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

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Executive Summary

Biogeochemical cycles interact with the climate system over a wide-range of temporal and spatial scales. Nonlinear interactions involving physical, chemical and biological processes 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 involve reciprocal interactions with the land surface, the carbon cycle, reactive gases and aerosol particles.

The Land Surface and Climate

- Changes in the land surface (vegetation, soils, water) resulting from human activities can significantly affect regional and local climate through shifts in radiation, cloudiness, and surface temperatures. Similarly, Changes in land use, climate, and atmospheric composition affect the distribution and functioning of terrestrial ecosystems.
- Changes in vegetation cover have a substantial effect on surface energy and water balance at the regional scale. Model results indicate increased boreal forest cover results in reduced albedo and significant regional warming, offsetting cooling effects of carbon uptake.
- The impact of land-use change on climate may be very significant at regional scales, but is expected to be small at the global scale in comparison with greenhouse gas warming.

The Carbon Cycle and Climate

- The land and oceans have continued to absorb ~45% of the CO_2 emissions from fossil fuel burning and cement production. This fraction was lower in the 1980's (0.39), higher in the 1990's (0.50) and recovered an intermediate value during 2000–2005 (0.41). There are no indications of a trend in the fraction of emissions that are absorbed by the land and ocean combined since 1958, which suggests that large non-linear feedbacks between climate and the carbon cycle have not yet taken place.
- The fraction of emissions taken up by the oceans appear to have decreased from 0.42 ± 0.07 for the period 1750–1994 to 0.37 ± 0.07 for the period 1980–2005, consistent with the limited rate at which CO_2 is transported from the surface to the deep ocean. This trend are expected to continue.
- A combination of techniques gives an estimate of the flux of CO_2 to the atmosphere from land use change of 1.6 (0.5 to 2.8) GtC yr^{-1} for the 1990's. A revision of the TAR estimate for the 1980s downwards to 1.3 (0.3 to 2.8) GtC yr^{-1} suggests little change between the 1980s and 1990s, and continuing uncertainty in the estimates.
- Interannual variability in the growth-rate of atmospheric CO_2 is dominated by the response of land carbon to climate variations. Large decadal changes are observed in the land-atmosphere CO_2 flux, with estimates of -0.2 ± 0.7, -1.4 ± 0.7, and -0.7 ± 0.7 GtC yr^{-1} for the 1980's, 1990's and 2000-2005 time periods, respectively. This decadal variability also appears caused by the response of land carbon to climate variations.
- Although the ocean is currently absorbing large amounts of CO_2 (~2 GtC yr^{-1}), its uptake capacity will decrease with rising CO_2. After the ocean equilibrates with the atmosphere (on timescales of centuries), one quarter of the anthropogenic CO_2 will remain in the atmosphere, eventually to be neutralized by carbonate and silicate weathering reactions in the ocean. Roughly one quarter of anthropogenic CO_2 will influence climate for thousands to hundreds of thousands of years.
- Increasing CO_2 concentrations in the ocean has lowered the pH (increasing the acidity) by 0.1 since 1750. The consequences for the carbon cycle include the reduced calcification by marine organisms and the dissolution of shallow-water sediments. The net effect is unknown.
- Coupled climate-carbon cycle models indicate that climate change will increase the fraction of anthropogenic CO_2 that remains in the atmosphere. This positive climate-carbon cycle feedback leads to an additional increase in atmospheric CO_2 concentration of 20 to 220 ppm by 2100, under the SRES A2 emissions scenario
- The largest contribution to the uncertainty in the climate-carbon cycle feedback concerns the response of vegetation and soil to climate change.

Reactive Gases and Climate

- Atmospheric CH_4 is dominated by anthropogenic sources. Since there is no general consensus on significant change in CH_4 sinks since the TAR, the recent slow down in growth rate of atmospheric concentration is likely due to changes in sources strengths.

- Most models predict that climate change affects methane emissions from wetlands. Emissions likely increase in warmer and wetter climate and decrease in warmer and dryer climate. However, this has not yet been confirmed by field observation.
- About 50% of current sources of atmospheric N_2O result from human activities – animal husbandry, fertilizer and crops, and coastal oceans being the three largest sources. Emissions from the coastal oceans represent ~20% of the 'anthropogenic' sources and result mainly from increasing anoxic conditions in or above the sediments.
- New model estimates of the global tropospheric ozone budget suggest that input 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 (both approximately 4500 Tg yr^{-1}) are higher than estimated by TAR (3500 Tg yr^{-1}).
- Future climate change is expected to cause a decrease in background tropospheric ozone (due to higher water vapor) but increases in regional ozone pollution (due to higher temperatures and weaker circulation)..
- 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 hydrocarbons, carbon monoxide, nitrogen oxides, water vapor, and ozone. The changes partially offset one another so that future methane lifetime remains relatively unchanged during the next few decades. On shorter time scales, the variability of the CH_4 growth rate is partially explained by the interannual variability of OH.
- There is potential for significant air quality degradation under all IPCC SRES emission scenarios. In addition to changing emissions, the resulting climate change modifies the dispersion rate of pollutants, the chemical environment for ozone and aerosol generation, and the strength of emissions from the biosphere, fires, and dust. The sign and magnitude of the effect of climate change are highly uncertain, and may vary greatly depending on region.

Aerosol Particles and Climate

- Aerosols affect the radiative fluxes by scattering and absorbing solar radiation (direct effect, see Chapter 2). They also interact with clouds and the hydrological cycle by acting as cloud condensation nuclei (CCN) and ice nuclei. A larger number of CCN increases cloud albedo (indirect cloud albedo effect) and reduces the precipitation efficiency (indirect cloud lifetime effect), both of which are likely to result in a reduction of the global, annual-mean net radiation at the top of the atmosphere. However, these effects may be partly offset by evaporation of cloud droplets due to absorbing aerosols (semi-direct effect) and by more ice nuclei (glaciation effect).
- The reduction in the global annual mean top-of-the-atmosphere net radiation as a response to the sum of these aerosol effects (direct, semi-direct and indirect cloud albedo and lifetime effect) since pre-industrial times amounts to between –0.2 and –2.3 W m^{-2} as deduced from several climate models. The highest estimated value of the sum of these effects has been reduced from more than –4 W m^{-2} in TAR to –2.3 W m^{-2} because of improvements in cloud parameterizations. Large uncertainties, however, remain, because of interactions within the climate system and feedbacks on clouds, large-scale dynamics and the hydrological cycle.
- The magnitude of the indirect aerosol effect on precipitation is even more uncertain, with model results ranging from an increase of +0.005 mm/d to a decrease of 0.13 mm/d. The decreases in precipitation are larger, when the atmospheric GCMs are coupled to mixed-layer ocean models where the sea surface temperature and, hence, the evaporation is allowed to vary.
- Nutrients deposited with dust particles enhance photosynthetic carbon fixation in nutrient-poor regions of the oceans and land. Iron fertilisation of the ocean through dust from desert sources is one of the key drivers of reduction in glacial-interglacial CO_2 concentrations. Climate change is likely to affect dust sources more than land use change in the future.
- Since TAR, advances have been made to link the marine and terrestrial biosphere via the aerosol cycle with the climate system. Vegetation emits organic compounds. These emissions are expected to increase in a warmer climate. In addition, recent studies show that the marine biosphere may also be a source for organic aerosols.

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 among 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 state. Positive feedbacks amplify applied perturbations, and could potentially produce transitions towards a new 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 identify the major biogeochemical feedbacks of significance to the climate system, and to assess current knowledge on their magnitudes and trends. Specifically, it will examine the relations between the physical climate system and the land surface, the carbon cycle, chemically reactive atmospheric gases and aerosol particles. It also presents the current state of knowledge on budget of important trace gases. 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 Climate

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.

7.1.1.1 Biogeophysical feedbacks

Changes in the type, structure and physiology of terrestrial ecosystems can feed back to climate via changes in the partitioning of energy between latent (evapotranspiration) and sensible heat, albedo (the reflectivity of the surface) or roughness (which affects the transfer of momentum between the flowing air and the fixed surface elements.). 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. Betts (2001) has estimated that past deforestation has led to decreases in near surface air temperature of up to 1°C over large areas of central North America and central Eurasia due primarily to the albedo effect. This is the same order-of-magnitude as the observed increase in surface temperature over the last century. Clearly, changing the nature of terrestrial ecosystems through land-use change can have a significant influence on climate. A classic example of a feedback between terrestrial ecosystems and climate 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 (numbers represent relative reflectivity to incoming solar radiation). 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 a 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).

7.1.1.2 Biogeochemical feedbacks

Biogeochemical feedbacks from terrestrial ecosystems to climate operate through a wide range of compounds and particles. Here we focus on 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 (e.g., nitrogen, phosphorus), for example. The interaction 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, especially when water is limited. Also, different types of plants (e.g., those with C3 and C4 photosynthetic pathways - the two major biochemical systems that convert CO_2 into carbohydrates within plants) 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. Increasing temperature generally 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. Changing moisture regimes can either increase or decrease mineralisation. Overall, the feedback effects on climate can be either positive or negative.

Heterotrophic respiration. Organic carbon compounds in the soil, originally derived from plant material, are slowly oxidised by microbial communities 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 microbial communities. Both temperature and soil moisture can significantly affect rates of heterotrophic respiration, which generally increases with increasing soil temperature. Changes in heterotrophic respiration with increasing temperature constitute a positive feedback to climate. The influence of moisture is more complex, and can lead to positive or negative feedbacks depending on the nature of the moisture change.

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.

Productivity changes. Terrestrial ecosystems can respond to a changing climate by changing their productivity. For example, if climate becomes more favourable for growth (e.g., increased rainfall in a semi-arid system), productivity increases, there is enhanced carbon uptake from the atmosphere, and thus a negative feedback is generated. The opposite effect occurs when climate becomes less favourable for growth.

Fire. 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.

7.1.2 Ocean Ecosystems and Climate

Ocean ecosystems (or food chains) depend strongly on climatic conditions including density stratification, ocean circulation, temperature, salinity (regulated by precipitation and evaporation), the wind field and sea ice cover (Longhurst, 1998). High biomass production rates correlate with upward nutrient fluxes in upwelling regions. Ocean ecosystems play a significant role in determining the chemical composition of the atmosphere (greenhouse gases CO_2, N_2O, O_2, dimethyl sulfate (DMS) and sulphur aerosols) under a variable climate and under high CO_2 conditions. Marine biota can also influence the near-surface radiation budget through changes of the marine albedo during plankton blooms and through absorption of solar radiation (bio-optical heating). Coastal and shelf sea ecosystems can be modified by climatically- and anthropogenically-induced changes in nutrient supply from river runoff. Ocean acidification due to uptake of anthropogenic CO_2 by seawater may lead to shifts in ocean ecosystem structure and dynamics and to extinction of biota that cannot adapt to a more acidic ocean. Changes in the supply of life limiting micronutrients, in particular iron, through dust deposition to the ocean surface can modify marine biological production patterns.

7.1.3 Atmospheric Chemistry and Climate

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. The emissions of chemical ozone precursors (carbon monoxide, methane, nonmethane hydrocarbons, nitrogen oxides) have increased as a result of larger use of fossil fuel, more frequent biomass burning and more intense agricultural practices. The atmospheric concentration 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 chemical composition that could result from climate changes. The photochemical production of the hydroxyl (OH) radical, which occurs in the presence of ozone and water vapour, and destroys efficiently many atmospheric compounds, should be enhanced in a wetter atmosphere, which is projected under future global warming. Other chemistry-related processes affected by climate changes have been identified as potentially important mechanisms. They include the frequency of lightning flashes in thunderstorms (which produce nitrogen oxides), scavenging mechanisms that remove soluble species from the atmosphere, the intensity and frequency of convective transport events, the natural emissions of chemical compounds (e.g., biogenic hydrocarbons by the vegetation, nitrous and nitric oxide by soils, ocean exchanges of chemical compounds), the surface deposition on molecules on the vegetation and soils, etc. Changes in the circulation and specifically the more frequent occurrence of stagnant air events in urban or industrial areas could also enhance the intensity of air pollution events. The importance of these effects is not yet well-quantified. Finally, the recovery of stratospheric ozone in the future decades could also be affected by future climate changes. A cooling of the lower polar stratosphere, caused by enhanced radiative cooling by CO_2 to space, could facilitate the heterogeneous destruction of ozone by anthropogenic halogen compounds and delay the expected ozone recovery.

7.1.4 Aerosol Particles and Climate

Atmospheric aerosol particles modify Earth's radiation budget by absorbing and scattering incoming solar radiation. Even though some particle types may have a warming effect, most aerosol particles, such as e.g., sulphate (SO_4) aerosol particles, tend to cool the Earth surface by scattering some of the incoming solar radiation back to space. In addition, by acting as condensation nuclei (CCN), aerosol particles (e.g., particles containing nitrogen compounds or sulphate) affect radiative properties of clouds and their lifetime, which contribute to additional surface cooling. As the major natural source of sulphate is provided by DMS, an organic compound whose production by ocean organisms 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 radiative 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.

Aerosols are also delivering more nitrogen, phosphate and iron to the Earth's surface (e.g., Tegen et al., 2004). These nutrients could increase biological ocean uptake and uptake by terrestrial ecosystems.

7.1.5 Coupling the Biogeochemical Cycles with the Climate System

Models that attempt to perform reliable projections of future climate changes should not treat the evolution in the atmospheric concentrations of greenhouse gases, reactive gases and aerosol particles as external forcing factors. They should account explicitly for the feedbacks between climate and the processes that determine the atmospheric abundance of these compounds. An example is provided by the carbon-climate interactions. It is well established that the level of atmospheric CO_2, which influences directly the Earth's temperature, depends critically on the rates of carbon uptake by the ocean and by the land, which are themselves dependent on climate. Climate models including the dynamics of the carbon cycle (Friedlingstein et al., 2006) suggest that the overall effect of carbon-climate interactions is a positive feedback. Hence the predicted atmospheric CO_2 concentration in 2100 is therefore higher (and consequently the climate warmer) than in models that do not include these couplings.

As our understanding of the role of the biogeochemical cycles in the climate system improves, we can include in climate models an explicit representation of vegetation dynamics, atmospheric chemistry, aerosol microphysics, as well as land and ocean biogeochemistry. The present chapter assesses our current understanding of the processes involved and highlights the role of biogeochemical processes in the climate system.

7.2 The Changing Land Climate System

7.2.1 Introduction to Land Climate

The land component of the climate system corresponds to the terrestrial biosphere system, i.e., the fabric of soils, vegetation, and other biological components, the processes that connect them, and the carbon, water and energy they store. This section addresses from a climate perspective the advancing understanding since the previous assessment of the biophysical aspects of the system. Chapter 8 addresses progress in the land component of the coupled climate models used for the future climate projections. The land climate system is closely coupled to many other parts of the climate system but for the purpose of discussing its most important features, it can be viewed as consisting of "external" drivers and "internal" variables that respond to the external drivers, that is the various surface energy, carbon, and moisture stores and how they respond to the precipitation incoming radiation, and near surface atmospheric variables. These internal variables exchange carbon, moisture and energy with the overlying atmosphere and between themselves. The drivers and response variables occur over various time and space scales. Some aspects of this variation in time and space can be at least as important as averaged quantities. As a simple example, changes in the amplitude of the diurnal or seasonal cycles of temperature may be as significant as a change of the annual averaged temperature. As another, if almost all the precipitation were to occur in one season, the climate would be very different than it would be if it was spread uniformly over the year, and shifts in this seasonality could be very significant.

What are the most important land climate response variables, what are the most important drivers for these variables, and how can the land climate feed back on its drivers to modify variability and long term change? The drivers and response variables for the terrestrial system, in general, can be divided into biophysical, biological, biogeochemical, and human processes. The recognition of the strong coupling between these processes has been one of the major successes of the study of the Earth System as a whole. The present biophysical viewpoint emphasizes the response variables that involve the stores of energy and water and the mechanisms by which these terms are coupled to the atmosphere. These couplings depend on the properties of soils and vegetation which can be modified not only by coupling to climate but through biological, biogeochemical, and human processes. Thus, from a broader perspective the latter terms should be treated

not simply as drivers but as interactive system components for predicting the future evolution of the soil and vegetation variables.

The exchanges of energy and moisture between the atmosphere and land surface (Box 7.1) are driven from the atmosphere by radiation, precipitation, and the temperatures, humidity, and winds of the overlying atmosphere. A descriptive understanding of this system is commonly facilitated by lumping many of the individual pieces into larger summary pieces. For example the full detail of how water is stored in a column of soil might require consideration of many hundred individual layers, or water on a plant by individual stores of water on its hundreds of leaves. We may collect all these to together into a single soil moisture storage or a canopy water storage term, and these two summary terms may be further added to constitute a single surface water storage. However, the rates of exchange of this stored water with the atmosphere will depend to some degree on the detailed information as to where the water is stored and what are the transfers between different locations. Temperatures that determine the storage of thermal energy are likewise generally summarized in terms of fewer quantities. Determining exactly how much detail to include for such situations is not easy and so many choices can be made and more detail becomes necessary when more processes are to be addressed. Observations for all time and space scales help guide such choices. Common meteorological observations are the temperatures and humidity near the surface that are a result of interactions between land surface properties and those of the overlying atmosphere.

Box 7.1: Surface Energy and Water Balance

The land surface on average is heated by net radiation (incoming minus outgoing), which will be balanced by exchanges to the atmosphere of sensible and latent heat. The balance between these terms is known as the "surface energy balance". Sensible heat is the energy carried by the atmosphere in its temperature and latent heat is the energy lost from the surface by evaporation of surface water. The latent heat of the water vapour is converted to sensible heat in the atmosphere through vapour condensation and this condensed water is returned to the surface through precipitation.

The surface also has a "surface water balance". Water coming to the surface from precipitation is eventually lost either through water vapour flux or by runoff. The latent heat flux (or equivalently water vapour flux) under some conditions can be determined from the energy balance. For a fixed amount of radiation, if the sensible heat flux goes up, the latent flux will go down by the same amount. Thus, if the ratio of sensible to latent heat flux can be established as depending only on air temperature, relative humidity and other known factors, the flux of water vapour from the surface can be found from the net radiative energy at the surface. Such a relationship is most readily obtained when the mechanisms of water removal (evaporation from soil or transpiration by plants) are not limited by availability of water. Under these conditions, the increase of water vapour concentration with temperature increases the relative amount of the water flux as does also low relative humidity. Vegetation can prolong the availability of soil water through the extent of its roots and so increasing the latent heat flux but also can resist movement through its leaves, and so shift to a larger fraction of the energy flux carried by the sensible heat flux. Fluxes to the atmosphere modify atmospheric temperatures and humidity and such changes feedback on the fluxes.

If a surface is too dry to exchange much water with the atmosphere, compared to what would be exchanged if the surface were moist, the water returned to the atmosphere should on average be not far below the incident precipitation and radiative energy beyond that needed for evaporating this water will heat the surface. Under these circumstances, less precipitation and hence less water vapour flux will make the surface warmer. Reduction of cloudiness from the consequently warmer and drier atmosphere may act as a positive feedback to provide more solar radiation. A locally moist area (such as an oasis or pond), however, would still evaporate according to energy balance with no water limitation and thus should increase its evaporation under such warmer and drier conditions.

Various feedbacks coupling the surface to the atmosphere may work in opposite directions and their relative importance may depend on season and location as well as on time and space scales. A moister atmosphere will commonly be cloudier making the surface warmer in a cold climate, and cooler in a warm climate. The warming of the atmosphere by the surface may reduce its relative humidity and reduce precipitation as happens over deserts. However, it can also increase the total water held by the atmosphere, which may lead to increased precipitation as happens over the tropical oceans.

7.2.2 Dependences of Land Processes and Climate on Scale

7.2.2.1 What are the important scales?

Land climate processes are largely observed at the surface at the "plot" scale, typically with horizontal dimensions of from a few m to a few tens of m. The satellite observations used to provide a global characterization of land are typically at scales from a few hundred m to a few km. Land couples to the atmosphere vertically through exchanges of fluid and gaseous components. The atmosphere redistributes such quantities horizontally. The near surface atmosphere is coupled to the land surface over distances out to tens of km or more and the full atmosphere out to regional (e.g., a major fraction of a continent) and global scales.

Temporal variability can be viewed as consisting of daily, weather, annual, inter-annual, and decadal or longer variations. How might the amplitudes of the shorter time scales change with the long-term changes from global warming is a key research question. The land climate system has controls on amplitudes of variables on all these time scales, varying with season and geography. As an example of such dependences: Trenberth and Shea (2005) evaluate from climatic observations the correlation between surface air temperature and precipitation. A strong (>0.3) positive correlation is seen over most winter land areas, i.e., poleward of 40°N, but a strong (>0.3) negative correlation over much of summer and tropical land. These differences result from various competing feedbacks with the water cycle. On large enough scales where surface temperatures control atmospheric temperatures, the atmosphere will hold more water vapour and may provide more precipitation with warmer temperatures. Low clouds have a strong control of surface temperatures, especially in cold regions where they make the surface warmer. In warm regions without precipitation, the land surface can become warmer because of lack of evaporation, or lack of clouds. Although a drier surface will become warmer from lack of evaporative cooling, warmer temperatures can evaporate more water from a moist surface (see Box 7.1).

Extremes are especially notable as a potential cause of damage. (cf. Chapters 3 and 8 for discussion of observations and modelling of extremes). The climate statistics of extremes can change as a consequence of changing amplitudes of any of the time scales of variability. For example, cold extremes may largely depend on nighttime minimum temperatures added to winter (annual cycle) and weather variability. Diffenbaugh et al. (2005) argue that changing climate extremes will be more determined by fine scale land climate processes than by changing atmospheric weather.

7.2.2.2 Spatial dependences

Drivers of the land climate system have larger effects on regional and more local scales than global climate and thus may be inappropriately discounted for their relatively small impact on a global spatial scale and on longer time scales. Global climate change is largely controlled by processes of global radiation balance. Myhre et al. (2005) point out that the albedo of agricultural systems is only slightly higher than forests and estimate that the impact since pre-agricultural times of land use change to agriculture on global radiative forcing has been only –0.09 W/m^2, i.e., about 5% of the warming contributed by carbon dioxide (cf. Chapter 2) since pre-industrial times. Land is only about 30% of the globe, and its ability to affect reflection of global solar radiation is largely through its ice and snow cover, and the shading of the latter by vegetation.

On a regional scale and at the surface, many additional more localized and shorter time scale processes besides radiative forcing can affect climate in other ways, and possibly be of comparable importance to the effects of the greenhouse gases. Changes over land that modify its evaporative cooling can cause large changes of surface temperature, both locally and regionally (cf. Boxes 7.1, 7.2). How this change feeds back on precipitation, the direct driver of surface moisture availability is a major research question. Land has a strong control on the vertical distribution of atmospheric heating, through its determination of how much of the radiation delivered to land goes into warming of the near surface atmosphere versus how much of that is released as latent heat fueling precipitation at higher levels. Low clouds are normally closely coupled to the surface and over land can be significantly changed by modifications of surface temperature or moisture resulting from changes of land properties. For examples, Chagnon et al. (2004) find a large increase in boundary layer clouds in the Amazon in areas of partial deforestation. (e.g., also, Durieux et al, 2003; Ek and Holtslag, 2004).

Box 7.2: Urban and Other Land Use Effects on Climate

If the properties of the land surface are changed locally, the surface net radiation and the partitioning between latent and sensible fluxes (Box 7.1) may also change, with consequences for temperatures and moisture storage of the surface and near surface air. Such changes commonly occur to meet human needs for agriculture, housing, or commerce and industry. The consequences of urban development may be especially significant for local climates. However, urban development may have quite different features in different parts of an urban area and also between geographical regions.

Some common modifications are the replacement of vegetation by impervious surfaces such as roads or the converse development of dry surfaces into vegetated surfaces by irrigation, such as lawns and golf courses. Buildings cover a relatively small area but in urban cores may locally strongly modify wind-flow and surface energy balance (Box 7.1). Besides the near surface effects, urban areas can provide high concentrations of aerosols with local or downwind impacts on clouds and precipitation. Change of land use to dark dry surfaces such as roads will generally increase daytime temperatures and lower humidity while irrigation will do the opposite. Changes at night may depend on the retention of heat by buildings and can be exacerbated by the thinness of the layer of atmosphere connected to the surface by mixing of air.

Details of surface properties on scales of as small as a few km can be important for larger scales. Over some fraction of moist soils, water tables can be high enough to be hydrologically connected to the rooting zone, or reach the surface as in wetlands (e.g., Koster et al. (2000); Marani et al., 2001; Milly and Shmakin, 2002; Liang et al., 2003; Gedney and Cox, 2003).

The consequences of changes in atmospheric heating from land changes on a regional scale are similar to those from ocean temperature changes such as from El Niño, potentially producing patterns of reduced or increased cloudiness and precipitation elsewhere to maintain global energy balance. Attempts have been made to find remote adjustments (e.g., Avissar and Werth, 2005). Such adjustments may occur in multiple ways, and are part of the dynamics of climate models. 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 or longer time commonly will give 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.

7.2.2.3 Daily and seasonal variability

Diurnal and seasonal variability result directly from the temporal variation of the solar radiation driver. Large-scale changes of climate variables are of interest as part of the observational record of climate changes (Chapter 3). Daytime during the warm season produces a thick layer of mixed air whose temperature is consequently relatively insensitive to perturbations in the amplitude of the daytime radiative forcing. Night-time and high latitude winter surface temperatures, on the other hand, are coupled by mixing to only a thin layer of atmosphere, and can be readily altered by changes in atmospheric downward thermal radiation as resulting from changes in atmospheric temperature, water vapor and clouds. Thus, land is more sensitive to changes in radiative drivers under cold stable conditions and weak winds than under warm unstable conditions and strong winds. Winter or nighttime temperatures (hence diurnal temperature range) strongly correlate with downward longwave radiation (cf. Betts, 2006; Dickinson et al., 2006), and consequently, average surface temperatures may change (e.g., Pielke and Matsui, 2005) with a change in downward longwave. Compensating effects may occur elsewhere.

Changes of downward longwave by change of clouds provide one example of how land surface temperatures can so change. For example, Qian and Giorgi (2000) discussed regional aerosol effects, and noted a reduction of the day-night temperature range of –0.26 K/decade over Sichuan China. The reduction of solar heating is too small to account for this change. 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. They show the nighttime temperature change to be a result of increased night-time cloudiness and hence downward longwave radiation connected to the increase of aerosols.

In moist warm regions, large changes are possible in the fraction of energy going into water fluxes, e.g., by change of vegetation cover, Bonan (2001), or by changes in precipitation, and hence soil moisture. Bonan (2001), Oleson et al. (2004) indicate that conversion of forests to agriculture could give a daytime cooling. This cooling is apparently a result of the higher albedos and increased transpiration. Various factors not accounted for, e.g., dry soil between crops, could reverse such results. Changes of reflected solar radiation by changing vegetation are likely to be most pronounced in areas with vegetation underlain by snow or light soil. Consequent feedbacks with vegetation are most readily identified at the tundra-boreal-forest margin and in semi-arid regions.

Seasonal and diurnal cycles of precipitation can be pronounced. Understanding how the latter works is important for understanding how land couples to the atmospheric hydrological cycle. It 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.

