						
Deposition	58.3	55	56 ± 41	40 ± 30	78	90 ± 20
Oxidation by OH	17.1	15	19 ± 5	25 ± 5	11	8 ± 3
Total	74.4	70	75 ± 41	65 ± 30	89	98

Estimates of the global amounts of H_2 necessary to fuel a future carbon-free energy system are highly uncertain and depend on the technological parameters as well as the fraction of energy that would be provided by hydrogen. In the future, hydrogen emissions could at most double compared to the present, and the impacts on the global oxidizing capacity and stratospheric temperatures and ozone concentrations are estimated to be small (Schultz et al., 2003; Warwick et al., 2004). As pointed out by Schultz et al. (2003), the side effects of a global hydrogen economy could have a much stronger impact on the global climate and air pollution. The global oxidizing capacity is predominantly controlled by the concentration of NO_x and the large-scale introduction of hydrogen powered vehicles would lead to a significant decrease of global NO_x emissions, leading to a reduction of OH on the order of 5–10%. Reduced NO_x levels could also significantly reduce tropospheric ozone concentrations in urban areas. In spite of the expected large-scale use of natural gas for H_2 production, the impact of a hydrogen economy on the global CH_4 budget is likely to be small, except for the feedback between the reduced oxidizing capacity (via the NO_x reduction) and the CH_4 lifetime.

7.4.4 Global Tropospheric Ozone

7.4.4.1 Present-day budgets of ozone and its precursors

Tropospheric ozone is (after CO_2 and methane) the third most important contributor to greenhouse radiative forcing since preindustrial times. Typical concentrations are 10–50 ppbv in the lower troposphere, with higher values in polluted regions, and 40–100 ppbv in the upper troposphere (Logan, 1999). Long-term trends in these concentrations over the 20th century are discussed in Chapter 2. Ozone is produced within the troposphere by photochemical oxidation of CO, methane, and nonmethane volatile organic compounds (NMVOCs) in the presence of nitrogen oxide radicals ($NO_x = NO + NO_2$). Stratosphere-troposphere exchange (STE) is another source of ozone to the troposphere. Loss of tropospheric ozone takes place by chemical reactions and by dry deposition to the surface. Estimating the global chemical production and loss rates of tropospheric ozone, and the implications for ozone concentrations, requires 3-D tropospheric chemistry models that describe the complex nonlinear chemistry involved and its coupling to transport. Evaluation of these models with observations of ozone, its precursors, and related species can then be used to test and improve our understanding of the budget and of the underlying processes.

The past decade has seen considerable development in capabilities for modeling tropospheric ozone chemistry. These were reviewed by the TAR, which reported global tropospheric ozone budgets from eleven models documented in the 1996–2000 literature. We present in Table 7.4.5 the means and standard deviations from these TAR budgets together with results from a number of more recent models including a recent intercomparison of 25 models (Stevenson et al., 2005). It is well established that chemical production and loss are the principal terms in the global budget. Recent models and measurements have shown that the spring maximum of tropospheric ozone in the northern hemisphere, long thought to be stratospheric origin, is in fact largely driven by in situ chemical production (Wang et al, 1998; Lelieveld and Dentener, 2000; Browell et al., 2003; Liu et al., 2004). Though STE is only a minor term in the global budget, it delivers ozone to the upper troposphere where its lifetime is particularly long and where it is of most importance from a radiative forcing perspective.

[INSERT TABLE 7.4.5 HERE]

The recent models in Table 7.4.5 show three significant differences relative to the older-generation TAR models: a weaker STE source, stronger chemical production and loss, and a larger tropospheric ozone burden. It is now well established that many of the older studies overestimated STE, as robust constraints from observed NO_y-N_2O-O_3 correlations in the lower stratosphere impose an STE ozone flux of 540 ± 140 Tg yr^{-1} (Olsen et al., 2001). Overestimation of the STE flux appears to be most serious in models using assimilated meteorological data, due to the effect of assimilation on vertical and horizontal motions (Douglass et al., 2003; Schoeberl et al., 2003; Tan et al., 2004; Van Noije et al., 2004). Simulations with free-running GCM fields tend to have a better stratospheric residual circulation and cross-tropopause transport (Douglass et al., 2003; Shindell et al., 2003; Hauglustaine et al., 2004; Rotman et al., 2004). Hauglustaine et al. (2004) found an increase in the STE ozone flux from 523 Tg yr^{-1} in their free running GCM to 783 Tg yr^{-1} in the same GCM with winds relaxed toward assimilated meteorology. The newer models using assimilated meteorological data correct for this effect by using dynamic flux boundary conditions in the tropopause region (McLinden et al., 2000) or by relaxing model results to observed climatology (Horowitz et al., 2003). Such corrections, although matching the global STE flux constraints, may still induce errors in the location of the transport (Hudman et al., 2004) with implications for the degree of stratospheric influence on tropospheric concentrations (Fusco and Logan, 2003).

Explaining the faster chemical production and loss of ozone in the current generation of models is less straightforward. Comparisons of newer vs. older generations of the same models suggests that this could reflect improved treatment of NMVOC sources and chemistry (Houweling et al., 1998), UV actinic fluxes (Bey et al., 2001), and deep convection (Horowitz et al., 2003), as well as higher NO_x emissions (Stevenson et al., 2005). These explanations would also account for the higher ozone burdens. Another contributing factor is that as the STE source decreases, chemical production increases to compensate, reflecting the nonlinearity of ozone chemistry. The compensating increase could be larger than the decrease in the STE source because ozone injected by STE has on average a longer lifetime than ozone chemically produced in the troposphere (Wauben et al., 1998; Lamarque et al., 2005).

Detailed budgets of ozone precursors were presented in the TAR. The most important precursors are methane and NO_x (Wang et al., 1998; Fiore et al., 2002; Grenfell et al., 2003; Dentener et al., 2004). Methane is in general not simulated explicitly in ozone models and is instead constrained from observations. NO_x is explicitly simulated and proper representation of its sources and chemistry is critical for the ozone simulation. Table 7.4.6 gives global NO_x source estimates from the TAR, including likely ranges (mainly from Holland et al., 1999) and the values used in the TAR OxComp intercomparison of ozone models. The latter assumed a large global fossil fuel source (33 Tg-N yr^{-1}) to account for increase of Asian emissions over the past decade, however the Asian increase has been compensated by a European decrease (Naja et al., 2003). Also shown in Table 7.4.6 are the NO_x sources used in the more recent model studies of Table 7.4.5.

Table 7.4.6. Global emissions of NO_x (Tg-N yr^{-1}) in the present-day atmosphere[a]

Reference	Fossil Fuel (surface)	Aircraft	Biomass Burning and Biofuels	Soils	Lightning	Total
TAR[b]	33 (20–24)	0.7 (0.2–0.9)	7 (3–13)	6 (4–21)	5 (3–13)	52 (31–73)
Lelieveld and	24	0.5	9	5	5	46

Dentener (2000)						
Bey et al. (2001)[c]	23	0.5	12 (6)	7 (5)	3 (6)	46 (42)
Horowitz et al. (2003)	23	NR	12	7	3	45
Shindell et al. (2003)	21	0.6	6	6	7	41
Von Kuhlmann et al. (2003)	24	0.5	8	6	5	43
Hauglustaine et al. (2004)	28	0.6	8	6	5	47
Park et al. (2004)	21	NR	8	6	6	41
Rotman et al. (2004)	22	0.5	6	6	5	38
Wong et al. (2004)	27	0.7	6	6	3	43
Stevenson et al. (2004)	27	0.7	8	6	7	50
Stevenson et al. (2005)	28	0.8	10	7[d]	5[d]	51

Notes:
(a) Values given in the TAR are compared with those used in the more recent model studies of Table 7.4.5. None of these model studies includes the NO_x source from oxidation of NH_3, which could contribute up to 3 Tg-N yr^{-1} according to the TAR. The source of NO_x from STE is less than 1 Tg-N yr^{-1} in all models, and this is well constrained from observations of N_2O-NO_y correlations in the lower stratosphere (Olsen et al., 2001).
(b) Values used in the TAR OxComp intercomparison of global tropospheric ozone models. Ranges from the emission inventories compiled by the TAR are given in parentheses.
(c) Values in parentheses are from a more recent GEOS-CHEM version (Martin et al., 2003b)
(d) Values recommended in the Stevenson et al. (2005) model intercomparison of 25 models; individual models used sources in the range 5.5-8.0 Tg-N yr^{-1} for soils and 3.7–7.0 Tg-N yr^{-1} for lightning.

The close agreement in NO_x sources between models in Table 7.4.6 is somewhat artificial, reflecting the use of similar inventories and parameterizations rather than actual constraints on our understanding. The lightning source is particularly uncertain (Nesbitt et al., 2000; Tie et al., 2002), yet is of great importance because of the high production efficiency of ozone in the tropical upper troposphere. The range of the global lightning NO_x source used in models (3–7 Tg-N yr^{-1}) is designed to match tropical observations of ozone and nitrogen oxides (Martin et al., 2002), although large uncertainties in the model simulations of deep convection and the vertical distribution of lightning emissions detract from the strength of this constraint. Process-based models tend to predict higher lightning emissions (5–20 Tg-N yr^{-1}; Price et al., 1997).

One significant development for constraining NO_x sources since the TAR has been the GOME satellite observations of tropospheric NO_2 columns (Richter and Burrows, 2002). Leue et al. (2001) first showed how these data could be used to estimate the magnitude of NO_x emissions. A detailed analysis by Martin et al. (2003b) found that the GOME NO_2 data yield a best estimate of 38 Tg N yr^{-1} for the global surface source of NO_x in 1996–1997 with a factor 1.6 uncertainty (Figure 7.4.4). This is consistent with the surface sources (excluding lightning and aircraft) used in the current generation of global models (34–42 Tg-N yr^{-1}). Martin et al. (2003b) found that the biomass burning source of NO_x had to be significantly lower than 6 Tg-N yr^{-1}, which is already at the low end of the range used in current models. They also pointed out large regional discrepancies with current fossil fuel combustion inventories in the Middle East, South Africa, and some other regions as shown in Figure 7.4.4. Richter et al. (2005) used 1996–2004 trends observed by GOME to deduce a 50% increase in NO_x emissions over industrial areas of China. Martin et al. (2003b) argued that GOME would be insensitive to lightning NO_x due to preferential partitioning of upper tropospheric NO_x to NO during daytime, but a careful analysis by Boersma et al. (2005) shows that the GOME data can constrain the global lightning NO_x source for 1997 to be in the range 1.1–6.4 Tg N yr^{-1}.

[INSERT FIGURE 7.4.4 HERE]

Other significant precursors for tropospheric ozone are CO and non-methane volatile organic compounds (NMVOCs), including in particular biogenic isoprene. Satellite measurements of CO from the MOPITT instrument launched in 1999 (Edwards et al., 2004) have provided important new constraints for CO emissions, pointing in particular to an underestimate of Asian sources in current inventories (Kasibhatla et

al., 2002; Petron et al., 2004; Arellano et al., 2004; Heald et al., 2004), as confirmed also by aircraft observations of Asian outflow (Palmer et al., 2003a; Allen et al., 2004). Recent measurements of biogenic NMVOC emissions and related ecosystem properties have been assimilated by Guenther et al. () to construct updated global emission inventories. Satellite measurements of formaldehyde columns from the GOME instrument (Chance et al., 2000) have been used to place independent constraints on isoprene emissions and indicate values consistent in general with current inventories though with significant regional discrepancies (Palmer et al., 2003b; Shim et al., 2005).

A few recent studies have explored the effect of aerosols on global tropospheric ozone involving both heterogeneous chemistry and perturbations to actinic fluxes. Jacob (2000) reviewed the heterogeneous chemistry involved. Hydrolysis of N_2O_5 in aerosols is a well-known sink for NO_x, but other processes involving reactive uptake of HO_2, NO_2, and O_3 itself could also be significant. Martin et al. (2003b) found that including these processes along with actinic aerosol effects in a global CTM reduced ozone production rates by 6% globally, with larger effects over aerosol source regions (Tie et al., 2005).

