

Chapter 6: Carbon and Other Biogeochemical Cycles

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Table of Contents

Executive Summary	3
6.1 Introduction	7
6.1.1 <i>Global Carbon Cycle Overview</i>	7
6.1.2 <i>Industrial Era</i>	9
6.1.3 <i>Connections Between Carbon and Other Biogeochemical Cycles</i>	10
Box 6.1: Nitrogen Cycle and Nitrogen Carbon Cycle Feedbacks	11
6.2 Variations in Carbon and Other Biogeochemical Cycles before the Fossil Fuel Era	13
6.2.1 <i>Glacial-Interglacial GHG Changes</i>	13
6.2.2 <i>GHG Changes over the Holocene (last 11,000 Years)</i>	16
6.2.3 <i>GHG Changes over the Last Millennium</i>	18
6.3 Evolution of Biogeochemical Cycles since the Industrial Revolution	19
6.3.1 <i>CO₂ Emissions and their Fate Since 1750</i>	19
Box 6.2: CO₂ Residence Time	20
6.3.2 <i>Global CO₂ Budget</i>	21
Box 6.3: The CO₂ Fertilization Effect	35

1 6.3.3 *Global CH₄ Budget* 39

2 6.3.4 *Global N₂O Budget* 43

3 **6.4 Projections of Future Carbon and Other Biogeochemical Cycles** **45**

4 6.4.1 *Introduction*..... 45

5 **Box 6.4: Climate-Carbon Cycle Models and Experimental Design** **47**

6 6.4.2 *Carbon Cycle Feedbacks in CMIP5 Models*..... 50

7 6.4.3 *Implications of the Future Projections for the Carbon Cycle* 53

8 6.4.4 *Future Ocean Acidification*..... 58

9 6.4.5 *Future Ocean Oxygen Depletion* 59

10 **Box 6.5: IPCC AR5 Ocean Deoxygenation**..... **59**

11 6.4.6 *Future Trends in the Nitrogen Cycle and Impact on Carbon Fluxes* 61

12 6.4.7 *Future Changes in CH₄ Emissions*..... 65

13 6.4.8 *How Future Trends in Other Biogeochemical Cycles Will Affect the Carbon Cycle*..... 68

14 6.4.9 *The Long Term Carbon Cycle and Commitments*..... 70

15 **6.5 Potential Effects of Carbon Dioxide Removal Methods and Solar Radiation Management on the**

16 **Carbon Cycle** **70**

17 6.5.1 *Introduction to Carbon Dioxide Removal Methods*..... 70

18 6.5.2 *Carbon Cycle Processes Involved in CDR Methods*..... 73

19 6.5.3. *Impacts of CDR Methods on Carbon Cycle and Climate* 76

20 6.5.4 *Impacts of Solar Radiation Management on Carbon Cycle* 78

21 **FAQ 6.1: What Happens to Carbon Dioxide After it is Emitted into the Atmosphere?** **79**

22 **FAQ 6.2: Could Rapid Release of Methane and Carbon Dioxide from Thawing Permafrost or Ocean**

23 **Warming Substantially Increase Warming?** **80**

24 **References**..... **83**

25 **Tables**..... **109**

26 **Figures** **116**

27

28

Executive Summary

This chapter focuses on the biogeochemical cycles of carbon dioxide, methane, and nitrous oxide, which are perturbed by human activities. The three most influential greenhouse gases are carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O), since they altogether amount to 80% of the total radiative forcing from long-lived greenhouse gases. With a *very high level of confidence*, the concentration increase of these greenhouse gases in the atmosphere is caused by anthropogenic emissions, and modulated by natural biogeochemical processes [6.1].

During the past 800,000 years, atmospheric CO₂ varied by 50–100 ppm between glacial (cold) and interglacial (warm) periods. This is well established from multiple ice core measurements. There is a high confidence that those variations in atmospheric CO₂ were caused primarily by changes in ocean carbon storage. It is *very likely* that carbon storage in the ocean decreased from glacial to interglacial periods, resulting from increased ocean mixing, decreased marine biological productivity caused by changes in atmospheric iron deposition, and increased carbonate formation. In parallel, it is *very likely* that carbon storage on land increased from glacial to inter-glacial, in part compensating the effect of ocean carbon changes on atmospheric CO₂. Uncertainties in reconstructing glacial conditions and deficiencies in understanding the partitioning of carbon between surface and deep ocean waters prevent an unambiguous interpretation of the variations of CO₂ between glacial and interglacial periods [6.2; Figure 6.5].

During the present interglacial period, the Holocene (circa 7000 BP to year 1750), atmospheric CO₂ increased continuously by 20 ppm. Although the *confidence in underlying processes is medium*, **the contribution of CO₂ emissions from early anthropogenic land use is unlikely sufficient to explain the CO₂ increase during the Holocene.** Atmospheric CH₄ levels rose between 4 ka and year 1750 by about 100 ppb [Figure 6.6]. *About as likely as not*, early anthropogenic land use significantly contributed to this increase. Causes for variability of CO₂ during the last millennium, especially for the decrease by 5 to 8 ppm around year 1600, have not yet been firmly established. Climatic and anthropogenic forcing are proposed to explain variability in the atmospheric CH₄ during the last millennium, such as the decrease in the late 16th century by about 40 ppb, but the *confidence in these mechanisms is low* [6.2; Figure 6.7].

Changes in atmospheric CO₂ since the beginning of the Industrial Era (1750) have been dominated by anthropogenic influence. CO₂ emissions from fossil fuel combustion and cement production estimated from energy statistics have released 365 ± 30 PgC to the atmosphere, while human land use change activities (mainly deforestation) are estimated to have released 180 ± 80 PgC. Of these 545 ± 85 PgC, only 240 ± 10 PgC have accumulated in the atmosphere as CO₂. This historical increase of CO₂ from 278 ± 5 ppm in 1750 to 390 ppm in 2011, is known with very high accuracy from ice core and atmospheric station measurements. The remaining amount of carbon released by fossil fuel and land use change emissions since 1750 has been absorbed by the ocean and by terrestrial ecosystems. Ocean measurements and models consistently indicate that the ocean carbon reservoir has increased in storage with a *very high level of confidence* and this increased is estimated to be of 155 ± 30 PgC. Natural terrestrial ecosystems (those not affected by land use change) are estimated by difference from changes in other reservoirs to have accumulated 150 ± 90 PgC. The gain of carbon by natural terrestrial ecosystems is *likely* to take place mainly through the uptake of CO₂ by enhanced photosynthesis at higher CO₂ levels and N deposition and longer growing seasons in high latitudes, and the regrowth of temperate forests. These processes vary regionally [6.3; Table 6.1; Figure 6.8].

During the most recent decade (2002–2011), CO₂ emissions from fossil fuel combustion and cement production were 8.3 ± 0.7 PgC yr⁻¹, and reached 9.4 ± 0.8 PgC in 2012 – 53% above 1990 levels. The growth rate in these emissions was 2.9% yr⁻¹ compared to 1.0% yr⁻¹ during 1990–1999 as reported by the IPCC Fourth Assessment Report. CO₂ emissions from land use change were 0.9 ± 0.8 PgC yr⁻¹ on average during 2002–2011. This estimate includes gross deforestation emissions of around 3 PgC yr⁻¹ compensated by 2 PgC yr⁻¹ of forest regrowth in some regions; mainly abandoned agricultural land. It is *more likely than not* that land use change emissions decreased since 2000 compared to the 1990s due to decreases in regional tropical deforestation rates. During 2002–2011, atmospheric CO₂ concentration increased at a rate of 2.0 ± 0.1 ppm yr⁻¹ (equivalent to 4.3 ± 0.2 PgC yr⁻¹); the ocean and the natural terrestrial ecosystems also increased at a rate of 2.4 ± 0.7 PgC yr⁻¹ and 2.5 ± 1.3 PgC yr⁻¹, respectively. It is *likely* that recent changes in temperature, surface winds and ocean circulation have affected the regional carbon uptake by the ocean in the past 20 years over the North Atlantic, Southern Ocean and equatorial Pacific, together these processes

1 reduce ocean uptake by $0.2 \pm 0.2 \text{ PgC yr}^{-1}$, partly compensating the growth in global ocean uptake of $0.3 \pm$
2 0.1 PgC yr^{-1} that driven by the increase in atmospheric CO_2 alone [6.3; Table 6.1; Table 6.2; Figure 6.8;
3 Figure 6.10]. It is *likely* that the global CO_2 sink in natural terrestrial ecosystems remained approximately the
4 same between 2002 and 2011 ($2.5 \pm 1.3 \text{ PgC yr}^{-1}$) and the 1990s ($-2.6 \pm 1.2 \text{ PgC yr}^{-1}$) [6.3; Table 6.1]

5
6 **Atmospheric CH_4 has been multiplied by a factor 2.5 since 1750, reaching 1794 ppb in 2010, mostly in**
7 **response to of increasing anthropogenic emissions.** The methane budget is $177\text{--}284 \text{ Tg}(\text{CH}_4)\text{yr}^{-1}$ for
8 natural wetlands emissions, $195\text{--}263 \text{ Tg}(\text{CH}_4)\text{yr}^{-1}$ for agriculture (rice and animals), $85\text{--}116 \text{ Tg}(\text{CH}_4)\text{yr}^{-1}$ for
9 fossil related emissions, $46\text{--}185 \text{ Tg}(\text{CH}_4)\text{yr}^{-1}$ for other natural emissions including geological emissions, and
10 $16\text{--}20 \text{ Tg}(\text{CH}_4)\text{yr}^{-1}$ for biomass burning. Uncertainties in estimates of major emission sources have been
11 reduced since the AR4 although they remain significant. By including natural geological sources not
12 accounted for in previous budgets, the fossil component of the total CH_4 emissions (both anthropogenic and
13 natural) has been re-evaluated as up to 30% of the total CH_4 emissions. Natural wetlands and biomass
14 burning emissions are confirmed to be the main drivers of global inter-annual variability of CH_4 emissions,
15 and a more consistent quantification of the magnitude of inter-annual variability of the chemical sink
16 compared to previous budgets has been established. However, the causes of the methane concentration
17 stabilization in the early 2000s are still debated, as those of the observed recent increase of methane
18 concentrations since 2007.