7.2.2.4 Coupling of precipitation intensities to leaf water - an issue involving both time and space scale

The bulk of the water exchanged with the atmosphere is stored in the soil around the roots of plants until it is extracted by roots, typically weeks latter. However, the rapidity of evaporation of the near surface stores allows them to be of comparable importance for surface water and energy balances. (Dickinson et al., 2003, conclude that feedbacks between surface moisture and precipitation may act differently on different time scales). Evaporation from the fast reservoirs acts primarily as a surface energy removal mechanism, and from the water viewpoint, may largely cancel some of the incident precipitation.

Much of the precipitation over vegetation is initially intercepted by leaves. A significant fraction of this leaf water is re-evaporated to the atmosphere in an hour or less. This loss reduces the amount of water stored in the soil for use by plants. Its magnitude depends inversely on the intensity of the precipitation, which can be larger on smaller time and space scales. Modelling results can be wrong either through neglect of or through exaggeration of the magnitude of the fast time scale moisture stores. Other paths for water change as this term is changed, and so affect the atmosphere. Various studies have reported a variety of conflicting results.

Leaf water evaporation may have little effect on the determination of monthly evapotranspiration (e.g., as found in the analysis of Desborough, 1999) but may still produce important changes of temperature and precipitation. Pitman et al. (2004) in a coupled study with land configurations of different complexity were unable to find any impacts on atmospheric variability, but Bagnoud et al., (2005) did find precipitation and temperature extremes to be affected. Some studies that change the intensity of precipitation find a very large impact of leaf water. Wang and Eltahir (2000) compare model results (Figure 7.2.1) for realistic versus uniform precipitation intensities. Both cases have about the same evapotranspiration, but evidently, for the latter case, the feedback on precipitation was so strong that their runoff dropped from 700 mm yr^{-1} to nearly zero. Hahmann (2003) found changing the fraction of land over which precipitation occurred had large impacts on surface moisture in turn affecting the precipitation (Figure 7.2.2) so that, opposite to the result of Figure 7.2.1, runoff was reduced with more realistic intensities.

[INSERT FIGURE 7.2.1 HERE]

[INSERT FIGURE 7.2.2 HERE]

7.2.3 Observational Basis for the Effects of Land Surface on Climate

7.2.3.1 Vegetative controls on soil water and its return flux to the atmosphere

The study by Scanlon et al. (2005) provides a nice example of how the soil moisture, can depend on vegetation. They 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.

Vegetation can enhance the extraction of water as seen in the above study. In absence of leaves, forests in early spring also appear as especially dry surfaces with consequent large sensible fluxes that stir the atmosphere to a large depth (e.g., Betts et al., 2001). Increased water fluxes with spring green-up are seen observationally in terms of a reduction in temperature. Trees in the Amazon can have the largest water fluxes in the dry season by development of deep roots (Da Rocha et al., 2004; Quesada et al., 2005).

Forests can also retard fluxes through control by its leaves. Such control by vegetation of water fluxes is most pronounced for taller or sparser vegetation in cooler or drier climates, and from leaves that are sparse or exert the strongest resistance to water movement. The boreal forest, in particular, has been characterized as a "green desert" because of its small release of water to the atmosphere (Gammon et al., 2004)

7.2.3.2 Land feedback on precipitation

People have for centuries associated changes of land use with changes of precipitation, and climate modelers have been able to find such a connection for several decades. However, convincing observational evidence from such a connection has remained somewhat sparse. Since, as reviewed in Section 7.2.5.2, modeling conclusions cannot yet be regarded as very robust, efforts to provide independent observational constraints on this question are valuable.

Findell and Eltahir (2003) studied over the US the correlation between early morning near surface humidity and an index of the likelihood of occurrence of precipitation They identified different geographical regions with positive, negative, or little correlation. Koster et al. (2003), Koster and Suarez (2004) show from summer over the US, and all 30–60 N land, respectively, a significant correlation of precipitation over a month with that of prior months. They further show that this correlation is only reproduced in their model if soil moisture feedback is allowed to affect precipitation. Some additional observational evidence for such feedback has been noted by D'Odorico and Porporato (2004) in support of a low-dimensional model of precipitation soil moisture coupling.

Liebmann and Marengo (2001) point out that the inter-annual variation of precipitation over the Amazon is largely controlled by the timing of the onset and end of the rainy season. Li and Fu (2004) provide evidence that time of the onset of rainy season has a strong dependence on transpiration by vegetation during the dry season. Fu and Li (2004) further argue from low dry season moisture fluxes from forest removal over should contribute to a lengthening of the Amazon dry season. Durieux et al, 2003 have found a reduction of dry season precipitation over deforested regtions compared to forested areas, whereas Negri et al. (2004) obtain an opposite result. Chagnon and Bras (2005) also report an increase in dry season precipitation over deforested areas. Such changes, if initiated by mesoscale circulations, could be indicative of reduced precipitation over the remaining forested areas, and a consequent increase of water stress.

7.2.3.3 Properties affecting radiation

Albedo (the fraction of reflected solar radiation) and emissivity (the ratio of thermal radiation entitled to that of a black body) 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 snow or a soil of light colour. For models that separately balance canopy and surface energy budgets, the partitioning of radiative fluxes between these components also becomes important.

A large scale transformation of tundra to shrubs, possibly connected to warmer temperatures, has been happening, e.g., Chapin et al. (2005). Sturm et al. (2005) report on winter and melt season observations of how varying extents of such shrubs can modify surface albedo. New satellite data show the importance of radiation heterogeneities on the plot scale for the determination of albedo and the solar radiation used for photosynthesis, and appropriate modelling concepts to incorporate the new data are being advanced (e.g., Yang and Friedl, 2003; Niu and Yang, 2004; Wang, 2005; and Pinty et al., 2006).

7.2.3.4 Improved global and regional data

Specification of land surface properties 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, Z. et al., 2004, Zhou et al., 2005), and emissivities (Zhou et al., 2003a,b), and constrain model calculated albedos in the presence of vegetation (Zhou et al., 2003d; Ogawa and

Schmugge, 2004; Oleson et al., 2003), vegetation underlain by snow (Jin et al, 2002), and the role of leaf area (Tian et al., 2004a, 2004b, 2004c). Radiative temperatures are an important measurement (recent analyses include Oku and Ishikawa, 2004). Precipitation data sets combining rain gauge and satellite (Chen 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 et al., 2002).

7.2.3.5 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 physical climate aspects are reviewed here. Goncalves et al. (2004) have discussed the importance of incorporating land cover heterogeneity in weather prediction models for South America. Da Rocha et al. (2004) and Quesada et al. (2004) 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, which may help control the length of the dry season (cf. Section 7.2.3.2). Da Rocha et al. (2004) 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) (Da Rocha et al., 2004; Goulden et al., 2004).

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, heating of the atmosphere by land mixes it to a much higher altitude than elsewhere, with implications for vertical exchange of energy. However, the daytime water vapour mixing ratio in this mixed region is found to rapidly decrease with increasing altitude (Yang et al., 2004), indicating a strong insertion of dry air from above or by lateral transport.

7.2.3.6 Connecting changing vegetation to changing climate

This topic at the plant scale has extensive literature. Only large scale patterns are assessed here. Analysis 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 that changes in climate may have eased several critical climatic constraints to plant growth and thus increased global terrestrial net primary production.

7.2.4 Modelling the Coupling of Vegetation, Moisture Availability, Precipitation and Surface Temperature

7.2.4.1 How do models of vegetation control surface water fluxes?

Box 7.1 provides a general description of fluxes of water from surface to atmosphere. The most important factors affected by vegetation are surface roughness, leaf area, and availability of water from the soil. 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 heat 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 in a model 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 decrease their stomatal conductance to counter this effect.

7.2.4.2 Feedbacks demonstrated through simple models

In semi-arid systems, the occurrence and amounts of precipitation can be highly variable from year to year. Are there mechanisms whereby the growth of vegetation in times of adequate precipitation can act to maintain the precipitation? Various analyses with simple models have demonstrated how this might happen (Zeng et al., 2002; Foley et al., 2003; Wang, G. 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. That is, the extraction of water by roots and shading of soil by plants can increase precipitation and maintain the vegetation, but if the vegetation is removed, it may not be able to be restored for a long period. The Sahel region between the deserts of North Africa and the African equatorial forests appears to most readily generate such an alternating precipitation regime.

7.2.4.3 Consequences of imposing changes of moisture availability

Soil moisture control of the partitioning of energy between sensible and latent flux is very important for local and regional temperatures, and possibly their coupling to precipitation. Oglesby et al. (2002) carried out a study starting with dry soil where the dryness of the soil over the US Great Plains for at least the first several summer months of their integration produced a warming of about 10–20 K. Williamson et al. (2005), has shown that flaws in model formulation of thunderstorms can cause excessive evapotranspiration that lower temperatures by more than 1 K.

7.2.4.4 Consequences of changing land cover

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. However, since such regional changes can be of both signs, the global average impact is expected to be small. Current literature has large disparities in conclusions. For example, Snyder et al., (2004) found that removal of Northern temperate forests gave a summer warming of 1.3 K and a reduction in precipitation of –1.5 mm/day. Oleson et al. (2004) on the other hand, found that removal of temperate forests in the US would cool summer by 0.4 to 1.5 K 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. The first study assumes conversion of forest to desert and the second to crops. The large numbers of such studies collectively demonstrate a potentially important impact of human activities on climate through land use modification. Some other recent such studies illustrating various aspects of this issue include the following.

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 Nino events.

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 would modify the response of African climate to that of the greenhouse warming, in particular by further increasing the temperatures.

Guillevic et al. (2002) address the issue of the importance of interannual variability of leaf area as inferred from AVHRR satellite data, and infer a substantial sensitivity of climate to this variation. 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 variability of surface temperature and precipitation as analysed by Crucifix et al. (2005).

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 the Northeast Brazil would substantially decrease precipitation.

7.2.4.5 Mechanisms for modification of precipitation by spatial heterogeneity

Clark et al. (2004) show an example of a "squall-line" simulation where variation of soil-moisture on the scale of the rainfall substantially modifies the rainfall pattern. Pielke (2001), Weaver et al. (2002), and Roy et al. (2003) have also addressed various aspects of small-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) and Silva Dias 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. Such studies have indicated mechanisms by which small-scale inhomogeneties may modify precipitation. However, characterizations of how land has changed globally to force such modifications are not readily obtained.

7.2.4.6 Interactive vegetation response variables

Prognostic approaches estimate leaf cover on the basis of physiological processes (e.g., Arora and Boer, 2005). Levis and Bonan (2004) discuss how the springtime leaf emergence in middle latitude forests, when it is interactively modeled, provides a negative feedback on the rapid increases of temperature by increased transpiration. 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). Dynamic vegetation models have advanced and explicitly simulate competition between plant functional types (PFTs) (e.g., Sitch et al., 2003; Bonan et al., 2003; Arora and Boer, 2006).

New developments in dynamic vegetation schemes and coupled climate-carbon models (Cox et al., 2000; Betts et al., 2004; Huntingford et al., 2003) have demonstrated the possibility of large feedbacks between future climate change and vegetation change, as discussed further in Section 7.3.5. In particular, they found a large die-back in the Amazon vegetation and large reductions in Amazon precipitation. 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., 2004). They also indicated that the physiological forcing of stomatal closure from the rising CO_2 levels could contribute 20% to that rainfall reduction. Levis et al. (2004) demonstrate how African rainfall and dynamic vegetation can change each other.

7.2.5 Evaluation of Models Through Intercomparison

7.2.5.1 Intercomparison of surface fluxes

A considerable body of literature including some of the papers already mentioned have reported on the consequences for various climate models of improvements in their land models by better descriptions of leaf cover and of types of vegetation cover. Henderson-Sellers et al. (2003) in comparing the surface fluxes among 20 models submitted for intercomparison, reports over an order of magnitude difference between sensible fluxes of different models (Figure 7.2.3). However, more recently developed models cluster much more tightly. Irannejad et al. (2003) have developed a statistical methodology to fit monthly fluxes from a large number of 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 (Figure 7.2.4). Apparently both the land and the atmosphere models are major sources of uncertainty for feedbacks. They find that the coupled models are more in agreement because of offsetting differences in the atmospheric and land models.

[INSERT FIGURE 7.2.3 HERE]

INSERT FIGURE 7.2.4 HERE]

7.2.5.2 Model surface flux feedback inter-comparisons

Individual modelling studies have long reported 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 and Suarez, 2001; Koster et al., 2002; Reale and Dirmeyer, 2002; Reale et al., 2002; Koster et al., 2003, Koster and Suarez, 2004. Koster et al, (2004, 2006), Guo et al. (2006) 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 soil moisture either that is either prescribed or interactive as it evolves in time. They report a wide range of differences between models (Figure 7.2.5). Apparently we can yet have little confidence in this important feedback component of a climate model and therefore its possible contribution to global warming simulations. Further discussion of this study is given in Chapter 8. The Hadley Centre model had one of the weakest coupling strengths. Lawrence and Slingo (2005) have shown that this weak coupling strength of the Hadley Centre Model is from its atmospheric component.

[INSERT FIGURE 7.2.5 HERE]

7.2.6 Linking Biophysical to Biogeochemical and Ecological Components

7.2.6.1 What is the status of important feedbacks?

Soil moisture and surface temperatures work together in response to precipitation and radiative inputs. Vegetation influences these terms through its controls on energy and water fluxes, and through these fluxes, precipitation. It also affects the radiative heating. Clouds and precipitation are affected through modifications of the temperatures and water vapour of near surface air. How the feedbacks of land on the atmosphere work remain difficult to quantify through either observations or modelling (as addressed in Sections 7.2.3.2, 7.2.5.1).

Radiation feedbacks depend on vegetation or cloud cover that have changed because of changing surface temperatures or moisture conditions. How such conditions may promote or discourage the growth of vegetation is established by various ecological studies. The question of how vegetation will change its distribution on a large scale and what will be the consequent changes in absorbed radiation is quantified through remote sensing studies. At desert margins, radiation and precipitation feedbacks may act jointly with vegetation. Dynamic vegetation models (see Section 7.2.4.6) synthesize current understanding. Radiation feedbacks connected to vegetation may be most pronounced at the margins between boreal forests and tundra and involve changes in the timing of snow melt. How energy is transferred from the vegetation to underlying snow surfaces is understood in general terms but remains problematical in detail from modelling and process understanding viewpoints.

Changing soil temperatures and snow cover impact the soil microbiota and their processing of soil organic matter. How are nutrient supplies modified by these surface changes or delivery from the atmosphere? In particular, the treatment of carbon fluxes (addressed in more detail in Section 7.3) may require comparable or more detail in the treatment of nitrogen cycling (as attempted by Wang, S.S. et al., 2002; Dickinson et al., 2003). The challenge is to establish better process understanding on local scales and appropriately incorporate this understanding into global models. The C^4MIP simulations described in Section 7.3.5 are a first such effort.

7.2.6.2 Aerosol connections to biomass burning

Biomass burning is a major mechanism for changing vegetation cover and generation of atmospheric aerosols and is directly coupled to the land climate variables of moisture and near surface winds, as addressed for the tropics by Hoffman et al. (2002). The aerosol plume produced by biomass burning at the end of dry season contains black carbon that absorbs radiation causing warming. The combinations of a cooler surface for lack of solar radiation and a warmer boundary layer due to absorption of solar radiation increases the thermal stability and reduces cloud formation, thus can reduce rainfall. Freitas et al., (2004) have indicated the possibility of rainfall decrease in the Plata Basin as a response to the radiative effect of the aerosol load transported from biomass burning the Cerrado and Amazon regions.

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 et al., (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). Angert et al (2004) provide an analysis that rejects this hypothesis relative to other possible mechanisms,

7.3 The Carbon Cycle and the Climate System

7.3.1 Overview of the Global Carbon Cycle

7.3.1.1 Human activities and the natural carbon cycle

In the geological history of the Earth the drawdown of CO_2 by plants contributed to making the climate habitable. Burning fossilized biomass (fossil fuels) returns carbon captured by plants in Earth's geological history to the atmosphere. New ice core records available since the IPCC Third Assessment Report now cover the last 650,000 years – six glacial-interglacial cycles. These data show that the Earth system has not experienced the current concentrations of CO_2 in the atmosphere, or indeed of CH_4 and N_2O, for at least 650,000 years. During that period the atmospheric CO_2 concentration has been constrained between 180 ppm (glacial maxima) and 300 ppm (warm interglacial periods) (Siegenthaler et al., 2005). It is generally accepted that during glacial maxima, the excess CO_2 has resided in the ocean. Several causal mechanisms have been identified that connect changes in the Earth's orbit, climate, CO_2 and other greenhouse gases: ocean circulation and temperature, biological productivity and nutrient supply, and interaction with deep sea sediments (see Chapter 6, Box 6.2).

Prior to the beginning of the industrial era, around 1750, the atmospheric concentration of CO_2 had been relatively stable between 260 and 280 ppm for 10,000 years (Monnin et al, 2004 and Chapter 6, Box 6.2). During this period, perturbations to the carbon cycle from human activities were insignificant relative to natural variability. Since 1750, the concentration of CO_2 in the atmosphere has risen, at an increasing rate, from around 280 ppm to nearly 380 ppm in 2005 (see Chapter 2, Figure 2.4 and Question 2.1, Figure 1), pushing the carbon cycle beyond its natural equilibrium. The increase in atmospheric CO_2 concentration results from changes in human activities: primarily burning of fossil fuels and deforestation, but also cement production and other changes in land use and management such as biomass burning, intensive crop production and conversion of grasslands to croplands (see Question 7.1). While human activities contribute to climate change in many direct and indirect ways, CO_2 emissions from human activities are considered to be the single largest anthropogenic factor contributing to climate change in terms of its radiative forcing (see Chapter 2, Question 2.1, Figure 2). Atmospheric CH_4 concentrations have similarly experienced a rapid rise after 10,000 years of stability, from ~700 ppb (Flückiger et al., 2002) to ~1780 ppb in 2004 (see Chapter 2, Section 2.3.2): sources include fossil fuels, landfills and waste treatment, peatlands/wetlands, ruminant animals and rice paddies. The increase in CH_4 radiative forcing is less than 1/3 that of CO_2, and it is the second most important greenhouse gas in terms of direct radiative forcing (see Chapter 2, Question 2.1, Figure 2). The CH_4 cycle is dealt with in detail in Section 7.4.1.

[INSERT FIGURE 7.3.1 HERE]

A simple schematic of the fluxes of CO_2 carbon between the major reservoirs is shown in Figure 7.3.1. Both CO_2 and CH_4 are part of natural cycles involving continuous flows of large amounts of carbon among the ocean, the terrestrial biosphere and the atmosphere that have maintained stable atmospheric concentrations of these gases in the past. Carbon is converted to plant biomass by the process of photosynthesis. Terrestrial plants capture CO_2 from the atmosphere (flux F_{AL}); marine plants (phytoplankton) take up carbon from the surface ocean (flux F_{AO}). Plant, soil, and animal respiration (including decomposition of dead biomass) returns carbon to the atmosphere (fluxes F_{LA}, F_{OA}) as CO_2, or as CH_4 under anaerobic conditions (thus coupling the CO_2 and CH_4 cycles on timescales of years to decades). Combustion of plant material, e.g., during vegetation fires, is an additional source of CO_2 and CH_4 and a contribution to F_{LA} if the fires are part of a natural cycle. that can be part of a natural cycle if the vegetation re-grows and re-captures the carbon.

CO_2 is continuously exchanged between the atmosphere and the ocean; it dissolves and dissociates in surface waters and is then transported into the deep ocean. It takes roughly one year for the CO_2 concentration in surface waters to equilibrate with the atmosphere. The speed by which anthropogenic CO_2 is taken up

effectively by the ocean, however, depends on how quickly theses surface waters are mixed into the ocean's interior. While intermediate waters mix on a timescale of decades to centuries, the large volume of deep waters mixes on millennial time scales. Several repeated mixing cycles are necessary in order to bring the full buffering capacity of the ocean into effect (see Chapter 5, Section 5.4 for long-term observations on the oceanic carbon cycle and their consistency with ocean physics). Some of the dissolved carbon that is taken up by marine plants sinks in the form of dead organisms, particles, or is transferred to dissolved organic carbon. The small amount which enters ocean sediments is replaced by river runoff loads at the ocean surface; the rest is respired at depth and eventually recirculated to the surface. The marine biological cycling of carbon can change the atmospheric CO_2 content only in cases of circulation changes, nutrient supply changes, ecological changes, physiological changes or changes in the marine particle flux mode. The biological pump does not take up and store anthropogenic carbon directly, but may undergo changes due to high CO_2 concentrations with a feedback to the carbon cycle. A considerable amount of anthropogenic CO_2 can be buffered or neutralized by dissolution of calcium carbonate from the top sediment layer in the deep sea, but this process requires several tens of thousands of years.

Figure 7.3.1 shows that 'anthropogenic emissions' consist of two fractions: CO_2 from fossil fuel burning and cement production (flux F_{ff}), newly-released from geological storage of hundreds of millions of years, as evidenced by carbon isotopes (see Chapter 2, Section 2.3), and CO_2 from deforestation and agricultural development (flux F_{df}), which has been stored for 10s to 100s of years, on the same timescales as climate change. Figure 7.3.1 also shows that even during the natural equilibrium period prior to 1750, the net exchanges of CO_2 between the atmosphere and respectively the ocean and the land were not zero because of the small riverine transfer of carbon from the land to the ocean (flux R_{LO}).

[INSERT FIGURE 7.3.2 HERE]

In Figure 7.3.2 the natural or unperturbed exchanges among oceans, atmosphere and land are shown by the black arrows. The gross natural flux between the terrestrial biosphere and the atmosphere is around 60 GtC yr^{-1}, and between the oceans and the atmosphere is around 70 GtC yr^{-1}. Just under 1 GtC yr^{-1} carbon is transported from the land to the oceans via rivers either dissolved or as suspended particles (e.g., Richey, 2004). While these fluxes vary on an annual basis with climate variability, they are approximately in balance when averaged over longer time periods. Additional small natural fluxes that are important on longer geological time scales include conversion from terrestrial plants to inert soils, rock weathering and sediment accumulation ("reverse weathering"), and release from volcanic activity. The net fluxes in the 10,000 years prior to 1750, when averaged over decades or longer, are assumed to have been less than ~0.1 GtC yr^{-1} due to these small natural fluxes. For more background on the carbon cycle see Prentice et al. (2001) and Field and Raupach (2004).

7.3.1.2 Perturbations to the natural carbon cycle from human activities

The additional burden of CO_2 added to the atmosphere by human activities, often referred to as "anthropogenic CO_2" leads to the current 'perturbed' global carbon cycle. The net land-atmosphere and ocean-atmosphere fluxes have become observably different from zero as indicated by the red arrows in Figure 7.3.2. with numbers representing the average annual net flux for the 1990s (see Section 7.3.2). Even though the anthropogenic fluxes of CO_2 between the atmosphere and both the land and ocean are just a few percent of the gross natural fluxes, they have resulted in changes in the carbon content of the reservoirs since pre-industrial times as shown in red.

It is estimated that about 60% of CO_2 emissions over the last two centuries came from fossil fuel burning, while about 40% came from land use change (primarily deforestation in the northern hemisphere) (e.g., Houghton, 1999, 2003). About 40% of total CO_2 emissions (fossil fuel plus land use) have remained in the atmosphere. Oceans are estimated to have taken up approximately 30%, an amount that can be fully accounted for by physico-chemical processes (e.g., Sabine et al., 2004a; Figure 7.3.2). The increased atmospheric concentration leads to increased uptake by the oceans, due to an increased difference in concentration (partial pressure pCO_2). Terrestrial ecosystems took up the rest through a combination of ecosystem processes including growth of replacement vegetation on cleared land, land management practices, and the fertilizing effects of elevated CO_2 and nitrogen deposition (see Section 7.3.3).

The increase in the atmospheric CO_2 concentration relative to the emissions from fossil fuels only is known as the 'airborne fraction'. Land emissions are not included in the technical definition due to the difficulty in quantifying their contribution. From 1959 to the present the airborne fraction has averaged 0.55 (see Section 7.3.2.1), i.e., the oceans and terrestrial biosphere have removed 45% of fossil fuel emissions. In this chapter we also discuss the 'airborne fraction of total emissions' which is defined as the atmospheric CO_2 increase as a fraction of total anthropogenic CO_2 emissions, including the net land-use emissions. These airborne fractions vary from year to year mainly due to the effect of interannual variability in land uptake (see Section 7.3.2).

7.3.1.3 New developments in knowledge of the carbon cycle since the TAR

Sections 7.3.2–4 give more detail on the magnitude and changes in CO_2 fluxes and the processes that regulate them, with emphasis on where our knowledge and understanding have advanced significantly since the TAR. In particular, the budget of anthropogenic CO_2 (shown by the red fluxes in Figure 7.3.2) can be calculated with improved accuracy. In the ocean, we have used enhanced inverse techniques and newly available high quality data on the ocean carbon system to construct robust estimates of the integrated ocean burden of 'anthropogenic' carbon (Sabine et al., 2004a) and associated changes to the carbonate system (Feely et al., 2004), and we have become aware of decreasing pH in the surface ocean and the need to understand both its interaction with a changing climate and the potential impact on organisms in the ocean (e.g., Orr et al., 2005; Royal Society, 2005). On land, we understand better the contribution to the buildup of CO_2 in the atmosphere since 1750 associated with changes in land use and the mechanisms by which the land surface and the terrestrial biosphere interact with a changing climate. Globally, the atmospheric inverse techniques used to infer the magnitude and location of major fluxes in the global carbon cycle have continue to mature, reflecting both refinement of the techniques and the availability of new high quality observations. During the TAR, inclusion of the terrestrial carbon cycle in climate models was a new innovation. Results from the first coupled climate–carbon cycle model intercomparison project are now available: the models consistently find that when the carbon cycle is included, climate feedback on land and ocean carbon cycles tends to reduce uptake of CO_2 by land and ocean from 1850 to 2100 (see Section 7.3.5).

7.3.2 The Contemporary Carbon Budget

7.3.2.1 Atmospheric increase

The atmospheric increase is measured with great accuracy at various monitoring stations (see Chapter 2 and also http://gaw.kishou.go.jp/wdcgg.html). The mean yearly increase in atmospheric CO_2 (the CO_2 "growth rate") is reported in Table 7.3.1. Atmospheric CO_2 has continued to increase since the TAR (Figure 7.3.3), and the rate of increase appears to be accelerating, with the average annual increment rising from $+3.3 \pm 0.1$ GtC yr^{-1} in the 1990s to 4.1 ± 0.1 GtC yr^{-1} in the period 2000–2005. The annual increase represents the net effect of several processes that regulate global land-atmosphere and ocean-atmosphere fluxes, which we examine below. The "airborne fraction" provides a basic benchmark for assessing short- and long-term changes in these processes. From 1959 to present, the airborne fraction has averaged 0.55, with remarkably little variation when block-averaged into 5-year bins (Figure 7.3.3). Thus the terrestrial biosphere and the oceans together have consistently removed 45% of fossil CO_2 for the last 45 years, and the accelerating rate of increase of atmospheric CO_2 largely reflects increased rates for fossil fuel emissions. Year-to-year fluctuations in the airborne fraction are notably associated with ENSO, volcanic eruptions, and other major climatic events (see Section 7.3.2.4 and Bacastow et al., 1981; Jones C. et al., 2001; Jones and Cox, 2001a; Lintner, 2002; Lucht et al., 2002; Reichenau and Esser, 2003; Rödenbeck et al., 2003a, b; Angert et al., 2004, 2005). The annual increase in 1998, 2.5 ppm, was the highest ever observed, but when viewed as an airborne fraction (0.82), it was no higher than values observed several times in prior decades. The airborne fraction dropped significantly below the average in the early 1990s, and preliminary data suggest it may have risen above the average in 2000–2005.