Overall, the current generation of tropospheric ozone models is generally successful in describing the principal features of the present-day global ozone distribution on the basis of underlying processes, although there are significant weaknesses (Brunner et al., 2003). Much less confidence is to be had in the ability of these models to reproduce the changes in ozone associated with perturbations to emissions or climate, the latter to be discussed below. The inability of current models to simulate observed long-term trends in ozone concentrations over the 20th century is of significant concern (Mickley et al., 2001; Hauglustaine and Brasseur, 2001; Shindell and Favulegi, 2002; Fusco and Logan, 2003; Shindell et al., 2003; Lamarque et al., 2005). Increasing our confidence in ozone models will require new approaches to model evaluation, involving for example correlations of ozone with other chemical or with meteorological variables.

7.4.4.2 Effects of climate change

Climate change can affect tropospheric ozone in a number of ways through changes in precursor emissions, chemistry, and transport. A detailed report on ozone-climate interactions by the European Commission (2003) identifies changes in lightning, biomass burning, biogenic VOC emissions, humidity, and transport (including STE) as having potentially major impacts on ozone (Figure 7.4.5). These and other effects are discussed below. They could represent positive or negative feedbacks to climate change.

[INSERT FIGURE 7.4.5 HERE]

7.4.4.2.1 Effects on ozone precursor emissions

Climate change affects the sources of ozone precursors through physical response (lightning), biological response (soils, vegetation, biomass burning), and human response (energy generation, land use, agriculture). It is generally expected that lightning will increase in a warmer climate (Price and Rind, 1994a; Brasseur et al., 2005), though a GCM study by Stevenson et al. (2005) for the 2030 climate finds no global increase but instead a shift from the tropics to mid-latitudes. Perturbations to lightning could have a large effect on ozone in the upper troposphere (Toumi et al., 1996; Thompson et al., 2000; Martin et al., 2002; Wong et al., 2004). Mickley et al. (2001) found that observed long-term trends in ozone over the past century might be explainable by a concurrent increase in lightning.

Biomass burning in the tropics and at high latitudes is likely to increase with climate change, both as a result of increased lightning and as a result of increasing temperatures and dryness (Price and Rind, 1994b; Stocks et al., 1998; Williams et al., 2001; Brown et al., 2004). Biomass burning is known to make a large contribution to the budget of ozone in the tropical troposphere (Thompson et al., 1996), and there is evidence that boreal forest fires can enhance ozone throughout the extratropical northern hemisphere (Jaffe et al., 2004). With climate warming, it is likely that boreal fires will increase due to a shorter duration for the seasonal snowpack and decreased soil moisture (Kasischke et al., 1995).

The effect of climate change on biogenic VOC emissions is potentially large but complex. From an ozone perspective the effect on methane is most important and was discussed in Section 7.3.1. The effect on NMVOCs was examined by Constable et al. (1999) and Sanderson et al. (2003b). Although biogenic NMVOC emissions increase with increasing temperature, both studies concluded that ecosystem structural responses unfavorable to NMVOC emissions would compensate for the effect of warming,

7.4.4.2.2 Effects on chemistry

Changes in temperature, humidity, and UV radiation intensity brought about by climate change could affect ozone significantly. GCM simulations by Stevenson et al. (2000) for the 21st century indicate a decrease in the lifetime of tropospheric ozone of 30% by 2100 as increasing water vapor enhances the ozone sink from the $O(^1D) + H_2O$ reaction. They find that the ozone radiative forcing over the 1990–2100 period in the TAR SRES A2 scenario drops from 0.43 to 0.27 W m^{-2} when the effect of climate change on ozone chemistry is included. Similar qualitative trends are found by Stevenson et al. (2005a) in an intercomparison of nine models for 2030 vs. 2000 climate.

7.4.4.2.3 Effects on transport

Changes in atmospheric circulation could have a major effect on tropospheric ozone. Recent GCM studies concur that the STE source of tropospheric ozone should increase in the future climate because of the stronger Brewer-Dobson stratospheric circulation (Sudo et al., 2003; Collins et al., 2003; Zeng and Pyle, 2003; Stevenson et al., 2005b). Changes in vertical transport within the troposphere are also important, in view of the rapid increase in both ozone production efficiency and ozone lifetime with altitude. Convection is expected to intensify as climate warms (Rind et al., 2001), although this might not be the case in the tropics (Stevenson et al., 2005b). The implications are complex, as recently discussed by Pickering et al. (2001), Lawrence et al. (2003), Doherty et al. (2005), and Li et al. (2005). On the one hand, convection brings down ozone-rich air from the upper troposphere to the lower troposphere where it is rapidly destroyed, and replaces it with low-ozone air. On the other hand, injection of NO_x to the upper troposphere greatly increases its ozone production efficiency. Compensation between these two effects can either lead to a decrease or increase of ozone, depending on NO_x levels in the lower troposphere.

Changes in the modes of the general circulation can also affect the distribution and lifetime of tropospheric ozone. TOMS satellite observations of tropical tropospheric ozone columns show a strong interannual sensitivity to ENSO (Ziemke et al., 1999; Chandra et al., 2003), as illustrated in Figure 7.4.6, and this is also found in ozone models (Peters et al., 2001). Warm phase conditions lead to increased ozone over the equatorial western tropical Pacific, reflecting contributions from both Indonesian biomass burning and reduced upwelling (Sudo and Takahashi, 2001). In the central and eastern Pacific, by contrast, warm-phase conditions lead to depleted ozone because of weaker subsidence (Figure 7.4.6). The ENSO effect on tropospheric ozone is mainly confined to the tropics; at northern mid-latitudes, the Arctic Oscillation (AO) has been found recently to be a major contributor to tropospheric ozone variability (Creilson et al., 2003; Lamarque and Hess, 2004).

[INSERT FIGURE 7.4.6 HERE]

7.4.5. The Hydroxyl Radical (OH)

7.4.5.1 Present-day OH budget

The hydroxyl radical (OH) is the primary cleansing agent of the lower atmosphere and it provides the dominant sink for many greenhouse gases (e.g., CH_4, HCFCs, HFCs) and pollutants (e.g., CO, non-methane hydrocarbons). The steady-state lifetime of these trace gases is determined by the morphology of their atmospheric distribution, the kinetics of their reaction with OH, and the OH distribution. The local abundance of OH is mainly controlled by the local abundances of NO_x, CO, CH_4 and higher hydrocarbons, O_3, water vapour as well as the intensity of solar ultraviolet radiation (UVR) at wavelengths shorter than 0.310 μm. The primary source of tropospheric OH is a pair of reactions that start with the photodissociation of O_3 by solar UVR:

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \quad (7.1)$$

$$O(^1D) + H_2O \rightarrow OH + OH \quad (7.2)$$

Additionally, in the remote troposphere and in particular in the upper troposphere, photodissociation of oxygenated volatile organic chemicals such as peroxides, acetone and other ketones, alcohols, and aldehydes and may provide dominant sources of OH radical (e.g., Jaeglé et al., 2001; Tie et al., 2003; Singh et al., 2004). In urban environments or within the forest canopy, measurements also suggest that the processing of

unsaturated hydrocarbons, photolysis of carbonyls or HONO can also sustain a large pool of radicals (e.g., Handisides et al., 2003; Heard et al., 2004). OH reacts with many atmospheric trace gases, in most cases as the first and rate-determining step of a reaction chain that leads to more or less complete oxidation of the compound. These chains often lead to formation of an HO_2 radical, which then reacts with O_3 or NO to recycle back to OH. Tropospheric OH and HO_2 are lost through radical–radical reactions leading to the formation of peroxides or with NO_2 to form HNO_3. The sources and sinks of OH involve most of the fast photochemistry of the troposphere.

7.4.5.2 Changes in OH over the past decades

7.4.5.2.1 Top-down estimates

The global distribution of OH radicals cannot be observed directly because of the difficulty in measuring its small concentrations (about 10^6 OH molecules cm^{-3} on average during daylight in the lower free troposphere) and because of strong variability of OH with geographical location, time of day, and season. However, indirect estimates of the average OH concentration can be obtained from observations of atmospheric concentrations of trace gases such as methyl chloroform (CH_3CCl_3) that are removed mostly by reaction with OH (with rate constants known from laboratory studies), and whose emission history is relatively well-known. The lifetime of CH_3CCl_3 is then often used as a reference number to derive the lifetime of other species and, by convention, provides a measure of the global OH burden. Prinn et al. (2001) analyzed a 22-year record of global CH_3CCl_3 measurements and emission estimates and inferred a large interannual and interdecadal variability in global OH. They estimated that OH values in 2000 were below those in the late 1970s by 10 ± 24 %. Prinn et al. (2005) have extended in time their former analysis over the period 1979–2003. Their results suggest that global average OH levels have remained fairly steady from 1979 to 2003 with only a small maximum around 1989 and a larger minimum around 1998, with OH concentrations in 2003 being comparable to those in 1979. Krol and Lelieveld (2003) calculated a variation of OH of +12% during the 1978–1990 period, followed by a decrease slightly larger than 12% in the decade 1991–2000. Over the entire 1978–2000 period that study provides an overall change close to zero. Bousquet et al. (2005) have also re-examined the OH trend over the 1980–2002 period from the inversion of CH_3CCl_3 atmospheric observations accounting for varying meteorological fields over the considered period. They also infer a substantial OH inter-annual variability and a trend of –0.9% yr^{-1} over the entire period in agreement with previous estimates (Figure 7.4.7). In a recent study, Manning et al. (2005) have used measured carbon monoxide containing radiocarbon (^{14}CO) to derive the OH trend. They found no significant long-term trend in OH concentrations over 1989–2003 period but provide evidence for short-term variations of about 10% persisting for a few months. As a summary of these various analyses, it appears that the phase of the OH fluctuations (positive trend in the 1980s and a negative trend since the early 1990s) is more robustly determined by the inversions than their amplitude (*see* Section 2.3.3 for discussion).

[INSERT FIGURE 7.4.7 HERE]

7.4.5.2.2 Bottom-up analyses

The fluctuations in global OH derived from CH_3CCl_3 or CO measurements are in conflict with observed methane growth rates and with forward model calculations. Karlsdottir and Isaksen (2000) used a 3D CTM accounting for varying nitrogen oxides (NO_x), carbon monoxide (CO) and non-methane hydrocarbon (NMHC) emissions and found a positive trend in OH of +0.43% yr^{-1} over the period 1980–1996. Dentener et al. (2003ab) used a 3D CTM accounting for varying emissions of ozone precursors and methane, meteorology and ozone column and derived a positive trend of +0.26% yr^{-1} over the 1979–1993 period. Wang et al. (2004) have also used a 3D CTM accounting for interannual variations in methane emissions, transport, and column ozone to analyze the trend of methane from 1988 to 1997. They did not account for interannual variability of a number of other variables that affect OH such as concentrations of NO_x, tropospheric ozone and NMHCs. They also derive a positive trend in OH over the considered period of +0.63% yr^{-1}. Their calculated trend in OH is primarily associated with the negative trend in the overhead column ozone over the considered period and reduced to +0.16% yr^{-1} when the total O_3 column is held constant.

7.4.5.3 Longer-term changes in OH

7.4.5.3.1 Impact of emissions

Because of its dependence on CH_4 and other pollutants, tropospheric OH is also expected to have changed since the pre-industrial era and to change in the future. Pre-industrial OH is likely to have been different than

today, but because of the counteracting effects of higher CO and CH_4 (decreasing OH) and increased NO_x and O_3 (increasing OH) there is still little consensus on the magnitude of this change. Several model studies suggest a decline in weighted global mean OH from pre-industrial time to present-day of less than +10% (Shindell et al., 2001; Lelieveld et al., 2002a; Lamarque et al., 2005). Other studies have reported larger decreases in global OH of –16% (Mickley et al., 1999), –25% (Wong et al., 2004) and –33% (Hauglustaine and Brasseur, 2001). The model study by Lelieveld et al. suggests that during the past century OH concentration decreased substantially in the marine troposphere by reaction with CH_4 and CO, however, on a global scale it has been compensated by an increase over the continents associated with strong emissions of nitrogen oxides. As far as future changes in OH are concerned, IPCC (Prather et al., 2001), using scenarios reported in the IPCC Special Report on Emissions Scenarios (Nakicenovic et al., 2000) and on the basis of a comparison of results from 14 models, predicts that global OH could decrease by 10% to 18% by 2100 for 5 emission scenarios and increase by 5% for one scenario assuming large decreases in CH_4 and other ozone precursor emissions. Based on a different emission scenario, Wang and Prinn (1999) also predicted an OH decrease of 16 ± 3% in 2100.