19
20 Global emissions of N_2O are difficult to estimate, but global and regional budgets are constrained by inverse
21 modelling studies. **During the 2000s, food production is *likely* responsible for 80% of the increase in**
22 **atmospheric N_2O .** The long atmospheric lifetime of N_2O implies that it will take decades before abundances
23 stabilize even if global emissions are reduced. This is of concern not only because of its contribution to the
24 global radiative forcing, but also because N_2O is currently the dominant ozone depleting substance.

25
26 **The availability of nitrogen for plant growth will *likely* limit 21st century land carbon uptake resulting**
27 **in higher atmospheric CO_2 concentration.** A key update since AR4 is the introduction of nutrient
28 dynamics in some land carbon models, in particular the limitations imposed by nitrogen availability. Models
29 including the nitrogen cycle predict a that the future uptake of anthropogenic CO_2 by land ecosystems is *very*
30 *likely* to be less than when no nitrogen limitation is modeled. These models also predict that this limitation
31 effect is partly offset by nitrogen supplied by atmospheric deposition, and increased soil nitrogen availability
32 due to warming. In all cases, the net effect is a smaller predicted land sink for a given trajectory of
33 anthropogenic CO_2 emissions. CMIP5 models that neglect nitrogen cycle interactions project excessive land
34 carbon uptake by 2100 by up to 400 PgC [6.4.6, Figure 6.36].

35
36 **Projections of the global carbon cycle to 2100 using so called ‘CMIP5 Earth System Models’ that**
37 **represent a wider range of complex interactions between the carbon cycle and the physical climate**
38 **system, consistently estimate a positive feedback between climate and the carbon cycle, i.e., reduced**
39 **natural sinks or increased natural CO_2 sources in response to future climate change,** like in the
40 previous AR4 coupled carbon climate simulation results. According to CMIP5 model results it is *very likely*
41 that the global ocean will continue as a net carbon sink for all 4 RCP concentration scenarios. For scenarios
42 with decreasing areas of anthropogenic land use (RCP4.5, 6.0), it is *very likely* global land will continue as a
43 net carbon sink. For scenarios with increasing areas of land use (RCP2.6, 8.5), a net land sink remains *likely*
44 but some models project a source by 2100. CMIP5 models predict that carbon sinks in tropical land
45 ecosystems are *very likely* to decrease because of climate change. CMIP5 model projections of ocean carbon
46 uptake show less spread in response to CO_2 and climate than the previous C4MIP generation of models, but
47 there is still significant model spread (4–5 times greater than ocean carbon) in future land carbon storage.
48 Future land use change, and the response of terrestrial ecosystems to it, is an important driver of future
49 terrestrial carbon cycle and contributes significant additional spread to model estimates [6.4; Figure 6.19,
50 Figure 6.20, Figure 6.21, Figure 6.22; Figure 6.24].

51
52 **The combined effect of all processes on future ocean and land carbon uptake allows us to quantify the**
53 **trajectory of fossil fuel emissions compatible with the RCP future CO_2 concentration pathway**
54 **scenarios.** For RCP2.6 all CMIP5 models project large reductions in emissions relative to present day levels.
55 It is about as *likely as not* that sustained globally negative emissions will be required to achieve the
56 reductions in atmospheric CO_2 in this scenario. CMIP5 models are generally consistent with RCP scenario
57 emissions except for RCP8.5 where the CMIP5 Earth System models project lower natural carbon uptake

1 and lower compatible emissions than in this RCP scenario. This difference would be greater if nitrogen
2 limitation on land carbon uptake was included in more of the CMIP5 models [6.4, Figure 6.25, Figure 6.26].
3

4 **With a very high level of confidence, the increased storage of carbon by the ocean will increase**
5 **acidification in the future, continuing the observed trends of the past decades. Ocean carbon cycle**
6 **models consistently project continued ocean acidification worldwide at high latitudes to 2100 for all**
7 **RCP pathways.** The largest decrease in pH and surface carbonate ion (CO_3^{2-}) is projected to occur in the
8 warmer low and mid-latitudes. However, it is the colder high-latitude oceans that are projected to first
9 become undersaturated with respect to aragonite. Aragonite undersaturation in surface waters is *likely* to be
10 reached by 2100 in the Southern Ocean as highlighted in AR4, but new studies project that undersaturation
11 will even *likely* occur before 2100 in the Arctic [6.4; Box 6.5, Figure 6.28].
12

13 **Regarding the ocean loss of dissolved oxygen (de-oxygenation), ocean carbon and oxygen models**
14 **suggest that it is likely that large decreases in oceanic dissolved oxygen will occur during the 21st**
15 **century, predominantly in the sub-surface mid-latitude oceans, due to enhanced stratification and**
16 **warming.** There is however no consensus on the future development of the volume of hypoxic and suboxic
17 waters because of large uncertainties in potential biogeochemical effects and in the evolution of tropical
18 ocean dynamics.
19

20 **With a very high level of confidence, ocean and land ecosystems will continue to respond to climate**
21 **change and atmospheric CO₂ increases created during the 21st century, even for centuries after any**
22 **stabilization of CO₂ and climate.** Ocean acidification will continue in the future as long as atmospheric
23 CO₂ concentrations remain higher than average ocean CO₂ partial pressure. The so called *committed* land
24 ecosystem carbon cycle changes, i.e., induced changes in CO₂ sources and sinks, will manifest themselves
25 further beyond the end of the 21st century. In addition, there is *medium confidence* that large areas of
26 permafrost will experience thawing, but uncertainty over the magnitude of frozen carbon losses through CO₂
27 or CH₄ emissions to the atmosphere are large, although most of AR5 model results produce significantly
28 increased CO₂ emissions by the end of the 21st century. Future methane emissions from natural sources are
29 *very likely* to be affected by climate change, but there is limited confidence in quantitative projections of
30 these changes. Models and ecosystem warming experiments show agreement that per unit area of wetland
31 CH₄ emissions will increase in a warmer climate, but wetland areal extent may increase or decrease
32 depending on regional climate-induced changes in wetland hydrology. Estimates of the future release of CH₄
33 from gas hydrates in response to seafloor warming are poorly understood, and might possibly lead to
34 significant release from the sea floor by the end of the 21st century but subsequent emissions to the
35 atmosphere are likely to remain low due to oxidation of hydrate emitted CH₄ in the water column and slow
36 propagation of warming to the seafloor.
37

38 **This chapter was termed to assess the scientific consequences for so called human induced ‘Carbon**
39 **Dioxide Removal (CDR)’ that have been proposed to accelerate / augment the removal of CO₂ from**
40 **the atmosphere to reduce climate change.** These methods are based on human induced changes in natural
41 carbon cycle processes. [6.5, list in Table 6.15, FAQ 7.3 Figure 1] and were analysed only here for their
42 potential effects on the global carbon cycle. Scientific considerations for evaluating CDR methods include
43 storage capacity, the permanence of the storage, potential adverse side effects, and the so called ‘rebound
44 effect’: when carbon is removed from the atmosphere, the subsequent rate of removal of CO₂ from the
45 atmosphere by natural carbon cycle processes on land and oceans will be reduced.
46

47 **CDR schemes may not present a viable option to rapidly affect climate on decadal and centennial time**
48 **scales because of the long time required by relevant natural carbon cycle processes to remove**
49 **atmospheric CO₂. Currently, the maximum physical potential of atmospheric CO₂ removal by any**
50 **single CDR scheme that rely on natural carbon cycle processes is at most about 1 PgC yr⁻¹.** However,
51 CDR based on land use options may not be achievable in the real world because of other constraints, such as
52 competing demands for land. The level of scientific knowledge on the effectiveness of CDR methods, their
53 side effects on climate, and their potential effects on carbon and other biogeochemical cycles, including
54 ocean acidification and de-oxygenation, is low and uncertainties are very large [6.5, Figure 6.40, Figure 6.41,
55 Table 6.16].
56

1 **So called ‘Solar Radiation Manipulation (SRM)’ are addressed in Chapter 7, and were only analysed**
2 **in this Chapter for their potential effects on carbon cycling. SRM methods are *likely* to impact the**
3 **carbon cycle through their climate effects, SRM proposals might counter the global-average radiative**
4 **effects of CO₂ but they will leave the direct ‘fertilization’ effects of CO₂ on natural ecosystems on land (e.g.,**
5 **enhanced plant productivity and reduced plant transpiration) and in oceans including ocean acidification.**
6

6.1 Introduction

The radiative properties of the atmosphere are strongly influenced not only by the natural water vapour, but also by the abundance of long-lived greenhouse gases, including carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O). The concentrations of these gases have substantially increased over the last 200 years caused primarily by anthropogenic emissions (see Chapter 2). Long-lived greenhouse gases represent the atmospheric phase of the natural global biogeochemical cycles, which describe the flows and transformations of the major elements between the different components of the Earth System (atmosphere, ocean, land, lithosphere) by physical, chemical, biological and geological processes. Since these processes are themselves also dependent on the prevailing climate, feedbacks induced by climate changes can also modify the concentrations of CO₂, CH₄ and N₂O, e.g., during the glacial-interglacial cycles (see Chapter 5) but also in the next century (see Chapter 12).

This chapter summarizes the scientific understanding of budgets, variability and trends of the three major biogeochemical trace gases, CO₂, CH₄ and N₂O, their underlying major source and sink processes and their perturbations caused by past and present climate changes and direct human impacts. After the introduction (Section 6.1), Section 6.2 assesses the present understanding of the mechanisms responsible for the variations of CO₂, CH₄ and N₂O in the past emphasizing glacial-interglacial changes, variations during the Holocene since the last glaciation and their variability over the last millennium. Section 6.3 focuses on the fossil fuel era since 1750 addressing the major source and sink processes, and their variability in space and time. This information is then used to evaluate critically the simulation models of the biogeochemical cycles, including their sensitivity to changes in atmospheric composition and climate. Section 6.4 assesses future projections of carbon and other biogeochemical cycles computed with off-line and coupled climate-carbon cycle models. This includes a quantitative assessment of the direction and magnitude of the various feedback mechanisms as represented in current models, as well as additional processes that might become important in the future but which are not yet fully described in current biogeochemical models. Finally, Section 6.5 addresses the effects of deliberate carbon dioxide removal methods and solar radiation management on the carbon cycle.