Table 7.3.1. Estimates of terms in the global atmospheric carbon budget estimates. By convention, CO_2 fluxes leaving the atmospheric reservoir have a negative sign. Numbers in parentheses are ranges.

	1980s		1990s		2000–2005
	TAR	TAR revised	TAR	AR4	AR4
Atmospheric Increase[a]	3.3 ± 0.1	3.3 ± 0.1	3.2 ± 0.1	3.2 ± 0.1	4.1 ± 0.1
Emissions (fossil	5.4 ± 0.3	5.4 ± 0.3	6.4 ± 0.3	6.4 ± 0.3	7.0 ± 0.3

fuel+cement)[b]					
Net ocean-atmosphere flux[c]	–1.9 ± 0.6	–1.8 ± 0.8	–1.7 ± 0.5	–2.2 ± 0.4	–2.2 ± 0.5
Net land-atmosphere flux[d]	–0.2 ± 0.7	–0.3 ± 0.9	–1.4 ± 0.7	–1.0 ± 0.5	–0.7 ± 0.5
Partitioned as follows					
Land Use Change Flux	1.7 (0.6 to 2.5)	1.3 (0.3 to 2.8)	NA	1.6 (0.5 to 2.8)	NA
Residual Land Sink	–1.9 (–3.8 to 0.3)	–1.6 (–4.0 to 0.3)	NA	–2.6 (–4.3 to –1.0)	NA

Notes:
(a)The mean atmospheric increase is estimated by taking the time derivative of CO_2 continuously measured at background atmospheric stations Mauna Loa (MLO, 19°N) and South Pole (SPO, 90°S). The errors denote uncertainty ($\pm 1\sigma$), not interannual variability.
(b) Fossil fuel and cement emission data are only available until 2002 (http://cdiac.esd.ornl.gov/trends/emis/em_cont.htm). The mean emission over 2000–2005 has been extrapolated from trends after 2000, with a linear increase rate of 0.15 GtC yr^{-2}.
(c) The ocean-atmosphere flux is estimated using atmospheric O_2:N_2 and CO_2 trends in the 1980s, and using ocean measurements and models in the 1990s (see text). For the 2000–2005 period, we used a model estimate of the change in ocean-atmosphere flux (Le Quéré et al., 2005) between 2000–2005 and the 1990's and added this to the ocean-atmosphere flux of the 1990s. We estimated the error based on the quadratic sum of the error of the 1990's and the external error, which is the root mean square of the 5-year variability from three inversions and one ocean model presented in Le Quéré et al. (2003).
(d) The land-atmosphere flux is the balance of a positive term due to land-use change and a residual land sink. These two terms cannot be separated on the basis of current atmospheric measurements.

[INSERT FIGURE 7.3.3 HERE]

The inter-hemispheric gradient of CO_2 provides additional evidence that the increase in atmospheric CO_2 is caused primarily by the burning of fossil fuel in the Northern Hemisphere. The excess CO_2 in the North versus the South, ΔCO_2^{N-S}, has increased in proportion to emission rates of fossil fuel (which are predominantly in the north), at about 0.5 ppm (GtC $yr^{-1})^{-1}$ (Figure 7.3.4). The intercept of the best-fit line indicates that, without anthropogenic emissions, CO_2 would be higher in the Southern Hemisphere than in the North by 0.8 ppm, presumable due to transport of CO_2 by the ocean circulation. The consistency of the airborne fraction and the relationship between ΔCO_2^{N-S} and fossil emissions suggest broad consistency in the functioning of the carbon cycle over the period. There are interannual fluctuations in ΔCO_2^{N-S} as large as ±0.4 ppm, at least some of which may be attributed to changes in atmospheric circulation (Dargaville et al., 2000), while others may be due to major geophysical events such as large forest fires.

[INSERT FIGURE 7.3.4 HERE]

7.3.2.1.1 Fossil fuel and cement emissions

Fossil fuel and cement emissions have continued to increase since the TAR, rising up from to 6.4 ± 0.4 GtC yr^{-1} in the 1990's to 7.0 ± 0.3 GtC yr^{-1} between the 1990's and the recent 2000–2005 period. These numbers are estimated based upon international energy statistics for the 1980–2002 period (Marland et al., 2005) with extrapolated trends for 2003–2005 (see Table 7.3.1). The error on fossil fuel and cement emissions is on the order of 5% globally. Emissions rose from 5.4 ± 0.3 in the 1980s to 6.4 ± 0.4 GtC yr^{-1} in the 1990's (http://cdiac.esd.ornl.gov/trends/emis/em_cont.htm). Cement emissions are very small compared to fossil fuel emissions, roughly 3% of the total.

7.3.2.1.2 Land use change

During the past two decades, the CO_2 flux caused by land use changes has been dominated by tropical deforestation. Large-scale clearing of tropical forests has been widespread worldwide. 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 such old-growth forests. In the TAR, the land use flux was estimated to be 1.7 (0.6–2.5) GtC yr^{-1} for the 1980s (Houghton, 1999). No estimate was available at the time for the 1990s. The method upon which the TAR estimate is based is a book-keeping carbon model with prescribed deforestation statistics (Houghton and Hackler, 1999). Houghton (2003) has now updated this calculation, and estimates the land use flux as 2.0 (0.9–2.8) GtC yr^{-1} during the 1980s and 2.2 (1.4–3.0) GtC yr^{-1} during the 1990's. Such updated values (Table 7.3.2) give a higher CO_2

source to the atmosphere than the one reported in the TAR. A markedly lower estimate of the land use flux of 0.8 (0.6–1.0) GtC yr^{-1} was obtained by McGuire et al. (2001) using four process driven terrestrial carbon models, prescribed with changes in cropland area (Ramankutty and Foley, 1999). It has been hypothesised (House et al., 2003) that the higher value of Houghton (2003) reflects the additional inclusion of conversion of forest to pasture in their study, but Jain and Yang (2005) attributed the discrepancy to differences in the cropland area changes, and provided their own range of 1.3–2.1 GtC yr^{-1} for the 1980's, with a median value close to Houghton (1999).

Table 7.3.2. Carbon emissions caused by land-use changes during the past two decades (GtC yr^{-1}). Numbers in parentheses are ranges.

	Tropical Americas	Tropical Africa	Tropical Asia	Pan-Tropical	North	Total Globe
1990s						
Houghton[a]	0.75 ± 0.3	0.35 ± 0.2	1.09 ± 0.5	2.19 ± 0.6	–0.03 (–0.53–0.47)	**2.16 ± 0.8**
De Fries et al.[b]	0.43 (0.21–0.62)	0.12 (0.08–0.14)	0.35 (0.19–0.59)	0.97 (0.51–1.55)	NA	
Achard et al.[c]	0.44 (0.35–0.52)	0.16 (0.13–0.19)	0.39 (0.32–0.56)	0.98 (0.81–0.12)	NA	
Mean[d]	0.59 (0.33–0.84)	0.24 (0.12–0.35)	0.72 (0.39–1.09)	1.58 (1.05–2.17)	–0.03 (–0.53–0.47)	**1.55 (0.52–2.64)**
1980s						
Houghton[a]	0.77 ± 0.3	0.28 ± 0.2	0.88 ± 0.5	1.93 ± 0.6	0.06 (–0.53–0.47)	**1.99 ± 0.8**
De Fries et al.[b]	0.34 (0.17–0.48)	0.10 (0.08–0.14)	0.18 (0.10–0.29)	0.65 (0.37–0.96)	NA	
McGuire et al.[e]	0.54 (0.21–1.05)	0.21 (0.08–0.55)	0.61 (0.19–1.59)	1.55 (0.5–2.8)	NA	**0.6–1.0**
Jain et al.[f]	0.22–0.24	0.08–0.48	0.58–0.34	-	-	**1.33–2.06**
Mean[d]	1.11 (0.32–0.78)	0.19 (0.08–0.31)	0.53 (0.24–0.84)	1.29 (0.85–1.75)	0.06 (–0.53–0.47)	**1.35 (0.32–2.32)**

Notes:
(a) Houghton (2003)
(b) DeFries et al. (2002)
(c) Achard et al. (2002)
(d) Mean of (a) and (b), the only two studies covering both the 1980's and the 1990's
(e) McGuire et al. (2001)
(f) Jain, A. K., and X. Yang (2005). Range between their two simulations using the same biosphere model, forced by land cover change datasets of (a) and (b).

In addition, DeFries et al. (2002) and Achard et al (2004) estimate a land use flux of 0.6 (0.3–0.8) and 0.9 (0.5–1.4) Gt-C yr^{-1} for the 1980s and 1990s, respectively (DeFries), and 0.98 ± 0.3 Gt-C yr^{-1} in the 1990s (Achard), using satellite data and terrestrial carbon models. The different land use flux estimates are reported in Table 7.3.2 for the 1990's. Although the two recent satellite-based estimates point to a smaller source than the one estimated by (Houghton, 2003), it is premature to say that Houghton's (2003) numbers are overestimated. Estimates of the land use carbon flux have the largest uncertainties in the atmospheric carbon budget equation. The different methods used to estimate that flux also produce a large spread of mean values. If a high value for the land use source is adopted in the global budget equation below, then the residual land uptake over undisturbed ecosystems should be a large sink, and vice-versa. For evaluating the global carbon budget in the next section, we chose to use the mean value of the two studies which both cover the 1980's and the 1990's (Table 7.3.2) and the full range of uncertainty.

7.3.2.2 Uptake of CO_2 by natural reservoirs and global carbon budget

The fraction of carbon emitted by fossil fuel burning, cement production, and land use changes that does not accumulate in the atmosphere must be taken up by land ecosystems and by the oceans.

7.3.2.2.1 Ocean-atmosphere flux

For assessing the mean ocean sink, eight methods have been used. The methods are based on: (1) observations of the partial pressure of CO_2 at the ocean surface (Takahashi et al., 2002), (2) observations of the spatial distribution of atmospheric CO_2 combined with estimates of atmospheric transport (Gurney et al., 2003), also called atmospheric inversions (see also Section 7.2.3.4), (3) observations of carbon, oxygen, nutrients and CFCs in seawater, from which the concentration of anthropogenic CO_2 is estimated (Sabine et al. 2004a) combined with estimates of oceanic transport (Gloor et al., 2003; Mikaloff Fletcher et al., in press), (4) combined estimates using observations from (2) and (3), (5) estimates of the distribution of water age based on CFC observations combined with the atmospheric CO_2 history (McNeil et al., 2003), (6) the simultaneous observations of the increase in atmospheric CO_2 and decrease in atmospheric O_2 (Manning and Keeling, 2006), (7) various methods using observations on change in ^{13}C in the atmosphere (Ciais et al., 1995; Miller et al., 2006) or the oceans (Gruber and Keeling, 2001; Quay et al., 2003), and (8) ocean general circulation models (Orr et al., 2001). The ocean uptake estimates obtained with methods (1) and (2) include in part a flux component due to the outgassing of river supplied inorganic and organic carbon (Sarmiento and Sundquist, 1992). The magnitude of this necessary correction to obtain the oceanic uptake flux of anthropogenic CO_2 is not well known, as these estimates pertain to the open ocean, whereas a substantial fraction of the river induced outgassing likely occurs in coastal regions not resolved by these estimates. These estimates of the ocean sink are shown in Figure 7.3.2.

With these corrections, estimates from all methods are consistent, resulting in a well-constrained global oceanic sink for anthropogenic CO_2 (see Table 7.3.1). The uncertainty around the different estimates is more difficult to judge and varies considerably with the method. Four estimates appear better constrained than the others. The estimate of 2.2 ± 0.5 GtC yr^{-1} centered around 1998 based on atmospheric O_2/N_2 ratio needs to be corrected for the oceanic O_2 changes (Manning and Keeling, 2006). The estimate of 2.0 ± 0.4 GtC yr^{-1} centered around 1995 based on CFC observations provides a constraint from observed physical transport in the ocean. These estimates of the ocean sink are shown in Figure 7.3.5. The mean estimates of 2.2 ± 0.25 and 2.2 ± 0.2 GtC yr^{-1} centered around 1995 and 1994 provide constraints based on a large number of oceanic carbon observations. These well-constrained estimates all point at a decadal oceanic CO_2 sink of 2.2 ± 0.4 GtC yr^{-1} centered around 1996, where the error is the root mean square of all errors. See section 5.4 for a discussion on changes in the decadal CO_2 sink.

[INSERT FIGURE 7.3.5 HERE]

7.3.2.2.2 Land-atmosphere flux

The land-atmosphere CO_2 flux is the sum of the land use change CO_2 flux (see Section 7.3.2.1) plus sources and sinks due for instance to legacies of prior land use, climate, rising CO_2, N-deposition (see section 7.3.3 for a review of processes). For assessing the global land-atmosphere flux, we cannot rely on direct terrestrial observations only. This is because observations of land ecosystem carbon fluxes are too sparse and the ecosystems are too heterogeneous to allow global assessment of the net land flux with sufficient accuracy. For instance, large-scale biomass inventories (Goodale et al., 2002; UN-ECE/FAO, 2000) are limited to forests with commercial value only, and they do not adequately survey tropical forests. Direct flux observations by the eddy covariance technique are only available at point locations, most do not yet have long-term coverage, and they require considerable upscaling to obtain global estimates (Baldocchi et al., 2001). As a result, one can use two methods to quantify the global land-atmosphere flux, (1) deduce that quantity as a residual between the fossil fuel and cement emissions and the sum of ocean uptake and atmospheric increase (Table 7.3.1), or (2) infer the land-atmosphere flux simultaneously with the ocean sink by inverse analysis or mass balance computations using atmospheric CO_2 data, with terrestrial and marine processes distinguished using O_2/N_2 and/or ^{13}C observations. Individual estimates of the land-atmosphere flux deduced from either method (1) or method (2) are shown in Figure 7.3.5. Method (2) was used in the TAR, based upon O_2/N_2 data (Langenfelds et al., 1999) (Battle et al., 2000). Corrections have been brought to the results of method (2) to account for the effects of thermal O_2 fluxes by the ocean (Le Quéré et al., 2003). In this chapter, we have included these corrections to update the 1980's budget. Doing so, we obtain a land net flux of -0.3 ± 0.9 GtC yr^{-1} during the 1980's. For the 1990's and after, we chose to use method (1) for assessing the ocean sink and the land-atmosphere flux. This is because method (1) now yields lower uncertainties than method (2) over that period, thanks to the convergence of four independent methods (including method (1), see above), which all robustly quantify the ocean sink based upon observations. Doing so, we estimate a mean land-atmosphere flux of -1.0 ± 0.5 GtC yr^{-1} during the 1990's, and of $-0.7 \pm$

0.5 GtC yr^{-1} over the recent period 2000-2005. The land-atmosphere flux evolved from a small sink in the 1980's of –0.3 ± 0.9 GtC yr^{-1} to a large sink during the 1990's of –1.0 ± 0.5 GtC yr^{-1}, and returned to an intermediate value of –0.7 ± 0.5 GtC yr^{-1} over the past five years. A recent weakening of the land-atmosphere uptake has also been suggested by other independent studies of the flux variability over the past decades (Jones and Cox, 2005; Miller et al., 2005). The global CO_2 budget is summarized in Table 7.3.1.

7.3.2.2.3 Residual land sink

In the context of land use change, deforestation dominates over forest re-growth (see Section 7.3.2.1), and the observed net uptake of CO_2 by the land biosphere implies that there must be an uptake by terrestrial ecosystems elsewhere, called the "residual land sink" (formerly the 'missing sink'). Estimates of the residual land sink necessarily depend on the land use change flux, and its uncertainty reflects predominantly the (large) errors associated with the land use change term. With the high land use source of (Houghton, 2003), the residual land sink equals –2.3 (–4.0 to –0.3) and –3.2 (–4.5 to –1.9) GtC yr^{-1} respectively for the 1980s and the 1990's. With the smaller land use source of De Fries (2002), the residual land sink is only –0.9 (–2.0 to –0.3) and –1.9 (–2.9 to –1.0) GtC yr^{-1} for the 1980s and the 1990's. Using the mean value of the land use source from Houghton (2003) and DeFries et al. (2002) as reported in Table 7.3.2, we obtain a mean residual land sink of –1.6 (–4.0 to 0.3) and –2.6 (–4.3 to –1.0) GtC yr^{-1} for the 1980's and 1990's respectively. Houghton (2003) and De Fries (2002) disagree on the absolute value of the land use source, but they agree that this source was 0.2–0.3 GtC yr^{-1} higher in the 1990's than in the 1980s (see Table 7.3.2). To compensate for that increase and to match the larger land-atmosphere uptake during the 1990's, the inferred residual land sink is found to have increased by 1 GtC yr^{-1} between the 1980's and the 1990's. This finding is insensitive to the method used to determine the land use flux, and shows considerable decadal variability in the residual land sink.

7.3.2.2.4 New findings on the carbon budget

The revised carbon budget in Table 7.3.1 show new estimates of two key numbers. First, the flux of CO_2 released to the atmosphere from land use change is estimated to be 1.6 (0.5 to 2.8) GtC yr^{-1} for the 1990's. A revision of the TAR estimate for the 1980s downwards to 1.3 (0.3 to 2.8) GtC yr^{-1} suggests little change between the 1980s and 1990s, but there continues to be considerable uncertainty in these estimates. Second, the underlying numbers used to calculate the flux of CO_2 from the atmosphere to the ocean can be used to give a new estimate of the fraction of CO_2 emissions taken up by the ocean during 1980–2005: the net emissions seen by the ocean during this period were 136.5 ± 9 GtC yr^{-1} and the amount taken up by the ocean was 51 ± 9 GtC yr^{-1}, giving the fraction of emissions taken up by the ocean to be 0.37 ± 0.07, which can be compared with a fraction of 0.42 ± 0.07 for the period 1750–1994 (see Sabine et al., 2004a; and Chapter 5, Section 5.4). The net emissions include emissions from fossil fuel burning, cement production, land use change and the "residual land sink'. It is equivalent to the sum of the atmospheric and oceanic increase. In Section 7.3.4, we consider changes occurring in the ocean that might cause this fraction to decrease.

7.3.2.3 Regional fluxes

Quantifying present-day regional carbon sources and sinks and understanding the underlying carbon mechanisms are needed to inform policy decisions. Furthermore, we can also isolate mechanisms by analyzing spatial and temporal detail.

7.3.2.3.1 The top-down view, atmospheric inversions

The atmosphere mixes and integrates surface fluxes that vary spatially and temporally. The distribution of regional fluxes over land and oceans can be retrieved using observations of atmospheric CO_2 and related tracers within models of atmospheric transport. This is called the 'top-down' approach to estimating fluxes. Atmospheric inversions belong to that approach, and determine an optimal set of fluxes, which minimizes the mismatch between modelled and observed gradients of concentrations, accounting for measurement and model errors. Fossil fuel emissions are generally considered perfectly known in inversions, so that their effect can be easily modelled and subtracted from atmospheric CO_2 data to solve for regional land-atmosphere and ocean-atmosphere fluxes, although making such an assumption biases the results (Gurney et al., 2005). Input data for inversions come from a global network of about a hundred of CO_2 concentration measurement sites (http://gaw.kishou.go.jp/wdcgg.html), with mostly discrete flask sampling sites, and a smaller number of in situ continuous sites. Generally, regional fluxes derived from inverse models have smaller uncertainties upwind of regions with denser data coverage. Measurement and modelling errors, and

uneven and sparse coverage of the network, determine random errors in inversion results. In addition, inverse methodological details, such as the choice of transport model, can introduce systematic errors. A number of new inversion ensembles, with different methodological details, have been produced since the TAR (Baker et al., 2005; Gurney et al., 2003; Peylin et al., 2005; Rödenbeck et al., 2003a, b). Generally, confidence in the long-term mean inverted regional fluxes is lower than confidence in the year-to-year anomalies (see 7.3.2.4). For individual regions, continents or ocean basins, the errors of inversions increase and the significance can be lost. Being aware of this, we chose to report in Figure 7.3.6 the oceans and land fluxes aggregated into large latitude bands, as well as a breakdown of five land and ocean regions in the Northern Hemisphere, which is constrained by denser atmospheric stations. Both random and systematic errors are reported in Figure 7.3.6.

[INSERT FIGURE 7.3.6 HERE]

7.3.2.3.2 The bottom-up view, ocean and land observations and models

The range of carbon flux and inventory data enables quantification of the distribution and variability of CO_2 fluxes between the Earth's surface and the atmosphere. This is called the 'bottom-up' approach. The fluxes can be determined by measuring carbon stock changes at repeated intervals, from which time-integrated fluxes can be deduced, or by direct observations of the fluxes. The stock change approach includes basin-scale in situ measurements of dissolved and particulate organic and inorganic carbon or tracers in the ocean (e.g., Sabine et al., 2004a), extensive forest biomass inventories (e.g., Fang et al., 2001; Goodale et al., 2002; Nabuurs et al., 2003; Shvidenko and Nilsson, 2003; UN-ECE/FAO, 2000) and soil carbon inventories (e.g., Bellamy et al., 2005). The direct flux measurement approach includes ocean pCO_2 surveys from ship-based measurements, drifters and time series (e.g., Lefèvre et al., 1999; Takahashi et al., 2002), and ecosystem flux measurements via eddy covariance flux networks (e.g., Baldocchi et al., 2001; Valentini et al., 2000).

Takahashi et al. (2002) present both surface ocean pCO_2 observations (used in many atmospheric inversions) and estimated atmosphere-ocean CO_2 fluxes normalized to 1995 using NCEP/NCAR 41-year mean monthly winds. Large CO_2 annual fluxes to the ocean occur in the N. Atlantic (into the Arctic) poleward of 40°N, in the N. Pacific poleward of 30°N, and in a band between 40 and 60°S in the Southern Ocean (see Figure 7.3.7). The North Atlantic and Southern Ocean correspond to areas of greatest storage of 'anthropogenic' carbon as derived from global ocean hydrographic surveys (Sabine et al. 2004a; and Chapter 5, Figure 5.4.2). The broad area of outgassing in the tropical Pacific corresponds to a region of almost no ocean uptake storage of 'anthropogenic' CO_2.

[INSERT FIGURE 7.3.7 HERE]

Models are generally used to extrapolate pointwise flux observation into regional estimates, using climate, remote-sensing properties, and knowledge of the processes controlling the CO_2 fluxes and their variability. A more recent development is the use of inverse, process-based models, whereby observations are "assimilated" to infer optimized fluxes (Rayner et al., 2005). One can refer to the TAR for a detailed description of oceanic and terrestrial carbon models. Since the TAR, the global air-sea fluxes synthesis of Takahashi et al. (1997) was updated, and new syntheses were made of continental scale carbon budgets of the Northern Hemisphere continents (Ciais et al., 2004; Goodale et al., 2002; Janssens et al., 2003; Pacala et al., 2001; Shvidenko and Nilsson, 2003), and of tropical forests (Malhi and Grace, 2000). These estimates are reported in Figure 7.3.6 and compared with inversion results.

Comparing bottom up regional fluxes with inversion results is not straightforward because: (1) inversion fluxes may contain a certain amount of a priori knowledge of bottom-up fluxes so that the two approaches are not fully independent; (2) the time period for which inversion models and bottom-up estimates are compared is often not consistent, in the presence of interannual variations in fluxes[1] (see Section 7.3.2.4); and (3) CO_2 fluxes to or from the atmosphere do not always match changes in carbon stocks in the presence of lateral carbon fluxes. Lateral surface fluxes (e.g., river flows, trade) act to transport carbon away from or into areas where CO_2 is exchanged with the overlying atmosphere, (Sarmiento and Sundquist, 1992; Tans et

[1] For instance, the chosen 1992–1996 time period for assessing inversion fluxes, dictated by the availability of the TRANSCOM-3 transport model intercomparison results (Gurney et al., 2002, 2003, 2004), corresponds to low growth rate and to a stronger terrestrial carbon sink.

al., 1995). Atmospheric transport and photochemistry displace reduced carbon compounds such as VOCs, CO, CH_4 emitted by ecosystems and human activities (Enting and Mansbridge, 1991; Folberth et al., 2005; Suntharalingam et al., 2005). Trade of forest and crop products displaces carbon harvested from ecosystems (Ciais et al., 2005; Imhoff et al., 2004). Rivers displace dissolved and particulate inorganic and organic carbon from land to ocean, though a cascade of 'filters', such as wetlands, dams, flood-plains and estuaries (e.g., Aumont et al., 2001). A summary of inversion and bottom-up main results on regional CO_2 fluxes is given below.

7.3.2.3.3 Robust findings of regional land-atmosphere flux

- Tropical lands are found in inversions to be either carbon neutral or sink regions, despite widespread deforestation. This implies carbon uptake by undisturbed ecosystems, in agreement with limited forest inventory data in the Amazon (Malhi and Grace, 2000; Phillips et al., 1998).
- Inversions place a substantial land carbon sink in the Northern Hemisphere of –1.7 (–0.4 to –2.3) GtC yr^{-1} (mean and range of data in Figure 7.3.7) in agreement with bottom up studies –0.98 (–0.38 to –1.6) GtC yr^{-1}, the latter number compiled as the sum of regional estimates (Pacala et al., 2001; Kurz and Apps, 1999) for North America, (Fang et al., 2001) for China, (Janssens et al., 2003) for Europe, and (Shvidenko and Nilsson, 2003; Nilsson et al., 2003) for Russia. The Northern land CO_2 sink inferred by inversions is on average higher than the land carbon sink inferred from bottom-up studies. Part of this discrepancy could be explained by laterally transported carbon from Northern Hemisphere to the Tropics (rivers, crop products trade, reduced carbon compounds).
- The longitudinal partitioning of the northern land sink between North America, Europe and Northern Asia has large uncertainties (see Figure 7.3.7). Inversion results give a very large spread over Europe (–0.9 to +0.2 GtC yr^{-1}), and Northern Asia (–1.2 to +0.3 GtC yr^{-1}) and a large spread over North America (–0.6 to –1.1 GtC yr^{-1}). Within the uncertainties of each approach, continental scale carbon fluxes from bottom-up and top-down methods over Europe, North America and Northern Asia are mutually consistent. The North American carbon sink estimated by recent inversions is large, but on average lower than an earlier, widely cited study by Fan et al. (1998). Nevertheless the Fan et al. (1998) estimate still remains within the inversion range of uncertainty[2].

7.3.2.3.4 Robust findings of regional ocean-atmosphere flux

- The tropical oceans are outgassing CO_2 to the atmosphere, with a mean flux on the order of 0.7 GtC yr^{-1}, estimated from an oceanic inversion (Gloor et al., 2003), in good agreement with atmospheric inversions (0–1.5 GtC yr^{-1}), and estimates based on oceanic pCO_2 observations (0.8 GtC yr^{-1}) Takahashi et al., 2002).
- The extratropical northern hemisphere ocean is a net sink for atmospheric CO_2, with a magnitude of the order of 1.2 GtC yr^{-1}, consistent among all estimates.
- The extratropical southern hemisphere is also a net sink for atmospheric CO_2. Its magnitude has been estimated to be about 1.5 GtC yr^{-1}. This estimate is consistent among the different methods at the scale of the entire southern hemisphere. However, substantial differences exist in the determination of the distribution within the southern hemisphere, particularly with regard to the flux distribution between the temperate latitudes and the high southern latitudes (Roy, T. et al., 2003).