7.4.5.3.2 Effects of climate change

In addition to the emission changes future increases in direct and indirect greenhouse gases could also induce changes in OH through direct participation in OH-controlling chemistry, indirectly through stratospheric ozone changes that could increase solar ultraviolet in the troposphere, and potentially through changes in temperature, humidity, and clouds or climate change effects on biogenic emissions of methane and other ozone precursors. Changes in tropospheric water could have important chemical repercussions. The reaction between water vapour and electronically excited oxygen atoms constitutes the major source of tropospheric OH (Eq. 7.2). So, in a warmer, and potentially wetter climate, the abundance of OH is expected to increase. This effect was already proposed by Pinto and Khalil (1991) to explain the variation of OH during the cold dry Last Glacial Maximum (LGM). This effect was quantified by Martinerie et al. (1995) who calculated that the change in water vapour during the LGM was responsible for a 7% decrease in global average OH concentration. Brasseur et al. (1998) and Johnson et al. (1999) estimated that in a warmer climate corresponding to a doubling in CO_2 concentration, the global and annual mean OH concentration increases by +7% and +12.5% respectively. More recently, Hauglustaine et al. (2005) used a climate-chemistry 3D model and calculated a 16% reduction in global OH from present day to 2100 accounting for changes in surface emissions solely. The effect of climate change and mainly of increased water vapour in this model is to increase global OH by 13%. In that study, the competing effects of emissions and climate change maintain the future global average OH concentration close to its present-day value. The importance of the water vapour distribution on global OH as also been illustrated by Lamarque et al. (2005). These authors showed that under reduced aerosol emissions the warmer and moister climate directly increases global OH concentration significantly.

Changes in lightning NO_x emissions in a warming climate have also the potential to significantly affect OH. Labrador et al. (2004) have calculated that global OH is very sensitive to the magnitude of the lightning NO_x emissions and increases by 10% and 23% when the global lightning source is increased respectively by a factor of 2 and 4 from a 5 TgN yr^{-1} best estimate. A similar sensitivity of global to the lightning source has been estimated by Wang et al. (2004) who calculated a 10.6% increase in OH for a doubling of the source (from 3 to 6 TgN yr^{-1}). Regarding the large uncertainty on lightning emissions and the sensitivity of OH to the total amount of N emitted, an improved understanding of this source appears important for our ability to accurately simulate OH and its changes over time.

7.4.5.4 Consequences on lifetimes

As described in more detail in Velders et al. (2005), for a given trace gas, each relevant sink process contributes to the additive first-order total loss frequency, l, which is variable in space and time such as oxidation by OH. A local lifetime τ_{local} can be defined as the inverse of l evaluated at a point in space (x, y, z) and time (t):

$$\tau_{local} = 1 / l(x,y,z,t) \qquad (7.3)$$

The global instantaneous atmospheric lifetime of the gas is obtained by integrating l over the considered atmospheric domain. The integral must be weighted by the distribution of the trace gas on which the sink

processes act. Consider a distribution of the trace gas $C(x,y,z,t)$, a global instantaneous lifetime derived from the budget can be defined as:

$$\tau_{global} = \int C \, dv / \int C \, l \, dv \quad (7.4)$$

where dv is an atmospheric volume element. This expression can be averaged over a year to determine the global and annually averaged lifetime. The global atmospheric lifetime characterizes the time required to turn over the global atmospheric burden. Because the total loss frequency l is the sum of the individual sink process frequencies, τ_{global} can also be expressed in terms of process lifetimes:

$$1/\tau_{global} = 1/\tau_{tropospheric\ OH} + 1/\tau_{photolysis} + 1/\tau_{other\ processes} \quad (7.5)$$

It is convenient to consider lifetime with respect to individual sink processes limited to specific regions, e.g., the oxidation by reaction with OH in the troposphere. However, the associated burden must always be global and include all communicating reservoirs in order for (Eq. 7.4) to remain valid. In (Eq. 7.4), the numerator is therefore integrated over the whole atmospheric domain and the denominator is integrated over the domain in which the individual sink process is considered. In the case of $\tau_{tropospheric\ OH}$, the convention is that integration is performed over the tropospheric domain. The use of different domains or different definitions for the troposphere can lead to differences of 10% in the calculated value (Lawrence et al., 2001).

The lifetimes can be determined in global models by simulating the injection of a pulse of that gas and watching the decay of this added amount. This decay can be represented by a sum of exponential functions, each with its own decay time. These exponential functions are the chemical modes of the linearised chemistry-transport equations of a global model (Prather, 1996; 2002). In the case of a CH_4 addition, the longest-lived mode has an *e*-fold time of 12 yr, very close to the steady-state perturbation lifetime of CH_4 described in more details in Prather et al. (2001) and Velders et al. (2005). In the case of a CO, HCFCs, or HCs addition, this same mode is also excited, but at a much reduced amplitude depending on the amount of gas emitted (Prather, 1996; Daniel and Solomon, 1998). The pulse of added CO, HCFCs, or HCs, by causing the concentration of OH to decrease and thus the lifetime of CH_4 to increase temporarily, causes a build-up of CH_4 while the added burden of the gas persists. After the initial period defined by the photochemical lifetime of the injected trace gas, this built-up CH_4 then decays in the same manner as would a direct pulse of CH_4. Thus, changes in the emissions of short-lived gases can generate long-lived perturbations as shown in global models (Wild et al., 2001; Derwent et al., 2001). Changes in tropospheric O_3 accompany the CH_4 decay on a 12-year time scale as an inherent component of this mode, a key example of chemical coupling in the troposphere. Thus, any chemically reactive gas, whether a greenhouse gas or not, will produce some level of indirect greenhouse effect through its impact on atmospheric chemistry.

Since OH is the primary oxidant in the atmosphere of many greenhouse gases including methane and hydrogenated halogen species, their lifetime in the atmosphere and hence impact on the climate system will directly be affected by changes in OH. Several studies have shown that variations on an annual basis in the chemical removal of methane by OH exert an important impact in the variability of the methane growth rate (Johnson et al., 2002; Warwick et al., 2002; Wang et al., 2004). These studies show that variations in CH_4 oxidation by OH contribute to a significant fraction of the observed variations in the annual accumulation rate of methane in the atmosphere. In particular, the observed slowdown in the growth rate of methane in the atmosphere is attributed to a combination of slower growth of sources and increases in OH and the 1992–1993 anomaly in CH_4 growth rate can be explained by fluctuations in OH and wetland emissions after the eruption of Mount Pinatubo (Wang et al., 2004). The methane variability simulated by Johnson et al. (2002) accounting only from OH sink processes also indicates that the El Niño-Southern Oscillation cycle is the largest component of that variability. These findings are consistent with the variability of global OH reconstructed by Prinn et al. (2005) and Manning et al. (2005) and strongly affected by large-scale wildfires as in 1997–1998, by El Niño events and the Mt Pinatubo eruption.

The importance of climate change on tropospheric chemistry and on the future evolution of methane has also been investigated in several studies. In most cases the future methane lifetime increases when emissions increase and climate change is ignored (Brasseur et al., 1998; Stevenson et al., 2000; Prather et al., 2001; Hauglustaine and Brasseur, 2001; Hauglustaine et al., 2005). This feature reflects the fact that increased levels of CH_4 and CO depress OH reducing the CH_4 sink. However, climate warming increases the

temperature-dependant CH_4 oxidation rate coefficient (Johnson et al., 1999), and increases in water vapour and NO_x concentrations tend to increase OH. In most cases, these effects partly offset or even exceed the methane lifetime increase due to emissions. As a consequence, the future methane lifetime calculated by Brasseur et al. (1998), Stevenson et al. (2000) and Hauglustaine et al. (2005) remains relatively constant (within a few %) over the 21st century. In their transient simulation over the period 1990–2100, Johnson et al. (2001) found a dominant effect of climate change on OH in the free troposphere so that the global methane lifetime declines from around 9 years in 1990 to around 8.3 years after by 2025 and does not change significantly thereafter. The direct consequence is that the calculated methane increase in 2100 is reduced by 27% when climate change is considered. A similar conclusion about the relatively constant methane lifetime was reached by Stevenson et al. (2005) in their model intercomparison. As a result of future changes in emissions, the methane lifetime simulated by 25 state-of-the art chemistry transport models increased by 3% in 2030 from an ensemble mean of 8.7 ± 1.3 years for the present-day. Under the 2030 warmer climate scenario the lifetime was reduced by 5% so that the total effect of both emission and climate changes was to reduce the methane lifetime by only 2%.

7.4.6 Stratospheric Ozone and Climate

During the last two decades a negative trend in globally averaged total ozone has been observed. It is generally accepted that an increase in chlorine and bromine loading is a major cause of this trend. In addition, atmospheric concentration of well-mixed greenhouse gases has also increased. This subsection presents a synthetic review of our understanding of the interactions between stratospheric ozone and climate. For more detailed discussions, see the reports published recently by WMO (2003), Chapters 3 and 4, by the IPCC (Special Report on Ozone and Climate, Chapter 1), and by the European Commission (2003).

[INSERT FIGURE 7.4.8 HERE]

7.4.6.1 Interactions

Figure 7.4.8 illustrates schematically the processes determining ozone climate interactions in the troposphere and stratosphere. Stratospheric ozone is affected by climate change through changes in tropospheric temperature, in the water vapour content and possibly in the circulation and dynamics (e.g., Granier and Shine, 1999; Stevenson et al., 2000; Johnson et al., 2001). An increase in the concentration of greenhouse gases (GHG), especially CO_2, cools the stratosphere and alters the ozone distribution (Rosenfield et al., 2002). In most of the stratosphere, a decrease in temperature reduces ozone depletion leading to higher ozone amounts and a positive correction to the GHG induced cooling. However, in the polar regions, there is a positive feedback process whereby cooling leads to enhanced ozone destruction via chlorine and bromine.

Ozone is a greenhouse gas and absorbs UV radiation in the stratosphere. The absorption of UV provides the heating responsible for the observed increase of temperature with height above the tropopause. Changes in stratospheric temperatures, whether induced by ozone change or GHG change, alter the Brewer-Dobson circulation. This controls the rate at which long-lived molecules, such as GHGs, CFCs, and halons are transported from the troposphere to various levels in the stratosphere**.** There is also statistical evidence that changes in the stratospheric circulation propagate downwards into the troposphere (e.g., Baldwin and Dunkerton, 1999).

Additionally, climate is affected by changes in stratospheric ozone. Stratospheric ozone radiates infrared radiation down to the troposphere. For a given percentage change in the vertical structure of ozone, the largest dependence of the radiative forcing (RF) is in the vicinity of the tropopause (Wang et al., 1980; Lacis et al., 1990). The climate sensitivity, (i.e. the surface temperature response per unit RF) on the vertical structure of the ozone perturbation is model dependent, but ozone perturbations in the lower stratosphere appear to be most efficient (e.g., Stuber et al. 2001; Joshi et al., 2003). Past ozone depletion has thus induced surface cooling, which has approximately balanced the greenhouse warming resulting from increasing abundances of ozone depleting substances (ODSs) and their substitutes. Taking into consideration the net change in ozone in the troposphere and stratosphere, the positive radiative forcing due to tropospheric ozone changes has dominated the negative stratospheric forcing over the period 1750–2000. Over the period 1970–2000, however, the two forcings were approximately of equal importance, but opposite in sign. Part of the long-term observed UV changes are driven by changes in stratospheric ozone.

7.4.6.2 Past ozone changes

Past ozone losses have been largest in polar regions during spring. For example, the ozone hole over Antarctica has occurred every spring since the early 1980s and is a recurring phenomenon (Fioletov et al., 2002). In the year 2002, the ozone hole was of shorter duration than normal due to a unique stratospheric warming event. This is not an indication of recovery in ozone amounts, but rather the result of this dynamical disturbance (e.g., Newman et al., 2004). Ozone destruction there is driven by climatologically low temperatures combined with high chlorine and bromine amounts produced from the photochemical breakdown of primarily man-made CFCs and halons. Similar losses, but of much smaller magnitude, have occurred over the Arctic due to the same processes during cold winters. Warm winters have been relatively unaffected. Ozone losses in other regions have occurred due to increases in nitrogen oxides (from nitrous oxide emissions) and heterogeneous chemical processes on the surface of atmospheric aerosols, again combined with high chlorine and bromine amounts. Mid-latitudes have been influenced by transport of ozone from polar and tropical regions, as well as from local chemistry (aerosols and nitrogen oxides).