6.1.1 Global Carbon Cycle Overview

6.1.1.1 CO₂ Cycle

Atmospheric CO₂ represents the atmospheric phase of the global carbon cycle. The global carbon cycle can be viewed as a series of reservoirs of carbon in the Earth System, which are connected by exchange fluxes of carbon. One can principally distinguish two domains in the global carbon cycle. (1) A fast domain with large exchange fluxes and relatively rapid reservoir turnovers, which consists of carbon in the atmosphere, the ocean and on land carbon in living vegetation, soils, and freshwaters. Reservoir turnover times, defined as reservoir mass of carbon divided by the exchange flux, range from a few years for the atmosphere, to decades-millennia for the major carbon reservoirs of the land vegetation and soil and the various domains in the ocean. (2) A second, slow domain consists of the huge carbon stores in rocks and sediments, which exchange carbon with the fast domain through volcanic emissions of CO₂, weathering, erosion and sediment formation on the sea floor (Sundquist, 1986). Geological turnover times of the reservoirs of the slow domain are 10,000 years or longer. On time scales of the anthropogenic interference with the global carbon cycle, the slow domain can be assumed to be at steady state. Natural exchange fluxes between the slow and the fast domain of the carbon cycle are relatively small (<0.3 PgC yr⁻¹) and can be assumed as approximately constant in time (volcanism, sedimentation), although erosion and river fluxes may have been modified by human induced changes in land use (Raymond and Cole, 2003).

During the Holocene prior to the Industrial Era (starting in 1750) the fast domain was close to steady state as witnessed by the relatively small variations of atmospheric CO₂ recorded in ice cores (see Section 6.2). By contrast, since the beginning of the Industrial Era, fossil fuel extraction from geological reservoirs, and their combustion has resulted in the transfer of significant amount of fossil carbon from the slow domain into the fast domain, thus causing an unprecedented and major human induced perturbation in the carbon cycle. A schematic of the global carbon cycle with focus on the fast domain is shown in Figure 6.1. The numbers represent the estimated current pool sizes in PgC (1 PgC = 10¹⁵ g C) and the magnitude of the different main exchange fluxes in PgC yr⁻¹ averaged over the time period 2000–2009.

[INSERT FIGURE 6.1 HERE]

Figure 6.1: Simplified schematic of the global carbon cycle. Numbers represent reservoir sizes (in PgC), and carbon exchange fluxes (in PgC yr⁻¹). Dotted arrow lines denote carbon fluxes between the fast and the slow carbon cycle domain (see text). Darkblue numbers and arrows indicate reservoir sizes and natural exchange fluxes estimated for the time prior to the Industrial Era. Red arrows and numbers indicate fluxes averaged over 2000–2009 time period resulting from the emissions of CO₂ from fossil fuel combustion, cement production, and changes in land use, and their partitioning among atmosphere, ocean and terrestrial reservoirs (see Section 6.3). Red numbers in the reservoirs denote cumulative changes over the Industrial Period 1750–2011.

In the atmosphere, CO₂ is the dominant carbon bearing trace gas with a current concentration of approximately 390 ppm (January 2011), which corresponds to a mass of 828 PgC. Additional trace gases include methane (CH₄, current content mass ~3.8 Pg C) and carbon monoxide (CO, current content mass ~2 PgC), and still smaller amounts of hydrocarbons, black carbon aerosols, and organic compounds.

The terrestrial biosphere reservoir contains carbon in organic compounds in vegetation living biomass (450–650 PgC; Prentice et al., 2001) and in dead organic matter in litter and soils (1500–2400 PgC; Batjes, 1996), with an additional amount of old soil carbon in wetland soils (200–450 PgC) and in permafrost soils (~1670 PgC; Tarnocai et al., 2009). CO₂ is removed from the atmosphere by plant photosynthesis (123 ± 8 PgC yr⁻¹; Beer et al., 2010), and carbon is then cycled through plant tissues, litter and soil carbon and released back into the atmosphere by autotrophic (plant) and heterotrophic (soil microbial) respiration and additional disturbance processes (e.g., sporadic fires) on a very wide range of time scales (seconds to millennia). The imbalance of CO₂ uptake by photosynthesis during the growing season with the near year-round CO₂ release by respiration in the northern hemisphere causes the characteristic sawtooth seasonal cycle observed in atmospheric CO₂ measurements (see Figure 6.3). A small amount of terrestrial carbon is transported from soils to the coastal ocean via freshwaters and rivers (~0.8 PgC yr⁻¹), under the form of dissolved inorganic carbon, dissolved and particulate organic carbon.

The oceanic carbon reservoir (~38,000 PgC) contains predominantly Dissolved Inorganic Carbon (DIC): carbonic acid (dissolved CO₂ with water), bicarbonate (dominant form) and carbonate ions, which are tightly coupled via ocean chemistry. In addition, the ocean contains Dissolved Organic Carbon (DOC, ~662 PgC; Hansell et al., 2009), of which a major fraction is very rapidly recycled. Marine organisms, phytoplankton and other microorganisms, represent a small carbon pool (~3 PgC), which is turned over very rapidly in days to a few weeks. Photosynthesis by phytoplankton in the ocean surface layer removes dissolved CO₂, which is subsequently cycled through the marine food chain and finally respired back to DIC by microbes through heterotrophic respiration processes. After death of the organisms, some of the organic carbon that they contain sinks to deeper waters where it is remineralized to inorganic carbon. This process creates and maintains a natural negative concentration gradient of DIC between the surface ocean and the deeper waters. Deeper waters are therefore supersaturated with carbon and release this in the form of CO₂ back to the atmosphere where these deeper waters outcrop to the atmosphere in upwelling, whereas on annual average CO₂ is removed from the atmosphere elsewhere in surface waters by marine organisms photosynthesis. This natural branch of the ocean carbon cycle is termed the ‘marine biological soft-tissue pump’. It is limited primarily by radiation and the prevailing nutrients (phosphate, nitrate and additional micronutrients e.g., iron and manganese). A second natural branch of the oceanic carbon cycle, the ‘marine carbonate pump’ is generated by the formation of calcareous shells of certain oceanic microorganisms in the surface ocean which, after sinking to depth are mostly dissolved and transformed back into DIC and calcium ions. Paradoxically, this marine carbonate pump operates counter to the marine biological pump: in the formation of calcareous shells, bicarbonate ions are split into carbonate ions and dissolved CO₂ with increases dissolved CO₂ in surface waters, while the reverse takes place during shell dissolution at depth. Only a small fraction (~0.2 PgC yr⁻¹) of the carbon exported by biological processes (both soft-tissue and carbonate pumps) from the surface reaches the sea floor and is stored in sediments for millennia and longer. A third natural branch of the oceanic carbon cycle exists due to higher solubility of CO₂ in colder waters. This ‘solubility pump’ pumps CO₂ from the atmosphere into the ocean in colder surface waters and releases CO₂ back to the atmosphere in warmer surface waters, and this process is coupled to the ocean general circulation.

6.1.1.2 CH₄ Cycle

1 Methane is a very important gas, because of the stronger radiative properties per molecule of CH₄ compared
2 to CO₂ (Chapter 8), its interactions with photochemistry. The global biogeochemical cycle of atmospheric
3 methane (CH₄) is a short ‘sub-cycle’ of the global carbon cycle, as methane turnover time is less than 10
4 years in the troposphere. The sources of CH₄ at the surface of the Earth can be thermogenic, including (1)
5 natural emissions of fossil CH₄ from geological sources (marine and terrestrial seepages, geothermal vents
6 and mud volcanoes), and (2) emissions caused by leakages from fossil fuel extraction and use (natural gas,
7 coal and oil industry; Figure 6.2). A second category of CH₄ sources consists in pyrogenic sources including
8 natural fires and incomplete burning of fossil fuels and biomass. A third category of CH₄ sources consists of
9 biogenic sources including natural biogenic emissions from wetlands, by far the largest natural source, and
10 by termites as well, with a small ocean source, and the anthropogenic biogenic emissions from rice paddy
11 agriculture, ruminants, landfills, man-made lakes and wetlands and waste treatment. In general, biogenic
12 CH₄ is produced from organic matter under low oxygen conditions by fermentation processes of
13 methanogenic microbes (Conrad, 1996). As compared to the AR4 assessment report, a new and large CH₄
14 source from plants under aerobic conditions has been hypothesized (Keppler et al., 2006), which, however,
15 has not been confirmed in subsequent studies (e.g., Dueck et al., 2007; Nisbet et al., 2009). CH₄ is primarily
16 removed from the atmosphere by photochemistry, through atmospheric chemistry reactions with the OH
17 radical to CO and subsequently to CO₂. Other smaller removal processes of atmospheric CH₄ take place in
18 the stratosphere through reaction with chlorine and oxygen radicals, at the surface by oxidation in well
19 aerated soils, and possibly by reaction with chlorine in the marine boundary layer (Allan et al., 2007).

21 [INSERT FIGURE 6.2 HERE]

22 **Figure 6.2:** Schematic of the global cycle of CH₄. Numbers represent fluxes in Tg(CH₄) yr⁻¹ estimated for the time
23 period 2000–2009 (see Section 6.3). Green arrows denote natural fluxes, red arrows anthropogenic fluxes, and orange
24 arrow denotes a combined natural+anthropogenic flux.

26 A very large geological pool, (1500–7000 PgC; Archer, 2007; with low confidence) of CH₄ exists in the
27 form of frozen hydrate deposits in permafrost soils, shallow Arctic ocean sediments and on the slopes of
28 continental shelves. These CH₄ hydrates are stable under conditions of low temperature and high pressure.
29 Warming or changes in pressure, e.g., due to lowering sea level could render some of these hydrates unstable
30 with a potential release of CH₄ to the overlying ocean and/or atmosphere.

32 6.1.2 Industrial Era

34 6.1.2.1 CO₂ Cycle

36 Since the beginning of the Industrial Era defined as 1750 in this chapter, human activities have been
37 producing energy by burning of fossil fuels (coal, oil and gas), a process which is releasing large amounts of
38 carbon dioxide into the atmosphere (Boden et al., 2011; Rotty, 1983). The amount of fossil fuel CO₂ emitted
39 to the atmosphere can be estimated with an accuracy of about 5% for recent decades from statistics of fossil
40 fuel use (Andres et al., 2012). Estimates of fossil fuel CO₂ emissions for the period prior to 1950 are less
41 certain (Rotty, 1983). Total cumulative emissions between 1750 and 2011 amount to 365 ± 30 PgC (see
42 Section 6.3 and Table 6.1), including a contribution of 8 PgC from the production of cement.