7.3.2.4 Interannual changes in the carbon cycle

7.3.2.4.1 Interannual changes in global fluxes

The atmospheric CO_2 growth rate exhibits large interannual variations (see e.g., TAR, Chapter 3, Figure 3.3 and http://lgmacweb.env.uea.ac.uk/lequere/co2/carbon_budget), but the variability of fossil emissions is too small to account for this signal, which must be caused by year-to-year fluctuations in land-atmosphere fluxes. Over the past two decades, higher than normal CO_2 growth rates occurred in 1983, 1987, 1994–1995, 1997–1998, and in 2002–2003. During such episodes, the land-atmosphere and ocean-atmosphere uptake fluxes are temporarily weakened. Conversely, small growth rates occurred in 1981, 1992–1993 and in 1996–1997, associated with enhanced uptake. Generally, high CO_2 growth rates correspond to El Niño climate conditions, and low growth rates to La Niña (Bacastow and Keeling, 1981; Lintner, 2002). However, two episodes of CO_2 growth rate variations during the past two decades did not reflect such an El Niño forcing.

[2] Also worth noting is that the actual years considered by Fan et al. (1998) were in the low-growth post-Pinatubo period, i.e., not necessarily representative of long-term behaviour.

In 1992–1993, a marked slow down in growth rate occurred, coincident with the cooling and radiation anomaly caused by the volcanic eruption of Mt Pinatubo in June 1991. In 2002-2003, a speed-up in growth rate occured in the absence of a significant El Niño event (Jones and Cox, 2005), but coincident with widespread droughts in Europe (Ciais et al., 2005), North America (Breshears et al., 2005) and in Asian Russia (IFFN, 2003).

[INSERT FIGURE 7.3.8 HERE]

Since the TAR, many studies have confirmed that the variability of CO_2 fluxes is mostly due to land fluxes, and that tropical lands contribute strongly to this signal (Figure 7.3.8). Such a predominant terrestrial origin of the growth rate variability can be inferred from (1) atmospheric inversions assimilating time-series of CO_2 concentrations from different stations (Baker et al., 2005; Bousquet et al., 2000; Rödenbeck et al., 2003b), (2) consistent relationships between $\delta^{13}C$ and CO_2 (Rayner et al., 1999), (3) ocean model simulations (e.g., Le Quéré et al., 2003; McKinley et al., 2004a) and (4) terrestrial carbon cycle and coupled model simulations (e.g., Jones, C. et al., 2001; McGuire et al., 2001; Peylin et al., 2005; Zeng et al., 2005). Furthermore, there is no evidence for basin-scale interannual variability in the oceans exceeding ± 0.4 GtC yr^{-1}.

7.3.2.4.2 Interannual variability in regional fluxes, atmospheric inversions and bottom up models

Year-to-year flux anomalies can be more robustly inferred by atmospheric inversions than mean fluxes. Yet, at the scale of continents or ocean basins, the inversion errors increase and the statistical significance of the inferred regional fluxes decreases. This is why we show in Figure 7.3.8 the land-atmosphere and ocean-atmosphere flux anomalies over broad latitude bands only for the inversions ensembles[3] of Baker et al. (2005), Bousquet et al. (2000), and Rödenbeck et al. (2003b). Interannual variability of global land-atmosphere fluxes (±4 GtC yr^{-1} between extremes) is larger than that of air-sea fluxes and dominates the global fluxes. This result is also true over large latitude bands (Figure 7.3.8). Tropical land fluxes exhibit on average a larger variability than temperate and boreal fluxes. Inversions give tropical land flux anomalies on the order of ±1.5–2 GtC yr^{-1}, which compare well in timing and magnitude with terrestrial model results (Peylin et al., 2005; Tian et al., 1998; Zeng et al., 2005). In these studies, enhanced sources occur during El Niño episodes and abnormal sinks during La Niña. In addition to the influence of these climate variations on ecosystem processes (Gérard et al., 1999; Jones et al., 2001), regional droughts during El Niño events promote large biomass fires, which appear to contribute to high CO_2 growth rates during the El Niño episodes (Barbosa et al., 1999; Langenfelds et al., 2002; Page et al., 2002; Patra et al., 2005; van der Werf et al., 2003, 2004).

Inversions robustly attribute a rather small variability in the ocean-atmosphere CO_2 fluxes (±0.5 GtC yr^{-1} between extremes), except for the recent work of Patra et al. (2005b). This is in agreement with bottom-up ocean model and data estimates (Le Quéré et al., 2003; Lee et al., 1998; McKinley et al., 2004b). However, inversions and ocean models differ on the dominant geographic contributions to the variability. Inversions estimate similar variability in both hemispheres, whereas ocean models estimate more variability in the Southern Ocean (Baker et al., 2005; Bousquet et al., 2000; Rödenbeck et al., 2003b). Over the North Atlantic, Gruber et al., (2002) suggest a regional CO_2 flux variability (extremes of ±0.3 GtC yr^{-1}) by extrapolating data from a single ocean station to the whole but McKinley et al. (2004a, b) model a small variability (extremes of ±0.1 GtC yr^{-1}). The Equatorial Pacific is the ocean region of the world where the variability is constrained from repeated ΔpCO_2 observations (variations of about ±0.4 GtC yr^{-1}) (Feely et al., 2002), with a reduced source of CO_2 during El Niño associated with decreased upwelling of CO_2-rich waters. Over this region, some inversion results (e.g., Bousquet et al. 2000) compare well in magnitude and timing with ocean and coupled model results (Le Quéré et al., 2000; Jones, C. et al., 2001; McKinley et al., 2004a, b) and with ΔpCO_2 observations (Feely et al., 2002).

[3] These studies all report a random error and a systematic error range derived from sensitivity tests with different settings. Bousquet et al., (2000) used large regions and different inversion settings for the period 1980–1998. Rödenbeck et al. (2003) used one transport model and inverted fluxes at the resolution of model grid for the period 1982–2002, with different inversion settings. Baker et al. (2005) used large regions but 13 different transport models for the period 1988–2002. An important finding of this study is that differences in transport models have a small impact on the inverted interanual variability of fluxes. In other words, the bias in inverse models has low interannual variability.

7.3.2.4.3 Slow down in CO_2 growth rates during the early 1990s

The early 1990s featured anomalously strong global sinks for atmospheric CO_2. Although a weak El Niño established from 1991 to 1995 may have helped to enhance ocean uptake at that time, inversions and analysis of O_2:N_2 and $\delta^{13}C$-CO_2 atmospheric data (Battle et al., 2000; Miller et al., 2005) indicate the enhanced uptake to be of predominantly terrestrial origin. The regions where the 1992–1993 abnormal sink is projected to be are not robustly estimated by inversions. Both Bousquet et al. (2000) and Rödenbeck et al. (2003b) project a large fraction of that sink in temperate North America, while Baker et al. (2005) place it predominantly in the Tropics. Model results suggest that cooler temperatures caused by the Pinatubo eruption reduce soil respiration and enhance Northern Hemisphere carbon uptake (Jones and Cox, 2001b; Lucht et al., 2002), despite a lower productivity analyzed from remotely sensed vegetation activity data. Also, aerosols from the volcanic eruption scattered sunlight and increased its diffuse fraction, which is used more efficiently by plant canopies in photosynthesis than direct light (Gu et al., 2003). It has been hypothesized that a transient increase in the diffuse fraction of radiation has enhanced CO_2 uptake by land ecosystems in 1992-93, but the global significance and magnitude of this effect remains unresolved (Angert et al., 2004; Krakauer and Randerson, 2003; Robock, 2005; Roderick et al., 2001).

7.3.2.4.4 Speed-up in CO_2 growth rates during the late 1990s

The notably high CO_2 growth in 1998 coincided with a global increase in CO concentrations attributable to wildfires (Yurganov et al., 2005). The main regions that contributed to enhanced wildfire emissions were South East Asia (60%), South America (30%) and a small Siberian contribution (van der Werf et al., 2004). Similarly, Langenfelds et al. (2002) analyze the correlations in the interannual growth rate of CO_2 and other species at 10 stations and link the 1997–1998 (and the 1994–1995) anomalies to high fire emissions as a single process. Achard et al. (2004) estimate a source of 0.88 ± 0.07 GtC emitted from the burning of 2.4×10^6 ha of peatland in the Indonesian forest fires in 1997–1998, and Page et al. (2002) estimate a source of +0.8 to +2.6 GtC. During the 1997–1998 high CO_2 growth rate episode, inversions place an abnormal source over tropical South East Asia, in good agreement with such bottom-up evidence. The relationship between El Nino and CO_2 emissions from fires is not uniform: fire emissions from low productivity ecosystems in Africa and northern Australia are limited by fuel load density and thus decrease during drier periods, in contrast to the response in tropical forests (Barbosa et al., 1999, Randerson et al., 2005). In addition, co-varying processes such as reduced productivity caused by droughts over tropical forests during El Niño episodes may be superimposed on fire emissions.

From 1998–2003, extensive droughts in mid-latitudes of the northern hemisphere (Hoerling and Kumar, 2003), accompanied by more wildfires in some regions (Balzter et al., 2005; Yurganov et al., 2005) may have led to decreased photosynthesis and carbon uptake (Angert et al., 2005; Ciais, 2005), helping to push up the CO_2 growth rate towards higher values.

7.3.3 Terrestrial Carbon Cycle Processes and Feedbacks to Climate

The net exchange of carbon between the terrestrial biosphere and the atmosphere is the difference between carbon uptake by photosynthesis and release by plant respiration, soil respiration and disturbance processes (fire, windthrow, insect attack and herbivory in unmanaged systems, together with deforestation, afforestation, land management and harvest in directly managed systems). Over at least the last 30 years, the net result of all these processes has been an uptake of atmospheric CO_2 by terrestrial ecosystems (Table 7.3.1, "land-atmosphere flux" row). It is critical to understand the reasons for this uptake and its likely future course. Will uptake by the terrestrial biosphere grow or diminish with time, or even reverse so that the terrestrial biosphere becomes a net source of CO_2 to the atmosphere? To answer this question it is necessary to understand the underlying processes and their dependence on the key drivers of climate, atmospheric composition and human land management.

Drivers that affect the carbon cycle in terrestrial ecosystems can be classified as (1) direct climate effects (changes in precipitation, temperature and radiation regime); (2) atmospheric composition effects (CO_2 fertilisation, nutrient deposition, damage by pollution); and (3) land use change effects (deforestation, afforestation, agricultural practices, and their legacies over time). In this section we first summarise current knowledge of the processes by which each of these drivers influence the terrestrial carbon balance, and then examine knowledge of the integrative consequences of all these processes in the key case of tropical forests.

7.3.3.1 Processes driven by climate, atmospheric composition and land use change

7.3.3.1.1 Dependence of photosynthesis and respiration on temperature and soil moisture

Global fluxes of carbon reflect competition between the effects of temperature and moisture on photosynthesis and respiration, with different regions responding differently. Most models predict strong release of CO_2 from increased oxidation organic matter in a warmer climate. Jenny's (1941) famous studies are often cited as predicting major reductions in soil organic matter in a warmer climate, but even his early studies recognized that rates of mineralization of soil organic matter depend at least as much on soil moisture as on temperature. Warmer temperatures lengthen the growing season at middle to high latitudes (e.g., Keeling et al., 1996; Myneni et al., 1997), potentially enhancing tree growth and carbon storage, but this trend over the last decade has been largely offset by increased plant water stress through a combination of warming and more severe droughts (Angert et al., 2005).

Recent experimental evidence on temperature effects at the whole-ecosystem level is equivocal (Giardina and Ryan, 2000). Soil warming manipulations in particular show strong "acclimation" (or down-regulation), with CO_2 fluxes stimulated by warming for a while, followed by return to initial values or lower after a few years (Oechel et al., 2000; Melillo et al., 2002; Jarvis et al, 2000; Luo et al, 2001; Rustad et al. 2001). Taken at face value, these studies suggest that coupled climate-carbon models may overestimate positive feedback of climate on mineralization of soil carbon. But warming studies last a few years to a decade, and thus observe the rapid depletion of labile pools of organic matter that lead to adjustments in these pool that can mimic acclimitatization. Knorr et al. (2005) argued that these studies have been misinterpreted, and that the data are consistent with models that include properly adjusted parameters and soil pools with a range of decay rates. Observations of carbon age using ^{14}C techniques (Trumbore 2000) usually suggest older ages (longer preservation) of soil carbon at lower temperatures (e.g., Bird et al., 2002). But there is spirited debate on the question (Fang et al., 2005; Reichstein et al., 2005; Knorr et al, 2005), and, since there are still no direct observations at long time scales (tens of years to centuries), the issue cannot be fully resolved.

Projections of changes in land carbon storage are intimately tied not only to the sensitivity of ecosystem processes to climate change, but also to the modelled projections of climate change itself. There are strong feedbacks between these components of the Earth system, an issue addressed in Section 7.3.5.

7.3.3.1.2 Atmospheric composition effects

On physiological grounds almost all models predict stimulation of carbon assimilation and sequestration, or "CO_2 fertilization", in response to rising CO_2 (Cramer et al., 2001; Oren et al., 2001; Luo et al., 2004; DeLucia et al., 2005). Elevated CO_2 experiments, including Free Air CO_2 Enrichment (FACE) and other studies, have been used to examine the response of ecosystems to large (usually about 50%) step increases in CO_2 concentration. The results of these have been quite variable (Nowak et al., 2004; Oren et al., 2001; Shaw et al., 2002; Norby et al, 2005). On average stimulation of net CO_2 uptake has been observed, but not as much as predicted from the kinetics of photosynthesis. These results clearly demonstrate that other factors (nutrients for example) can limit plant growth, and throttle the CO_2 fertilization effect. Eleven FACE experiments, encompassing bogs, grasslands, desert, and young temperate tree stands report an average increased NPP of 12% when compared to ambient CO_2 (Nowak et al. 2004), but there is a large-range of responses with some vegetation types showing NPP increases of 23–25% (Norby et al., 2005). A recent meta-analysis of over a hundred studies shows about 2/3 of the experiments responding positively to increased CO_2 (Lou et al. 2005). This analysis also shows that ecosystems under elevated CO_2 can accumulate N, so demonstrating a certain capacity of terrestrial ecosystems to generate the additional N required to continue accumulating C along with the some capacity to increase the C:N ratio. But some systems seem to show saturation of CO_2 stimulation due to nutrient or other limitations (Koerner et al., 2005; Dukes et al., 2005), in some systems enhanced plant growth does not lead to carbon sequestration due to life-cycle limits of the organisms. Thus it is not clear how strong the CO_2 fertilization effect actually is.

Atmospheric composition also affects terrestrial ecosystems through nitrogen deposition. Early modeling studies suggested that anthropogenically enhanced N deposition on forests would significantly enhance carbon sequestration, particularly in mid-latitude Northern Hemisphere forests where N deposition is high and N limitation is common (Holland et al., 1996; Townsend et al., 1996). However, later field experiments suggest a more conservative 0.25 GtC yr^{-1} as the upper limit of C uptake by through enhanced N deposition (Nadelhoffer et al., 1999).

7.3.3.1.3 Nutrient limitations to carbon sequestration

Supply of nutrients, especially nitrogen, exert strong constraints on growth in many ecosystems. These limitations are likely to increase in the future Hungate et al. (2003) calculate the amount of N required to meet the C accumulation over the 21st Century as predicted by several terrestrial ecosystem models used in the TAR. They conclude that, even after accounting for large increases in atmospheric N deposition and biological fixation, and decreased C:N ratios, the N supply from all processes over 100 years (1.2 to 6.1 GtN) is inadequate to meet the demand imposed by the C accumulation (2.3 to 16.9 GtN). Failure to account for this constraint (phosphorus is also important in the tropics) will result in a gross overestimation of the CO_2 fertilization effect.

7.3.3.1.4 Fire

Fire is a major agent for conversion of biomass and soil organic matter to CO_2 (Kasischke et al., 2005; Cochrane, 2003; Nepstad et al., 2004; Randerson et al., 2002a-d, 2005; Jones and Cox, 2005). Globally, wildfires (savanna and forest fires, excluding biomass burning for fuel and land clearing) oxidise 1.7 to 4.1 GtC yr^{-1} (Mack et al. 1996), or about 3% to 8% of total terrestrial NPP. There is an additional large enhancement of CO_2 emissions associated with fires stimulated by human activities, such as deforestation and tropical agricultural development. Thus, there is a large potential for future alteration in the terrestrial C balance through altered fire regimes. A striking example occurred during the 1997–1998 El Niño, when large fires in the Southeast Asian archipelago released 0.8 to 2.6 GtC (see Section 7.3.2.4). Fire frequency and intensity are strongly sensitive to climate change and variability, and also to land use practices. Over the last century, trends in burned area have been largely driven by land use practices, through fire suppression policies in mid-latitude temperate regions and increased use of fire to clear forest in tropical regions (Mouillot and Field, 2005). The decrease in fire frequency in regions like USA and Europe has contributed to the land carbon sink there, while increased fire frequency in regions like Amazonia and South East Asia has contributed to the carbon source. In high latitudes, the role of fire appears to have increased in recent decades: fire disturbance in boreal forests was higher in the 1980s than in any previous decade on record (Kurz and Apps, 1999; Kurz et al., 1995), attributed to climatic fluctuations and trends.

7.3.3.1.5 Direct effects of land use and land management

Evolution of landscape structure, including woody thickening: Changes in the structure and distribution of ecosystems are driven in part by changes in climate and atmospheric CO_2, but also by human alterations to landscapes through land management and the introduction of invasive species and exotic pathogens. The single most important process in the latter category is woody encroachment or vegetation thickening, the increase in woody biomass in (mainly semi-arid) grazing lands, mostly arising from fire suppression and associated grazing management practices. For example, woody encroachment could account for as much as 22 to 40% of the regional C sink in the US (Pacala et al., 2001), and a high proportion in northeast Australia (Burrows et al., 2002). Comprehensive data are lacking to define this effect accurately.

Deforestation: Clearing of forest (mainly in the tropics) is a huge contributor to the current atmospheric CO_2 budget, accounting for about 1/3 of total anthropgenic emissions (see Table 7.3.2; Section 7.3.2.1; also Table 7.3.1, row "land use change flux"). The future evolution of this term in the CO_2 budget is therefore of critical importance. Deforestation in tropical America, Africa and Asia is expected to decrease towards the end of the 21st century to a small fraction of the levels in 1990 (IPCC SRES, 2000). The declines in Asia and Africa are driven by the depletion of forests, while trends in America have the highest uncertainty given the extent of the forest resource.

Afforestation: Recent (since 1970) afforestation and reforestation as direct human-induced activities have not yet had much impact on the global terrestrial carbon sink. However, regional sinks have been created in areas such as China, where afforestation since the 1970s has sequestered 0.45 GtC (Fang et al., 2001). The largest effect of afforestation is not immediate but through its legacy.

Agricultural practices: Improvement of agricultural practices on carbon-depleted soils has created a carbon sink. For instance, the introduction of conservation tillage in the USA is estimated to have increased soil organic matter (SOM) stocks by about 1.4 GtC over the last 30 years (Donigan et al., 1994). However, yearly increases in SOM can be sustained only for 50-100 years, after which the system reaches a new equilibrium (Smith et al., 1997; Cole et al., 1996). Moreover, modern conservation tillage often entrains large inputs of

chemicals and fertilizer, which are made from fossil fuels, reducing the apparent CO_2 benefit from carbon sequestration in agricultural soils.

7.3.3.1.6 Forest regrowth

A major consequence of the timing of afforestation arises through the legacy of prior land use, through forest regrowth (see below). Some studies suggest that this may be a dominant effect in currently inferred global carbon sequestration (e.g., Pacala et al., 2001; Schimel et al., 2001; Hurtt et al., 2002). Forest areas generally increased during the 20th century at middle and high latitudes (unlike in the tropics). 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 led to carbon sequestration by regrowing forests. 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 atmospheric radiative forcing.

Regional studies have confirmed the plausibility of strong mid-latitude sinks due to forest regrowth. Data from the eddy flux tower network (Baldocchi et al., 2003) 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), so forests in these areas are accumulating biomass simply because of their ages and stages of succession. Within wide error bands (see Section 7.3.2.3), 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). It is important to note that at least some of this sequestration is "refilling" the deficits in biomass and soil organic matter, accumulated in previous epochs (see Figure 7.3.2), and the associated CO_2 uptake would be expected to decline in the coming decades unless sustained by careful management strategies designed to accomplish that purpose.

7.3.3.2 Terrestrial ecosystems with potentially large impacts on the carbon cycle

This section considers the overall result of the above processes for three key ecosystems: tropical forests, permafrost and peatlands.

7.3.3.2.1 Undisturbed tropical forests: are they a CO_2 sink?

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.

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 Mg C ha^{-1} yr^{-1}, implying net carbon uptake into global neotropical biomass of 0.6 ± 0.3 GtC yr^{-1}, although they noted large variability between plots, due to the natural dynamics of tree death and regrowth. It is possible that rising CO_2 levels could stimulate uptake of this magnitude, simply by accelerating photosynthesis, since ecosystem respiration will lag behind. The CO_2 concentration of the atmosphere has increased on average by ~1.5 ppm (0.4%) yr^{-1}; the associated incremental stimulation of photosynthesis might average about 0.25% (e.g., next year's photosynthesis should be 1.0025 times this year's) (Lin et al., 1999; Farquhar et al., 2001). Using of ~10 years for the mean turnover rate for organic matter in tropical forests (Taylor and Lloyd, 1996), the present imbalance between uptake of CO_2 and respiration might be

2.5% (1.0025^{10}), consistent with rate of live biomass increase (~3%) inferred from the plot studies by Philips et al. (1998).

However, many other factors affect these forests. The recent pan-tropical rise in air temperatures, ~0.26°C per decade (Malhi and Wright, 2004), could enhance nutrient mineralization and stimulate uptake, but also might increase water stress and respiration. Forest response to CO_2 might be limited by 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 ecological shifts favouring short lived trees or agents of disturbance (insects, lianas) (Koerner, 2004). Baker et al. (2004) noted higher mortality rates and increased prevalence of lianas in their plots, and since dead organic pools were not measured, effects of increased disturbance may give the opposite sign of the imbalance inferred from plot measurements that only count changes in part of the system (cf. Rice et al., 2004).

Methodological bias associated with sub-sampling of natural disturbance and recovery on small plots might also lead to erroneous inference of net growth (Koerner, 2004). , Indeed, 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)).
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. 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). Lacking these studies today, we cannot authoritatively assess the net carbon balance of undisturbed tropical forests based on in situ studies.

If the results from the plots could in fact be extrapolated, the mean above ground carbon sink would be 0.61 ± 0.22 Mg 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 GtC yr^{-1} (Malhi and Phillips 2004). Scaling-up, taking into account soil type, would increase this value to about 0.62 ± 0.18 GtC 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 GtC 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 from disturbed and undisturbed areas would be ~0, which is intriguingly consistent with inferences from inverse studies of little net flux from low latitudes.

7.3.3.2.2 Permafrost

Frozen soils hold over 400 GtC which have been accumulated over thousands of years (Sabine et al., 2004b). With the rapid warming of the northern latitudes at rates well above the global averages (TAR), carbon in frozen soils can be exposed to aerobic and warmer conditions which result in increased soil organic decomposition. There is already widespread observation of permafrost thawing leading to thermokarst and lake expansion, followed by lake drainage as the permanent permafrost further degrades (Camill, 2005; Smith et al., 2005). Preliminary estimates show that permafrost area could shrink up to 25% with a mean global warming of 2°C (Anisimov et al., 1999). Melting permafrost will increase CO_2 and CH_4 emissions, and it is estimated for the Canadian permafrost alone that up to 48 GtC could be sensitive to oxidation under a 4°C warming scenario (Tarnocai, 1999). In addition, important quantities of carbon are also lost as Dissolved Organic Carbon (DOC) into the rivers. For Western Siberia, climate models predict a doubling of the area above mean average temperature of –2˚C (which coincides with permafrost distribution) and an associated 700% increase in DOC concentrations in streams. Part of the DOC reaching the Arctic Ocean will oxidize and return to the atmosphere (Frey and Smith, 2005).

7.3.3.2.3 Peatlands

High latitude and tropical peatlands store over 450 GtC, being among the ecosystems with the highest carbon densities (Sabine et al., 2004b). This carbon is now susceptible to rapid emissions due to fast warming in high latitudes, and deforestation and drainage in the tropics. A preliminary estimate suggests that up to 100 GtC of CO_2 equivalent could be released to the atmosphere from wetlands and peatlands over the next 100 years (Gruber et al., 2004). Hence there are reasons to be concerned about rising sources of CO_2 from permafrost and peatlands in a warmer world.

7.3.4 Ocean Carbon Cycle Processes and Feedbacks to Climate

7.3.4.1 Functioning of the ocean carbon cycle

Before the industrial revolution, the ocean contained about 50 times as much carbon as the atmosphere and 20 times as much carbon as the terrestrial biosphere/soil compartment. Oceanic carbon is stored as dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and particulate organic carbon (POC) (living and dead) in an approximate ratio DIC:DOC:POC = 2000:38:1 (circa 37400 GtC DIC, Falkowski et al., 2000; 685 GtC DOC, Hansell and Carlson, 1998; 13-23 GtC POC, Eglinton and Repeta, 2004).

Seawater can, by inorganic processes, absorb large amounts of CO_2 from the atmosphere, because CO_2 is a weakly acidic gas and the minerals dissolved in the ocean have created a slightly alkaline ocean over geologic time (Degens et al., 1984). The air-sea exchange of CO_2 is determined by the air-sea gradient in CO_2 partial pressure between atmosphere and ocean. Equilibration of surface ocean and atmosphere occurs roughly on a timescale of 1 year. Gas exchange rates increase with wind speed (Wanninkhof and McGillis, 1999; Nightingale et al., 2000) and depend on other factors such as precipitation, sea ice, and surfactants. Respective functional relationships are not yet well established, especially at high wind speeds where exchange rates and uncertainties are maximal. In contrast, the equilibrium values for partitioning of CO_2 between air and seawater and associated seawater pH values are well established (Zeebe and Wolf-Gladrow, 2001) (see Box 7.3).