7.4.6.3 Stratospheric water vapour trend

Stratospheric water vapour is controlled to a high degree by temperatures near the tropical tropopause. Long-term observed changes show that the tropical tropopause has cooled slightly during the past two decades. Most climate models do not simulate an increase in water vapour, neither for the past nor for the future. Long-term changes in lower stratospheric water vapour are currently not known, as e.g. decadal-scale changes of water vapour in the lower stratosphere for the time period 1992–2002 are very different between balloon and satellite datasets near Boulder (Oltmans et al., 2000; Rosenlof et al., 2001; Randel et al., 2004). A positive (negative) water vapour trend, if present, is expected to give rise to a positive (negative) trend in total ozone of comparable magnitude.

7.4.6.4 Future ozone changes

Continued increases in greenhouse gases and a slow decrease in atmospheric halogen loading are expected to occur in the future decades. Both influence the abundance of stratospheric ozone. Over Antarctica, ozone should start to recover within the next 10 years, whereas in the Arctic, the recovery should be start within the next two decades (Figure 7.4.9).

[INSERT FIGURE 7.4.9 HERE]

In the Arctic, the climate feedback associated with GHG increase on the ozone recovery should be more prominent than in the Antarctic. The recovery to the levels last observed in 1980 is not expected to occur until about 2040. Thereafter there may be some further ozone losses due to increases in nitrous oxide emissions. When recovery does finally occur, the vertical distribution of ozone will be different from that which was observed in the 1980s due to the sensitivity of the chemical processes to the atmospheric temperature. One of the major scientific conclusions of recent model studies (Austin et al., 2003) is that we do not expect a future Arctic ozone hole comparable to the hole observed in Antarctica.

7.4.6.5 Uncertainties in current coupled Chemistry-Climate Models (CCMs)

Coupled chemical climate models (CCMs) have been used to simulate past ozone changes and to provide prediction of the future evolution of ozone in response of human activities. Only a limited number of these models have assessed the sensitivity of stratospheric ozone to natural forcings such as large volcanic eruptions, solar variability (11-year cycle), and the quasi-biennial oscillation (QBO). These mechanisms have significant impacts on processes that determine the dynamics and chemistry of the atmosphere. A more detailed investigation of the role of natural variability in past ozone changes and other atmospheric changes is therefore important for assessments of ozone changes. The largest uncertainties in current Climate Chemistry Models (CCMs) stem from the performance of the underlying dynamical model components. Other components of CCMs (i.e., chemistry and transport) have not yet been tested to the same extent. These models are often characterized by temperature biases, which lead to substantial errors in the calculated degree of ozone depletion. The major uncertainties are associated with the representation of the resolved and unresolved portions of the dynamical wave spectrum and the excitation of waves at resolved and unresolved scales (including gravity waves).

7.5 Aerosol Particles and the Climate System

Anthropogenic aerosol particles such as sulphate and carbonaceous aerosols have substantially increased the global mean burden of aerosol particles from preindustrial times to the present-day. Aerosol particles affect the climate system via the following physical mechanisms: First, they scatter and can absorb solar radiation. Second, they can scatter, absorb and emit thermal radiation. Third, aerosol particles act as cloud condensation nuclei (CCN) and ice nuclei (IN), thereby affecting the hydrological cycle and radiation processes. The first two mechanisms are referred to as direct effects and are discussed in detail in Chapter 2. The last one is referred to as an indirect effect. It will be the subject of this chapter together with other atmospheric properties influenced by aerosols (e.g. semi-direct effect, suppression of convection). Even though the semi-direct effect is a consequence of the direct effect of absorbing aerosols, it changes cloud properties in response to these aerosols. This aspect will be discussed here while its radiative effects are subject of Chapter 2.

7.5.1 What Major Climatic Factors Control Natural Aerosol Emissions and Burdens?

Aerosol sources are more complex than greenhouse gas sources, because aerosols often are formed within the atmosphere. Clouds are at the same time a source and a sink for aerosols. They are an important factor for determining the size, composition, lifetime and degree of mixing of aerosols. Also, aerosols left behind from an evaporating cloud are more effective CCN in subsequent cloud formation events. Thus, the anthropogenic burden hethero depends on the climate itself. In addition natural emissions, such as wind driven dust and sea salt or emissions from the marine and terrestrial biosphere, also depend on climate. This complexity is lost if simple empirical relationships between anthropogenic emissions and aerosol radiative effects are used in global climate models. Some examples of climatic influences on natural aerosol emissions and burdens are discussed below while anthropogenic aerosol emissions are subject of Chapter 2. The importance of natural aerosols and their dependence on the parameterizations used in different climate models is highlighted in Figure 7.5.1 (Kinne et al., 2005).

[INSERT FIGURE 7.5.1 HERE]

7.5.1.1 Dust

Estimates of global source strength of bulk dust aerosol range from ~1000 to 3000 Mt yr^{-1} (Andreae, 1995; Duce, 1995; Textor et al., 2005) with high spatial and temporal variability. Zhang et al. (1997) estimated that ~800 Mt of Asian dust is injected into the atmosphere annually, about 30% of which is re-deposited onto the deserts and 20% is transported over regional scales, while the remaining ~50% is subject to long-range transport to the Pacific Ocean and beyond. Uncertainties for the estimates of global dust emissions are over more than a factor of two (Zender et al., 2004) due to problems in validating and modeling the global emissions. The representation of the high wind tail of the wind speed distribution alone—responsible for most of the dust flux—leads to differences in emissions in one model by more then 30% (Timmreck and Schulz 2004). Observations suggest that African dust may have varied by a factor of four during 1960–2000 (Chiapello et al., 2005), possibly due to variability of rainfall in the Sahel zone. Single model simulations suggest a decrease of dust emissions by 20–60% for 2100 due to changes in vegetation cover in response to precipitation, temperature and CO_2 fertilization (Mahowald and Luo, 2003). Natural mineral dust is the most important aerosol component in terms of aerosol burden and radiative impact and the modulation of its source due to climate factors is thus likely to be of importance. The radiative effect of dust, suggested for example to intensify the African Easterly Waves, may be a feedback mechanism between climate and dust (Jones et al., 2005b).

Dust may alter the climate, which in turn can feed back upon dust emission. For example, radiative forcing by dust from anthropogenic sources alters the atmospheric circulation, which feeds back upon dust emission from natural sources. Perlwitz et al. (2001) estimated that this feedback changes the global dust load by roughly 15%. In addition to natural dust production, human activities have created another potential source for dust through the process known as desertification, but the contribution of desertification through human activities to global dust emission is very uncertain with the estimation varying from 50% (Tegen et al., 1996), to less than 10% (Tegen et al., 2004), to insignificant values (Ginoux, 2001; Prospero et al., 2002). A 43-year estimation of Asian dust emissions reveals that meteorology and climate have a greater influence on Asian dust emissions and associated Asian dust storm occurrences than desertification (Figure 7.5.2; Zhang et al., 2003). Estimates of future changes in dust emissions under several climate and land-use scenarios suggest dust emissions may increase or decrease. Either way the effects of climate change are more

important in controlling dust emissions than changes in land-use (Tegen et al., 2004). High Asian dust-induced heating of the land relative to the ocean would tend to reduce the thermal gradient between the land and ocean, thereby weakening the Asian winter monsoon circulation, with a feedback to reduce the dust emission from its sources (Zhang et al., 2002).

[INSERT FIGURE 7.5.2 HERE]

In addition, the deposition of aerosols has impacts on global ecosystems. Deposition of mineral dust in the ocean plays an important role in the biogeochemical cycle of the oceans. Also for terrestrial ecosystems the input of trace elements by dust deposition is of essential importance. For example, it has been proposed that the vegetation of the Amazon basin is highly dependent on Saharan dust deposition as it provides phosphorus, necessary for the maintenance of long-term productivity (see Section 7.3).

7.5.1.2 Natural organic carbon

Biogenic organic material is both directly emitted into the atmosphere and produced by volatile organic compounds (VOC). Primary emissions have been thought to be a relatively minor source but some studies suggest that these emissions could be much higher (Jaenicke, 2005; Folberth et al., 2005). Kanakidou et al. (2005) estimate a global biogenic secondary organic aerosol production of ~30 Tg yr^{-1} and recognize the potentially large, but highly uncertain, flux of primary biogenic particles. They suggest that primary emissions are of limited importance for climate since they consist mostly of the coarse aerosol fraction. Annual global biogenic VOC emission estimates range from about 0.5 to 1.2 Pg. However, there is a large range (<5% to >90%) of organic aerosol yield for individual compounds and atmospheric conditions resulting in estimates of global annual secondary organic aerosol production from biogenic VOC of about 32 Tg that range from 2.5 to 44.5 Tg of organic matter per year (Tsigardis and Kanakidou, 2003). All biogenic VOC emissions are highly sensitive to changes in temperature, and some emissions respond to changes in solar radiation and precipitation (Guenther et al., 1995). In addition to the direct response to climatic changes, biogenic VOC emissions are also highly sensitive to climate-induced changes in plant species composition and biomass distributions. Several studies have examined the response of global biogenic VOC emissions to climate change (e.g., Turner et al., 1991; Adams et al., 2001; Sanderson et al., 2003b). These model studies predict that solar radiation and climate induced vegetation change can affect emissions, but they do not even agree on the sign of the change. The impact of precipitation on biogenic VOC emissions is even more uncertain and has not been included in global studies. The substantial increase in emissions with increasing temperature (~10% increase per degree C) predicted by these studies is based on algorithms described by Guenther et al. (1993) which describe the response of emissions to short term changes in temperature. There is evidence of physiological adaptations to higher temperatures that would lead to a greater temperature response for long-term temperature changes (Guenther et al., 1999). The response of biogenic secondary organic carbon production to a temperature change, however, could be considerably lower than the response of biogenic VOC emissions since aerosol yields can decrease with increasing temperature.

New evidence reveals the ocean as a source of organic matter from biogenic origin (O'Dowd et al., 2004; Leck and Bigg, 2005). These findings are, however, still too recent to extrapolate any global organic flux from the ocean surface.

7.5.1.3 Sea salt

Sea salt aerosol is a key aerosol constituent of the marine atmosphere. Sea salt aerosol particles are hygroscopic and function as cloud condensation nuclei, affecting the formation of clouds and development of rain; they serve as sinks for reactive gases and small particles, possibly suppressing new particle formation; and they scatter light, affecting the albedo and radiative balance of Earth. Sea salt aerosol production is affected by meteorological or environmental factors that modify surface properties of the ocean, wave breaking, or the turbulence level in the ocean surface waters; the formation, size distribution, entrainment, rise velocity, gas exchange characteristics, or bursting of bubbles; or the formation, entrainment, or behaviour of drops. The major meteorological and environmental factors that have been proposed in this regard are wind speed, atmospheric stability and wind friction velocity, sea and air temperatures, present and prior rain or snow, and the amount and nature of surface-active materials in the near-surface ocean waters (Lewis and Schwartz, 2005). The average annual global sea-salt flux from 12 models is estimated to be 16300 ± 200 Tg (Textor et al., 2005) of which 15% is emitted into the fine mode.

These submicrometer particles contribute significantly to the background aerosol mass and number concentrations in the marine atmosphere and substantially to the total optical depth of the atmosphere over the open ocean.

7.5.1.4 Dimethylsulphide (DMS)

DMS produced by phytoplankton is the most abundant form in which the ocean releases gaseous sulphur. DMS sea-air fluxes may vary by orders of magnitude in space and time depending mainly on DMS sea surface concentration and on wind speed. Estimates of the global DMS flux vary widely depending mainly on the utilized DMS sea surface climatology, sea-air exchange parameterization, and wind speed data, ranging from 16 Tg S/yr up to 54 Tg S/yr (see Kettle and Andreae, 2000 for a review). Up to now none of the transient climate studies include a description of the DMS cycle in the ocean. The response of the DMS emission to climate change could therefore be only assessed through changes in the sea-air exchange rate, which varies with wind speed and temperature. Penner et al. (2001) showed a small increase in DMS emissions between 2000 and 2100 (from 26.0 Tg-S yr^{-1} to 27.7 Tg-S yr^{-1}) using a constant DMS sea surface concentration field together with a constant monthly climatological ice cover. As discussed in Section 7.5.1.4., Gabric et al. (2004) predicted an increase of the globally integrated DMS flux perturbation of +14% for a tripling of the pre-industrial carbon dioxide concentration.