44 The second major anthropogenic emission of CO₂ to the atmosphere is caused by changes in land use and
45 land management, which cause a net reduction in land carbon storage. In particular deforestation for
46 procurement of land for agricultural or pasture is associated with a loss of terrestrial carbon. Estimation of
47 this CO₂ source to the atmosphere requires knowledge of changes in land area as well as estimates of the
48 carbon stored per area before and after the land use change transition. In addition, longer term effects, such
49 as the decomposition soil organic matter after land use change, have to be taken into account as well. Since
50 1750, anthropogenic land use changes have been important: currently an area of about 43 million km² is used
51 for cropland and pasture, corresponding to about 35% of the total ice-free land area (Foley et al., 2007) in
52 contrast to an estimated cropland and pasture area of 7.5–9 million km² in the 18th century (Goldewijk,
53 2001; Ramankutty and Foley, 1999). The net CO₂ emissions from land use changes between 1750 and 2011
54 are estimated at approximately 180 ± 80 PgC (see Section 6.3 and Table 6.1).

56 The almost exponentially increasing anthropogenic CO₂ emissions from fossil fuel burning and land use
57 change are the cause of the observed increase in atmospheric CO₂. Several lines of evidence support this

1 conclusion beyond the fact that the rate of CO₂ emissions from fossil fuel burning and land use change is
2 about twice the rate of atmospheric CO₂ increase:

- 3 • Since most of the fossil fuel CO₂ emissions take place in the industrialized countries north of the equator,
4 on annual average, atmospheric CO₂ measurement stations in the Northern Hemisphere record slightly
5 higher CO₂ concentrations than stations in the Southern Hemisphere, as witnessed by the observations
6 from Mauna Loa, Hawaii, and the South Pole (Figure 6.3). The annually averaged concentration
7 difference between the two stations follows extremely well the estimated difference in emissions between
8 the hemispheres (Fan et al., 1999; Keeling et al., 1989; Tans et al., 1989).
- 9 • CO₂ from fossil fuels and from the land biosphere has a lower ¹³C/¹²C stable isotope ratio than the CO₂ in
10 the atmosphere, which induces a decreasing temporal trend in the atmospheric ¹³C/¹²C ratio of the CO₂
11 concentration as well as, on annual average, slightly lower ¹³C/¹²C values in the Northern Hemisphere
12 (Figure 6.3).
- 13 • Because fossil fuel CO₂ is devoid of radiocarbon (¹⁴C), reconstructions of the ¹⁴C/C isotopic ratio of
14 atmospheric CO₂ from tree rings show a declining trend (Levin et al., 2010; Stuiver and Quay, 1981)
15 prior to the massive addition of ¹⁴C in the atmosphere by nuclear weapon tests which has been offsetting
16 that declining trend signal.
- 17 • An additional indication of the anthropogenic influence on atmospheric CO₂ is provided by the observed
18 decrease in atmospheric O₂ content over the past two decades (see Figure 6.3 and Section 6.1.3.2).

20 [INSERT FIGURE 6.3 HERE]

21 **Figure 6.3:** Atmospheric concentration of CO₂, oxygen, ¹³C/¹²C stable isotope ratio in CO₂, CH₄ and N₂O recorded
22 over the last decades at representative stations in the northern (solid lines) and the southern (dashed lines) hemisphere.
23 (a: CO₂ from Mauna Loa and South Pole atmospheric stations (Keeling et al., 2005), O₂ from Alert and Cape Grim
24 stations (<http://scrippso2.ucsd.edu/> right axes), b: ¹³C/¹²C: Mauna Loa, South Pole (Keeling et al., 2005), c: CH₄ from
25 Mauna Loa and South Pole stations (Dlugokencky et al., 2010), d: N₂O from Adrigole and Cape Grim stations (Prinn et
26 al., 2000).

28 6.1.2.2 CH₄ Cycle

29
30 Throughout the Holocene before the Industrial Era, atmospheric CH₄ levels varied only moderately (up to 50
31 ppb) around 700 ppb, indicating a long term balance between natural emissions and sinks of atmospheric
32 CH₄ (see Section 6.2.3.2; MacFarling-Meure et al., 2006). After 1750, atmospheric CH₄ levels rose almost
33 exponentially, reaching 1650 ppb by the mid 1980s. Between the mid 1980s and the mid 2000s the
34 atmospheric growth of CH₄ has been declining to nearly zero. However, during the last few years
35 atmospheric CH₄ has been observed to increase again, although it is not clear if this recent trend reflects a
36 new imbalance between emissions and sinks or a short term variability episode (Dlugokencky et al., 2009).

37
38 There is very high level of confidence that the atmospheric CH₄ increase during the Industrial Era is being
39 caused by anthropogenic activities. The massive expansion of the number ruminants, the emissions from
40 fossil fuel extraction and use, emissions from landfills and waste, as well as the expansion of rice paddy
41 agriculture are the dominant anthropogenic CH₄ sources. Total anthropogenic sources contribute at present
42 between 45 and 65% of the total CH₄ sources. The fraction of fossil fuel to the total emission, fossil being
43 the sum of both natural geological fossil emissions and anthropogenic fossil fuel emissions, has since AR4
44 been revised upwards to be 30% based on measurements of ¹⁴C in atmospheric CH₄ and on detailed surveys
45 of geological sources (Etiope et al., 2008; Lassey et al., 2007; Wahlen et al., 1989). The history of fossil fuel
46 CH₄ emissions has also been constrained indirectly from ice core measurements of ethane (C₂H₆), which is
47 co-emitted with fossil fuel CH₄ (Aydin et al., 2011). The dominance of anthropogenic CH₄ emissions in the
48 Northern Hemisphere is evidenced furthermore by the observed north-south gradient in CH₄ concentrations
49 (Figure 6.3), although this atmospheric signal contains also a contribution from the natural wetland
50 emissions located in the Northern Hemisphere. Satellite based CH₄ concentration measurements averaged
51 over the entire atmospheric column also indicate higher concentrations of CH₄ above and downwind of
52 densely populated and intensive agriculture areas where anthropogenic emissions occur REF.

54 6.1.3 Connections Between Carbon and Other Biogeochemical Cycles

56 6.1.3.1 Global Nitrogen Cycle including N₂O

1 The biogeochemical cycles of nitrogen and carbon are tightly coupled with each other due to metabolic
2 needs of organisms. Changes in the availability of one element will influence not only biological
3 productivity but also influence the availability of the other element (Gruber and Galloway, 2008) and in the
4 longer term, the structure and function of ecosystems as well.

5
6 Before the Industrial Era, creation of reactive nitrogen Nr (all nitrogen species other than N₂) from non-
7 reactive atmospheric N₂ occurred primarily through two processes, lightning and biological nitrogen fixation
8 (BNF). This input of Nr to the land and ocean biosphere was in balance at steady state with the loss of Nr
9 though the denitrification process, returning N₂ back to the atmosphere (Ayres et al., 1994). This is no longer
10 the case. Nr is produced by human activities and delivered to ecosystems at local, regional, and global scales.
11 During the last decades, production of Nr by humans has been much greater than the natural production
12 (Galloway et al., 1995). There are three main anthropogenic sources of Nr: (1) the widespread cultivation of
13 legumes, and other crops that convert N₂ to Nr in organic compounds through BNF; (2) the combustion of
14 fossil fuels, which converts atmospheric N₂ and fossil fuel N to nitrogen oxides (NO_x); and (3) the Haber-
15 Bosch industrial process, employed massively to produce NH₃ from N₂ for N-fertilizers and for NH₃ as a
16 feedstock for some industrial activities. In addition, mobilization of sequestered nitrogen from soils due to
17 disturbance is also a potential source (Morford et al., 2011).

18
19 Anthropogenic sources of Nr over land exceed the magnitude of natural sources by at least of factor of two
20 (Figure 6.4; Galloway et al., 2008) and perhaps more (Vitousek et al., *subm.*). The amount of anthropogenic
21 Nr that is converted back to non-reactive N₂ is uncertain, with current estimates being of about 30–50% of
22 the total source (Canfield et al., 2010; Galloway et al., 2004). The emission of Nr to the atmosphere by NH₃
23 and NO_x emissions is driven by agriculture and fossil fuel combustion, respectively. There is a net transfer of
24 N_r from the continental atmosphere into the marine atmosphere by large-scale atmospheric transport,
25 resulting in subsequent Nr deposition over the ocean. This Nr atmospheric deposition flux is greater than the
26 Nr flux from riverine discharge to the coastal ocean (Galloway et al., 2004). The connection between the
27 nitrogen and carbon cycles are discussed in Box 6.1.

28 29 [INSERT FIGURE 6.4 HERE]

30 **Figure 6.4:** Global nitrogen cycle. The upper panel (A) shows natural and anthropogenic process that create reactive
31 nitrogen Nr. The middle panel (B) shows the flows of reactive Nitrogen species. The bottom panel (C) shows a
32 schematic of the global cycle of N₂O. Blue arrows are natural, red arrows anthropogenic fluxes, and yellow arrows
33 represent fluxes with an anthropogenic and natural component. Units: TgN yr⁻¹.

34 35 [START BOX 6.1 HERE]

36 37 **Box 6.1: Nitrogen Cycle and Nitrogen Carbon Cycle Feedbacks**

38
39 In the period preceding human agriculture, the total amount of Nr that was cycling naturally among various
40 compartments of the atmosphere and the biosphere was quite small. The biodiversity and intricate webs of
41 relationships found in nature are thought to have evolved as a result of intensive competition among many
42 different life forms, many of them evolving under N-limited conditions (Vitousek et al., *subm.*). Following
43 the discovery of N as an element, of microbial processes that transform Nr from one species to another
44 biological nitrogen fixation, nitrification, denitrification), and of the importance of Nr as a nutrient for
45 sustaining plant productivity, the discovery of the Haber-Bosch process (synthesis of NH₃ from N₂) marked
46 the onset of large scale human interference with the nitrogen cycle. Currently, human creation of Nr (Haber-
47 Bosch process, fossil fuel combustion, agricultural biological nitrogen fixation) is dominating Nr creation
48 relative to biological nitrogen fixation in natural ecosystems on a global basis. This dominance has profound
49 impacts on human health, ecosystem health and the radiation balance of the Earth.

50
51 The time-course of Nr production from 1850 to 2005 shows both the rate and magnitude of this change (Box
52 6.1, Figure 1). After mid-1970s, human production of Nr became more important than natural production.
53 Currently food production (mineral fertilizers, legumes) accounts for three-quarters of Nr created by humans,
54 with fossil fuel combustion and industrial uses accounting equally for the remainder.