Box 7.3: Marine Carbon Chemistry and Ocean Acidification

Why is seawater absorbing large amounts of anthropogenic CO_2 and becoming more acidic during this process? In seawater, gaseous CO_2 is hydrated to carbonic acid (H_2CO_3) which is dissociated in two steps into bicarbonate HCO_3^- and carbonate CO_3^{2-} ions in the approximate ratio [CO_2 plus H_2CO_3], [HCO_3^-] and [CO_3^{2-}] of roughly 1:100:10. This means that CO_2 is stored in the ocean mainly as HCO_3^-. The sum of CO_2, HCO_3^-, and CO_3^{2-} is called total dissolved inorganic carbon (DIC). The degree of CO_2 dissociation depends on temperature, salinity and total alkalinity of seawater (TAlk). TAlk is a quantitative measure for the seawater's ability to dissociate CO_2 due to the excess of alkaline components in seawater. The largest contribution for short term changes of TAlk comes from the carbonate ion CO_3^{2-}. For a definition of TAlk see Dickson (1981). Addition of excess CO_2 from atmosphere to seawater leads to formation of bicarbonate through:

(1) $CO_2 + H_2O + CO_3^{2-} \rightarrow 2HCO_3^-$ and

(2) $CO_2 + H_2O \rightarrow H^+ + HCO_3^-$

A small portion 0.x of the HCO_3- generated, however, will dissociate again back to CO_3^{2-} and generate a proton H^+:

$0.x\ HCO_3^- \rightarrow 0.x\ CO_3^{2-} + 0.x\ H^+$

A higher proton concentration means more acid conditions, i.e., a decrease in pH value ($pH=-\log_{10}[H^+]$, a decrease of one pH unit means 10 times less protons H^+). In parallel to increasing seawater [CO_2], the concentrations [HCO_3^-] and [H^+] increase while [CO_3^{2-}] decreases. The acidification can be compensated again through an addition of alkalinity, mainly by dissolution of $CaCO_3$ (biogenic calcium carbonate shell material in water column and sediment):

$CaCO_3$ (solid) + $CO_2 + H_2O \rightarrow Ca^{2+}$ (dissolved) + CO_3^{2-}(dissolved) + $CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$

The ocean acidification through uptake of anthropogenic CO_2 from the atmosphere leads to a decrease in the saturation state of $CaCO_3$ in the ocean. Two primary effects are expected: (1) The bio-calcification within the water column may be inhibited or slowed down (less biological production of corals as well as calcifying phytoplankton and zooplankton), and (2) the dissolution of $CaCO_3$ at the ocean floor (available $CaCO_3$ sediments and corals) will be increasingly furthered (Royal Society, 2005). The metastable $CaCO_3$ form

aragonite which is produced by corals and pteropods (planktonic snails, Lalli and Gilmer, 1989) will be particularly susceptible to a pH lowering (Kleypas et al., 1999; Hughes et al., 2003; Orr et al., 2005). The impact of anthropogenic ocean acidification on the ocean saturation state with respect to $CaCO_3$ is already detectable (Feely et al., 2004). In laboratory experiments with the coccolithophore species *Emiliana huxleyi* and *Gephyrocapsa oceanica*, a significant reduction in $CaCO_3$ production and a stimulation of particulate organic carbon production resulted under high ambient CO_2 partial pressure (Zondervan et al., 2001; Riebesell et al., 2000). Similar studies are being repeated under different boundary conditions. There are indications that other species also may show different responses, 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 relatively small negative feedback of reduced $CaCO_3$ production on atmospheric pCO_2 may be compensated for by a change of the ballast for settling biogenic particles ($CaCO_3$ could act towards acceleration of sinking particle aggregates, Armstrong et al., 2002; Klaas and Archer, 2002) and the associated shallowing of remineralization depth levels in the water column for organic carbon (Heinze, 2004). 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 trophic levels. Apart from the absolute magnitude of a pH lowering, the expected rapid rate of pH change at the sea surface can cause difficulties for marine ecosystems to adjust accordingly. Since the beginning of the industrial revolution, sea surface pH has dropped by about 0.1 pH units (corresponding to a 30% increase of the hydrogen ion concentration). The expected continued decrease may lead within a few centuries to an ocean pH which is estimated to have occurred most recently a few hundred million years before present (Caldeira and Wickett, 2003; Key et al., 2004) (Box 7.3, Figure 1).

[INSERT BOX 7.3, FIGURE 1 HERE]

Assuming a mid-range emission scenario for anthropogenic CO_2 such as the IS92a scenario, bio-calcification will become difficult in particular within the Southern Ocean by year 2100 (Orr et al., 2005), for aragonite producing organisms already by year 2050. 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 context.

In addition to lateral advection by ocean currents, the ocean can alter the atmospheric CO_2 concentration through three mechanisms (Volk and Hoffert, 1985), which are illustrated in Figure 7.3.9a:
(1) Absorption or release of CO_2 due to changes in solubility for gaseous CO_2 ("solubility pump").
(2) Binding of CO_2 to POC in surface waters during photosynthesis and export of this carbon through particle flux out of the surface layer ("organic carbon pump"). This process is limited by availability of light and nutrients (phosphate, nitrate, silicic acid and micronutrients such as iron).
(3) Release of CO_2 in surface waters during formation of calcium carbonate ($CaCO_3$) shell material by plankton ("$CaCO_3$ counter pump").

Organic particles are remineralized (oxidized to DIC through the action of bacteria) primarily in the upper 1000 m of the oceanic water column, with an accompanying decrease in dissolved oxygen. $CaCO_3$ particles on the average sink deeper before they undergo increased dissolution in deep waters which are undersaturated with respect to $CaCO_3$. The remainder of the particle flux enters the marine sediment and is subject to either redissolution to the water column or accumulation within the sediment. Although the POC reservoir is small, it plays an important role in maintaining carbon concentrations low in surface waters and high in deep waters. The loop is closed through the three dimensional ocean circulation: upwelling water brings inorganic carbon and nutrients to the surface again, leading to potential outgassing and biogenic particle production. DOC enters the ocean water column from rivers and marine metabolic processes. A large fraction of DOC has a long residence time in the ocean, while another fraction is more labile (Loh et al., 2004). Due to its smaller reservoir size as compared with DIC, DOC is likely to play a minor role in altering the atmospheric CO_2 concentration.

[INSERT FIGURE 7.3.9 HERE]

In conjunction with the world ocean mixing or overturning time of the order of 1000 years (Broecker and Peng, 1982), small changes in the large ocean carbon reservoir can induce important changes in the atmospheric CO_2. Likewise, perturbations in the atmospheric CO_2 partial pressure can be buffered by the ocean to a significant extent. Glacial-interglacial changes of the atmospheric CO_2 content can potentially be attributed to a combined change of marine carbon pump functioning with a change in ocean circulation (see Chapter 6). The key role for the timing of the anthropogenic carbon uptake by the ocean is played by the downward mixing of surface water, with a high burden of anthropogenic carbon, into the ocean's interior. The organic carbon cycle and the $CaCO_3$ counter pump modulate the anthropogenic carbon uptake, especially in case of a change in the physical and biogeochemical forcing, but do not dominate this process (Figure 7.3.9b and c).

Sabine et al. (2004a) estimate that since the beginning of the industrial revolution ca. 118 ± 19 GtC of anthropogenic CO_2 emissions from fossil fuel burning, land use, and cement manufacture have entered the oceanic reservoir with highest water column burdens of anthropogenic carbon concentrations (C_{ant} = DIC resulting from human activity) in the northern North Atlantic Ocean (see Chapter 5). This inventory estimate is currently being revised by several authors.

7.3.4.2 Carbon cycle feedbacks to changes in atmospheric CO_2

CO_2 which enters the ocean is buffered due to scavenging by the CO_3^{2-} ions and conversion to bicarbonate HCO_3^-, i.e., the resulting change in gaseous seawater CO_2 concentration is smaller than the amount of CO_2 added per unit of seawater volume would suggest. CO_2 buffering in seawater is quantified through the Revelle factor ("buffer factor"), relating given changes in seawater CO_2 partial pressure to parallel changes in total dissolved inorganic carbon after re-equilibration (Revelle and Suess, 1957; Zeebe and Wolf-Gladrow, 2001):

$$\text{Revelle factor (or buffer factor)} = \Delta[CO_2]/[CO_2] \,/\, \Delta[DIC]/[DIC]$$

The lower the buffer factor is, the better is the buffer capacity of the respective seawater volume. While the solubility of CO_2 in seawater decreases with rising temperature, the dissociation increases. As a net effect, the buffer factor decreases with rising seawater temperature and increases with CO_2 partial pressure. In the present ocean, the buffer factor varies between 8 and 13 (Sabine et al., 2004a) (Figure 7.3.10). With respect to atmospheric CO_2 partial pressure alone, two inorganic chemical mechanisms are at work: (1) The ocean re-equilibrates, buffering a significant amount of CO_2 from the atmosphere depending on the water volume exposed to equilibration. (2) The percentage of additional CO_2 inputs to the atmosphere, which can be buffered by the oceans decreases, the higher the atmospheric CO_2 partial pressure gets (positive feedback). Both processes are quantitatively important and instantaneous. While the first one is generally considered as a system response, the latter one is a feedback process.

[INSERT FIGURE 7.3.10 HERE]

The ocean will become more acidic due to CO_2 uptake from the atmosphere (see Box 7.3). The biogeochemical ocean climate will change for certain due to this acidification caused by marine uptake of anthropogenic CO_2 from the atmosphere. The consequences of ocean acidification are potentially severe. Details are given in Box 7.3.

Increased carbon storage in the deep ocean leads to the dissolution of calcareous sediments below their saturation depth (Broecker and Takahashi, 1978; Feely et al., 2004). 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). Due to the slow $CaCO_3$ buffering mechanism (and the slow silicate weathering), atmospheric CO_2 partial pressure will approach a new equilibrium asymptotically only after a very long time. This slow approach to a new equilibrium takes 30,000-35,000 years (Archer, 2005) (Figure 7.3.11).

[INSERT FIGURE 7.3.11 HERE]

Elevated ambient CO_2 levels appear also to have an influence on the production rate of POC by marine calcifying planktonic organisms (e.g., Zondervan et al., 2001). This increased carbon binding under higher CO_2 levels was also observed for three diatom species (diatoms are silicifying phytoplankton) (Riebesell et al., 1993). It is critical to know whether these increased carbon fixation rates translate also into increased export production rates, i.e., removal of carbon from the closed seasonal cycling loop. Studies on the nutrient to carbon ratio in marine phytoplankton have not yet shown any significant changes of the nutrient utilization efficiency (expressed through the "Redfield ratio" C:N:P:Si) in organic tissue with CO_2 concentration (Burkhardt et al., 1999).

7.3.4.3 Carbon cycle feedbacks induced by nutrient cycling and land ocean coupling

Input of carbon (DIC, DOC), phosphate, nitrate as well as ammonium, and silicic acid to the ocean takes place mainly through river runoff. 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 (Raymond and Cole, 2003; 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 would lead to a negative feedback on atmospheric CO_2 on long time scales (Dupre et al., 2003). The net effect of riverine carbon inputs to the world ocean is proposed to be almost balanced at present (Borges, 2005). Variations in nutrient supply can lead to species shifts and to deviations from the large scale average Redfield ratios mainly in coastal waters, but also in the open ocean (Pahlow and Riebesell, 2000). Nutrient supply to the ocean has been changed through retention of silicic acid in freshwater systems due to the construction of water reservoirs (e.g., Humborg et al., 2000) and to increased nitrate release from land due to fertilizer use as well as nitrogen deposition from the atmosphere in highly polluted areas (De Leeuw et al., 2001; Green et al., 2004). Possibly the growth of calcifying organisms relative to silicifying plankton could be stimulated and result in a local instantaneous positive feedback to atmospheric CO_2. Species shifts in marine ecosystems could change also the particle flux mode and thus induce changes in the efficiency of the vertical biological carbon transfer with related positive or negative feedbacks to atmospheric CO_2.

Transfer of dust from the continents to the ocean through atmospheric transport provides an important source of micronutrients and ballast material to the ocean. Iron (also zinc and others, e.g., Frew et al., 2001; Boyd et al., 2004) is a biolimiting micronutrient. Areas where iron is not supplied by aeolian dust transport in sufficient amounts tend to be iron limited resulting in elevated surface ocean concentrations of nitrogenous 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 increased dust loads may result as well due to land use changes (Tegen et al., 2004) and natural changes in vegetation cover (Woodward et al., 2005). A decrease of dust loads would decrease the supply of bio-available iron to the oceans. It thus could lead to net positive feedback towards further increasing CO_2 by a weakening of marine biological production. On the other hand, a decrease of dust brings also less clay ballast material into the ocean. This would induce a change to smaller marine particle aggregates and to slower settling velocities of particles through the water column (Ittekkot, 1993; Haake and Ittekkot, 1990) which in conjunction with a shallowing of the remineralization horizon for POC in the water column may act as a positive feedback to atmospheric CO_2.

Changes in plankton species composition and regional shift of high production zones can lead to a series of further feedbacks. Light absorption due to changes in bio-optical heating may change and induce a respective temperature change of ocean surface water (Sathyendranath et al., 1991; Wetzel et al., in press). 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 temporarily increase 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 a 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.

7.3.4.4 Carbon cycle feedbacks to changes in physical forcing

The solubility of CO_2 gas in seawater as well as the two dissociation constants of carbon acid in seawater depends on temperature and salinity (Weiss, 1974; Millero et al., 2002). For a 1°C increase of the sea surface temperature, a change 6.9–10.2 μatm for a combined effect of the temperature increase on solubility and all other carbon chemistry 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.

Warming may increase the biological uptake rate of nutrients and carbon from surface waters, but evidence from observations is contradictory (Behrenfeld and Falkowski, 1997). It is not yet conclusively determined, in which way the export production of organic carbon and the degradation rate of organic matter in the water column will change with changing temperature. Laws et al. (2000) proposed that export efficiency increases with net photosynthesis at low temperatures, which implies a positive feedback due to warming. A modelling study predicts an increase in small phytoplankton over large phytoplankton under climatic warming leading to a decrease in particle sinking velocities and thus a positive CO_2 feedback (Bopp et al., 2005).

Dissolved organic carbon (DOC) is considered to be stored in the ocean in two forms: as a refractory pool with a very low turnover rate (Bauer et al., 1992), and as a "semi-labile" pool (Carlson et al., 1994; Børsheim and Myklestad, 1997; Loh et al., 2004). The composition of dissolved organic matter in the ocean is still widely unknown (Loh et al., 2004). Both DOC fractions may be degraded more quickly at higher temperatures due to increased bacterial activity. Because of the relatively small carbon pool size of DOC, the quantitative potential of a related feedback to the carbon cycle is expected to be relatively small.

A change in ocean circulation, 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. 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 (Bolin and Eriksson, 1959; see also the carbon cycle climate model simulations by Cox et al., 2000; Friedlingstein et al., 2001; Friedlingstein et al., in press). As long as the sinking speeds for marine biogenic particles remain unchanged, in a more sluggish ocean the biological carbon pump will be more efficient (Boyle 1988; Heinze et al., 1991), thus inducing a negative feedback, which is expected to be smaller than the physical transport feedback (Broecker, 1991) (Figure 7.3.9). Changes in ocean circulation can affect shelf sea circulation systems regionally, leading either to increased export of nutrients plus carbon from the shallow seas into the open ocean or to increased upwelling of nutrients plus carbon onto the shelf and towards coastal areas (Chen et al., 2003; Smith and Hollibaugh, 1993; Walsh, 1991). A reduction in sea ice cover such as a “blue Arctic” may potentially increase the uptake area for anthropogenic CO_2 and act as a minor negative carbon feedback (ACIA, 2005).

7.3.4.5 Summary on marine carbon cycle climate couplings

Coupling between the marine carbon cycle and climate are summarised in Table 7.3.3 and below:

7.3.4.5.1 Robust findings

- Inorganic chemical buffering and dissolution of marine calcium carbonate sediment are the main oceanic processes for neutralizing anthropogenic CO_2. These processes work only on long time scales (5,000–10,000 yrs and 40,000 yrs) and cannot prevent a temporary build up of a large atmospheric CO_2 pool.
- The surface ocean has become more acid since the industrial revolution by ca. –0.1 pH units. Ocean acidification will continue and is directly and inescapably coupled to the invasion of anthropogenic CO_2 into the ocean.
- A slowing down of the ocean circulation and the decrease of seawater buffering with rising CO_2 concentration will suppress oceanic uptake of anthropogenic CO_2.

7.3.4.5.2 Key uncertainties

- The overall reaction of the organic carbon cycle to a warm and high CO_2 world is not yet understood. Several smaller feedback mechanisms are identified. These may compensate each other or add up to a significant feedback.
- The reaction of marine biota to ocean acidification is not yet clear, especially concerning physiological changes. Potential impacts are expected especially for organisms which build $CaCO_3$ shell material.
- Estimates of gas exchange rates between ocean and atmosphere at high wind speeds continue to have a large uncertainty.

[INSERT TABLE 7.3.3 HERE]

7.3.5 Coupling Between the Carbon Cycle and Climate

7.3.5.1 Introduction

Atmospheric carbon dioxide is increasing at only about half the rate implied by fossil fuel plus land-use emissions, with the reminder being taken-up by the ocean, and vegetation and soil on the land. Therefore the land and ocean carbon cycles are currently helping to mitigate against CO_2-induced climate change. However, these carbon cycle processes are also sensitive to climate. The glacial-interglacial cycles are an example of tight coupling between climate and carbon cycle over long-timescales, but there is also clear evidence of the carbon cycle responding to short-term climatic anomalies such as the El Niño Southern Oscillation and Arctic Oscillation (Jones C.D. et al., 2001; Bousquet et al., 2000; Rayner et al., 1999; Lintner, 2002; Russell and Wallace, 2004) and the climate perturbation arising from the Pinatubo volcanic eruption (Hansen et al., 1996; Jones and Cox, 2001a; Lucht et al., 2002; Angert et al., 2004).

Climate projections have typically used a prescribed CO_2 scenario to drive an atmosphere-ocean general circulation model (AOGCM), neglecting two-way coupling between climate and the carbon cycle. This section discusses the first generation of coupled climate-carbon cycle simulations, using the results to highlight a number of critical issues in the interaction between climate change and the carbon cycle.

7.3.5.2 Coupled climate-carbon cycle projections.

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., 2005b; 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 eleven models involved in C^4MIP differ in the complexity of their components (Friedlingstein et al., 2006), including both Earth System Models of Intermediate Complexity and AOGCMs.

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 atmospheric CO_2 increases do not influence climate (so that the carbon cycle experiences no CO_2-induced climate change). A comparison of the runs defines the climate-carbon cycle feedback, 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 of the eleven C^4MIP models produce a positive climate-carbon cycle feedback, but with feedback factors varying from 1.04 (Model E) to 1.44 (Model A). This translates into an extra CO_2 concentration of between 20 and 224ppm by 2100, with a mean of 87 ppm (Table 7.3.4).

Table 7.3.4. Simulated mean air, land, and ocean -borne fraction of total emissions to 2100, from the C^4MIP models. Coupled runs (with climate-carbon feedbacks) and uncoupled runs (without climate change) are shown with the latter in brackets. Column 5 shows the impact of climate effects on the CO_2 concentration by 2100, and column 6 shows the related amplification of the atmospheric CO_2 increase, i.e., the climate-carbon cycle feedback factor.

Model	Air-borne Fraction	Land-borne Fraction	Ocean-borne Fraction	Impact of climate change on the CO_2 concentration by 2100 (ppmv)	Climate-Carbon Feedback Factor
A. HadCM3LC	0.72 (0.50)	0.05 (0.30)	0.24 (0.20)	224	1.44
B. IPSL-CM2C	0.47 (0.40)	0.22 (0.30)	0.32 (0.30)	74	1.18
C. MPI	0.54 (0.46)	0.22 (0.30)	0.24 (0.24)	83	1.18
D. LLNL	0.45 (0.40)	0.39 (0.45)	0.16 (0.16)	51	1.13
E. NCAR CSM-1	0.54 (0.52)	0.25 (0.26)	0.21 (0.22)	20	1.04
F. FRCGC	0.58 (0.45)	0.14 (0.26)	0.27 (0.28)	128	1.26
G. UVic-2.7	0.59 (0.48)	0.17 (0.28)	0.23 (0.25)	129	1.25
H. UMD	0.64 (0.55)	0.01 (0.06)	0.36 (0.40)	98	1.17
I. BERN-CC	0.48 (0.42)	0.26 (0.32)	0.26 (0.26)	65	1.15
J. CLIMBER2-LPJ	0.57 (0.50)	0.23 (0.29)	0.20 (0.21)	59	1.11
K. IPSL-CM4-LOOP	0.52 (0.49)	0.26 (0.27)	0.23 (0.24)	32	1.07
MEAN				87	1.18

7.3.5.3 Sensitivity analysis

The coupled and uncoupled model experiments can be used to separate the effects of climate change and CO_2 increase on land and ocean carbon storage (Friedlingstein et al., 2003). Table 7.3.5 shows the linear sensitivity parameters diagnosed from each of the C^4MIP models (Friedlingstein et al., 2006).

7.3.5.3.1 Increase in ocean carbon uptake with atmospheric CO_2.

The ocean takes 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; Section 7.3.4.1; Box 7.3) and on the action of the biological pump (Sarmiento et al. 2000). Ocean carbon cycle model intercomparisons have shown that the simulated circulation in the Southern Ocean can have a large impact on the efficiency with which anthropogenic CO_2 is drawn down (Orr et al., 2001). The C^4MIP models show ocean carbon storage increases ranging from 0.9 to 1.6 GtC ppm^{-1}, which is equivalent to ocean uptake increasing at between 42 and 75 % of the rate of atmospheric CO_2 increase. Basic ocean carbonate chemistry suggests that the ocean-borne fraction of emissions will fall in the future, even in the absence of climate change, because of decreasing ocean pH (Box 7.3).

7.3.5.3.2 Increase in land carbon uptake with atmospheric CO_2.

In the absence of land-use change and forest fires, 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) (Section 7.3.3). There is an ongoing debate concerning the importance of CO_2-fertilisation at the patch-scale where other constraints such as nitrogen limitation may dominate; recent surveys indicate a wide range of possible responses to a CO_2 increase of around 50%, with average increases of 12% to 23% (Norby et al., 2005; see Section 7.3.3.1)

Table 7.3.5. Effective parameters of the C^4MIP models : transient sensitivity of mean global temperature to CO_2, and the sensitivities of land and ocean carbon storage to CO_2 and climate.

Model	Transient Climate Sensitivity to doubling CO_2 (K)	Land Carbon Storage Sensitivity to CO_2 (GtC ppm^{-1})	Ocean Carbon Storage Sensitivity to CO_2 (GtC ppm^{-1})	Land Carbon Storage Sensitivity to Climate (GtC K^{-1})	Ocean Carbon Storage Sensitivity to Climate (GtC K^{-1})
A.	2.3	1.3	0.9	–175	–24
B.	2.3	1.6	1.6	–97	–30
C.	2.6	1.4	1.1	–64	–22
D.	2.5	2.5	0.1	–81	–14

E.	1.2	1.1	0.9	–24	–17
F.	2.3	1.4	1.2	–111	–47
G.	2.3	1.2	1.1	–97	–43
H.	2.0	0.2	1.5	–36	–60
I.	1.5	1.6	1.3	–104	–38
J.	1.9	1.2	0.9	–64	–22
K.	2.7	1.2	1.1	–19	–17
MEAN	**2.1**	**1.4**	**1.1**	**–79**	**–30**

The C^4MIP models show increases in global NPP of between 6% and 33% when CO_2 increases over the same range. These figures are not exactly comparable as some C^4MIP models include vegetation dynamics which is likely to increase the vegetation cover as well as the NPP per unit of vegetation area, and would therefore lead to higher overall sensitivity of global NPP to CO_2. Hence, given the scatter of the experimental information, most C^4MIP models are in the right range of CO_2 response.

The overall response of land carbon storage to CO_2 is given by the third column of Table 7.3.5. The C^4MIP models show time-mean land carbon storage increases ranging from 0.2 to 2.5 GtC ppm^{-1}, with all but two models between 1.1 and 1.6 GtC ppm^{-1} . This response is driven by the CO_2-fertilisation of NPP in each model, with a counteracting tendency for the mean soil carbon turnover rate (i.e., the heterotrophic respiration by unit soil carbon) to increase even in the absence of climate change. This somewhat surprising effect of CO_2 is seen to varying degrees in all C^4MIP models. It appears to arise because CO_2 fertilisation of NPP acts particularly to increase vegetation carbon, and therefore litterfall and soil carbon, in productive tropical regions which have high intrinsic decomposition rates. This increases the average turnover rate of the global soil carbon pool even though local turnover rates are unchanged. In some models (e.g., model C) this acts to offset a significant fraction of the land carbon increase arising from CO_2 fertilisation.

Models with large responses of ocean or land carbon storage to CO_2 tend to have weaker climate-carbon cycle feedbacks because a significant fraction of any carbon released through climate change effects is reabsorbed through direct CO_2 effects (Thompson et al. 2004).

7.3.5.3.3 Transient Climate Sensitivity to CO_2

The strength of the climate-carbon cycle feedback loop depends on both the sensitivity of the carbon cycle to climate, and the sensitivity of climate to CO_2. The equilibrium climate sensitivity to doubling CO_2 remains a critical uncertainty in projections of future climate change, but also has a significant bearing on future CO_2 concentrations, with higher climate sensitivities leading to larger climate-carbon cycle feedbacks (Andreae et al., 2005). The second column of Table 7.3.5 shows the transient global climate sensitivity (i.e., the global climate warming that results when the transient simulation passes 2 x CO_2) for each of the C^4MIP models. All but 2 models (models E and I) have climate sensitivities in the range 1.9 to 2.7 K. However, differences in carbon cycle responses are likely to occur because of potentially large differences in regional climate change, especially where this affects water availability on the land.

7.3.5.3.4 Dependence of ocean carbon uptake on climate.

Climate change can suppress vertical mixing and thus ocean carbon uptake through increases in thermal stratification and decreases in surface salinity. On longer timescales (>70 years) the ocean carbon sink may also be affected by climate-driven changes in large-scale circulation (e.g., a slowing down of the thermohaline circulation). The sixth column of Table 7.3.5 shows the sensitivity of ocean carbon storage to climate change as diagnosed from the C^4MIP models. All models indicate a suppression of the ocean carbon sink by climate change with a magnitude between –19 and –60 GtC K^{-1}, implying a positive climate-ocean carbon feedback.

7.3.5.3.5 Dependence of land carbon storage on climate.

The major land-atmosphere fluxes of CO_2 are strongly climate dependent. NPP and heterotrophic respiration are both very sensitive to 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

(Table 7.3.5, fifth column) is negative in all the models, implying a positive climate-land carbon feedback, but the range is very large: –19 to –175 GtC K^{-1}. These values are determined by the combined effects of climate change on NPP and the soil carbon turnover (or decomposition) rate, as shown in Table 7.3.6.

Table 7.3.6. Effective sensitivities of land processes in the C^4MIP models: % change of vegetation net primary productivity (NPP) to CO_2 doubling (Column 2), and sensitivities of vegetation NPP and specific heterotrophic soil respiration called to a 1K global temperature increase (Columns 3 and 4).

Model	Sensitivity of Vegetation NPP to CO_2 % change for a CO_2 doubling	Sensitivity of Vegetation NPP to climate % change for a 1K increase	Sensitivity of Specific Heterotrophic Respiration Rate to climate % change for a 1K increase
A.	57	–5.8	10.2
B.	50	–4.5	2.3
C.	76	–4.0	2.8
D.	73	–0.4	7.0
E.	34	0.8	6.2
F.	21	1.2	7.2
G.	47	–2.3	6.5
H.	12	–1.6	4.8
I.	46	1.2	8.7
J.	44	1.9	9.4
K.	64	–0.3	2.9
MEAN	48	–1.3	6.2

The C^4MIP models utilise different representations of soil carbon turnover, ranging from single-pool models (model A) to nine-pool models (model E). However, most soil models assume a similar acceleration of decay with temperature, approximately equivalent to a doubling of the specific respiration rate for every 10 °C warming. This temperature sensitivity is broadly consistent with a long history of lab and field measurements of soil effux (Raich and Schlesinger, 1992), although there is an ongoing difficulty in separating root and soil respiration. 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). These apparent discrepancies may reflect the rapid depletion of labile pools of organic matter, with strong temperature responses still likely so long as litter inputs to the labile soil are maintained (Knorr et al., 2005). Nevertheless, the temperature sensitivity of the slow carbon pools is still very poorly known.