7.5.1.5 Climatic factors controlling aerosol burdens

Knowledge of the various primary and secondary aerosol sources, combined with the size and composition dependent aerosol sinks, chemical transformations and transport processes in principle allow prediction of the chemical and physical nature of the atmospheric aerosol and their amounts in the atmosphere (burden). Some of these controlling factors, such as chemical reaction rates, depend on climate factors, especially temperature. As these are relevant to biogeochemical cycles, some of them will be highlighted here.

The burden of carbonaceous aerosols is influenced by the conversion of hydrophobic carbon to hydrophilic carbon. While this conversion depends on condensation, coagulation and oxidation, it can reasonably well be approximated as a first order reaction with a constant 24-h half-life in the present-day climate (Croft et al., 2005; Park et al., 2005). However, one key factor in controlling the burden of secondary organic aerosols in global climate models is the gas-particle partitioning (Kanakidou et al., 2004). We cannot simply assume that all semi-volatile products always condense in the same proportion, because that depends on the presence of primary organic and inorganic aerosols as well as on temperature and relative humidity.

Lohmann and Feichter (1997) showed that the sulphate burden increased by 50% when an aerosol scheme is coupled to a cloud scheme in a global climate model. A positive feedback loop is established in which more sulphate aerosols decrease the precipitation formation rate, which in turn increases the lifetime of sulphate aerosols and results in more long-range transport of sulphate to remote regions where wet removal is less efficient. If, however, a fraction of the anthropogenic black carbon (BC) is considered to act as contact ice nuclei, the precipitation formation via the ice phase is enhanced, removing aerosols from the atmosphere and thus terminating the positive feedback loop. This mechanism can reduce the increase in anthropogenic aerosol burden from pre-industrial to present-day times by 38% to 58% (Lohmann, 2002).

Stier et al. (2005) concluded that the lifetime of sulphate aerosols decreased 10% from pre-industrial to present-day conditions, the black carbon lifetime decreased 23% and mineral dust 2%, whereas the lifetime of particulate organic matter increased 11%. The alterations in aerosol lifetimes cannot unambiguously be attributed to microphysical processes, as lifetimes are also affected by geographical shifts of the dominant aerosol source regions. Moreover, the burdens of different aerosol species do not add linearly. Close to the anthropogenic source regions, deviations from additivity are found up to 30% and 15% for the accumulation mode number burden and aerosol optical thickness, respectively. These results challenge the appropriateness of bulk aerosol models for addressing climate change.

7.5.2 How Do Aerosols (Indirect Effects) Modify Clouds and Precipitation?

Aerosol particles act as cloud condensation nuclei (CCN) and ice nuclei (IN). These indirect effects are the subject of this section together with aerosol induced changes in large-scale circulation and convection. They can be subdivided into processes contributing to the indirect aerosol effect as summarized in Table 7.5.1. The cloud albedo effect is the only true indirect aerosol forcing and therefore is subject of Chapter 2. The

other effects involve feedbacks and will be discussed here. All processes that decrease the cloud droplet size per given liquid water content simultaneously lead to an increase in cloud albedo (cloud albedo effect) and reduce the precipitation formation. Thus, they immediately affect cloud dynamics and prolong cloud lifetime (cloud lifetime effect), making it difficult to separate these different effects from observations. Heating due to black carbon can cause cloud droplet evaporation (semi-direct), which could counteract some of the aerosol-induced cooling described above. It also affects static stability as discussed in Section 7.5.4.1. If some aerosol particles initiate freezing in a supercooled cloud, this cloud will rapidly glaciate due to the difference in vapour pressure over ice and water (Bergeron-Findeisen process). Unlike cloud droplets, these ice crystals grow in an environment of high supersaturation with respect to ice, quickly reaching precipitation size, and with that, turning a non-precipitating into a precipitating cloud (glaciation effect and Section 7.5.2.3.). The thermodynamic effect refers to aerosol-induced increases in the intensity of convective clouds due to more latent heat of freezing that increases the amount of precipitation from polluted clouds (Section 7.5.2.5.). The surface energy budget effect (Section 7.5.3.1.) describes the aerosol-induced decrease in surface solar radiation with consequences for evaporation and precipitation.

Table 7.51a. Overview of the different aerosol indirect effects and their sign of the radiative forcing at the top-of-the atmosphere (TOA)

Effect	Cloud Types Affected	Process	Sign of Change in TOA Radiation	Potential Magnitude	Certainty
Cloud albedo effect	All clouds	For the same cloud water or ice content more but smaller cloud particles reflect more solar radiation	Negative for water clouds, positive or negative for ice clouds	medium	certain
Cloud lifetime effect	All clouds	Smaller cloud particles decrease the precipitation efficiency thereby prolonging cloud lifetime	Negative	medium	indication
Semi-direct effect	All clouds	Absorption of solar radiation by soot leads to an evaporation of cloud particles and increases static stability	Positive or negative	small	potential
Glaciation indirect effect	Mixed-phase clouds	An increase in ice nuclei increases the precipitation efficiency	Positive	medium	potential
Thermodynamic effect	Mixed-phase clouds	Smaller cloud droplets inhibit freezing causing supercooled droplets to extend to colder temperatures	Positive or negative	medium	uncertain
Surface energy budget effect “Solar dimming”	All clouds	The aerosol induced increase in cloud optical thickness decreases the amount of solar radiation reaching the surface, changing the surface energy budget	n/a	n/a	indication

Table 7.5.1b. Overview of the different aerosol indirect effects and their implications for the shortwave radiation at the surface F_{sfc} and for the hydrological cycle.

Effect	Sign of Change in F_{sfc}	Potential Magnitude	Certainty	Sign of Change in Precipitation	Potential Magnitude	Certainty
Cloud albedo effect	Negative	medium	certain	N/a	zero	certain
Cloud lifetime effect	Negative	medium	indication	Negative	small	indication
Semi-direct effect	Negative	large	potential	Negative	large	potential
Glaciation indirect effect	Positive	medium	potential	Positive	medium	potential
Thermodynamic effect	Positive or negative	medium	uncertain	Positive or negative	medium	uncertain
Solar dimming	Negative	large	indication	Negative	large	indication

7.5.2.1 Observational aerosol effects on water clouds

The indirect aerosol effect of changing cloud albedo is discussed in Chapter 2. Evidence of a cloud lifetime effect due to anthropogenic emissions of aerosols and their precursors stem, for instance, from the absence of a drizzle mode in ship tracks perturbing marine stratus cloud decks off the coast of California (Ferek et al., 1998) as well as from polluted versus clean clouds off the Atlantic coast of Canada (Peng et al., 2002). One remaining problem is that most climate models suggest an increase in liquid water when adding anthropogenic aerosols, whereas newer ship track studies show that polluted marine water clouds can have less liquid water than clean clouds (Platnick et al., 2000; Coakley et al., 2002). Ackerman et al. (2004) attribute this phenomenon to enhanced entrainment of dry air in polluted clouds in these instances.

On the individual cloud scale, the largest unknown is the contribution of organic aerosols as CCN (McFiggans et al., 2005 and Chapter 2). Recent studies that combine measurements with Lagrangian air parcel models off the coasts of Ireland, Eastern Canada and in the Arctic Ocean show that organics can increase the number of cloud droplets (O'Dowd et al., 2004; Lohmann and Leck, 2004; Leaitch et al., 2005). Over the Arctic Ocean this increase in cloud droplet number arises from the ability of the organic aerosols to lower the surface tension (Facchini et al., 1999; Decesari et al., 2003), whereas off the coasts of Ireland the cloud droplet increase is attributed to the addition of a new source of marine organics, mostly insoluble, active during phytoplankton blooms. Off the coast of Nova Scotia, the increase in cloud droplet number concentration is either caused by organics that are reasonably water-soluble and grow in a way similar to that of sulphate. Another possibility is that the organics are only weakly soluble and grow at a much slower rate than sulphate, which leads to a slightly higher cloud supersaturation and the activation of smaller aerosol particles. These chemical effects could be of the same order of magnitude as the cloud albedo effect (Nenes et al., 2002) and may be as important as unresolved cloud dynamics (Lance et al., 2004).

For the tropical Indian Ocean, Ramanathan et al. (2001) estimated a total indirect aerosol effect of –5 W m^{-2} at the top-of-the-atmosphere (TOA) and of –6 W m^{-2} at the surface. While the combined direct and semi-direct effect is negligible at the TOA, its surface forcing amounted to 14 W m^2, pointing out the importance of considering surface radiative forcings in addition to TOA forcings.

7.5.2.2 Global climate model estimates of the total anthropogenic aerosol effect

The total anthropogenic aerosol effect as defined here includes estimates of the indirect cloud albedo and cloud lifetime effect. For those climate models that also simulate black carbon and link their aerosols to the radiation scheme, the total anthropogenic aerosol effect is the sum of the direct, semi-direct and indirect effects. The global mean direct and semi-direct effects at the TOA are, however, smaller than the indirect effects (Lohmann and Feichter, 2001; Penner et al., 2003). The influence of black carbon is dominated via its absorption of solar radiation within the atmosphere, which also leads to a large negative global mean forcing of –1.2 to –4 W m^{-2} at the surface (Ramanathan et al., 2001a; Lohmann and Feichter, 2001; Liepert et al., 2004).

Climate model estimates of the total anthropogenic aerosol effect at the top-of-the atmosphere are generally larger than estimated from inverse models (Anderson et al., 2003; Lohmann and Feichter, 2005). Climate model estimates of the importance of the cloud lifetime effect as compared with the cloud albedo effect are diverse. Whereas some models concluded that the cloud albedo effect is four times as important as the cloud lifetime effect other models simulate a cloud lifetime effect that is larger than the cloud albedo effect (Lohmann and Feichter, 2005). This discrepancy is independent of the chemical nature of the anthropogenic aerosol species that are used in these different simulations. Differences among the simulations include an empirical treatment between the aerosol mass and the cloud droplet number concentration versus a mechanistic relationship, the dependence of the indirect aerosol effect on the assumed background aerosol or cloud droplet number concentration and the competition between natural and anthropogenic aerosols as CCN (Ghan et al., 1998; O'Dowd et al., 1999). Likewise differences in the cloud microphysics scheme, especially in the autoconversion rate, cause uncertainties in estimates of the indirect aerosol effect (Lohmann and Feichter, 1997; Jones et al., 2001; Menon et al., 2002; 2003). Another problem in current climate models arises from neglecting particulate sulphate emissions. Adams and Seinfeld (2003) point out that particulate sulphate emissions are more efficient per unit mass than gas-phase emissions at increasing CCN concentrations. However, Stier et al. (2005) show that this effect is negligible when not just sulphate but the full suite of aerosol components is taken into account.

The global mean total indirect aerosol effect, defined as the change in net radiation at TOA from pre-industrial times to present-day, is shown in Figure 7.5.3. The simulations by Lohmann (2004) and Lohmann and Diehl (2005) now include the influence of aerosols on the cloud droplet size distribution (dispersion effect as introduced by Liu and Daum (2002)) for the cloud albedo effect. The simulations by Rotstayn and Liu (2005) include the dispersion effect for the cloud albedo and the cloud lifetime effect (Liu et al., 2004). If the dispersion effect is taken into account, the total indirect aerosol effect is reduced by 15–35% (Peng and Lohmann, 2003; Rotstayn and Liu, 2003; 2005). This explains the small global mean total indirect aerosol effect in the simulation by Rotstayn and Liu (2005). The global mean indirect aerosol effect in the CAM-Oslo model has been reduced from –1.8 W m^{-2} (Kristjansson, 2002) to –0.13 W m^{-2} (Storelvmo et al., 2005), due to the introduction of microphysical sinks for cloud droplets and a cloud droplet activation scheme which accounts for the competition of the CCN for the available supersaturation.

All models agree that the total indirect effect is larger over the Northern Hemisphere than over the Southern Hemisphere (Figure 7.5.3). The values of the total indirect aerosol effect on the Northern Hemisphere radiative forcing vary between –0.2 and –4.4 W m^{-2} and on the Southern Hemisphere between –0.1 and -1.1 W m^{-2}. Estimates of the ocean/land partitioning of the total indirect effect vary from 0.2 to 1.6. Values exceeding one are in better agreement with the estimate of the total indirect aerosol effect as derived from combining POLDER satellite data and the ECHAM4 GCM results (Lohmann and Lesins, 2002). However, the retrieval of clouds from the POLDER satellite is limited to clouds with a rather narrow cloud droplet size distribution (Rosenfeld and Feingold, 2003) and therefore may not be universally applicable. The agreement with the POLDER satellite data weakens when the cloud lifetime effect is ignored (Lohmann and Lesins, 2002; Quaas et al., 2004), which provides indirect evidence for the existence of a cloud lifetime effect on a global scale. Similar conclusions were reached by Suzuki et al. (2004) when comparing simulations with and without a cloud lifetime effect with AVHRR satellite data of liquid water path as a function of column aerosol number (Nakajima et al. 2001).