55 56 [INSERT BOX 6.1, FIGURE 1 HERE]

1 **Box 6.1, Figure 1:** Reactive nitrogen (Nr) creation fluxes (in TgN yr⁻¹) from fossil fuel burning (green line),
2 cultivation-induced BNF, C-BNF (red line), Haber-Bosch process (blue line), and total creation (purple line). Source:
3 Galloway et al. (2003), Galloway et al. (2008).

4
5 Of all the questions that could be asked about this, the three most relevant questions regarding anthropogenic
6 perturbation of the N cycle with respect to global change are: 1) What is the fate of anthropogenic Nr? 2)
7 What are the impacts of the excess of Nr on humans and ecosystems? 3) What are the direct and indirect
8 effects of increased Nr on climate change?
9

10 With respect to its fate, Nr is released to the environment on various time scales: immediately for fuel
11 combustion, within about a year for human made N-fertilizers, and from immediately to years for industrial
12 sources depending on the use. Once released, Nr is transported, and transformed or stored. Large amounts of
13 Nr are injected into the atmosphere and to coastal systems (Figure 6.4). A portion of this flux (30–50%) is
14 converted back to N₂ but this amount is uncertain and is one of the most critical issues concerning the human
15 influence on the nitrogen cycle today.
16

17 The impacts of anthropogenic Nr production on climate and biogeochemistry can be both positive and
18 negative. Nr derived from the Haber-Bosch process is necessary to sustain global crop production. However,
19 most of the Nr created today by humans also enters non-agricultural environments, and impact tropospheric
20 ozone, tropospheric aerosol content, contributes to the acidification of the atmosphere, soils and fresh waters,
21 lead to fertilisation of productivity in forests, grasslands, coastal waters and open ocean and could lead to
22 reduction in biodiversity in terrestrial and aquatic ecosystems. Although outside the scope of this chapter, it
23 is worth noting that Nr induced increases in nitrogen oxides, aerosols, ozone, and nitrates in drinking water
24 have negative impacts on human health (Davidson, 2012; Galloway et al., 2008). A single Nr molecule can
25 contribute to several of these impacts as it cycles in sequence between atmospheric, terrestrial and
26 hydrologic systems. Returning Nr to the atmosphere as N₂ is critical to halt this ‘Nitrogen Cascade’
27 essentially once a molecule of N₂ is split and the nitrogen atoms become reactive (e.g., NH₃, NO_x), any given
28 nitrogen atom can contribute to all of the impacts noted above in sequence (Box 6.1, Figure 2). Because of
29 the Nitrogen Cascade, the creation of any molecule of Nr from N₂, at any location, has the potential to affect
30 climate, either directly or indirectly, as explained below. This potential exists until the Nr is converted back
31 to N₂.
32

33 [INSERT BOX 6.1, FIGURE 2 HERE]

34 **Box 6.1, Figure 2:** Illustration of the nitrogen cascade showing the sequential effects that a single atom of N can have
35 in various reservoirs after it has been converted from nonreactive N₂ to a reactive form (yellow arrows). Abbreviations:
36 NH₃, ammonia; NH_x, ammonia plus ammonium; NO₃⁻, nitrate; NO_x, nitrogen oxides; NO_y, NO_x and other combinations
37 of N and O (except N O); N₂O, nitrous oxide (after Galloway et al.; 2003).
38

39 The most important processes causing direct links between anthropogenic Nr and climate change include: (1)
40 N₂O emissions by soils and environments (e.g., groundwater) where Nr can accumulate, (2) formation of
41 tropospheric O₃ from anthropogenic NO_x, and (3) formation of nitrate aerosols. The first two processes have
42 warming effects; the third one can have a warming or a cooling effect. The most important processes causing
43 an indirect link between anthropogenic Nr and climate change include: (1) nitrogen dependent changes in
44 soil organic matter decomposition affecting heterotrophic respiration, (2) changes in marine and terrestrial
45 primary productivity, generally an increase, in response to Nr deposition, (3) changes in wetland CH₄
46 production and consumption due to Nr deposition, (4) changes in CH₄ emission by ruminants given more
47 feed produced by nitrogen fertilizers, (5) a reduction of terrestrial productivity in response to ozone
48 formation caused by Nr from NO_x, and (6) changes in the removal rate of CH₄ from the atmosphere by
49 atmospheric OH radical caused by O₃ and NO_x mediated anthropogenic Nr (Erisman et al., 2011).
50

51 [END BOX 6.1 HERE]

52 53 6.1.3.2 Oxygen Cycle

54
55 The cycle of atmospheric oxygen is tightly coupled with the global carbon cycle. The burning of fossil fuels
56 uses oxygen from the atmosphere in a tightly defined stoichiometric ratio depending on fuel carbon content.
57 As a consequence of the burning of fossil fuels, atmospheric O₂ levels have been observed to decrease
58 steadily over the last 20 years (Keeling and Shertz, 1992; Manning and Keeling, 2006). Compared to the

1 atmospheric oxygen content of 21% this decrease is very small, however, but it provides independent
2 evidence that the rise in CO₂ must be due to an oxidation process, i.e., fossil fuel combustion, and is not
3 caused by volcanic emissions or by outgassing of ocean dissolved O₂. The atmospheric oxygen
4 measurements furthermore also show the north-south concentration O₂ gradient (higher in the south in mirror
5 to the CO₂ north-south gradient) as expected from the stronger fossil fuel consumption in the Northern
6 Hemisphere (Keeling et al., 1996).

7
8 On land, during photosynthesis and respiration, O₂ and CO₂ are exchanged in rather tightly defined
9 stoichiometric ratios. However, with respect to exchanges with the ocean, O₂ behaves quite differently from
10 CO₂, since compared to the atmosphere only a small amount of O₂ is dissolved in the ocean whereas by
11 contrast the oceanic CO₂ content is much larger due to the carbonate chemistry. This different behaviour of
12 the two gases with respect to ocean exchange provides a powerful method to assess independently the
13 partitioning of the uptake of CO₂ by land and ocean (Manning and Keeling, 2006).

14 6.2 Variations in Carbon and Other Biogeochemical Cycles before the Fossil Fuel Era

15
16 Numerous mechanisms that were responsible for past changes in atmospheric CO₂, CH₄, N₂O related to
17 changes in carbon and other biogeochemical cycles changes will likely operate in the future climate as well.
18 Past archives of GHG and climate changes therefore provide useful knowledge, including constraints for
19 biogeochemical models applied for future projections in Section 6.4.

20 6.2.1 Glacial-Interglacial GHG Changes

21 6.2.1.1 Key Processes Contributing to the Low Glacial GHG Concentrations

22 6.2.1.1.1 Main glacial-interglacial CO₂ drivers

23
24 Ice cores recovered from the Antarctic ice cap reveal that the concentration of atmospheric CO₂ at the height
25 of the Last Glacial Maximum (LGM) around 20 thousand years ago (20 ka) was about one third lower than
26 during the subsequent interglacial (Holocene) period started around 11 ka ago (Delmas et al., 1980; Monnin
27 et al., 2001; Neftel et al., 1982). Longer (to 800 ka) records exhibit similar features, with CO₂ values of
28 ~180–200 ppm during glacial intervals (Petit et al., 1999). Prior to around 400 ka, interglacial CO₂ values
29 were 240–260 ppm rather than 270–290 ppm after that date (Luthi et al., 2008).

30
31 A variety of proxy reconstructions as well as diverse models of different complexity from conceptual to
32 complex Earth System Models (ESM) have been used to test hypotheses for the cause of lower LGM
33 atmospheric CO₂ concentrations. The ways in which the global carbon cycle operated at the LGM and its
34 relative implications for CO₂ can be broken down by individual drivers (Figure 6.5). It should be recognized
35 however that this breaking down is potentially misleading, as many of the component drivers shown in
36 Figure 6.5 may combine non-linearly (Bouttes et al., 2011). Only well-established individual drivers are
37 quantified (Figure 6.5), and discussed below.

38
39 *Reduced terrestrial carbon storage.* The $\delta^{13}\text{C}$ record of ocean waters as preserved in benthic foraminiferal
40 shells has been used to infer that terrestrial carbon storage was reduced in glacial times, thus playing against
41 recorded changes in atmospheric CO₂. Estimates of LGM land carbon storage deficit relative to pre-
42 industrial range from a few hundreds to 1000 PgC (e.g., Bird et al., 1996; Ciais et al., 2012). Dynamic
43 vegetation model simulations tend to favor values at the higher end (~800 PgC) (Kaplan et al., 2002; Otto et
44 al., 2002) and indicate a larger role for the physiological effects of low CO₂ on photosynthesis at the LGM
45 than that of climate-induced biome shifts (Prentice and Harrison, 2009).

46
47 *Lower ocean temperatures.* Reconstructions of sea-surface temperatures during the LGM suggest that the
48 global surface ocean was on average 3–5°C cooler compared to the Holocene. Because the solubility of CO₂
49 increases at colder temperature (Zeebe and Wolf-Gladrow, 2001), a colder glacial ocean will hold more
50 carbon. However, uncertainty in reconstructing the pattern of ocean temperature change, particularly in the
51 tropics (Archer et al., 2000; Waelbroeck et al., 2009), together with problems in transforming this pattern to
52 the resolution of (particularly box) models in light of the non-linear nature of the CO₂-temperature
53 relationship (Ridgwell, 2001), creates a ~24 ppm spread in estimates of changes in CO₂, although it can be
54 noted that most 3-D ocean GCM projections cluster more tightly.

1
2 *Lower global sea level, increased ocean salinity and alkalinity.* Changes in ocean volume also induces a well
3 understood effect on CO₂ solubility, given the fact that LGM sea level was about ~120 m lower than today.
4 This driver impacts the LGM ocean carbon cycle in three distinct ways. First, the resulting higher LGM
5 ocean surface salinity induces an increase in atmospheric CO₂ (Bopp et al., 2003). Second, total dissolved
6 inorganic carbon and alkalinity become more concentrated in equal proportions, which has the effect of
7 driving atmospheric CO₂ higher. Finally, decreasing the ambient hydrostatic pressure at the ocean floor with
8 a lowered sea level enhances the preservation of CaCO₃ in sediments and hence on the longer-term (~2–8
9 kyr; Archer et al., 2000; Ridgwell and Hargreaves, 2007) reduces alkalinity and acts to increase atmospheric
10 CO₂ during LGM.