Table 7.3.6 shows that all C^4MIP models simulate an overall increase in soil carbon turnover rate as the climate warms, ranging from 2% to 10% per degree K, which translates into an amplification of 1.3 (model B) to 2.7 (model A) for a 10 K warming. The use of a single soil carbon pool in the Hadley model (A) cannot completely account for the relatively large sensitivity of soil respiration to temperature in this model (Jones et al., 2005), as evidenced by the lower effective sensitivity diagnosed from the UVic model (model G), which uses the same soil-vegetation component. It seems more likely that differences in soil moisture simulations are playing the key part in determining the effective sensitivity of soil turnover rate to climate.

Table 7.3.6 also shows the effective sensitivities of NPP to climate, ranging from a significant reductions of 6% K^{-1} to smaller climate-change driven increases of 2% K^{-1} under climate change. This variation may reflect different timescales for boreal forest response to warming (leading to a positive impact on global NPP), as well as different regional patterns of climate change (Fung et al., 2005). The models with the largest negative responses of NPP to climate (models A, B and C) also show the tendency for tropical regions to dry under climate change, in some cases significantly (Cox et al., 2004).

7.3.5.4 Knowns and unknowns in climate-carbon cycle feedback

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

- Climate change alone will tend to suppress land and ocean carbon uptake increasing the fraction of anthropogenic CO_2 emissions which remain airborne (see Table 7.3.4), and producing a positive feedback on climate change.
- CO_2 increase alone will lead to continued uptake by the land and the ocean, although the efficiency of this uptake will decrease through the carbonate buffering mechanism in the ocean, and through saturation of CO_2 fertilisation on the land and a variety of other effects.

However, there is much less agreement over the magnitude of these various effects. Larger climate carbon cycle feedbacks arise in models with higher climate sensitivities to CO_2, more negative responses of vegetation Net Primary Productivity to climate, and smaller responses of ocean and land sinks to CO_2 (Figure 7.3.12).

[INSERT FIGURE 7.3.12 HERE]

Eight out of the eleven models produce a feedback factor in the range 1.11 to 1.28, 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=1.04). 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). Some models also point towards a decline of tropical ecosystems, a potentially major impact on world biotic and economic resources (Cox et al., 2004).

There were some important processes excluded from the C^4MIP models as part of the agreed protocol for the first generation C^4MIP exercise. For example the models currently exclude, by design, the effects of prior land use change, including forest regrowth which may account for a large part of the land carbon sink in some regions (e.g., Pacala et al., 2001; Schimel et al., 2001; Hurtt et al., 2002). The effects of land-use change have already been included in some models (Sitch et al., 2005), and will be part of the second C^4MIP protocol. Likewise fires were excluded from the first coupled experiments, despite the fact that combustion of ecosystems and soil organic matter may account for a significant fraction of the interannual variability in CO_2 (Kasischke et al., 2005; Cochrane, 2003; Nepstad et al., 2004; Randerson et al., 2005). In other cases there were important processes excluded in part because modelling these processes is even less straightforward. Amongst these are interactive nitrogen cycling on the land (would could enhance CO_2 uptake by plants) and the potential impacts of increasing ozone concentrations on plants (which could suppress CO_2 uptake).

It is vital that these missing processes begin to be included in coupled climate-carbon cycle models in a manner that avoids an explosion of parameter uncertainty. In the meantime observing the evolution of atmospheric CO_2 will help us to constrain climate-carbon cycle feedbacks – if the feedback is strongly positive this should begin to show up as an increase in the airborne fraction of emissions within the next decade or so (Figure 7.3.13).

[INSERT FIGURE 7.3.13 HERE]

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 (Figure 7.4.1) 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.

[INSERT FIGURE 7.4.1 HERE]

7.4.1 Methane (CH_4)

7.4.1.1 Biogeochemistry and budgets of CH_4

Atmospheric CH_4 originates from both non-biogenic and biogenic sources. Non-biogenic CH_4 includes emissions from fossil fuel burning (natural gas, petroleum and coal), 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 emissions from most of these sources involve ecosystem processes that result from complex sequences 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 finally converted to CH_4 by the so-called methanogenic archaea: $CH_3COOH \rightarrow CH_4+CO_2$ and $CO_2+4H_2 \rightarrow CH_4+2H_2O$.

CH_4 production is generally limited by availability of substrates and anaerobiosis conditions (Conrad, 1996). Not all CH_4 produced is emitted to the atmosphere. Most methane produced in land-based and managed ecosystems (50–90%) is oxidized (i.e., in the presence of molecular oxygen) before emission to the atmosphere, by methanotrophs or CH_4 oxidizing bacteria, which convert CH_4 into CO_2, H_2O and microbial biomass (Hanson and Hanson, 1996). CH_4 oxidation in this case is limited by both O_2 and CH_4 availability and regulated largely by environmental variables such as moisture and temperature. Although anaerobic CH_4 oxidation 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 are strongly influenced by climatic and edaphic factors (temperature, water table, substrates and pH). Generally, estimates of net emissions from sources derive from three approaches; (1) extrapolation from direct flux measurements, (2) a process-based modelling approach that represents the actual physical and biological processes of CH_4 production and emission (bottom-up approach), and (3) inverse modelling that relies on observations in the atmosphere (top-down approach). Extrapolation of direct flux measurements to larger scales contains considerable uncertainty due to the inherent large temporal and spatial variations. 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, b). However, as few such locations exist, extrapolation to regional or global scales involves high uncertainties. On the other hand, the top-down approach helps to overcome the weaknesses in bottom-up methods by bypassing limitations in our understanding of methanogenic-methanotrophic processes and their interactions with environmental factors. Inadequate observations and insufficient capabilities of the models to simulate complex topography and meteorology are the main obstacles for extensive application of the top-down approach (Chen and Prinn, 2005; 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 (Bergamaschi et al., 2000; Lassey et al., 2000; Mikaloff Fletcher et al., 2004a, 2004b).

Since TAR, availability of new data from various measurement networks has enabled re-estimates of CH_4 source magnitudes and insights into individual source strengths. As reported in Chapter 2, atmospheric CH_4 growth rates since TAR have slowed to nearly zero, presumably either from reduced emissions from sources, leading to a near balance between source inputs and sink removal, or from increased sink strengths and no net change in source emissions.

CH_4 sources can be divided into anthropogenic and natural sources. The anthropogenic sources include rice agriculture, livestock, landfill and waste treatment, biomass burning and fossil combustion (energy). Natural CH_4 is emitted from sources such as wetlands, ocean, termites and geological sources. Total global pre-

industrial emissions of CH_4 are estimated as 200–250 Tg CH_4 yr^{-1} (Chappellaz et al., 1993; Etheridge et al., 1998; Howeling et al., 2000; Ferretti et al., 2005; Valdes et al., 2005). Of this, natural CH_4 sources emitted between 190 and 220 Tg CH_4 yr^{-1}, and anthropogenic sources (rice agriculture, livestock, biomass burning and waste) account for the rest (Howeling et al., 2000; Ruddiman and Thomson, 2001). In contrast, anthropogenic emissions dominate present-day CH_4 budgets, accounting for >60% of the total global budget (Table 7.4.1).

[INSERT TABLE 7.4.1 HERE]

The single largest CH_4 source is natural wetlands. Recent estimates combine previously reported bottom-up and top-down values in combination with the worldwide observation results in a 3-D atmospheric transport and chemical model (ATCM) simulation by Chen and Prinn, (2005, 2006). These estimate indicate that southern and tropical regions account for >70% of total global wetland emissions. Other studies that include both direct observations and $^{13}C/^{12}C$ ratios of CH_4 also suggest an increase in emissions from tropical wetlands (Mikaloff Fletcher et al., 2004a; 2004b). The authors attribute such increased emissions to temporary wetlands that are flooded for only part of the year and thus are not accounted for in bottom up estimates. However, recent findings of Frankenberg et al. (2005) and Keppler et al. (2006) suggest that tropical forests may be the additional source missing in previous estimates: Keppler et al. estimate forest CH_4 emissions to be 10–30% (62–236 Tg yr^{-1}) of the global total.

Included in Table 7.4.1 are also the $^{13}C/^{12}C$ ratios ($\delta^{13}C$ values) of CH_4 emitted from individual sources. Due to isotope effects associated with CH_4 production and consumption processes, CH_4 produced and emitted from each source exhibits a different $\delta^{13}C$ value. Therefore, it is possible to distinguish fractions of atmospheric CH_4 emitted from different generic sources.

The major CH_4 sinks are oxidation with OH in the troposphere, biological CH_4 oxidation in upland soil, and loss to the stratosphere (Table 7.4.1). Oxidation with chlorine (Cl) atoms in the marine atmospheric boundary layer is suggested as another addition sink for CH_4, which could contribute a CH_4 loss of about 19 Tg CH_4 yr^{-1} (Gupta et al., 1997; Tyler et al., 2000; Platt et al., 2004; Allan et al., 2005).

The change in growth rate of atmospheric CH_4 concentration during 1990s and 2000s shows no clear correlation with change in sink strengths (Prinn et al., 2001, 2004; Allan et al., 2005). With no strong evidence to suggest the changes in sink strength, it appears that changes in emissions are primarily responsible for the observed slowing of CH_4 growth rate as described in Chapter 2. However, evidence is lacking to indicate a significant reduction in sources sufficient to explain the recent reduced growth rate. Instead, new sources including geological emissions and forests have been identified as contributing significantly to atmospheric CH_4 (Frankenberg et al., 2005, Keppler et al., 2006).

Since there is no general consensus of significant change in CH_4 sinks since the time of TAR, in AR4 the sink strength is treated as reported in TAR. Accordingly, the AR4 budget is based on a mean concentration of CH_4 in 2004 of 1777 ppb and an imbalance of 0.8 ppb yr^{-1} during 2000–2004 (see Chapter 2, Section 2.3). To maintain the sink strength as reported in TAR, the atmospheric lifetime during this period is estimated as 8.5 years, within the range of 8.7 ± 1.3 years reported in Section 7.4.5.4. For the conversion factor of 2.78 Tg per ppb (Etheridge et al., 1998), the atmospheric burden of CH_4 in 2004 is 4914 Tg, with annual average increase of 2 Tg yr^{-1}. Accordingly, the total average annual emissions during the period considered here is 578 Tg CH_4 yr^{-1}. However, Table 7.4.1 does not include active Cl as a chemical sink. If such a sink were introduced into the table with strength 19 Tg CH_4 yr^{-1}, the aggregate sink would strengthen to 595 Tg CH_4 yr^{-1} and the implied aggregate source of 597 Tg CH_4 yr^{-1} would essentially match the TAR value.

7.4.1.2 Effects of climate

We investigate the effects of climate on CH_4 biogeochemistry mainly by examining records of the past and from model simulations under various climate change scenarios. The Vostock and Dome C ice core records back to 650,000 years BP (Petit et al., 1999; Spahni et al., 2005) reveal that the atmospheric concentration of CH_4 is closely tied to atmospheric temperature, falling and rising in phase with temperature at the inception and termination of glacial episodes (Wuebbles and Hayhoe, 2002). Brook et al. (2000) showed that following each transition temperature increased more rapidly than CH_4 concentration. Since biogenic CH_4 production and emission from major sources (wetland, landfill, rice agriculture and biomass burning) are

influenced by climate variables such as temperature and moisture, the effects of climate on emission from these sources are significant.

Several studies indicate a high sensitivity of wetland CH_4 emissions to temperature and water table. Before the 1990s, elevated surface temperature and emissions from wetlands were believed to partially contribute to the increase in global CH_4 emissions (Walter et al., 2001a, b; Christensen et al., 2003; Zhuang et al., 2004). Based on the relationship between emissions and temperature at two wetland sites in Scotland, Chapman and Thurlow (1996) predicted that CH_4 emissions 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 their 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, emissions decrease if elevated temperature results in either reduced precipitation or NEP.

Walter and Heimann (2000) assessed how changes in water table and temperature would affect emissions in several northern wetlands. When the water table is above the soil surface, CH_4 emissions follow soil temperature. If the water table is below the soil surface, the pattern of emissions 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 emissions while a water table increase of 10 cm would increase emissions 0–25%, depending on initial wetness and dryness of wetlands. Under dry conditions, an increase in the water table enhances CH_4 emissions significantly while under wet conditions water table changes have only a small effect.

For the standard doubling in CO_2 concentration, the GCM of Shindell et al. (2004) simulates a 3.4°C warming. Changes in the hydrologic cycle due to this doubling of CO_2 cause CH_4 emissions from wetlands to increase by 78% from current estimates. 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 increased by an average 0.08 Tg CH_4 yr^{-1} during the 20th century. Their decadal net CH_4 emission rate correlates with soil temperature and water table depth.

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 controls net emissions (Matthews and Wassmann, 2003). Sass et al. (2002) show that CH_4 emissions correlate strongly with plant growth (height) in a Texas rice field. Any climate change scenario that results in an increase in plant biomass in rice agriculture is likely to increase CH_4 emissions (Xu et al., 2004). However, the magnitude of increased emission depends largely on water 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 zones which subsequently suppresses methanogenesis).

Past observations results indicate large inter-annual variations in CH_4 growth rates (Dlugokencky et al., 2001). The mechanisms causing these variations are poorly understood and the role of climate is not well known. Emissions from biomass burning may play an important role by contributing to emission peaks in 1993–1994 and 1997–1998 (Langenfelds et al., 2002; Butler et al., 2004). Unusually warm and dry conditions in the northern hemisphere during ENSO periods increased biomass burning. Kasischke et al. (2002) attributed CH_4 releases of 3–5 Tg in 1998 to boreal forest fires in Eastern Siberia resulting from unusually warm and dry conditions.

Climate also can affect 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 CH_4 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). Meteorological conditions can affect removal rates (Dentener et al, 2003), primarily through imhomogenous distributions of OH-precursor gases that lead to inhomogeneities in OH. There also appear to be significant inter-annual variations in the active-Cl sink, although mechanisms are poorly understood and a climate influence has yet to be identified (Allan et al., 2005).

Climate also effects stability of CH_4 hydrates in the ocean, where large amounts of CH_4 are stored (4×10^6 Tg CH_4, Buffett and Archer, 2004). Ancient seafloor carbonates show a number of negative excursions in their $\delta^{13}C$ values, which are believed to represent massive hydrate dissociation events (Dickens et al., 1997; Dickens, 2001). These events generally occurred in connection with rapid warming episodes in the Earth's history. Model results indicate that these hydrate decomposition events were too fast to be controlled by the propagation of the temperature change into the sediments (Paul et al., 2003; Katz et al., 1999), but additional studies have inferred other indirect and inherently more rapid effects such as enhanced migration of free gas, or reordering of gas hydrates due to slump slides (Kirschvink et al., 2003; Ryskin et al., 2003; Hesselbo et al., 2000; Jahren et al, 2001). The main marine gas hydrate reservoir is restricted to sediment depths below ~50 m, and a recent model of the formation of hydrates under steady state conditions suggests that today's CH_4 inventory would be diminished by 85% in case of a global warming of bottom water temperatures of 3°C (Buffett and Archer, 2004). Based on this inventory, the time-dependent feedback of hydrate destabilization on global warming has been addressed using different assumptions for the time constant of destabilization: it appears likely that the anthropogenic release of 2000 GtC could trigger the release of carbon from gas hydrates on a similar scale in a timeframe of 1–100 kyrs. Thus, gas hydrate decomposition is an important positive CH_4 feedback to be considered in global warming scenarios on longer timescales (Archer and Buffett, 2005).

In summary, advances have been made since TAR in constraining estimates of CH_4 source strengths and in the 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 2005, 2006; Mikaloff Fletcher, 2004a, 2004b). Emissions from anthropogenic sources remain the major contributor to atmospheric CH_4 budgets. Total emissions from sources are suggested to have decreased since the time of TAR, as nearly zero growth rates in atmospheric CH_4 concentrations have been observed with no change in the sink strengths. It is not well understood why emissions have decreased despite continued warming of the Earth's surface and the atmosphere.

7.4.2. Nitrogen Compounds

The nitrogen cycle is important to the functioning of the Earth system and to climate (Figure 7.4.2; Holland et al., 2005). Nitrogen, like phosphorus and iron, 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. Bio-atmosphere exchanges of nitrogen via emissions and deposition are a key component of the climate system as described below. In addition to the climate impact, changes to the N cycle have led to problems such as compromised air quality and human health, acidification of ecosystems, degradation of coastal estuaries, decreases in species diversity, and acceleration of aquatic and terrestrial eutrophication (Vitousek et al., 1997; Rabalais, 2002; Townsend et al., 2003; Galloway et al., 2004).

[INSERT FIGURE 7.4.2 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). Nitrous oxide is the nitrogen trace gas with the longest atmospheric lifetime, 120 years (Prather et al., 2001), and serves as the only atmospheric tracer of human perturbations to the global nitrogen cycle (Holland et al. 2005). Nitrous oxide is the dominant source of NO_x to the stratosphere and plays a role in stratospheric ozone depletion. Nitric oxides (NO_x) have short atmospheric lifetimes of hours to days (Prather et al. 2001). Nitric oxides are precursors for tropspheric ozone production and for atmospheric NO_y deposition (NO_y=NO_x+ HNO_3 + HONO + HO_2NO_2 + nitrate and nitrate radicals + organic nitrates + peroxyacetyl

nitrates + N_2O_5). They thus play important indirect roles in greenhouse gas formation both through their impact on tropospheric ozone formation and as a nutrient source for the carbon cycle. Ammonia is the atmosphere's most abundant base. It plays an important role in atmospheric acid neutralization, in aerosol formation and as a precursor for atmospheric NH_x deposition (NH_x=NH_3 + NH_4^+). The budgets for these N containing trace species are presented together because they are all generated by the global N cycle with dominant anthropogenic sources including fossil fuel combustion and agriculture.

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

N_2O concentrations have risen exponentially since the pre-industrial era (Figure 7.4.3). The average annual growth rate for 1999–2000 was 0.85–1.1 ppbv yr^{-1} (WMO Ozone Assessment 2002). Tropospheric abundances of N_2O have increased from pre-industrial values of about 270 ppb (TAR) to 318.8 in 2004 (Elkins, CMDL, in situ GC; Holland et al., 2005). Emission from natural and agricultural soils remains the dominant source of N_2O to the atmosphere (Bouwman et al., 2002b, c). There has been considerable focus on refining the estimates of N_2O from small-scale agricultural sources, the single biggest anthropogenic source of N_2O (Bouwman et al. 2002b; Del Grosso, 2005; Smith and Conen, 2004). Land use change continues to have a significant impact on both N_2O and NO emissions (Neill et al. 2005): logging is estimated to increase N_2O and NO emissions by 30–350% depending on conditions (Keller et al. 2005). Both studies underscore the importance of temperature and moisture as regulators of trace gas emissions.

The biggest change in the global N_2O budget since the TAR has been the quantification of the substantial human driven emission of N_2O from rivers, estuaries and coastal zones (Table 7.4.2; Bange 2006; Kroeze et al. 2005; Naqvi et al. 2000; Nevison et al. 2004). The inclusion of of a number of relatively minor sources (human excreta, landfills, and atmospheric deposition) increased the total budget to an estimated 20.6 Tg N yr^{-1} (Bouwman et al., 2002b). Bange (2006) suggests that the total ocean source of N_2O is 5.6 Tg N yr^{-1} with a range of 1.4–14 Tg N yr^{-1}, consistent with the sum of the natural and anthropogenic aquatic sources provided in Table 7.4.2. The sources and sinks remain out of balance, thus generating a continuing increase in atmospheric concentrations of N_2O which is larger in the AR4 than in the TAR. A recent analysis with an atmospheric box model suggests that the increased N_2O sources are consistent with the observed rise in atmospheric N_2O concentrations (Kroeze et al. 2005). Much of the global imbalance can be attributed to intensification of human activity, particularly agriculture, which impacts both the terrestrial and oceanic components of the Earth system (Galloway et al. 2004). Nitrous oxide is likely to become increasingly important as a greenhouse gas as the emissions of atmospheric halogens decline in compliance with the Montreal Protocol.

Table 7.4.2. Global sources (in Tg N yr^{-1}) of NO_x, NH_3, and N_2O.

Source	NO_x		NH_3		N_2O	
	TAR[b]	AR4[c]	TAR[7]	AR4	TAR[m]	AR4
Anthropogenic sources						
Fossil fuel + Industrial processes	33 (20–24)	25.6 (21–28)	0.3 (0.1–0.5)	2.5[i] (0.1–2.4)[j]	1.3/0.7 (0.2–1.8)	0.7[i] (0.2–1.8)[g]
Aircraft	0.7 (0.2–0.9)	[d](0.5–0.8)				
Agriculture	2.3 (0–4)		34.2 (16–48)	36.2[e, k] (21–62)[j]	6.3/2.9 (0.9–17.9)	5.6[e] (0.9–17.9)[g]
Biomass burning[1]	7.1 (2–12)	5.9 (6–12)	5.7 (3–8)	4.6[i] (2.0–8.0)[j]	0.5 (0.2–1.0)	0.7[e] (0.2–1.8)[g]
Human excreta	–	–	2.6 (1.3–3.9)	2.6[e] (1.3–3.9)[g]	–	0.2[e] (0.1–0.3)[g]
Landfills	–	–	–	2.7 (1.3–4.1)[j]	–	0.2[i] (0.1–0.3)[7]
Rivers, estuaries, coastal zones	–	–	–	–	–	1.7[n] (0.5–2.9)
Atmospheric deposition	–	0.3[5]	–	–	–	0.6[d] (0.3–0.9)[g]
Anthropogenic total	**43.1**	**31.8**	**42.8**	**48.6**	**8.1/4.1**	**9.7**
Natural sources						
Soils under natural vegetation	3.3(3–8)	8.9[f] (5–7)	2.4 (1–10)	2.4[e] (2.4–10)[j]	6.0/6.6 (3.3–9.0)	6.3 (3.3–9.0)

Oceans	–	–	8.2 (3–16)	8.2[e] (8.2–13)[j]	3.0/3.6 (1.0–5.7)	4[o] (2.0–6.0)
Wild animal excreta	–	–	0.1 (0–1)	2.5[e] (0.1–6)[j]	–	–
Lightning	5 (2–12)	1.1–6.4(3–7)	–	–	–	–
Atmospheric chemistry	<0.5	–	–	–	0.6 (0.3–1.2)	0.6 (0.3–1.2)
Natural total	**8.8**	**10-15.3**	**10.7**	**13.1**	**9.6/10.8**	**10.3**
Total source	51.9 (27.2–60.9)	41.8–47.1 (35.8–55.1)	53.5 (40–70)[h]	61.7 (36.4–109.5)	17.7/14.9 (5.9–37.5)	20.0 (7.6–40.9)

Notes:
(a) Includes biofuel combustion
(b) The values provided for NO_x are from the TAR, Chapter 4, Table 4.8: those in parentheses are the range of emissions used in the model runs described in the TAR, Chapter 4, Table 4.8 and Chapter 5, Table 5.2.
(c) The values provided in parentheses for NO_x are the range of emissions used in the model runs described in Table 7.4.4. See text for explanation. Where possible, the best estimate NO_x emission provided is based on satellite observations. None of the model studies includes the NO_x source from oxidation of NH_3 which could contribute up to 3 Tg N y^{-1}. The source of NOx from stratosphere troposphere exchange is less than 1 Tg-N yr^{-1} in all models and this is well constrained from observations of N_2O-NOy correlations in the lower stratosphere (Olsen et al., 2001).
(d) The aircraft source is included in the total for industrial processes. The parentheses indicate values used in model runs.
(e) Bouwman et al. (2002b) for 1990.
(f) All soils, including fertilized agricultural soils.
(g) The NH_3 values are from the TAR, Chapter 5, Table 5.2, based on Bouwman et al. (1997)
(h) The values provided in parentheses are the range of emissions used in the model runs described in the TAR, Chapter 5, Table 5.2.
(i) Van Aardenne et al. (2001)
(j) Holland et al. (1999)
(k) Bouwman et al. (2002a)
(l) Estimated as ±50%
(m) The N_2O values are from Table 4.4 in the TAR. The first value is from Mosier et al. (1998) & Kroeze et al. (1999). The second value is from Olivier et al. (1998), a single value indicates agreement between the sources and methodologies.
(n) Kroeze et al. (2005); Nevison et al. (2004), estimated uncertainty is ±70% from Nevison et al. (2004)
(o) Nevison et al. (2003, 2004)

[INSERT FIGURE 7.4.3 HERE]

Changes in atmospheric concentrations of NO_x and NH_x (NH_3 + NH_4^+) are challenging to measure because the atmospheric lifetimes of hours to days instead of years generate pronounced spatial and temporal variations in their distributions. NO_x and NH_x atmospheric concentrations are much more variable regionally and temporally than are concentrations of N_2O.

Total global NO_x emissions have increased exponentially from an estimated pre-industrial value of 12 Tg N yr^{-1} (Holland et al., 1999; Galloway et al., 2004) to between 42–47 Tg N yr^{-1} for 2000, and are forecast to be 105–131 Tg N yr^{-1} by 2100 (Lamarque et al., 2005a). The TAR intercomparison of ozone models 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). Current estimates of fossil fule NOx emissions are significantly smaller (Table 7.4.2). In a model intercomparison of 25 models, individual models assumed NO_x soil sources of 5.5–8.0 N yr^{-1} and NO_x lightning sources of 2.7–7.0 N yr^{-1}Interactions between soil emissions and scavenging by plant canopies have significant impact on soil NO_x emissions to the free troposphere: the impact may be greatest in subtropical and tropical regions where fossil fuel emissions are rising (Ganzeveld et al., 2002). The relatively small ranges used by the models is somewhat artifical, reflecting the use of similar inventories and parameterizations rather than actual constraints on our understanding.

One major development for constraining NO_x sources since the TAR has been the measurement of tropospheric NO_2 columns from space by GOME (launched 1995) and SCIAMACHY (launched 2002) (Richter and Burrows, 2002; Heue et al., 2005). Leue et al. (2001) first showed how these data could constrain the magnitude of NO_x emissions. Martin et al. (2003a) used GOME data to estimate a global

surface source of NO_x of 38 Tg N yr^{-1} for 1996–1997 with a factor of 1.6 uncertainty (Figure 7.4.4). This is consistent with the 33–45 Tg N yr^{-1} range of surface sources (excluding lightning and aircraft) in the current generation of global models listed in Table 7.4.4. Jaeglé et al. (2005) partitioned the surface NO_x source inferred from GOME into 25.6 Tg N yr^{-1} from fuels, 5.9 Tg N yr^{-1} from biomass burning, and 8.9 Tg N yr^{-1} from soils. Richter et al. (2005) (see also Irie et al., 2005) used trends for 1996–2004 observed by GOME and SCIAMACHY to deduce a 50% temporal increase in NO_x emissions over industrial areas of China. Observations of NO_2 in shipping lanes from GOME (Beirle et al., 2004) and SCIAMACHY (Richter et al., 2004) indicate values at the low end of current emission inventories. Boersma et al. (2005) found that the GOME data could constrain the global lightning NO_x source for 1997 to the range 1.1–6.4 Tg N yr^{-1}. GOME and SCIAMACHY data have further revealed large pulses of soil NO_x emissions associated with rain (Jaeglé et al., 2004) and fertilizer application (Bertram et al., 2005).