[INSERT FIGURE 7.5.3 HERE]

7.5.2.3 Aerosol impacts on large-scale mixed-phase clouds

Lohmann (2002) and Lohmann and Diehl (2005) show that if, in addition to mineral dust, hydrophilic black carbon aerosols are assumed to act as ice nuclei at temperatures between 0°C and –35°C, then increases in aerosol concentration from pre-industrial times to present-day pose a glaciation indirect effect. Here increases in contact and immersion ice nuclei in the present-day climate result in more frequent glaciation of supercooled clouds and increase the amount of precipitation via the ice phase. This decreases the global mean cloud cover and leads to more absorption of solar radiation. The glaciation effect dominates if dust is assumed to be composed of kaolinite. On the contrary, if dust consists of montmorillonite, which is a better ice nucleus, then the climate impact by black carbon is smaller and the changes in the hydrological cycle are as expected from the warm indirect cloud lifetime effect (Lohmann and Diehl, 2005).

Observations by Borys et al. (2003) in midlatitude orographic clouds show that for a given supercooled liquid water content, both the riming and the snowfall rates are smaller if the supercooled cloud has more cloud droplets. Examination of this effect in global climate model simulations with pre-industrial and present-day aerosol concentrations show that while the riming rate in stratiform clouds has indeed decreased due to the smaller cloud droplets in polluted clouds, the snowfall rate has actually increased. This is caused by the pollution induced increase in aerosol and cloud optical thickness, which reduces the solar radiation and causes a cooling that favours precipitation formation via the ice phase (Lohmann, 2004).

7.5.2.4 Aerosol impacts on cirrus clouds

A change in the number of ice crystals in cirrus clouds could also exert a cloud albedo effect in the same way that the cloud albedo effect acts for water clouds. In addition, a change in the cloud ice water content could exert a radiative effect in the infrared. The magnitude of these effects in the global mean has not yet been fully established, but the development of a physically based parameterization scheme of cirrus formation for use in global models led to significant progress in understanding underlying mechanisms of aerosol induced cloud modifications (Kärcher and Lohmann, 2002).

A global climate model study concludes that such an effect based solely on ubiquitous homogeneous freezing is small globally (Lohmann and Kärcher, 2002). This is expected to hold in the presence of heterogeneous ice nuclei (IN) that freeze at relative humidities over ice close to homogeneous values (above 130–140%) (Kärcher and Lohmann, 2003). In situ measurements reveal that organic-containing aerosols are less abundant than sulphate aerosols in ice cloud particles, suggesting that organics do not freeze preferentially (Cziczo et al., 2004). A model study explains this finding by the disparate water uptake of organic aerosols, and suggests that organics are unlikely significantly to modify cirrus formation unless they are present in very high concentrations at low temperatures (compared with sulphate-rich particles) and hamper water condensation (Kärcher and Koop, 2004).

With regard to aerosol effects on cirrus clouds, a strong link has been established between gravity wave induced, mesoscale variability in vertical velocities and climate forcing by cirrus (Kärcher and Ström, 2003). Hemispheric-scale studies of aerosol-cirrus interactions using ensemble trajectories suggest that changes in upper tropospheric cooling rates and ice-forming aerosols in a future climate may induce changes in cirrus occurrence and optical properties that are comparable in magnitude with observed decadal trends in global cirrus cover (Haag and Kärcher, 2004). Optically thin and subvisible cirrus are particularly susceptible to IN and therefore likely affected by anthropogenic activities.

Radiative forcing estimates and observed trends of aviation-induced cloudiness are discussed in Section 2.6.4. In terms of indirect effects on cirrus clouds developing from aircraft emissions, Lohmann and Kärcher (2002) show that the impact of aircraft sulphur emissions on cirrus properties via homogeneous freezing is small. Provided that black carbon particles from aviation serve as efficient IN, then maximum increases or decreases in ice crystal number concentrations of more than 40% are simulated in a climate model study assuming that the 'background' (no aviation impact) cirrus cloud formation is dominated by heterogeneous or homogeneous nucleation, respectively (Hendricks et al., 2005). Progress in assessing the impact of aircraft black carbon on cirrus is hampered by the poor knowledge of natural freezing modes in cirrus conditions and the inability to describe full complexity of cirrus processes in global models.

7.5.2.5 Aerosol impacts on convective clouds

Rosenfeld (1999) and Rosenfeld and Woodley (2000) analyzed aircraft data together with satellite data suggesting that pollution aerosols suppress deep convective precipitation by decreasing cloud droplet size and delaying the onset of freezing. This hypothesis was confirmed with a cloud resolving model (Khain et al., 2001) such that supercooled cloud droplets down to –37.5°C could only be simulated if the cloud droplets were small and numerous. On a global scale, Nober et al. (2003) find large instantaneous local aerosol forcings that reduce the warm phase precipitation in convective clouds by this mechanism. The precipitation change at the surface is, however, guided by feedbacks within the system.

Tropical biomass burning aerosols could lead to a reduction of ice crystal size in tropical deep convective clouds (Sherwood, 2002). These smaller and more numerous ice crystals would then lead to more scattering of solar radiation, i.e., exert a cloud albedo effect. They also evaporate more readily, thus increasing relative humidity. The increased relative humidity is partially transported into the stratosphere through the tropical pipe, which partially accounts for the increase of the stratospheric water vapour over the last 50 years (Rosenlof et al., 2001). Being a greenhouse gas, water vapour provides a positive radiative forcing that would partially offset the cloud albedo effect associated with the smaller ice crystal size in these deep convective clouds.

7.5.2.6 Aerosol impacts on precipitation and hydrological cycle

CCN and IN are largely responsible for precipitation processes in clouds. Smoke from burning vegetation reduces cloud droplet sizes and delays the onset of precipitation (Warner and Twomey, 1967; Andreae et al., 2004; Rosenfeld, 1999) as do aerosols from urban and industrial air pollution (Rosenfeld, 2000). Also, desert dust suppresses precipitation in thin low altitude clouds (Mahowald and Kiehl, 2003; Rosenfeld et al., 2001). On the other hand, correlations between dust and ice clouds, as derived from satellite data, are not yet conclusive (Mahowald and Kiehl, 2003), although no concurrent surface precipitation measurements were provided in these studies. Only the recent study by Givarti and Rosenfeld (2004) indicates surface precipitation losses over topographical barriers by 15–25% downwind of major coastal urban areas in California and in Israel. On the contrary Jin et al. (2005) conclude from analyzing four years of satellite and in-situ observations that the change in urban rainfall amount in summer in New York and Houston is not

primarily caused by aerosols. Likewise Ayers (2005) concludes that rainfall anomalies over Australia cannot be linked to anthropogenic aerosols.

Modelling studies largely suggest that anthropogenic aerosols suppress precipitation in the absence of giant CCN and aerosol-induced changes in ice microphysics (e.g., Lohmann, 2002; Menon and DelGenio, 2005) as well as in mixed-phase clouds where the ice phase only plays a minor role (Phillips et al., 2002). Giant sea salt nuclei, on the other hand, may override the precipitation suppression effect of the large number of small pollution nuclei (Feingold et al., 1999; Rosenfeld et al., 2002). Gong and Barrie (2003) predict a reduction of 20–60% in the marine cloud droplet number concentrations (CDNC) (because of the presence of sea salt), with greatest reductions in the roaring 40s south (40–70%) and in the midlatitude north (20–40%). This reduction in CDNC enhances the precipitation formation. If these giant CCN were covered by film-forming compounds, then their impact would be less than previously estimated (Medina and Nenes, 2004).

Khain et al. (2005) postulate that smaller cloud droplets, such as those originating from human activity, would reduce the production of drizzle drops. When these droplets freeze, the associated latent heat release results in more vigorous convection. In a clean cloud, on the other hand, drizzle would have left the cloud so that less latent heat is released when the cloud glaciates resulting in less vigorous convection. Therefore, no squall line is formed with maritime aerosol concentrations, but the squall line arises under the influence of higher continental aerosol concentrations and results in more precipitation after two hours of simulations with a detailed cloud microphysics model. More precipitation from polluted clouds is also simulated for different three-week periods over the Atmospheric Radiation Measurement Program (ARM) site in Oklahoma (Zhang et al., 2005) as well as for multicell cloud systems by Seifert and Beheng (2005). On the other hand, precipitation from single mixed-phase clouds is reduced under continental and maritime conditions when aerosol concentrations are increased (Khain et al., 2004; Seifert and Beheng, 2005). Modelling results of a thunderstorm in Florida suggest that the whole dynamic structure of the storms is influenced by varying dust concentrations (Van den Heever et al., 2004). In particular, the updrafts are consistently stronger and more numerous when Saharan dust is present compared with a clean air mass. This suggests that dust results in enhanced glaciation of convective clouds leading to dynamical invigoration of the clouds, larger amounts of processed water, and thereby enhanced rainfall at the ground (as discussed above). However, the precipitation enhancement lasted only 2 hours, after which precipitation decreased as compared with clean conditions. This highlights the complexity of the system and indicates that the sign of the global change in precipitation due to aerosols is not yet known.

Global climate model estimates of the change in global mean precipitation due to all anthropogenic indirect aerosol effects are summarized in Figure 7.26. Consistent with the conflicting results from the detailed cloud system studies, the change in global mean precipitation varies between –0.03 mm day^{-1} and +0.004 mm day^{-1}. These differences are amplified over land, ranging from –0.12 mm day^{-1} to 0.02 mm day^{-1}. Only Quaas et al. (2004) and Storelvmo et al. (2005) simulate an increase in land precipitation, which agrees best with the observed increase in terrestrial-mean precipitation trend in this century (Hulme et al., 1998). Continental precipitation did however decrease from 1947 to 1996, and especially from 1955 to 1970, before the clean-air acts were introduced in Europe and North America. This decrease in continental precipitation could be explained with indirect aerosol effects that are largest in the Northern Hemisphere (Figure 7.5.4).

[INSERT FIGURE 7.5.4 HERE]

7.5.3 How Are Changes in Aerosols/Clouds Affecting Processes at the Earth's Surface?

7.5.3.1 Energy budget: decreased solar radiation

By increasing aerosol and cloud optical depth, emissions of aerosols from human activity and their precursors cause a reduction of solar radiation at the surface ("solar dimming'"). As such, worsening air quality contributes to regional aerosol effects. Such a reduction is observed many regions worldwide (remote sites like Mauna Loa and Arctic and Antarctic stations as well as industrial regions) (Gilgen et al., 1998; Liepert, 2002; Stanhill and Cohen, 2001; Wild et al., 2004). According to Liepert (2002) this decline of solar radiation from 1961 to 1990 amounts to 1.3% per decade mainly over land surfaces of the Northern Hemisphere, whereas the clear-sky atmospheric transmission in Chile is perturbed only after the El Chichon and Mt Pinatubo volcanic eruptions (Schwartz, 2005). This affects the partitioning of direct versus diffuse solar radiation: Liepert and Tegen (2002) concluded that over Germany both aerosol absorption and

scattering must have declined from 1975 to 1990 in order to explain the simultaneously weakened aerosol forcing and increased direct/diffuse solar radiation ratio. The direct/diffuse solar radiation ratio over the United States also increased from 1975 to 1990, here likely due to increases in absorbing aerosols. Increasing aerosol optical depth associated with scattering aerosols alone in otherwise clear skies produces a larger fraction of diffuse radiation at the surface, which results in larger carbon assimilation into vegetation (and therefore greater transpiration) without a substantial reduction in the total surface solar radiation (Niyogi et al., 2004).