11
12 *Ocean circulation.* Potential re-organization in global circulation during glacial periods that promoted the
13 retention of dissolved inorganic carbon in the deep ocean during the LGM has increasingly become the focus
14 of recent research on the glacial-interglacial CO₂ problem. That ocean circulation likely plays a key role in
15 low glacial period atmospheric CO₂ concentration is exemplified by the tight coupling observed between
16 reconstructed deep ocean temperatures and atmospheric CO₂ (Shackleton, 2000). Evidence from bore hole
17 sites (Adkins et al., 2002) and from surface ocean paleo-environmental data in polar regions (Jaccard et al.,
18 2005) show that the glacial ocean was highly stratified compared to interglacial conditions and may thus
19 have held a larger store of carbon during glacial times. Radiocarbon records from deep-sea corals (Burke and
20 Robinson, 2012), as well as δ¹³C ice core records (Schmitt et al., 2012) demonstrate the role of a deep and
21 stratified Southern Ocean in LGM carbon storage. However, conflicting hypotheses exist on the drivers of
22 increasing ocean stratification, e.g., northward shift and weakening of Southern Hemisphere westerly winds
23 (Toggweiler et al., 2006), reduced air-sea buoyancy fluxes (Watson and Garabato, 2006), or massive brine
24 rejections during sea ice formation (Bouttes et al., 2011). Ocean carbon cycle models have simulated a
25 circulation-induced effect on LGM CO₂ that can explain lower values than during interglacial by 3 ppm
26 (Bopp et al., 2003) to 57 ppm (Toggweiler, 1999).

27
28 *Aeolian iron fertilisation.* Both marine and terrestrial sediment records indicate higher rates of deposition of
29 dust and hence iron (Fe) supply at the LGM (Mahowald et al., 2006), implying a potential link between Fe
30 fertilisation of marine productivity and lower glacial CO₂ (Martin, 1990). However, despite the fact that
31 models generally employ similar reconstructions of glacial dust fluxes (i.e., Mahowald et al., 1999;
32 Mahowald et al., 2006), there is considerable disagreement among the ocean carbon cycle models in the
33 associated CO₂ change. Ocean General Circulation Models-based Fe cycle models tend to cluster at the
34 lower end of simulated CO₂ changes between glacial and interglacial (e.g., Archer et al., 2000; Bopp et al.,
35 2003), whereas box models (e.g., Watson et al., 2000) or intermediate complexity models (EMICs) (e.g.,
36 Brovkin et al., 2007) tend to produce CO₂ changes which are at the higher end (Parekh et al., 2008). An
37 alternative view comes from inferences drawn from the timing and magnitude of changes in dust and CO₂ in
38 ice cores (Rothlisberger et al., 2004), assigning a 20 ppm limit for the lowering of CO₂ during the LGM in
39 response to a Southern Ocean Fe fertilisation effect, and a 8 ppm limit for the same effect in the North
40 Pacific.

41
42 *Increased sea ice extent.* A long-standing hypothesis is of increased LGM sea ice cover acting as a barrier to
43 air-sea gas exchange and hence reducing the 'leakage' of CO₂ during winter months from the ocean to the
44 atmosphere during glacial periods (Broecker and Peng, 1986). However, concurrent changes in ocean
45 circulation and biological productivity complicate the estimation of the atmospheric CO₂ impact of increased
46 sea ice extent (Kurahashi-Nakamura et al., 2007). Excepting for the results of an idealized box model
47 (Stephens and Keeling, 2000), models are relatively consistent in projecting a small effect on maintaining
48 atmospheric CO₂ lower during LGM, due to increased sea ice extent.

49
50 *Other glacial CO₂ drivers.* A number of further aspects of altered climate and biogeochemistry at the LGM
51 are also likely to have affected atmospheric CO₂. Reduced bacterial metabolic rates/remineralization depth of
52 organic matter (Matsumoto, 2007; Menviel et al., *subm.*), increased glacial supply of dissolved Si (required
53 by diatoms to form frustules) (Harrison, 2000), 'silica leakage' (Brzezinski et al., 2002; Matsumoto et al.,
54 2002), changes in net global weathering rates (Bernier, 1992), reduction in coral reef growth and other forms
55 of shallow water CaCO₃ accumulation (Berger, 1982), carbonate compensation (Ridgwell and Zeebe, 2005),
56 and changes to the CaCO₃ to organic matter 'rain ratio' to the sediments (Archer and Maierreimer, 1994), will
57 act to amplify or diminish the CO₂ effect of many of the above drivers.

1
2 *Summary.* All of the major drivers of the glacial-to-interglacial atmospheric CO₂ changes (Figure 6.5) are
3 likely to have already been identified. However, significant uncertainties exist in reconstructing glacial
4 boundary conditions and deficiencies in fully understanding some of the primary controls on carbon storage
5 in the ocean and in the land. This uncertainty prevents an unambiguous interpretation and attribution to
6 individual mechanisms of the causes of low glacial CO₂. Assessment of the balance of mechanisms before
7 deglacial transitions or glacial inceptions will likely provide additional insights into the drivers of low glacial
8 CO₂. Several of these identified drivers (e.g., organic matter remineralization, ocean stratification) are likely
9 to be sensitive to climate change in general, improved understanding drawn from the glacial-interglacial
10 cycles will help constrain the magnitude of future ocean feedbacks on atmospheric CO₂. Other drivers (e.g.,
11 iron fertilization) are involved in geoengineering methods, improved understanding could also help constrain
12 the potential of these methods (see Section 6.5.2)

13 [INSERT FIGURE 6.5 HERE]

14 **Figure 6.5:** Carbon dioxide concentrations changes from LGM to late Holocene (top) and from early/mid Holocene (7
15 ka) to late Holocene (bottom). Filled black circles represent individual model-based estimates for individual ocean,
16 land, geological or human drivers. Solid color bars represent expert judgment (to the nearest 5 ppm) rather than a
17 formal statistical average. References for the different model assessment used for the glacial drivers are as per Kohfeld
18 and Ridgwell (2009) with excluded model projections in grey. References for the different model assessment used for
19 the Holocene drivers are Joos et al. (2004), Brovkin et al. (2008), Kleinen et al. (2010), Broecker et al. (1999), Ridgwell
20 et al. (2003), Brovkin et al. (2002), Schurgers et al. (2006), Yu (2011), Kleinen et al. (2011), Ruddiman (2003, 2007),
21 Strassmann et al. (2008), Olofsson and Hickler (2008), Pongratz et al. (2009), Kaplan et al. (2011), Lemmen (2009),
22 Stocker et al. (2011) and Roth and Joos (2012).

23 6.2.1.1.2 *Glacial CH₄ and N₂O*

24
25 Polar ice core analyses show that atmospheric CH₄ and N₂O were much lower under glacial conditions
26 compared to interglacial ones. Their reconstructed history encompasses the last 800 kyr (Loulergue et al.,
27 2008; Schilt et al., 2010a). Glacial CH₄ mixing ratios are in the 350–400 ppbv range during the eight glacial
28 maxima covered by the ice core record. This is about half the levels observed during interglacial conditions.
29 The N₂O concentration amounts to 202 ± 8 ppbv, compared to the Early Holocene levels of about 270 ppbv
30 (Fluckiger et al., 1999).

31
32 CH₄ and N₂O isotopic ratio measurements in polar ice provide additional constraints on the mechanisms
33 responsible for their temporal changes. N₂O isotopes suggest a similar increase in marine and terrestrial N₂O
34 emissions for the last deglaciation (Sowers et al., 2003), whereas marine sediment proxies of ocean
35 oxygenation suggests that most of the observed N₂O deglacial rise was of marine origin (Jaccard and
36 Galbraith, 2011). δD and ¹⁴C isotopic composition measurements of CH₄ have shown that catastrophic
37 methane hydrate degassing events are unlikely to have caused the last deglaciation CH₄ increase (Bock et al.,
38 2010; Petrenko et al., 2009; Sowers, 2006). δ¹³C and δD measurements of CH₄ combined with interpo-
39 lar gradient changes suggest that most of the methane increase observed during the last deglaciation was caused
40 by increased source from boreal and tropical wetlands and an increase in CH₄ residence time due to a
41 reduced oxidative capacity of the atmosphere (Fischer et al., 2008). The biomass burning source apparently
42 changed little on the same time scale, whereas this CH₄ source experienced large fluctuations over the last
43 millennium (Mischler et al., 2009; Wang et al., 2010b).

44
45 Several modelling studies (Kaplan et al., 2006; Valdes et al., 2005) addressed the mechanisms behind
46 methane variations on glacial-interglacial time-scales. Changes in atmospheric oxidising capacity of the
47 atmosphere are probably negligible (Levine et al., 2011) and tropical temperature influencing tropical
48 wetlands and global vegetation were found to be the dominant controls for global CH₄ atmospheric
49 concentrations changes on glacial-interglacial time-scales (Konijnendijk et al., 2011).

50 6.2.1.2 *Processes Controlling Changes in CO₂, CH₄ and N₂O During Abrupt Glacial Events*

51
52 Greenhouse gases (CO₂, CH₄ and N₂O) reveal sharp millennial-scale changes in the course of glaciations,
53 associated with the so-called Dansgaard/Oeschger (DO) climatic events (see Chapter 5, Section 5.6.1), but
54 their amplitude, shape and timing differ. During these millennial scale climate events, atmospheric CO₂
55 concentrations varied by about 20 ppm, in phase with Antarctic temperatures, but not with Greenland ones.
56 CO₂ increased during cold (stadial) events in Greenland, attaining a maximum at around the time of the rapid
57
58

1 warming in Greenland, which lasted about 1000 years and decreased afterward (Ahn and Brook, 2008).
2 Methane and N₂O showed rapid transitions trending with Greenland temperatures with little or no lag. CH₄
3 changes are in the 50–200 ppbv range (Fluckiger et al., 2004) and are in phase with Greenland warmings at a
4 decadal time scale (Huber et al., 2006). N₂O fluctuations can reach glacial-interglacial amplitudes, and for
5 the warmest and longest DO events N₂O starts to increase several centuries before Greenland temperature
6 and CH₄ (Schilt et al., 2010b).

7
8 However, conflicting hypotheses exist on the drivers of these sharp millennial-scale changes. Some model
9 simulations suggest that both CO₂ and N₂O fluctuations can be explained by changes in the Atlantic
10 meridional overturning ocean circulation (Schmittner and Galbraith, 2008), CO₂ variations being mainly
11 explained by changes in the efficiency of the biological pump which affects deep ocean carbon storage
12 (Bouttes et al., 2011), whereas N₂O variations could be due to changes in productivity and oxygen
13 concentrations in the subsurface ocean (Schmittner and Galbraith, 2008). Other studies, however, suggest
14 that the millennial-scale CO₂ fluctuations can be explained by changes in the land carbon storage (Bozbiyik
15 et al., 2011; Menviel et al., 2008), and that terrestrial processes can explain most of the N₂O changes
16 (Goldstein et al., 2003).