[INSERT FIGURE 7.4.4 HERE]

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 (Figure 7.4.3b and Table 7.4.2; Bouwman et al., 2002a, b & c). Total global NH_3 emissions have increased from an estimated preindustrual value of 11 Tg N yr^{-1} to 54 Tg N yr^{-1} for 2000, and are projected to increase to 116 Tg N yr^{-1} for 2050 (Holland et al., 1999; Galloway et al., 2004).

The short atmospheric lifetime also means that deposition of NH_x and NO_x and their reaction products, including aerosols, is the primary mechanism for removing these chemical species from the atmosphere. Estimates of the removal rates 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 (Hauglustaine et al. 2004; Holland et al., 2005; Lamarque et al. 2005a). 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 reaction 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., 2005a). In an intercomparison of 25 models, N deposition rates over Asia are forecast to increase by 1.4 to 2 fold by 2030. Climate contributions to the changes in oxidized N deposition are limited by the models' ability to represent changes in precipitation patterns. In Brazil, changes in land use can change the amount of N deposited by as much as fourfold (Lara et al., 2006).

7.4.2.2. Carbon- nitrogen-ozone interactions

Estimated and projected terrestrial carbon storage requires inputs of nutrients, 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 in 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 suggest that canopy uptake may be an important mechanism for uptake of atmospheric nitrogen 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). As well as its direct effect on climate, ozone may have an indirect effect thourgh biogeochemical couplings with the biosphere. One study (Feltzer et al., 2004) found that surface ozone increases since 1950 have reduced CO_2 sequestration in the US by 18–20 Tg C yr^{-1}. More work is needed to evaluate the interactions among changing ozone, nitrogen, water availability and the carbon cycle.

7.4.3. Molecular Hydrogen

Atmospheric H_2 has recently received increased attention, because of its potential role as an indirect greenhouse gas (Derwent et al., 2001) 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 Polar Stratospheric Clouds (PSCs) in the stratosphere 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 7.4.3), and they generally agree on a total source strength between 70 and 90 Tg H_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 Tg H_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 the budgets of the troposphere and stratosphere are largely decoupled (Warneck, 1988).

Table 7.4.3. 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 40–150 ppbv in the upper troposphere (Logan, 1999). Trends over the 20th century are discussed in Chapter 2. Ozone is produced in 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 dry deposition. Understanding of tropospheric ozone and its relationship to sources requires 3-D tropospheric chemistry models that describe the complex nonlinear chemistry involved and its coupling to transport, and are evaluated extensively with observations of ozone, its precursors, and related species.

The past decade has seen considerable development in global models for tropospheric ozone, and the current generation of models can reproduce most climatological features of ozone observations. The TAR reported global tropospheric ozone budgets from eleven models in the 1996–2000 literature. We present in Table 7.4.4 an update to the post-2000 literature, including a recent intercomparison of 25 models (Stevenson et al., 2005). Models concur that chemical production and loss are the principal terms in the global budget. 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.

Table 7.4.4. 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
Folberth et al. (2006)	LMDz-INCA	715	4436	3890	1261	303	28
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.
(c) Calculated as the ratio of the burden to the sum of chemical and deposition losses
(d) Means and standard deviations for 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

The post-2000 model budgets in Table 7.4.4 show major differences relative to the older-generation TAR models: on average a 34% weaker STE, a 35% stronger chemical production, a 10% larger tropospheric ozone burden, a 16% higher deposition velocity, and a 10% shorter chemical lifetime. It is now well established that many of the older studies overestimated STE, as observational constraints in the lower stratosphere impose an STE ozone flux of 540 ± 140 Tg yr^{-1} (Gettelman et al.., 1997; 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 motions (Douglass et al., 2003; Schoeberl et al., 2003; Tan et al., 2004; Van Noije et al., 2004). The newer models 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). Subtracting ozone chemical production and loss terms in Table 7.4.4 indicates that the current generation of models has net production of ozone in the troposphere, while the TAR models had net loss, simply reflecting the decrease in STE. Net production is not a useful quantity in analyzing the ozone budget because (1) it represents only a small residual between production and loss, (2) it is imposed by the balance between STE and dry deposition, both of which are usually parameterized in models.

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. 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 presently used in models (3–7 Tg N yr^{-1}) is adjusted to match atmospheric observations of ozone and NO_x, although large model uncertainties in deep convection and lightning vertical distributions 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).

Other significant precursors for tropospheric ozone are CO and NMVOCs, the most important of which is 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). 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 examined 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 effects of aerosols on UV radiation in a global CTM reduced ozone production rates by 6% globally, with larger effects over aerosol source regions (Tie et al., 2005).

Although the current generation of tropospheric ozone models is generally successful in describing the principal features of the present-day global ozone distribution, much less confidence is to be had in the ability to reproduce the changes in ozone associated with perturbations to emissions or climate. There are

major discrepancies with observed long-term trends in ozone concentrations over the 20th century (Mickley et al., 2001; Hauglustaine and Brasseur, 2001; Shindell and Favulegi, 2002; Fusco and Logan, 2003; Shindell et al., 2003; Lamarque et al., 2005b). Improved simulation of these long-term trends is important for establishing confidence in the models.

7.4.4.2 Effects of climate change

Climate change can affect tropospheric ozone by modifying precursor emissions, chemistry, and transport. A 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 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; Hauglustaine 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 an 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., 2001a; 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. The effect on methane is discussed in Section 7.3.1. The effect on NMVOCs was examined by Constable et al. (1999), Sanderson et al. (2003b), and Lathière et al. (2005). 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.

Catalytic ozone loss driven by bromine released from sea ice has been observed extensively in the Arctic boundary layer in spring, and also more recently in the Antarctic (Wessel et al., 1998; Roscoe et al., 2001). Climate change would affect the latitudinal extent of the sea ice and the formation of leads in the ice, which would affect the source of bromine and hence the extent of these ozone depletion events.

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) and Grewe et al. (2001) for the 21st century indicate a decrease in the lifetime of tropospheric ozone as increasing water vapor enhances the dominant ozone sink from the $O(^1D) + H_2O$ reaction. Stevenson et al. (2000) 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. However, regional ozone pollution may increase in the future climate as a result of higher temperatures (see Box 7.4).

7.4.4.2.3 Effects on transport

Changes in atmospheric circulation could have a major effect on tropospheric ozone. GCM studies concur that STE 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;

Hauglustaine et al., 2005). 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), Olivie et al. (2004), 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.

7.4.5. The Hydroxyl Radical (OH)

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. New laboratory and field work shows that there is also significant formation of $O(^1D)$ from ozone photolysis in the wavelength range between 0.310 μm and 0.350 μm (Matsumi et al. 2002; Hofzumahaus et al. 2004). The primary source of tropospheric OH is a pair of reactions that start with the photodissociation of O_3 by solar UV radiation:

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

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

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 may be the dominant sources of OH radical (e.g., Jaeglé et al., 2001; Tie et al., 2003; Singh et al., 2004; Collins et al., 1999). In continental environments, measurements in the lower troposphere also suggest that the processing of unsaturated hydrocarbons or photolysis of carbonyls can also sustain a large pool of radicals (e.g., Handisides et al., 2003; Heard et al., 2004). Furthermore, the net formation of OH by photolysis of HONO was found to be the dominant OH radical source in urban atmospheres (e.g., Ren et al., 2003) and in a forest canopy (Kleffmann et al., 2005). 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.

7.4.5.3 Changes in OH over time

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., 2005a). 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. (2002a) 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.

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. (2003a, b) use a 3D Chemical Transport Model (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, J.S. et al. (2004) also use 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 do 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.

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. (2005a). 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 Tg N yr^{-1} best estimate. A similar sensitivity of global OH to the lightning source has been estimated by Wang, J.S. et al. (2004) who calculated a 10.6% increase in OH for a doubling of the source (from 3 to 6 Tg N 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):

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

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:

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

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:

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

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; Collins et al., 2002). 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, J.S. 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, J.S. 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. This showed that the evolution of the methane lifetime depended on the relative timings of emission changes of NOx and hydrocarbons in the emission scenarios. The direct consequence is that the calculated methane increase in 2100 is reduced by 27% when climate change is considered. Stevenson et al. (2005) in their model intercomparison reach a similar conclusion about the relatively constant methane lifetime. As a result of future changes in emissions, the methane steady-state lifetime simulated by 25 state-of-the art chemistry transport models increases 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 is reduced by 5% so that the total effect of both emission and climate changes reduces the methane lifetime by only 2%.

7.4.6 Stratospheric Ozone and Climate

From about 1980 to the mid 1990s a negative trend in globally averaged total ozone has been observed. It is generally accepted that an increase in chlorine and bromine loading (Montzka et al., 1999) was the major cause of this trend. There are first indications for a reduction of halogen loading (Montzka et al., 2003) and stratospheric ozone depletion (e.g., Newchurch et al., 2003; Yang et al., 2005; Reinsel et al., 2005; Huck et al., 2005), but there is also some evidence that a sustainable recovery of the ozone layer is expected not before the end of the present decade (Steinbrecht et al., 2004; Dameris et al., 2006). Atmospheric concentrations of well-mixed greenhouse gases have also increased (see Chapter 2). This subsection presents a brief summary of our current understanding of interactions and feedbacks between stratospheric ozone and climate. More detailed discussions can be found in reports published recently, for example a report on "Ozone-Climate Interactions" by the European Commission (2003), or the special report "Safeguarding the Ozone Layer and the Global Climate System" by IPCC/TEAP (2005, see Chapter 1: Ozone and Climate). In particular, the WMO/UNEP Scientific Assessment of Ozone Depletion: 2006 (2007, see Chapter 5: Ozone-Climate Connections) discusses in detail mechanisms, processes and feedbacks of climate-ozone links.

7.4.6.1 Interactions

Figure 7.4.6 illustrates schematically the processes determining ozone-climate interactions in the troposphere and stratosphere. Stratospheric ozone is affected by climate change through changes in dynamics and the chemical composition of the troposphere and stratosphere. An increase in concentrations of greenhouse gases (GHG), especially CO_2, cools the stratosphere and alters the ozone distribution (Rosenlof et al., 2001; Rosenfield et al., 2002; Randel et al., 2004, 2006; Fueglistaler and Haynes, 2005). In most of the stratosphere, a decrease in temperature reduces ozone depletion which leads to higher ozone column amounts and a positive correction to the GHG induced cooling. Moreover, ozone itself 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 (Butchart and Scaife, 2001). This controls the rate at which long-lived molecules, such as GHGs, CFCs, and halogens are transported from the troposphere to various levels in the stratosphere**.**

[INSERT FIGURE 7.4.6 HERE]

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 upper troposphere and ozone layer regions (see e.g., TAR, Figure 6.1). Past ozone depletion has induced surface cooling, which has approximately balanced the greenhouse warming resulting from increasing abundances of ozone depleting substances (ODSs) and their substitutes (see Chapter 2). The observed decrease of stratospheric ozone and the resultant increase in UV

irradiance (e.g., Zerefos et al., 1998; McKenzie et al., 1999) has affected the biosphere and biogenic emissions. Such UV increases also lead to an enhanced OH production, which reduces the lifetime of methane and influences tropospheric ozone, both of which are important greenhouse gases (European Commission, 2003). In addition to global mean equilibrium surface temperature changes, local surface temperature changes have been identified by Gillett and Thompson (2003) as a result of lower stratospheric ozone loss. There is also observational (e.g., Baldwin and Dunkerton, 1999, 2001; Thompson et al., 2005) and modeling (Polvani and Kushner, 2002; Norton, 2003; Song and Robinson, 2004; Thompson et al., 2005) evidence for month-to-month changes to the stratospheric flow feedback onto the troposphere to affect its circulation. There is also modeling evidence that trends in the Southern Hemisphere stratosphere affect high-latitude surface climate (Gillett and Thompson, 2003).

7.4.6.2 Past changes of stratospheric ozone

Past ozone losses have been largest in the polar lower stratosphere 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 halogens. Similar losses, but smaller in magnitude, have occurred over the Arctic due to the same processes during cold winters. Warm winters have been relatively unaffected. A summary on recent stratospheric ozone changes is given in Chapter 2 of this report.

7.4.6.3 Future changes of stratospheric ozone

The evolution of stratospheric ozone in the near future (i.e., present day and first decades of this century) will depend on natural as well as man-made impact factors, for example the influence of solar activity (e.g Steinbrecht et al., 2004; Dameris et al., 2005) as well as changes in both, stratospheric temperature and dynamics and the stratospheric halogen loading, which is expected to decrease over the next decades (WMO, 2003; IPCC/TEAP, 2005). The evolution of ozone will also depend on the changes in many stratospheric constituents, including ODSs, GHGs, water vapor, and aerosols. It is certainly expected that the reduction of ODSs in the 21st century will cause ozone to increase. However, this increase could be strongly affected by temperature changes (due to GHGs), chemical changes (e.g., due to water vapor), and transport changes. Coupled chemistry-climate models (CCMs) provide a possibility to assess the future development of chemical composition and climate. To obtain consistency of anthropogenic and natural reference simulations, a set of model forcings have been defined as part of the CCM Validation Activity for SPARC (Eyring et al., 2005). The forcings are defined by natural and anthropogenic emissions based on existing scenarios, on atmospheric observations, and on the Kyoto and Montreal Protocols and Amendments. Future simulations follow the IPCC SRES GHG scenario A1B (medium) (IPCC, 2001). Figure 7.4.7a shows minimum Antarctic total ozone for September to November for various transient CCM reference simulations compared to observations). Over Antarctica, ozone amounts are expected to stay about the same for perhaps the next five years. Temperature changes are not particularly important, except at the edge of the ozone hole. Consequently, Antarctic ozone is expected to follow the behavior of chlorine and bromine amounts and a recovery back to pre-1980 levels is expected around 2050. However, there are first indications that this might be slightly later around 2065 (Austin and Wilson, 2006). Moreover, increased atmospheric fluxes of CFCs have recently been reported (Hurst et al., 2006) which point to a still later recovery, but this would be counteracted by the increased strength of the Brewer-Dobson circulation (Butchart and Scaife, 2001). Over the Arctic, a confused picture is still present (Figure 7.4.6b), but with increased Brewer-Dobson circulation counteracting to a degree the expected cooling by CO_2 (Austin and Wilson, 2006).

[INSERT FIGURE 7.4.7 HERE]

7.4.6.4 Uncertainties

Although coupled chemistry-climate models (CCMs) are able to reproduce most of the recent development with regard to the global ozone depletion and in particular the evolution of the 'ozone hole', future predictions must be used with caution. On the one hand side, there are uncertainties, which are directly related to assumptions in the CCMs themselves. For example, sub-grid processes like gravity-wave propagation and breaking or convection are parameterized (e.g., Warner and McIntyre, 2001), i.e., are

prescribed in a way which is tuned to past and present conditions. On the other hand there is an insufficient understanding of ongoing changes occurring in the stratosphere. For example, observations of stratospheric water vapor do not give a consistent picture with regard to long-term changes. Future stratospheric water vapor changes are uncertain (Randel et al., 2004, 2005) and it remains unclear how stratospheric ozone will be affected. Most CCMs are neither able to reproduce the observed water vapor distribution sufficiently nor the observed changes in the last 20 years. Nevertheless, a water vapor trend, if present, is expected to give rise to a trend in total ozone of comparable magnitude. Another point of uncertainty is that tropospheric climate changes will likely alter the generation of planetary-scale waves. Enhanced planetary-scale waves could increase the "dynamical heating" of the stratosphere, if the changes to the stratosphere allow a greater flux of planetary wave activity into the stratosphere. This effect is seen, in some simulations, to (over-) compensate or at least partly compensate for the overall radiative cooling of the stratosphere (Austin et al., 2003). The future development of stratospheric dynamics remains uncertain. Therefore, the confidence in the simulations is low, so even the sign of polar stratospheric temperature change is unclear. Currently available numerical model assessments do not draw a consistent picture of the future development, particularly in the Northern Hemisphere (Figure 7.4.7 and Chapter 6 therein). This is a major issue, because it is expected that future changes to the climate of the stratosphere will feedback to affect the troposphere.

7.5 Aerosol Particles and the Climate System

Aerosols are an integral part of the atmospheric hydrological cycle and the atmosphere's radiation budget, with many possible feedback mechanisms that are not fully understood yet. This section will give an overview of 1) the impact of meteorological (climatic) factors like wind, temperature and precipitation on the natural aerosol burden and 2) possible effects of aerosols on climate parameters and biogeochemistry. The easiest understood interaction between aerosols and climate is the direct effect (scattering and absorption of shortwave and thermal radiation), which is discussed in detail in Chapter 2. Interaction with the hydrological cycle, and additional impacts on the radiation budget, occur through the role of aerosols in cloud microphysical processes, as aerosol particles act as cloud condensation nuclei (CCN) and ice nuclei (IN). The suite of possible impacts of aerosols through the modification of cloud properties are called 'indirect effects'. The forcing aspect of the indirect effect at the top-of-the-atmosphere is discussed in Chapter 2 while the processes that involve feedbacks or interactions, like the 'cloud lifetime effect' and the 'semi-direct effect', aerosol impacts on the large scale circulation, convection, the biosphere through nutrient supply and the carbon cycle, are discussed here (Figure 7.5.1).

[INSERT FIGURE 7.5.1 HERE]

7.5.1 Aerosol Emissions and Burdens Affected by Climatic Factors

Most natural aerosol sources are driven or controlled by climatic parameters like wind, moisture and temperature. Hence an (anthropogenic) induced change in climate is expected to impact also on the natural aerosol burden. The sections below give a systematic overview of the major natural aerosol sources and their relations to climate parameters while anthropogenic aerosol emissions are the subject of Chapter 2.

7.5.1.1 Dust

Estimates of the global source strength of bulk dust aerosols below 10 μm of between 1000 and 3000 Tg yr^{-1} agree well with a wide range of observations (Duce, 1995; Textor et al., 2005; Cakmur et al., 2006). 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 more than a factor of two (Zender et al., 2004) due to problems in validating and modelling 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 by more then 30% (Timmreck and Schulz 2004). Observations suggest that annual mean 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. Simulations with one model 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). On the other hand, Woodward et al. (2005) simulate a large increase in the global annual mean dust emissions in 2100 resulting from expansion of the South American dust sources due to a combination of

desertification and climate change. Tegen et al. (2004) simulate an increase of 9% or a decrease of 19% in dust emissions in 2100 depending on the climate model that is used to drive the vegetation and dust model.

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., 2004). It also alters the atmospheric circulation, which feeds back upon dust emission from natural sources. Perlwitz et al. (2001) estimated that this feedback reduces the global dust load by roughly 15%, as dust radiative forcing reduces the downward mixing of momentum within the planetary boundary layer, the surface wind speed, and thus dust emission (Miller et al, 2004a). 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; Mahowald et al., 2004), to less than 10% (Tegen et al., 2004), and 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 likely to be more important in controlling dust emissions than changes in land-use (Tegen et al., 2004). The potential large impact of climate change shows up in particular when comparing present-day with last glacial maximum conditions for dust erosion (e.g., Werner 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 (Figure 7.5.1). It provides the nutrient iron, which affects ocean biogeochemistry with feedbacks on climate and dust production (Jickells et al., 2005). The input of trace elements by dust deposition is also of essential importance for terrestrial ecosystems. 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 (Okin et al. (2004) and Section 7.3). Also the Hawaiin islands depend on the phophorus provided by Asian dust transport (Chadwick et al. 1999). Moreover, mineral dust can act as a sink for acidic trace gases, such as SO_2 and HNO_3, and thereby interact with the sulfur and nitrogen cycles (e.g., Dentener et al., 1996; Umann et al., 2005). Coatings with soluble substances, such as sulphate or nitrate, will change the ability of mineral dust aerosols to nucleate cloud droplets (Levin et al., 1996 and Section 7.5.2.1).

7.5.1.2 Sea salt

Sea salt aerosol is a key aerosol constituent of the marine atmosphere. Sea salt aerosol particles affect the formation of clouds and rain; they serve as sinks for reactive gases and small particles and possibly suppressing new particle formation. The major meteorological and environmental factors that affect sea salt formation are wind speed, atmospheric stability and wind friction velocity, sea surface 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 Tg ± 200% (Textor et al., 2005) of which 15% is emitted into the submicron mode.

7.5.1.3 Natural organic carbon

Biogenic organic material is both directly emitted into the atmosphere and produced by volatile organic compounds (VOC). Primary emissions from the continents 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. 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 that range from 2.5 to 44.5 Tg of organic matter per year (Tsigaridis 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 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 aerosol 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.

A potentially important feedback among forest ecosystems, greenhouse gases, aerosols and climate exists through increased photosynthesis and forest growth due to increasing temperatures and CO_2 fertilization (Kulmala et al. 2004). An increase in forest biomass would increase non-methane biogenic volatile organic compound emissions and thereby organic aerosol production. This couples the climate effect of CO_2 with that of aerosols (Figure 7.5.1).

New evidence reveals the ocean is also a source of organic matter from biogenic origin (O'Dowd et al., 2004; Leck and Bigg, 2005b). O'Dowd et al. (2004) showed that during phytoplankton blooms (summer conditions), the organic contribution can be as high as 63%. Surface-active organic matter of biogenic origin (such as lipidic and proteinaceous material and humic substances), enriched in the oceanic surface layer and transferred to the atmosphere by bubble-bursting processes, are the most likely candidates to contribute to the observed organic fraction in marine aerosol. Insoluble heat-resistant organic submicrometre particles (peaking at 40-50 nm in diameter), mostly combined into chains or aggregated balls of "marine microcolloids" linked by an amorphous electron-transparent material with properties entirely consistent with exopolymer secretions, EPS, (Decho, 1990; Verdugo et al., 2004) are found in near-surface water of lower latitude oceans (Wells and Goldberg, 1991; 1994; Benner et al., 1992), in leads between ice floes (Bigg et al., 2004), above the Arctic pack ice (Leck and Bigg, 2005a) and over lower latitude oceans (Leck and Bigg, 2005b).

7.5.1.4 Aerosols from dimethylsulfide (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 DMS sea surface climatology utilized, 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). 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 constant DMS sea surface concentrations together with a constant monthly climatological ice cover. 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.

Bopp et al. (2004) were the first to estimate the feedback of DMS on cloud albedo by using a coupled atmosphere-ocean-biogeochemical climate model that includes phytoplankton species in the ocean and a sulfur cycle in the atmospheric climate model. They obtained an increase in the sea-air DMS flux of 3% for $2xCO_2$ conditions, with large spatial heterogeneities (–15% to +30%). The mechanisms affecting those fluxes are marine biology, relative abundance of phytoplankton types, and wind intensity. The simulated increase in fluxes causes an increase in sulphate aerosols and, hence, cloud droplets resulting in a radiative pertubation on cloud albedo of –0.05 W m^{-2}, which represents a small negative climate feedback on global warming.

7.5.1.5 Aerosols from iodine compounds

Intense new aerosol particle formation has been frequently observed in the coastal environment (O'Dowd et al. 2002a). Simultaneous coastal observations of reactive iodine species (Saiz-Lopez et al, 2005), chamber studies using iodocarbon precursors and laboratory characterisation of iodine oxide particles formed from exposure of Laminaria species macroalgae to ozone (McFiggans et al., 2004) have demonstrated that coastal particle formation is linked to iodine compound precursor released from abundant infralittoral beds of macroalgae. The particle bursts overwhelmingly occur during daytime low tides (O'Dowd et al. 2002b, Saiz-

Lopez et al, 2005). Tidal exposure of kelp leads to the well-documented release of significant fluxes of iodocarbons (Carpenter et al., 1999), the most photolabile of which, 7.3.10.I_2, may yield a high iodine atom flux. However, the IO, OIO and new particles are thought more likely to result from emissions of molecular iodine (McFiggans et al., 2004), which will yield a much greater iodine atom flux (Saiz-Lopez and Plane, 2004). It is unclear whether such particles grow sufficiently to act as CCN (O'Dowd, 2002, Saiz-Lopez et al., 2005). Furthermore, a hitherto undiscovered remote ocean source of iodine atoms (such as molecular iodine) must be present if iodine-mediated particle formation is to be important in the remote marine boundary layer (McFiggans, 2005).

7.5.1.6 Climatic factors controlling aerosol burdens and cycling

7.5.1.6.1 Wind

As discussed above, near-surface wind speed determines the source strength for primary aerosols (sea salt, dust, primary organic particles) and precursors of secondary aerosols (mainly DMS). Progress has been made in the development of source functions (in terms of wind speed) for sea-salt and desert dust (e.g., Tegen et al., 2002; Gong, 2003; Balkanski et al., 2004). Wind speed also affects dry deposition velocities and hence the lifetime of aerosols.

7.5.1.6.2 Temperature

Biogenic emissions are strongly dependent on temperature (together with humidity/moisture). New evidence indicates that isoprene is a source for secondary organic aerosols, which are very sensitive to temperature (Claeys et al., 2005). Temperature also is a key factor in the gas-aerosol partitioning of semi-volatile secondary organics (Kanakidou et al., 2005). Also the lifetime of aerosols depends on temperature: it may be shorter in a warmer climate (Feichter et al., 2004; Stier et al. 2006).

7.5.1.6.3 Precipitation

Precipitation directly affects the wet removal and hence the lifetime of atmospheric aerosols. One study showed that the sulphate burden increased by 50% when an aerosol scheme was coupled to a cloud scheme in a global climate model (Lohmann and Feichter, 1997). A positive feedback loop was 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. This feedback loop is terminated when enough cloud water builds up or when a fraction of the anthropogenic black carbon (BC) is allowed to act as contact ice nuclei, which enhances the precipitation formation via the ice phase and can reduce the anthropogenic aerosol burden from pre-industrial to present-day times by 38% to 58% (Lohmann, 2002). Precipitation also affects the soil moisture, with impacts on source strength of dust, but also on stomatal opening /closure of plant leaves, hence affecting biogenic emissions.

7.5.1.6.4 Cloudiness

Cloud processing is an important pathway in the gas-to-particle conversion. It is the most important oxidation pathway for sulphate aerosols and shifts the aerosol size distribution to larger sizes, such that aerosols are more easily activated in subsequent cloud events (e.g., Kerkweg et al., 2003). It is also important in the conversion of hydrophobic to hydrophilic carbon.

In addition to meteorological influences on aerosol burden and lifetime, the different aerosol compounds interact with each other. For example, a reduction in sulfur dioxide emissions in a future climate could lead to a prolonged residence time of soot (Stier et al., 2006).

7.5.2 Indirect Effects of Aerosols on Clouds and Precipitation

There are many ways in which aerosols can interact with clouds and precipitation, either acting as cloud condensation or ice nuclei, or as absorbing particles, redistributing solar energy as thermal energy inside cloud layers. These indirect effects (in contrast to the direct interaction with radiation, see Chapter 2) are the subject of this section, together with aerosol-induced changes in large-scale circulation and convection. They can be subdivided into different contributing processes, as summarized in Table 7.5.1 and shown in Figure 7.5.3.