Over the Indian Ocean region during the dry winter monsoon season it has been estimated that anthropogenic aerosols, especially the highly absorbing aerosols, can decrease the average solar radiation absorbed by the surface in the range of 15 to 35 W m^{-2} (Ramanathan et al., 2001b). This results in an increase in the atmospheric heating between the surface and 3 km altitude by as much as 60 to 100%. Similar perturbations in the atmosphere have been observed over other regions, namely East Asia, South America and sub-Saharan Africa, which are subjected to large loading of absorbing aerosols. Such a perturbation imposed over the Indian Ocean (in the 15ºS–40ºN and 50ºE–120ºE region) can lead to a large regional cooling at the surface in the range of 0.5 to 1°C accompanied by a warming of the lower troposphere by about 1°C, as shown in a GCM study with fixed ocean surface temperatures (Chung et al., 2002). This vertical heating gradient alters the latitudinal and inter-hemispheric gradients in solar heating; these gradients play a prominent role in driving the tropical circulation (Ramanathan et al., 2001b) and determining the amount of precipitation (Chung and Zhang, 2004).

Global climate model estimates of the mean decrease in shortwave radiation at the surface in response to indirect aerosol effects vary between –1.6 and –3.1 W m^{-2} (Figure 7.5.5). As for the TOA net radiation, the decrease is largest on the Northern Hemisphere with values approaching –5 W m^{-2}. Consistent with the above-mentioned regional studies, most models predict larger decreases over land than over the oceans.

[INSERT FIGURE 7.5.5 HERE]

The decrease in solar radiation at the surface resulting from the increases in optical depth due to the direct and indirect anthropogenic aerosol effects is more important for controlling the surface energy budget than the greenhouse gas induced increase in surface temperature. This has been shown in equilibrium simulations with a global climate model coupled to a mixed-layer ocean model with increasing aerosol particles and greenhouse gases due to human activity from pre-industrial times to present-day (Liepert et al., 2004; Feichter et al., 2004), and in transient simulations (Roeckner et al., 1999). The conductive flux from below the surface is negligible in the long-term mean. The other components of the surface energy budget (thermal radiative flux, sensible and latent heat fluxes) decrease in response to the reduced input of solar radiation. This mechanism could explain the observations of decreased pan evaporation over the last 50 years reported by Roderick and Farquhar (2002). As global mean evaporation must equal precipitation in equilibrium climate simulations, a reduction in the latent heat flux leads to a reduction in precipitation (Liepert at al., 2004).

Recent surface observations show that the long term decline in solar radiation at land surfaces turned into an increase in surface solar radiation during the 1990s (Wild et al., 2005), in agreement with recent emission reductions in the “old” industrial regions in the northern hemisphere (Krüger and Graßl, 2002) as well as with long-term black carbon trends in the Canadian Arctic (Sharma et al., 2004) and sulphate deposition declines over Europe and North America since 1978. This also led to an improvement in air quality in these areas. Although Pinker et al. (2005) detect an overall global brightening signal of 0.16 W m^{-2} yr^{-1} from satellite data between 1983 to 2001, that change is a combination of a decrease in surface solar radiation until about 1990, followed by a sustained increase. Thus, the increasing greenhouse effect may no longer be masked by an aerosol-induced decline in solar radiation, resulting in the enhanced warming observed since the 1990s. The decrease in global mean precipitation from pre-industrial times to the present may reverse into an increase in global mean precipitation of about 1% in 2021–2050 as compared with 1961–1990, because the increased warming due to black carbon and greenhouse gases will dominate over the sulphate cooling (Roeckner et al., 2005). In South Asia, absorbing aerosols in atmospheric brown clouds may have played a major role in the observed South Asian climate and hydrological cycle changes and may have masked as much as 50% of the surface warming due to the global increase in greenhouse gases (Ramanathan

et al. 2005). Their simulations raise the possibility that, if current trends in emissions continue, the South Asian subcontinent may experience a doubling of the drought frequency in future decades.

7.5.3.2 Aerosol effects on the diurnal temperature range

Hansen et al. (1995) found that, although the aerosol direct effect or an increase in continental cloud albedo could contribute to a dampening of the surface temperature diurnal range (DTR), only an increase in continental cloud cover would be consistent with observations (Karl et al., 1993). The required cloud increase depends on cloud height and would need to be of the order of 1% global coverage for low clouds (i.e., 2–5% over land). More recently, Piers and Solomon (2003) observed a "weekend effect" in DTR whose most likely cause is aerosol-cloud interactions. Over the industrialized part of China in winter the cloud lifetime effect increases the nighttime temperature due to enhanced downward longwave forcing, thus reducing DTR by 0.7°C (Huang et al., 2005).

7.5.3.3 Interactions of aerosols with land surfaces

As discussed in detail in Chapter 2, through absorption of solar radiation, deposition of black carbon on snow surfaces decreases the albedo of the snow, causing a further warming that will lead to more melting of snow. The global mean radiative impact of a plausible estimate of an increase in the snow and ice albedo of 1.5% in the Arctic and 3% in Northern Hemisphere land areas yields an increase in climate forcing of 0.3 W m^{-2} (Hansen and Nazarenko, 2004).

7.5.4 How Are Aerosols Affecting Circulation Patterns?

7.5.4.1 Effects on stability

Changes in the atmospheric lapse rate modify the longwave emission and affect the water vapour feedback (Hu, 1996) and the formation of clouds. Observations and model studies show that an increase in the lapse rate produces an amplification of the water vapour feedback (Sinha, 1995). As aerosols cool the Earth's surface and warm the aerosol layer the lapse rate will decrease and suppress the water vapour feedback. Thus a more stable boundary layer suppresses greenhouse gas warming and may enhance aerosol cooling. On a global scale, Feichter et al. (2004) find that aerosol cooling in the free troposphere generally decreases the lapse rate if only anthropogenic aerosols are considered. However, the atmosphere becomes more stable if aerosols and greenhouse gases increase due to an aerosol cooling near the surface, especially in polluted regions of the Northern Hemisphere, and to greenhouse gas warming aloft. The change in atmospheric stability strongly depends on the altitude of the black carbon heating (Penner et al., 2003).

Dust modelling results suggest the existence of a contrast in radiative forcing between continents and oceans. Depending on the assumptions and the dust loading used in the calculation, the continental heating change could range from –4 to +10 W m^{-2} (Wang et al., 2004) to 0 to +20 W m^{-2} (Weaver et al., 2002) to +20 to +40 W m^{-2} (Sokolik and Toon, 1996) while the oceanic cooling could range from 0 to –4 W m^{-2} (Wang et al., 2004) to 0 to –18 W m^{-2} (Weaver et al., 2002) to –35 W m^{-2} to –15 W m^{-2} (Sokolik and Toon, 1996). The dust-induced thermal contrast changes between the Eurasian continent and the surrounding oceans are also found either to trigger or modulate a rapidly varying or unstable Asian winter monsoon circulation (Zhang et al., 2002). Heating of a lofted dust layer could also increase the occurrence of deep convection (Stephens et al., 2004).

Aerosols also cause a contrast of radiative forcing between TOA and surface, as deduced from SeaWiFS satellite data. Mean clear-sky solar radiative heating for the winters of 1998 and 1999 has also been found to decrease at the ocean surface by 12 to 30 W m^{-2}, but only by 4 to 10 W m^{-2} at the top of the atmosphere over the tropical northern Indian Ocean. This threefold difference (due largely to solar absorption by soot) and the large magnitude of the observed negative surface forcing both imply that tropical aerosols might increase the strength of the thermal inversion and slow down the hydrological cycle (Satheesh and Ramanathan, 2000; Ramanathan et al., 2005). This contrast between TOA and surface during the period of the large Indonesian fires (September–December 1997) may also have enhanced the atmospheric stability, weakened the atmospheric circulation, and augmented drought conditions (Chou et al., 2002).

7.5.4.2 Effects on the large-scale circulation

Through the aerosol radiation-circulation feedback, the scattering and absorption of radiation by aerosols can cause atmospheric pressure and circulation changes, which have the potential, for example, to modify Arctic

teleconnection patterns like the Barents Sea Oscillation (Rinke et al., 2004). The decadal to interannual variability of sea-salt aerosol concentrations in northern Greenland ice cores also identifies the eastern and northeastern Pacific region as the most important centre of action responsible for variations in sea-salt aerosol export onto the Greenland ice sheet which is related to the Pacific/North American teleconnection pattern (Fischer 2001). The influence of aerosols and other anthropogenic pollutants, through land-sea interaction (differential heating), topography (Western Ghats), and horizontal thermal gradients (SST versus land surface temperature) on the coastal circulations over Equatorial Indian Ocean, can produce significant diurnal variability and heterogeneity that may have interactive feedback teleconnections between local and large scale features (Mohanty et al., 2001).

Large tropical volcanic eruptions produce winter warming patterns over Northern Hemisphere continents forced by gradients of radiative heating from sulphate aerosols in the lower stratosphere. These effects must be considered for accurate dynamical seasonal predictions of Northern Hemisphere winter temperature over both North America and Eurasia (Robock, 2001).

Menon et al. (2002b) find that circulation changes due to different types of aerosols can vary. In a model simulation with absorbing aerosols, the upper-level westerlies to the north and easterlies to the south of the Tibetan plateau are stronger. The simulation with scattering aerosols yields weaker anticyclones with westerlies present south of the plateau. These results indicate that absorbing aerosols, mainly black carbon, can reduce the solar radiation reaching the surface and can warm the atmosphere, affecting the vertical temperature profile, latent heat fluxes, atmospheric stability and convection. These changes in convection can in turn modify the large-scale atmospheric circulation as shown in Figure 7.5.6. In India and China, where aerosols have been added, increasing rising motions are seen while comparable increased subsidence to the south and north are present in simulations. Wang (2004) models the effect of black carbon on climate and finds that BC heats the atmosphere mainly between 5ºN and 50ºN, corresponding to the most polluted areas. The radiative effect due to BC in the model alters the meridional sensible and latent heat transport, convective fluxes especially over the tropics, and hence the atmospheric circulation. In the northern part of the intertropical convergence zone (ITCZ) deep convection is enhanced due to BC while south of ITCZ the strength of the convection is substantially reduced. The precipitation change is found to depend mainly on the imposed atmospheric solar heating. Figure 7.5.7 shows the percentage change in precipitation revealing more clearly the regions of enhanced and suppressed precipitation (Chung et al., 2002) over the Indian Ocean region: the effects spread beyond the region of imposed forcing. Over arid regions in Southwest Asia the precipitation decreases. The atmospheric lifetime of aerosols increases due to suppression of precipitation. The drier conditions resulting from suppressed rainfall can induce more dust and smoke due to the burning of drier vegetation (Ramanathan et al., 2001a), thus affecting both regional and global hydrological cycles (Wang, 2004).

[INSERT FIGURE 7.5.6 HERE]

[INSERT FIGURE 7.5.7 HERE]

In Southern China, increases in both greenhouse gases and anthropogenic aerosols may be responsible for the observed droughts in recent years (Cheng et al., 2005), caused by a strengthening of the West Pacific Subtropical High in the early summer over the last 40 years, with the high-pressure system extending further westward over the continent in Southern China. Because the early summer average temperature contrast between the land and ocean decreases, the southwesterly monsoon from the ocean onto mainland China weakens and a surface horizontal wind divergence anomaly occurs over Southern China stabilizing the boundary layer. Thus, less moisture is transported to Southern China, causing the drying trend.

Observed precipitation trends over land for the period 1900–1998 show a complex pattern in the tropics indicating, for example, a drying of the Sahel in North Africa (Hulme et al., 1998). Dry conditions in the Sahel are associated with a near-global, quasi-hemispheric pattern of contrasting sea surface temperature anomalies (cooler in the northern hemisphere and warmer in the southern hemisphere). Using a global climate model/mixed-layer ocean model, Williams et al. (2001) and Rotstayn and Lohmann (2002) show that the dynamical and hydrological changes in this region in response to the indirect effect of anthropogenic sulphate aerosols are similar to the observed changes that have been associated with the Sahelian drought (Giannini et al., 2003). In addition, aerosol induced cooling of the Mediterranean Sea surface has reduced

evaporation, which has decreased moisture transport to North Africa and the Middle East (Lelieveld et al., 2002b). That is, the anthropogenic aerosol cooling reduces the solar radiation and the surface temperature predominately in the Northern Hemisphere, causing a southward shift of the ITCZ and a weakening of the African summer monsoon (Figure 7.5.8). If, on the contrary, the Northern Hemisphere surface temperature increases more than the Southern Hemisphere surface temperature due to the increase in fossil fuel combustion of black carbon, then the ITCZ shifts northward, strengthens the Indian summer monsoon and increases the rainfall in the Sahel (Roberts and Jones, 2004).