17 **6.2.2 GHG Changes over the Holocene (last 11,000 Years)**

18 *6.2.2.1 Understanding Processes Underlying Holocene CO₂ Changes*

19
20 The evolution of the atmospheric CO₂, CH₄, and N₂O concentrations during the Holocene, the interglacial
21 period which began 11.7 ka ago, is known with high certainty from ice core analyses (Figure 6.6). A
22 decrease in atmospheric CO₂ of about 7 ppm from 11 to 8 ka was followed by a 20 ppm CO₂ increase until
23 the onset of the Industrial Era (Elsig et al., 2009; Indermuhle et al., 1999; Monnin et al., 2004). These
24 variations in atmospheric CO₂ over the past 11,000 years preceding industrialization are more than five times
25 smaller than the observed CO₂ increase during the Industrial Era. Despite the small scale of atmospheric CO₂
26 variations prior to the Industrial Era, these changes are nevertheless essential for understanding the role of
27 natural forcing in carbon and other biogeochemical cycles during interglacial climate conditions.
28
29

30 **[INSERT FIGURE 6.6 HERE]**

31 **Figure 6.6:** Variations of CO₂, CH₄, and N₂O concentrations during the Holocene. The data are for Antarctic ice cores:
32 EPICA Dome C (Fluckiger et al., 2002; Monnin et al., 2004), triangles; Law Dome (MacFarling-Meure et al., 2006),
33 circles, and for Greenland ice core GRIP (Blunier et al., 1995), squares. Lines are for spline fits.
34
35

36 Since the IPCC AR4, mechanisms underlying the observed 20 ppm CO₂ increase during the Holocene
37 between 7 ka and the Industrial Era have been a matter of intensive debate. During three separate interglacial
38 periods prior to the Holocene, CO₂ did not increase, and this led to a hypothesis that pre-industrial
39 anthropogenic CO₂ emissions associated with early land use change were a main driver of the Holocene CO₂
40 changes (Ruddiman, 2003, 2007). However, ice core CO₂ data (Siegenthaler et al., 2005b) indicate that
41 during Marine Isotope Stage 11 (Chapter 5), an interglacial period that lasted from 400 to 420 ka, CO₂ was
42 increasing similarly to the Holocene period. Drivers of atmospheric CO₂ changes during the Holocene can be
43 divided into oceanic and terrestrial processes (Figure 6.5) and their role is examined below.
44

45 *6.2.2.1.1 Oceanic processes*

46 Very likely, the change in oceanic carbonate chemistry state explains the slow CO₂ increase during the
47 Holocene since 7 ka. Proposed mechanisms include: (1) a shift of oceanic carbonate sedimentation from
48 deep sea to the shallow waters due to sea level rise onto continental shelves and excessive accumulation of
49 CaCO₃ on shelves including coral reef growth (Kleinen et al., 2010; Ridgwell et al., 2003), (2) a ‘carbonate
50 compensation’ to release of carbon from the deep ocean during deglaciation and build-up of terrestrial
51 biosphere in the early Holocene (Broecker et al., 1999; Elsig et al., 2009; Joos et al., 2004; Menviel and Joos,
52 2012). The proxies for the carbonate ion concentration in the deep sea (Yu et al., 2010) and increased
53 dissolution of carbonate sediments in the deep tropical Pacific (Anderson et al., 2008) support the hypothesis
54 of the ocean being a source of CO₂ to the atmosphere during the Holocene. Changes in sea surface
55 temperatures (SST) over the last 7 ka (Kim et al., 2004) could led to slightly lower (Brovkin et al., 2008) or
56 higher (Menviel and Joos, 2012) atmospheric CO₂ concentration but, very likely, SST-driven CO₂ change
57 represents only a minor contribution to the observed CO₂ increase during the Holocene after 7 ka.

6.2.2.1.2 *Terrestrial processes: ice core isotope evidence*

$\delta^{13}\text{C}$ of atmospheric CO_2 trapped in ice cores is a proxy for changes in terrestrial biospheric carbon pools. Calculations based on inferred $\delta^{13}\text{C}$ of atmospheric CO_2 during the Holocene suggest an increase in terrestrial carbon stocks of about 300 PgC between 11 and 5 ka and small overall terrestrial changes in the period thereafter (Elsig et al., 2009).

6.2.2.1.3 *Natural terrestrial processes*

After 7 ka, increasing atmospheric CO_2 concentrations stimulated gross primary productivity of terrestrial vegetation resulting in increases in carbon storage. Modelling studies suggest that this CO_2 fertilisation process contributed a substantial land additional storage of carbon (>100 PgC) on Holocene timescales (Joos et al., 2004; Kaplan et al., 2002; Kleinen et al., 2010). Orbitally forced climate variability, including the intensification and decline of the Afro-Asian monsoon and the mid-Holocene warming of the high-latitudes of the Northern Hemisphere are estimated in models to have resulted in additional changes in vegetation distribution and terrestrial carbon storage. These climate-induced carbon storage changes are estimated using models to have been smaller than changes due to the CO_2 fertilisation (Brovkin et al., 2002; Schurgers et al., 2006). The Holocene evolution of carbon in peatlands has been reconstructed globally, suggesting a land carbon additional storage of several hundred PgC between the early Holocene and the Industrial Era, although uncertainties remain on this estimate (Kleinen et al., 2011; Tarnocai et al., 2009; Yu, 2011). Volcanic CO_2 emissions to the atmosphere between 12 and 7 ka were inferred to be two to six times higher than during the last millennium, of about 0.1 PgCyr (Huybers and Langmuir, 2009; Roth and Joos, 2012) but the confidence in changes of volcanic CO_2 emissions is low.

6.2.2.1.4 *Land use*

Global syntheses of the observational, paleoecological and archaeological records for Holocene land use change are not currently available (Gaillard et al., 2010). Available global reconstructions of anthropogenic land use and land cover change (LULCC) prior to the last millennium hence currently extrapolate using models and assumptions the relationship of the land cover change and population density from a single region and specific time period to the entire globe and Holocene (Kaplan et al., 2011) or extrapolate the changes of per-capita land requirements occurring with agro-technological progress over time from single regions to changes in all regions of the world (Goldewijk et al., 2011). Because of regional differences in land use systems and uncertainty in historical population estimates, the confidence in spatially explicit LULCC reconstructions is low.

Some recent studies focused on reconstructing LULCC while making very simple assumptions regarding the effect of land use on carbon, and therefore patterns of terrestrial carbon storage (Lemmen, 2009; Olofsson and Hickler, 2008), while other studies relied on more sophisticated terrestrial biosphere models to simulate carbon storage and loss in response to pre-industrial LULCC during the late Holocene period (Pongratz et al., 2009; Stocker et al., 2011; Strassmann et al., 2008). The conclusion of the above studies was that cumulative Holocene carbon emissions as a result of pre-industrial LULCC were not large enough (~50–150 Pg before 1850) to have had a significant influence on late Holocene CO_2 concentrations. However, a recent modelling study by Kaplan et al. (2011) suggested that these attempts represented significant underestimates and that more than 350 PgC could have been released as a result of LULCC between 8 ka and year 1850.

6.2.2.1.5 *Human impacts on holocene biomass burning*

In addition to clearing of forests for crop and pasture, biomass burning by humans before the Industrial Era has been hypothesized as a source of both CO_2 and CH_4 over the Holocene. Studies that synthesized charcoal records from lake and bog sediments initially indicate that there could be large-scale correlations between burning activity and atmospheric CO_2 (Carcaillet et al., 2002), but this human induced biomass burning hypothesis is opposed by two later global syntheses that used similar methods and concluded that fire activity followed climate variability, rather than human activities (Marlon et al., 2008; Power et al., 2008). In contrast, regional syntheses of charcoal and other paleo-evidence of biomass burning suggest fire is closely related to the dynamics of human societies (Archibald et al., 2012; McWethy et al., 2009; Nevle and Bird, 2008; Nevle et al., 2011).

6.2.2.2 *Holocene CH_4 and N_2O Drivers*

1 The Holocene atmospheric CH₄ levels were lowest at around 5 ka, and increased between 4 ka and year 1850
2 by about 100 ppb (Figure 6.6). Major Holocene agricultural developments, in particular rice paddy
3 cultivation and widespread domestication of ruminants, have been proposed as an explanation for the Late
4 Holocene CH₄ rise (Ruddiman, 2007). The most recent syntheses of archaeological data point to an
5 increasing anthropogenic CH₄ source from domesticated ruminants after 5 ka and from rice cultivation after
6 4 ka (Fuller et al., 2011; Ruddiman, 2007). The modelling support for either natural or anthropogenic
7 explanations of the Late Holocene increase in the atmospheric CH₄ concentration is equivocal. A study by
8 Kaplan et al. (2006) suggested that a part of the Late-Holocene CH₄ rise could be explained by
9 anthropogenic sources. Natural wetland CH₄ models driven by simulated climate changes are able
10 (Singarayer et al., 2011) or unable (Konijnendijk et al., 2011) to simulate Late Holocene increase in the CH₄
11 concentration. No new studies are known about mechanisms of Holocene N₂O changes.
12

13 **6.2.3 GHG Changes over the Last Millennium**

14 *6.2.3.1 A Decrease of CO₂ around Year 1600 and Possible Explanations for this Event*

15 High resolution records of the atmospheric composition from ice cores reveals that atmospheric CO₂ during
16 the last millennium varied with a drop in atmospheric CO₂ concentration by about 7–10 ppm around year
17 1600 followed by a CO₂ increase during the 17th century (Ahn et al., 2012; Siegenthaler et al., 2005a;
18 Trudinger et al., 2002) as shown in Figure 6.7. The CO₂ decrease during the 17th century was used to
19 evaluate the response of atmospheric CO₂ concentration to changes in global temperature (Cox and Jones,
20 2008; Frank et al., 2010; Scheffer et al., 2006) which was found to be dependent on the choice of global
21 temperature reconstructions used in the model.
22
23
24