[INSERT FIGURE 7.5.3 HERE]

The cloud-albedo effect, i.e., the distribution of the same cloud liquid water content over more, hence smaller, cloud droplets leading to higher cloud reflectivity, is a purely radiative forcing and is therefore subject of Chapter 2. The other effects involve feedbacks in the climate system and will be discussed here. The albedo effect cannot be easily separated from the other effects; in fact, the processes that decrease the cloud droplet size per given liquid water content also decrease precipitation formation, hence prolonging cloud lifetime (cloud lifetime effect, Section 7.5.2.1 and Figure 7.5.3). The semi-direct effect refers to the absorption of solar radiation by soot, re-emitted as thermal radiation, hence heating the air mass and increasing static stability relative to the surface. It may also cause evaporation of cloud droplets (see Chapter 2, Section 2.4; Section 7.5.4.1 and Figure 7.5.3). The glaciation effect refers to an increase in ice nuclei resulting in a rapid glaciation of a supercooled liquid water cloud due to the difference in vapour pressure over ice and water. Unlike cloud droplets, these ice crystals grow in an environment of high supersaturation with respect to ice, quickly reaching precipitation size, and with that can turn a non-precipitating into a precipitating cloud (Section 7.5.2.2 and Figure 7.5.3). The thermodynamic effect refers to a delay in freezing by the smaller droplets causing supercooled clouds to extend to colder temperatures (Section 7.5.2.2 and Figure 7.5.3). The surface energy budget effect (Section 7.5.3) describes the aerosol-induced decrease in surface solar radiation with consequences for evaporation and precipitation (Figure 7.5.3).

Table 7.5.1a. 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	Scientific Understanding
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	low
Cloud lifetime effect	All clouds	Smaller cloud particles decrease the precipitation efficiency thereby prolonging cloud lifetime	Negative	medium	very low
Semi-direct effect	All clouds	Absorption of solar radiation by absorbing aerosols increases static stability and may lead to an evaporation of cloud particles	Positive or negative	small	very low
Glaciation indirect effect	Mixed-phase clouds	An increase in ice nuclei increases the precipitation efficiency	Positive	medium	very low
Thermodynamic effect	Mixed-phase clouds	Smaller cloud droplets delay freezing causing supercooled clouds to extend to colder temperatures	Positive or negative	medium	very low

Table 7.5.1b. Overview of the different aerosol indirect effects and their implications for the global mean net shortwave radiation at the surface F_{sfc} (Columns 2-4) and for the precipitation (Columns 5-7).

Effect	Sign of Change in F_{sfc}	Potential Magnitude	Scientific Understanding	Sign of Change in Precipitation	Potential Magnitude	Scientific Understanding
Cloud albedo effect	Negative	medium	low	n/a	n/a	n/a
Cloud lifetime effect	Negative	medium	Very low	Negative	small	very low
Semi-direct effect	Negative	large	Very low	Negative	large	very low
Glaciation indirect effect	Positive	medium	Very low	Positive	medium	very low
Thermodynamic effect	Positive or negative	medium	Very low	Positive or negative	medium	very low

7.5.2.1 Aerosol effects on water clouds and warm precipitation

The indirect aerosol forcing of increasing cloud albedo for warm clouds (clouds that contain no ice crystals) is discussed in Chapter 2. In addition aerosols increase the lifetime of clouds because increased concentrations of smaller droplets lead to a decreased drizzle production and reduced precipitation efficiency

(Albrecht, 1989). It has proven difficult to devise observational studies that can separate the cloud lifetime from the cloud albedo effect; thus, observational studies in most instances provide estimates of the combined effects. Similarly, climate modelling studies cannot easily separate the cloud lifetime indirect effect once the aerosol scheme is fully coupled to a cloud microphysics scheme.

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 and Walsh, 2002). Ackerman et al. (2004) attributed this phenomenon to enhanced entrainment of dry air in polluted clouds in these instances. On the other hand, satellite observations have been used to conclude that the aerosol indirect effect is likely primarily due to an increase in cloud cover, rather than an increase in cloud albedo (Kaufman et al., 2005).

Cloud cover has been shown to decrease when biomass burning aerosols inhibit the formation of low clouds (Koren et al., 2004). For values of the aerosol optical depth above 1.2, very few low-lying clouds were observed in a large area with high biomass burning aerosol loading. Likewise increasing emissions of absorbing aerosols from the late 1980s to the late 1990s in China caused a reduction in cloud amount leading to a decrease in the local planetary albedo, as deduced from satellite data (Krüger and Graßl, 2004).

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 cloud droplet number concentration (O'Dowd et al., 2004; Lohmann and Leck, 2005). Over the Arctic Ocean this increase in cloud droplet number arises from the ability of the organic aerosols surrounded by microcolloids to lower the surface tension (Facchini et al., 1999; Decesari et al., 2003), whereas off the coasts of Ireland the cloud droplet number increase is attributed to the addition of a source of mostly insoluble marine organics (O'Dowd et al., 2004).

Smoke from burning vegetation reduces cloud droplet sizes and delays the onset of precipitation (Warner and Twomey, 1967; Rosenfeld, 1999; Andreae et al., 2004). Also, desert dust suppresses precipitation in thin low altitude clouds (Rosenfeld et al., 2001; Mahowald and Kiehl, 2003). The 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 likely caused by aerosols. On the other hand 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. Contradictory results are also found regarding the suppression of rainfall from aerosols in Australia (Rosenfeld, 2000; Ayers, 2005).

Modelling studies 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, 2006) 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). Likewise, Gong and Barrie (2003) predict a reduction of 20–60% in the marine cloud droplet number concentrations and an increase in precipitation when interactions of sulphate with sea salt aerosols are taken into account. A reduction of precipitation formation, on the other hand, leads to increased cloud processing of aerosols. Feingold et al. (1998) and Wurzler et al. (2000) showed that this could either lead to an increase or decrease of precipitation formation, depending on the size and concentration of activated CCN.

7.5.2.2 Aerosol impacts on mixed-phase clouds

Obervations of aerosol effects on mixed-phase clouds from satellite are not yet conclusive (Mahowald and Kiehl, 2003). Thus, this section only refers to modelling results and field studies. 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 had more cloud droplets. Examination of this effect in a global climate model found that although the riming rate decreased the modeled snowfall

actually increased. This was caused by a feedback in the model whereby the increased cloud optical thickness reduced the solar radiation and caused a cooling that favored precipitation in the ice phase (Lohmann, 2004).

Motivated by laboratory studies, Lohmann (2002) and Lohmann and Diehl (2006) 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 ice nuclei in the present-day climate result in more frequent glaciation of supercooled stratiform 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. Whether the glaciation or warm cloud lifetime effect is larger depends on the chemical nature of the dust (Lohmann and Diehl, 2006). Likewise, the number and size of ice particles in convective mixed phase clouds is sensitive to the chemical composition of the insoluble fraction (e.g., dust, soot, biological particles) of the aerosol particles (Diehl and Wurzler, 2004).

Rosenfeld (1999) and Rosenfeld and Woodley (2000) analysed 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 supported 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.

Khain et al. (2005) postulated 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 depleted the cloud so that less latent heat is released when the cloud glaciates resulting in less vigorous convection. Therefore, a squall line is only simulated under the influence of higher continental aerosol concentrations and results in more precipitation after two hours of simulations. More precipitation from polluted clouds is also simulated for different periods in Oklahoma (Zhang et al., 2005) as well as for multicell cloud systems (Seifert and Beheng, 2006). 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, 2006). 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., 2006). In particular, the simulated updrafts are consistently stronger and more numerous when Saharan dust is present compared with a clean air mass. This suggests that dust enhanced glaciation of convective clouds leading to dynamical invigoration of the clouds, and thereby enhanced rainfall at the ground (as discussed above). However, the simulated precipitation enhancement only lasted two hours after which it decreased as compared with clean conditions.

Besides changes in the distribution of precipitation also the frequency of extreme events may be influenced by the presence of aerosols. Paeth and Feichter (2005) report based on climate simulations that daily extreme events of precipitation and temperature tend to be reduced with a higher aerosol load.

Cloud processing of dust particles, sulphate particles and trace gases can lead to an acceleration of precipitation formation in continental mixed-phase clouds, whereas in maritime clouds, which already form on rather large CCN, the simulated effect on precipitation was minimal (Yin et al. 2002). 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. Note that microphysical processes can only change the temporal and spatial distribution of precipitation while the total amount of precipitation can only change if evaporation from the surface changes.

7.5.2.3 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 concluded that such an effect based solely on ubiquitous homogeneous freezing is small globally (Lohmann and Kärcher, 2002). This is expected to also hold in the presence of heterogeneous ice nuclei (IN) that cause cloud droplets to 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 to significantly 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; Hoyle et al, 2005). 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. 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. Assuming 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 the full complexity of cirrus processes in global models.

7.5.2.4 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 warm clouds from several climate models. 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 TOA are, however, probably smaller than the indirect effects (Lohmann and Feichter, 2001; Penner et al., 2003). Black carbon absorbs 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 (see Section 7.5.3; Ramanathan et al., 2001a; Lohmann and Feichter, 2001; Liepert et al., 2004). The total aerosol effect is restricted to warm clouds except for the simulations by Lohmann and Diehl (2006) who are the only ones to include the above mentioned glaciation indirect effects on stratiform mixed-phase clouds.

Global climate model (GCM) estimates of the total TOA anthropogenic aerosol effect are generally larger than estimated from inverse models (Anderson et al., 2003; Lohmann and Feichter, 2005). GCM 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 compounds 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, A. et al., 2001; Menon et al., 2002a; 2003).

[INSERT FIGURE 7.5.4 HERE]

The global mean total anthropogenic aerosol effect (direct, semi-direct and indirect cloud albedo and cloud lifetime effect), defined as the change in net radiation at TOA from pre-industrial times to present-day, is shown in Figure 7.5.4. It ranges from –0.2 W m^{-2} in the combined GCM+satellite simulations (Quaas et al., 2005) to –2.3 W m^{-2} in the simulations by Ming et al. (2005) and Quaas et al. (2004). Even though some model estimates include also the direct effect, its contribution to the TOA radiation is generally small compared to the indirect effect ranging from +0.1 to –0.5 W m^{-2} due to variations of the different locations of black carbon with respect to the cloud (Lohmann and Feichter, 2005). The simulated cloud lifetime effect varies between –0.3 and –1.4 W m^{-2} (Lohmann and Feichter, 2005), which explains some of the differences in Figure 7.5.4.

All models agree that the total aerosol effect is larger over the Northern Hemisphere than over the Southern Hemisphere (Figure 7.5.4). The values of the Northern Hemisphere total aerosol effect vary between –0.3 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 1.8. While the combined ECHAM4 GCM+POLDER satellite estimate suggests that the total aerosol effect should be larger over oceans (Lohmann and Lesins, 2002), combined estimates of the LMD and ECHAM4 GCMs with MODIS satellite data reach the opposite conclusion (Quaas et al., 2005). The average total aerosol effect over the ocean of –1.2 W m^{-2} agrees with estimates between –1 to –1.6 W m^{-2} from AVHRR/POLDER (Sekiguchi et al., 2003).

As compared to the estimates of the total aerosol effect in Lohmann and Feichter (2005), some new estimates (Rotstayn and Liu, 2005; Lohmann and Diehl, 2006) now also include the influence of aerosols on the cloud droplet size distribution (dispersion effect, Liu and Daum, 2002). It refers to a widening of the size distribution in the polluted clouds that partly counteracts the reduction in the effective cloud droplet radius in these clouds. Thus, if the dispersion effect is taken into account, the indirect cloud albedo aerosol effect is reduced by 12-35% (Peng and Lohmann, 2003; Rotstayn and Liu, 2003). The global mean total indirect aerosol effect in the simulation by Rotstayn and Liu (2005) has also been reduced due to a smaller autoconversion given by a new treatment of autoconversion.

Global climate model estimates of the change in global mean precipitation due to the total aerosol effects are summarized in Figure 7.5.5. Consistent with the conflicting results from detailed cloud system studies, the change in global mean precipitation varies between +0.005 mm day^{-1} and –0.13 mm day^{-1}. These differences are amplified over land, ranging from –0.17 mm day^{-1} to 0.02 mm day^{-1}. The decreases in precipitation are larger, when the atmospheric GCMs are coupled to mixed-layer ocean models (green bars), where the sea surface temperature and, hence, evaporation is allowed to vary.

[INSERT FIGURE 7.5.5 HERE]

7.5.3 Effects of Aerosols/Clouds on the Solar Radiation at the Earth's Surface

By increasing aerosol and cloud optical depth, emissions of aerosols and their precursors from human activity contribute to a reduction of solar radiation at the surface ("solar dimming"). As such, worsening air quality contributes to regional aerosol effects. The partially conflicting observations on solar dimming/brightening are discussed in detail in Chapter 3, Section 3.4 and Box 3.2. Here we focus on the possible contribution by aerosols. This decline of solar radiation from 1961 to 1990 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).

For the tropical Indian Ocean, Ramanathan et al. (2001b) estimated a total TOA indirect aerosol effect of –5 W m^{-2} and of –6 W m^{-2} at the surface. While the combined direct and semi-direct effect is negligible at

TOA, its surface forcing amounted to –14 W m^{-2}, pointing out the importance of considering surface radiative forcings in addition to TOA forcings. Absorbing aerosols imposed over the Indian Ocean in a GCM study with fixed sea surface temperatures can cool the land surface by 0.5–1°C and warm the lower troposphere by 1°C (Chung et al., 2002). This simulated vertical heating gradient altered the latitudinal and inter-hemispheric gradients in solar heating with consequences for the tropical circulation (Ramanathan et al., 2001b) and the amount of precipitation (Chung and Zhang, 2004). In South Asia, absorbing aerosols may have masked up to 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, Southern Asia may experience an enhanced drought frequency in future decades (Ramanathan et al., 2005).

Global climate model estimates of the mean decrease in shortwave radiation at the surface in response to all aerosol effects vary between –1.5 and –3.1 W m^{-2} (Figure 7.5.6). 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 7.5.6 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. There is a slight increase in downwelling longwave radiation due to aerosols, which in the global mean is small compared to the decrease in shortwave radiation at the surface. 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 from pre-industrial times to present-day (Liepert et al., 2004; Feichter et al., 2004), and in transient simulations (Roeckner et al., 1999). 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 which may explain the observations of decreased pan evaporation over the last 50 years reported in several studies (see Chapter 3, Section 3.3). As global mean evaporation must equal precipitation, a reduction in the latent heat flux in the model led to a reduction in precipitation (Liepert et al., 2004). This is in contrast to the observed precipitation evolution in the last century (see Chapter 3, Section 3.3) and points to an overestimation of aerosol influences on precipitation, or to an important ice cloud aerosol indirect effect. The decrease in global mean precipitation from pre-industrial times to the present may, however, reverse into an increase of about 1% in 2031–2050 as compared to 1981–2000, because the increased warming due to black carbon and greenhouse gases then dominates over the sulphate cooling (Roeckner et al., 2006).

7.5.4 Effects of Aerosols on 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 (cf. Chapter 8, Section 8.6). 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).

In addition, absorption of solar radiation by aerosols can change the cloud amount (semi-direct effect; Hansen et al., 1997; Ackerman et al., 2000; Ramanathan et al., 2001a, Figure 7.5.3. and Chapter 2, Section 2.8.5). It has been modelled both by GCMs and high-resolution cloud resolving models, since it is implicitly included whenever absorbing aerosols are included (see Chapter 2, Section 2.8). Direct aerosol heating modifies clouds in all GCMs analysed (Hansen et al., 1997; Lohmann and Feichter, 2001; Jacobson, 2002; Menon et al., 2002b; Penner et al., 2003; Cook and Highwood, 2004; Hansen et al., 2005). Aerosol heating within cloud layers reduced cloud fractions, whereas aerosol heating above the cloud layer tended to increase

cloud fractions. When diagnosed within a GCM framework, the semi-direct effect can also include cloud changes due to circulation effects and/or surface albedo effects. Moreover, the semi-direct effect is not exclusive to absorbing aerosol, as potentially any radiative heating of the mid-troposphere can produce a similar response in a GCM (Hansen et al., 2005; see also Chapter 2, Section 2.8). Cloud resolving models of cumulus and stratocumulus case-studies also diagnose semi-direct effects indicating a similar relationship between the height of the aerosol layer relative to the cloud and the sign of the semi-direct effect (Ackerman et al., 2000; Ramanathan et al., 2001a; Johnson et al., 2004; Johnson, 2005). Johnson (2005) points out that the necessarily coarse resolution of GCM cloud schemes means that they may incorrectly model such effects, thus global estimates of the semi-direct effect should be viewed with caution.

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 at TOA could range from –4 to +40 W m^{-2} while the oceanic cooling could range from 0 to–35 W m^{-2} (Sokolik and Toon, 1996; Weaver et al., 2002; Wang, H. et al., 2004). The dust-induced thermal contrast changes between the Eurasian continent and the surrounding oceans are found to trigger or modulate a rapidly varying or unstable Asian winter monsoon circulation, with a feedback to reduce the dust emission from its sources (Zhang et al., 2002). Heating of a lofted dust layer could also increase the occurrence of deep convection (Stephens et al., 2004).

7.5.4.2 Effects on the large-scale circulation

Several studies have considered the response of a GCM with a mixed-layer ocean to indirect aerosol effects (Rotstayn et al., 2000; Williams et al., 2001b; Rotstayn and Lohmann, 2002) or to a combination of direct and indirect aerosol effects (Feichter et al., 2004; Takemura et al., 2005; Kristjansson et al., 2005). All of these found a substantial cooling that was strongest in the Northern Hemisphere, with a consequent southward shift of the Intertropical Convergence Zone (ITCZ) and the associated tropical rainfall belt. Rotstayn and Lohmann (2002) went on to suggest that aerosol effects might have contributed to the Sahelian droughts of the 1970s and 1980s (see Chapter 9, Section 9.5). The southward shift of the ITCZ was less pronounced in the Feichter et al. (2004) study than in the other studies, perhaps due to their more complex treatment of cloud droplet nucleation, which tends to give less weight to the effects of sulphate than simpler schemes do. In contrast, Chung and Seinfeld (2005) considered the response of a GCM to direct forcing by black carbon aerosols, and found a northward shift of the ITCZ due to enhanced warming of the Northern Hemisphere.

As an example of aerosol interactions with the large-scale circulation we focus on regional effects in South East Asia. Menon et al. (2002b) found 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 can reduce the solar radiation reaching the surface and can warm the atmosphere, thus affecting atmospheric stability (see Section 7.5.4.1) and convection. These changes in convection can in turn modify the large-scale atmospheric circulation, an example of which is shown in Figure 7.5.7. In India and China, where absorbing aerosols have been added, increasing rising motions are seen while comparable increased subsidence to the south and north are present in these simulations (Menon et al., 2002b; Wang, 2004). Similarly, radiative heating within a dust layer can strengthen the Asian summer monsoon circulation and cause a local increase in precipitation, despite the global reduction of evaporation that compensates aerosol radiative heating at the surface (Miller et al., 2004b). 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 7.5.7 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 weakens so that less moisture is transported to Southern China, causing the drying trend.

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 and precipitation (Schwartz, 1993; Roeckner et al., 1999 and Feichter et al., 2004).

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.

Box 7.4: 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 7.4, 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 7.4, FIGURE 1 HERE]

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 offsets 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; Hauglustaine et al., 2005). Empirical relationships between ozone air quality standard exceedances and temperature, as shown in Box 7.4, Figure 2, integrate all of these effects and could be used to estimate how future regional changes in temperature would affect ozone air quality. However, one would also have to account for decreases in the global ozone background (Stevenson et al., 2005b).

[INSERT BOX 7.4, FIGURE 2 HERE]

A few GCM studies have examined more specifically the effect of changing climate on regional 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.

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 little effect in the United States.

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.

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. Brasseur and Roeckner (2005), for example, estimate that the hypothetical removal from the atmosphere of the entire burden of anthropogenic sulphate aerosol particles (in an effort to improve air quality) 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 7.6.1). 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 7.6.1 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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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. In fact the observed increase in atmospheric carbon dioxide concentrations only accounts for 57–60% of the carbon dioxide released by human activity. The rest is taken up by land plants and the oceans. Fossil fuel combustion and cement manufacture are responsible for more than 75% of human-caused carbon dioxide emissions. Land use change is responsible for the remainder. For methane, another important greenhouse gas, human activities contributed more than half of the annual emissions over the last 25 years. For nitrous oxide, human activity contributes about one third to one half of the total emission 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. About one half of present-day tropospheric ozone is created from atmospheric reactions of short-lived pollutants emitted from human activity.

Carbon Dioxide (Panel a)
The natural carbon cycle cannot explain the observed atmospheric increase of 3.3 GtC per year over the last 25 years (Panel a). (One GtC equals 10^{15} grams of carbon, that is, 1 billion metric tonnes.) Fossil fuel combustion, with contributions from cement manufacture, is responsible for more than 75% of the increase in atmospheric carbon dioxide concentration. The remainder comes from land use changes dominated by deforestation (and associated biomass burning) with contributions from changing agricultural practices.

Natural processes such as photosynthesis, respiration, decay, and sea-surface gas exchange lead to massive exchanges of carbon dioxide between the land and atmosphere (estimated at ~60 GtC per year) and the ocean and atmosphere (estimated at ~90 GtC per year). These exchanges are in balance, with roughly equal amounts entering and leaving the atmosphere (see Section 7.3.1). These numbers are generally stable for the global carbon cycle under current climatic conditions; thus there is currently no naturally-produced increase of atmospheric carbon dioxide concentrations with respect to time.

A variety of techniques and measurements indicate that human activity has caused the observed increase in atmospheric carbon dioxide concentrations. These include: a decrease in the ratio of oxygen to nitrogen in the atmosphere (oxygen is depleted by burning fossil fuels), and decreases over time in the relative concentrations of certain carbon isotopes in atmospheric carbon dioxide (fossil fuels are depleted in these isotopes).

[INSERT QUESTION 7.1, FIGURE 1 HERE]

Halogen-Containing Gases (Panel b)
The halogen-containing gases include chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and halons. Before industrialization, there were only a few naturally occurring halogen-containing gases, e.g., methyl bromide and methyl chloride. The atmospheric concentrations 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 amendments, the concentrations at the Earth's surface of several important halogen-containing gases, including CFCs, are now stabilizing or decreasing. Concentrations of HCFCs, whose production is to be phased out by 2030, and of the unregulated HFCs and PFCs, are currently increasing.

Methane (Panel c)
Human activities are responsible for more than half 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, waste disposal in land fills, raising ruminant animals (e.g., cattle and sheep), rice agriculture, and biomass burning. The main sink for methane is chemical oxidation in the troposphere. Minor sinks for methane include uptake by soils, and eventual destruction in the stratosphere. The atmospheric increase and the atmospheric concentration of methane are determined by the balance between emissions and destruction.

Nitrous Oxide (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. Human activities that emit nitrous oxide include transformation of fertilizer nitrogen into nitrous oxide and its subsequent emission from agricultural soils, biomass burning, raising cattle, and some industrial activities, including nylon manufacture. The increase in atmospheric concentration of nitrous oxide is determined by the balance between emissions and removal. Emitted nitrous oxide remains in the atmosphere for an average of 114–120 years before being removed, mainly by destruction in the stratosphere.

Tropospheric Ozone (Panel e)

Tropospheric ozone is produced by photochemical reactions in the atmosphere involving forerunner chemicals such as carbon monoxide, methane, volatile organic compounds (VOCs) and nitrogen oxides. Because tropospheric ozone is relatively short-lived, lasting for a few days to weeks in the atmosphere, its distributions are highly variable and tied to the abundance of its forerunner compounds. Tropospheric ozone concentrations are significantly enhanced in urban air and aircraft corridors, and downwind of urban areas and regions of biomass burning. The total global amount of tropospheric ozone is now roughly twice that before the industrial era; thus about 50% of tropospheric ozone is human-caused.

Tables

Table 7.3.3. Couplings between climate change (increased atmospheric CO_2 partial pressure, warming) and ocean carbon cycle processes. The response in terms of direct radiative forcing is considered (furthering or counteracting uptake of anthropogenic CO_2 from the atmosphere). The two quantitative most important marine processes for neutralization of anthropogenic CO_2 work on long time scales only and are virtually certain to be in effect.

Marine carbon cycle process	**Major forcing factors**	**Response + = enhancing – = damping and quantitative potential**	**Start**	**Re-equilibration time scale**	**Likelihood**	**Comment**
Seawater buffering	Atmospheric CO_2, ocean circulation	– high	immediate	5,000–10,000 yrs	Virtually certain	System response, leads to ocean acidification
Changes in inorganic carbon chemistry (solubility, dissociation, buffer factor)	Warming, atmospheric CO_2, ocean circulation	+ medium	immediate	5,000–10,000 yrs	Virtually certain	Positive feedback dependent on "bottleneck" ocean mixing
Biological export production of organic carbon and changes in organic carbon cycling	Warming, ocean circulation, nutrient supply, radiation, atmospheric CO_2, pH value	(Sum of effects not clear) +/– medium	immediate	1 yr–10,000 yrs	Likely	Complex feedback chain, reactions can be fast for surface ocean, nutrient supply from land works on longer time scales, patterns of biodiversity and ecosystem functioning may be affected
Biological export production of calcium carbonate	Warming, atmospheric CO_2, pH value	(Sum of effects not clear) +/– small	immediate	1 yr–1,000 yrs	Likely	Complex feedback chain, extinction of species likely, patterns of biodiversity and ecosystem functioning may be affected
Dissolution of calcium carbonate sediments	pH value, ocean circulation	– high	immediate	40,000 yrs	Virtually certain	Patterns of biodiversity and ecosystem functioning in deep sea may be affected
Weathering of silicate carbonates	Atmospheric CO_2, warming	– medium	immediate	100,000 yrs	Likely	Very long term negative feedback

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

References	Indicative $d^{13}C$, ‰ [a]	Hein et al., 1997 (S1)	Houweling et al. 2000	Olivier et al., 2005 (Edgar)	Wuebbles and Hayhoe, 2002	Scheehle et al., 2002	Wang et al., 2004	Mikaloff Fletcher et al. 2004a (S2)	Chen and Prinn, 2005b	TAR	AR4
Base year		1983–1989		2000	-	1990	1994	1999	1996–2001	1998	2000–2004
Natural sources			**222**		**145**		**200**	**260**	**168**		
Wetlands	–58	231	163		100		176	231	145		
Termites	–70		20		20		20	29	23		
Ocean	–60		15		4						
Hydrates	–60				5		4				
Geological sources	–40		4		14						
Wild animals	–60		15								
Wild fires	–25		5		2						
Anthropogenic sources		**361**		**320**	**358**	**264**	**307**	**350**	**428**		
Energy						74	77		84		
Coal mining	–37	32		34	46			30			
Gas, oil, industry	–44	68		64	60			52			
Landfills & waste	–55	43		66	61	69	49	35			
Ruminants	–60	92		80	81	76	83	91	189		
Rice agriculture	–63	83		39	60	31	57	54	112		
Biomass burning & biofuel	–25	43			50	14	41	88	43		
C3 vegetation	–25			27							
C4 vegetation	–12			9							
Total sources		**592**			**503**		**507**	**610**	**596**	**598**	**578**
Imbalance		+33								+22	+2
Sinks											
Soils	–18	26			30		34	30		30	30
Tropospheric OH	–3.9	488			445		428	507		506	506
Stratospheric loss		45			40		30	40		40	40
Free Cl atom											
Total sink		**559**			**515**		**492**	**577**		**576**	**576**

Notes:

(a) Indicative $\delta^{13}C$ values for sources are taken mainly from Mikaloff Fletcher et al. (2004a). Entries for sinks are the fractionation, (k_{13}/k_{12}^{-1}) where k_n is the removal rate of $^nCH_4$; the fractionation for OH is taken from Saueressig et al. (2001) and that for the soil sink from Snover and Quay (2000) as the most recent determinations.