[INSERT FIGURE 7.5.8 HERE]

In summary, an increase in aerosol load decreases air quality and the amount of solar radiation reaching the surface. This negative forcing competes with the greenhouse gas warming for determining the change in evaporation (Schwartz, 1993; Roeckner et al., 1999 and Feichter et al., 2004). While model simulations suggest that global mean evaporation and precipitation have decreased from pre-industrial to present-day times when considering both greenhouse gases and aerosols (Liepert et al., 2004), in future both evaporation and precipitation could increase (Roeckner et al., 2005).

7.6 Concluding Remarks

Biogeochemical cycles interact closely with the climate system over a variety of temporal and spatial scales. An illustration of this interaction on geological timescales is provided by the Vostok ice core record, which provides a dramatic evidence of the coupling between the carbon cycle and the climate system. The dynamics of the Earth system that can be inferred from this record results from a combination of external forcing (in this case long-term periodic changes in the orbital parameters of the earth and hence of the energy intercepted by our planet) and a large array of feedback mechanisms within the earth environment (see Chapter 6). On smaller timescales, a wide range of forcings that originate from human activities (conversion and fragmentation of natural ecosystems, emissions of greenhouse gases, nitrogen fixation, degradation of air quality, stratospheric ozone depletion) is expected to produce planetary-wide effects and perturb numerous feedback mechanisms that characterize the dynamics of the earth system.

[START OF BOX 7.2]

Box 7.2: Effects of Climate Change on Air Quality

Weather is a key variable affecting air quality. Surface air concentrations of pollutants are highly sensitive to boundary layer ventilation, winds, temperature, humidity, and precipitation. Anomalously hot and stagnant conditions in the summer of 1988 were responsible for the highest ozone year on record in the northeastern United States (Lin et al., 2001). The summer heat wave in Europe in 2003 was associated with exceptionally high ozone (Ordonez et al., 2005; Box 7.2, Figure 1). Such high interannual variability of surface ozone correlated with temperature demonstrates the potential air quality implications of climate change over the next century.

[INSERT BOX 7.2, FIGURE 1 HERE]

Only a few GCM studies have investigated how air pollution meteorology might respond to future climate change. Rind et al. (2001) found that increased continental ventilation as a result of more vigorous convection should decrease surface concentrations, while Holzer and Boer (2003) found that weaker winds should result in slower dilution of pollution plumes and hence higher concentrations. A more focused study by Mickley et al. (2004) for the eastern United States found an increase in the severity and persistence of regional pollution episodes due to the reduced frequency of ventilation by cyclones tracking across Canada. This effect more than offset the dilution associated with the small rise in mixing depths. A decrease in cyclone frequency at northern mid-latitudes has indeed been noted in observations from the past few decades (McCabe et al., 2001).

A number of studies in the United States have shown that summer daytime ozone concentrations correlate strongly with temperature (NRC, 1989). This correlation appears to reflect contributions of comparable magnitude from (1) temperature-dependent biogenic VOC emissions, (2) thermal decomposition of

peroxyacetylnitrate (PAN) which acts as a reservoir for NO_x, and (3) association of high temperatures with regional stagnation (Jacob et al., 1993; Sillman and Samson, 1995). Empirical relationships between ozone air quality standard exceedances and temperature, as shown in Box 7.2, Figure 2, integrate all of these effects and could be used to estimate how projected regional changes in temperature would affect ozone air quality. However, the ozone background may respond differently, decreasing with increasing temperatures because of associated increases in humidity (Stevenson et al., 2005b). Changes in solar irradiance at the surface due to changes in cloudiness and recovery of the ozone layer could also have a significant impact on ozone production in polluted regions.

[INSERT BOX 7.2, FIGURE 2 HERE]

A few GCM studies have examined more specifically the effect of changing climate on ozone air quality, assuming constant emissions. Knowlton et al. (2004) used a GCM coupled to a regional climate model (RCM) to investigate the impact of 2050 vs. 1990 climate change on ozone concentrations in the New York City metropolitan area. They found a significant ozone increase that they translated into a 4.5% increase in ozone-related acute mortality. Langner et al. (2005) used a RCM driven by two different GCMs to examine changes in the AOT40 statistic (ozone-hours above 40 ppbv) over Europe in 2050–2070 relative to present. They found an increase in southern and central Europe, and a decrease in northern Europe, that they attributed to different regional trends in cloudiness and precipitation. Dentener et al. (2005) found in an intercomparison of nine GCM ozone simulations for 2030 vs. 2000 climate that the annual mean surface ozone concentrations over populated continents decreased slightly, by ~1 ppbv. Trends in annual mean concentrations may be driven more by decreases in the global ozone background (Stevenson et al., 2005b) than by increases the frequency and severity of high-ozone episodes.

There has been less work on the sensitivity of aerosols to meteorological conditions. Regional model simulations by Aw and Kleeman (2003) find that increasing temperatures should increase surface aerosol concentrations due to increased production of aerosol precursors (in particular semi-volatile organic compounds and nitric acid) although this is partly compensated by the increasing vapor pressure of these compounds at higher temperatures. Perturbations to precipitation frequencies and patterns might be expected to have a major impact on aerosol concentrations, but the GCM study by Mickley et al. (2004) for 2000–2050 climate change finds in fact relatively little effect in the United States.

Intercontinental transport of pollution is increasingly recognized as an important issue for regional air quality. Climate change would be expected to affect this transport through perturbation to the general circulation. A model study by Li et al. (2002) found that transatlantic transport of pollution from North America to Europe is correlated with the positive phase of the North Atlantic Oscillation (NAO), and such a correlation is apparent in TOMS observations of tropospheric ozone columns over the northeast Atlantic (Creilson et al., 2003). Perturbation to the NAO phase resulting from climate change would thus be expected to have a major effect on transatlantic transport of pollution.

[END OF BOX 7.2]

The interactions between physical, chemical, and biological processes and feedback mechanisms that provide the conditions necessary for life on earth, are not yet fully understood or quantified, but will have to be more accurately represented in the future generations of climate models. The response of the climate system to anthropogenic forcing is expected to be more complex than a simple cause-effect relationship; rather, it could exhibit chaotic behavior with cascades of effects across the different scales and with the potential for abrupt and perhaps irreversible transitions.

[INSERT FIGURE 7.6.1 HERE]

This chapter has assessed how processes related to vegetation dynamics, carbon exchanges, gas-phase chemistry and aerosol microphysics could affect the climate system. These processes, however, cannot be considered in isolation because of the potential interactions that exist between them. A striking example highlighting the need to consider the links between the carbon cycle and aerosols is provided by Andreae et al. (2005). These authors suggest that future climate change in response to atmospheric CO_2 increase depends strongly on the intensity of present-day aerosol cooling. They stress that our insufficient

understanding of the present climate forcing of aerosols limits our ability to quantify the carbon-climate feedback and hence to perform accurate climate projections for the future. Figure 7.6.1 shows that future climate warming projected by a model in response to anthropogenic CO_2 emissions should be considerably more pronounced when the present-day aerosol cooling is assumed to be large than when it is ignored. Brasseur and Roeckner (2005) estimate that the hypothetical removal from the atmosphere of the entire burden of anthropogenic sulphate aerosol particles would produce a rather immediate increase of about 0.8°C in the globally averaged temperature with geographical patterns that bear resemblance with the temperature changes found in greenhouse gas scenario experiments (Figure 7.6.2). Thus, environmental strategies aimed at maintaining 'global warming' below a prescribed threshold must therefore account not only for CO_2 emissions but also for measures implemented to improve air quality.

[INSERT FIGURE 7.6.2 HERE]

In order to cope with the complexity of earth system processes and their interactions, and particularly to evaluate sophisticated models of the earth system, observations and long-term monitoring of climate and biogeochemical quantities will be essential. Climate models will have to reproduce accurately important processes and feedback mechanisms that are discussed in the present chapter.

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Tables

Table 7.3.3. Couplings between climate and ocean biogeochemical processes.

Process	Primary Forcings	Direction	Quantitative Potential	Timescale (years)	Certainty	Important Associated Impacts and Secondary Feedbacks
Sea water buffering	Atmospheric pCO_2 increase	-	high	0–1000	certainty	Dominant inorganic feedback, leads to significant ocean acidification
Changes in CO_2 solubility, dissociation, and buffer factor	Warming, atmospheric pCO_2 increase, slowing of ocean circulation	+	medium		certainty	pH lowering with impact on biology and sediments
Biological export production of POC, DOC storage	Warming, pCO_2 increase, runoff loads, dust deposition, slowing of ocean circulation, change in radiation	unknown	unknown	0–1000	indication	Complex feedback chain, involving food chain and biodiversity, N_2O production, light absorption and heating, particle dynamics
Biological export production of PIC ($CaCO_3$)	pCO_2 increase (pH decrease)	unknown	unknown	0–1000	indication	Ballast effect and particle dynamics, DMS production, species shifts
Coral growth	Warming, atmospheric pCO_2 increase (pH decrease)	–	unknown	0–100	certainty	Albedo change, biodiversity, species shifts
Dissolution of $CaCO_3$ sediments	pCO_2 increase (pH decrease)	–	high	1000–100000	certainty	biodiversity
DMS production	$CaCO_3$ production, dust flux	unknown	unknown	0–100	indication	tropospheric cloud formation
Destabilization of gas hydrates	warming	+	unknown	unknown	potential	Bacterial blooms
Purposeful CO_2 storage	Human intention to mitigate climate change	unknown	unknown	unknown	potential	Ecological impact on water column and bottom fauna, may increase fossil fuel burning

Table 7.4.5. Global budgets of tropospheric ozone (Tg yr^{-1}) for the present-day atmosphere[a]

Reference	Model	Stratosphere-Troposphere Exchange (STE)	Chemical Production[b]	Chemical Loss[b]	Dry Deposition	Burden (Tg)	Lifetime[c] (days)
TAR[d]	11 models	770 ± 400	3420 ± 770	3470 ± 520	770 ± 180	300 ± 30	24 ± 2
Lelieveld and Dentener (2000)	TM3	570	3310	3170	710	350	33
Bey et al. (2001)[e]	GEOS-Chem	470	4900	4300	1070	320	22
Sudo et al. (2002)	CHASER	593	4895	4498	990	322	25
Horowitz et al. (2003)	MOZART-2	340	5260	4750	860	360	23
Von Kuhlmann et al. (2003)	MATCH-MPIC	540	4560	4290	820	290	21
Shindell et al. (2003)	GISS	417	NR[f]	NR	1470	349	NR
Hauglustaine et al. (2004)	LMDz-INCA	523	4486	3918	1090	296	28
Park et al. (2004)	UMD-CTM	480	NR	NR	1290	340	NR
Rotman et al. (2004)	IMPACT	660	NR	NR	830	NR	NR
Wong et al. (2004)	SUNYA/UiO GCCM	600	NR	NR	1100	376	NR
Stevenson et al. (2004)	STOCHEM	395	4980	4420	950	273	19
Wild et al. (2004)	FRSGC/UCI	520	4090	3850	760	283	22
Stevenson et al. (2005)	25 models	520 ± 200	5060 ± 570	4560 ± 720	1010 ± 220	340 ± 40	22 ± 2

Notes:
(a) From global model simulations describing the atmosphere of the last decade of the 20th century.
(b) Chemical production and loss rates are calculated for the odd oxygen family, usually defined as $O_x = O_3 + O + NO_2 + 2NO_3 + 3N_2O_5 + HNO_4$ + peroxyacylnitrates (and sometimes HNO_3), to avoid accounting for rapid cycling of ozone with short-lived species that have little implication for its budget. Chemical production is mainly contributed by reactions of NO with peroxy radicals, while chemical loss is mainly contributed by the $O(^1D)+H_2O$ reaction and by the reactions of ozone with HO_2, OH, and alkenes. Several models in this table do not report production and loss separately ("NR" entry in the table), reporting instead net production. However, net production is not a useful quantity for budget purposes because (1) it represents a small residual between large production and loss, (2) it represents the balance between STE and dry deposition, both of which are usually parameterized as a flux boundary condition.
(c) Calculated as the ratio of the burden to the sum of chemical and deposition losses
(d) Means and standard deviations from an ensemble of 11 global model budgets from the 1996–2000 literature reported in the TAR. The mean budget does not balance exactly because only 9 CTMs reported their chemical production and loss statistics.
(e) A more recent version of GEOS-Chem by Martin et al. (2003b) gives identical rates and burdens.
(f) Not reported