25 **[INSERT FIGURE 6.7 HERE]**

26 **Figure 6.7:** Variations of CO₂, CH₄, and N₂O during 900–1900 AD from ice cores. The data are for Antarctic ice cores:
27 Law Dome (Etheridge et al., 1996; MacFarling-Meure et al., 2006), circles; West Antarctic Ice Sheet (Ahn et al., 2012;
28 Mitchell et al., 2011), triangles; Dronning Maud Land (Siegenthaler et al., 2005a), squares. Lines are spline fits to
29 individual measurements.
30

31 One of the possible explanations for the drop in atmospheric CO₂ around year 1600 is enhanced land and/or
32 ocean carbon uptake in response to the cooling caused by reduced solar irradiance during the Maunder
33 Minimum (Chapter 5). However, simulations using EMIC models (Brovkin et al., 2004; Gerber et al., 2003)
34 and by complex ESM models (Jungclaus et al., 2010) suggest that solar irradiance forcing alone is not
35 sufficient to explain the magnitude of the CO₂ decrease. The drop in atmospheric CO₂ around year 1600
36 could also be caused by a cooling in response to increased volcanic eruptions (Brovkin et al., 2010; Jones
37 and Cox, 2001). Another hypothesis calls for a link between CO₂ and epidemics and wars and associated
38 forest growth over abandoned lands, especially in Central America. Here, results are model- and scenario
39 dependent. Simulations by (Pongratz et al., 2011) do not reproduce a decrease in CO₂, while simulations by
40 Kaplan et al. (2011) suggest a considerable increase in land carbon storage during late 16th to early 17th
41 century. The temporal resolution of Central American charcoal and pollen records is insufficient to support
42 or falsify these model results (e.g., Nevle and Bird, 2008).
43

44 Ensemble simulations over the last 1200 years have been conducted using an ESM including a fully-
45 interactive carbon cycle (Jungclaus et al., 2010). For two ensemble simulations using a lower and higher end
46 estimate for the multi-centennial solar irradiance forcing variation, the sensitivity of atmospheric CO₂
47 concentration to Northern Hemisphere temperature changes was modelled to be of 2.7 and 4.4 ppm K⁻¹,
48 respectively. This sensitivity falls within the range of 1.7–21.4 ppm K⁻¹ of a recent reconstruction based on
49 tree-ring Northern Hemisphere temperature reconstructions (Frank et al., 2010), though at its lower end.
50

51 *6.2.3.2 Mechanisms Controlling CH₄ and N₂O during the Last Millennium*

52
53 Recent high-resolution ice core records confirm a CH₄ decrease in the late 16th century by about 40 ppb
54 (MacFarling-Meure et al., 2006; Mitchell et al., 2011). Correlations between this variation in CH₄ and
55 temperature in the 15th and 16th centuries suggest that climate change affected CH₄ emissions by wetlands
56 during this period. Additionally to changes in the wetland CH₄ source, long-term trends in biomass burning
57 have been invoked to explain the Last Millennium CH₄ record (Ferretti et al., 2005; Marlon et al., 2008).

Changes in anthropogenic CH₄ emissions during times of war and plague hypothetically contribute to variability in atmospheric CH₄ concentration, although they cannot explain all variability (Mitchell et al., 2011). No studies are known about mechanisms of N₂O changes for the last millennium.

6.3 Evolution of Biogeochemical Cycles since the Industrial Revolution

6.3.1 CO₂ Emissions and their Fate Since 1750

Prior to the Industrial Era, that began in 1750, the concentration of atmospheric CO₂ fluctuated between 180 ppm and 290 ppm for at least 2.1 million years (Honisch et al., 2009; Luthi et al., 2008; Petit et al., 1999; see Section 6.2). Between 1750 and 2011, the combustion of fossil fuels (coal, gas, oil, and gas flaring) and the production of cement have released 365 ± 30 PgC to the atmosphere (Boden et al., 2011), with an additional 190 ± 80 PgC due to land use change, mainly deforestation (Table 6.1; see Section 6.3.2 for data sources). This carbon is called anthropogenic carbon.

Table 6.1: Global anthropogenic CO₂ budget, accumulated since the Industrial Revolution (onset in 1750) and averaged over the 1980s, 1990s, 2000s, and the last ten years until 2011. Note that, by convention, a negative ocean or land to atmosphere CO₂ flux is equivalent to a gain of carbon by the ocean or land reservoirs. The budget for the 1850–2005 time period is also provided for comparison with coupled carbon-climate models historical simulations and future projections (see Section 6.4.3). The uncertainty range of 90% confidence interval presented here differs from how uncertainties were reported in AR4 (68%).

	1750–2011 Cumulative PgC	1850–2005 Cumulative PgC	1980–1989 PgC yr ⁻¹	1990–1999 PgC yr ⁻¹	2000–2009 PgC yr ⁻¹	2002–2011 PgC yr ⁻¹
Atmospheric increase ^a :	240 ± 10 ^f	200 ± 10 ^f	3.4 ± 0.2	3.1 ± 0.2	4.0 ± 0.2	4.3 ± 0.2
Fossil fuel combustion and cement production ^b :	365 ± 30 ^f	320 ± 25 ^f	5.5 ± 0.4	6.4 ± 0.5	7.7 ± 0.6	8.3 ± 0.7
Ocean-to-atmosphere flux ^c :	-155 ± 30 ^f	-125 ± 25 ^f	-2.0 ± 0.7	-2.2 ± 0.7	-2.3 ± 0.7	-2.4 ± 0.7
Land-to-atmosphere flux: <i>partitioned as follows</i>	30 ± 45	5 ± 40	-0.1 ± 0.8	-1.1 ± 0.9	-1.4 ± 0.9	-1.6 ± 1.0
Net land use change ^d	180 ± 80 ^f	150 ± 80 ^f	1.4 ± 0.8	1.5 ± 0.8	1.1 ± 0.8	0.9 ± 0.8
Residual terrestrial sink ^e :	-150 ± 90 ^f	-145 ± 90 ^f	-1.5 ± 1.1	-2.6 ± 1.2	-2.5 ± 1.2	-2.5 ± 1.3

Notes:

(a) Data from Charles .D. Keeling, (<http://scrippsco2.ucsd.edu/data/data.html>), Thomas Conway and Pieter Tans, NOAA/ESRL (www.esrl.noaa.gov/gmd/ccgg/trends/) using a conversion factor of 2.123 PgC per ppm.

(b) CO₂ emissions are estimated by the Carbon Dioxide Information Analysis Center (CDIAC) based on UN energy statistics for fossil fuel combustion and US Geological Survey for cement production (Boden et al., 2011).

(c) Averaged from existing global estimates (see 6.3.2.5 and 6.3.2.6 for the mean values and Table 6.5 for the decadal trends). This flux does not include the natural river flux of carbon and the associated natural outgas of CO₂ to the atmosphere (see Figure 6.1).

(d) Based on the bookkeeping land use change flux accounting method of Houghton et al. (2012) (see text and Table 6.2).

(e) Sum of the Land-to-atmosphere flux minus Net Land Use Change, assuming the errors on each term are independent and added quadratically. (f) The 1750–2011 and 1850–2005 estimates and their uncertainties were rounded to the nearest 5 PgC.

Of the 545 ± 85 PgC of anthropogenic carbon emitted to the atmosphere from fossil fuel and cement and land use change, less than half have accumulated in the atmosphere (240 ± 10 PgC), resulting in an average atmospheric CO₂ concentration of 390.4 ppm in 2011 (Conway and Tans, 2011). The remaining anthropogenic carbon has been absorbed by the ocean and in terrestrial ecosystems: the carbon ‘sinks’ (Figure 6.8). The ocean stored 155 ± 30 PgC of anthropogenic carbon since 1750 (see Section 6.3.2.4.3). This ocean sink will continue to remove atmospheric CO₂ until the entire ocean has re-equilibrated with the higher atmospheric CO₂ (see Box 6.2).

[INSERT FIGURE 6.8 HERE]

Figure 6.8: Sources and sinks fluxes (PgC yr^{-1}) for the component of the global anthropogenic CO_2 budget from 1750 to 2010. (Top) Fossil fuel and cement CO_2 emissions by category, estimated by the Carbon Dioxide Information Analysis Center (CDIAC) based on UN energy statistics for fossil fuel combustion and US Geological Survey for cement production (Boden et al., 2011). (Bottom) Fossil fuel and cement CO_2 emissions as above. CO_2 emissions from net land use change, mainly deforestation for 1750–1850 are from the average of estimates (Pongratz et al., 2009; Shevliakova et al., 2009b; vanMinnen et al., 2009; Zaehle et al., 2011) and from Houghton et al. (2012) after 1850. The atmospheric CO_2 growth rate prior to 1960 is based on a spline fit to ice core observations (Etheridge et al., 1996; Friedli et al., 1986; Neftel et al., 1982) and a synthesis of atmospheric observations from 1960 (Conway and Tans, 2011). The fit to ice core observations does not capture the large interannual variability in atmospheric CO_2 and is represented with a dashed line on the figure. The ocean CO_2 sink prior to 1960 is from Khatiwala et al. (2009) and from a combination of model and observations from 1960 updated from (LeQuere et al., 2009). The residual land sink is computed from the residual of the other terms. The sources and sinks only include the fluxes that have changed since 1750, and not the natural CO_2 fluxes (e.g., atmospheric CO_2 uptake from weathering, natural river transport of carbon from land to ocean, and compensatory CO_2 outgassing by the ocean) between the atmosphere, and ocean reservoirs that existed before that date and still exist today. The uncertainties in the various terms are discussed in the text and reported in Table 6.1.

Terrestrial ecosystems not affected by land use change have accumulated 150 ± 90 PgC of anthropogenic carbon since 1750 (Table 6.1), thus not fully compensating the CO_2 losses from terrestrial ecosystems to the atmosphere from land use change during the same period estimated to 180 ± 80 PgC (Table 6.1). This increased storage in terrestrial ecosystems not affected by land use is thought to have been caused by enhanced photosynthesis at higher CO_2 levels and N deposition, changes in climate favoring carbon sinks such as longer growing seasons in mid-to-high latitudes, the expansion and increased biomass density of forests in temperate and boreal regions. This increased terrestrial carbon storage is called residual terrestrial sink in Table 6.1 because it is deduced by mass balance as the difference between fossil and land use change emissions and measured atmospheric and oceanic storage increase (Table 6.1).

[START BOX 6.2 HERE]

Box 6.2: CO_2 Residence Time

On average, CO_2 molecules are exchanged between the atmosphere and the Earth surface every few years. This fast CO_2 cycling through the atmosphere is linked to a much slower cycling of carbon through land vegetation, litter and soils, and the upper ocean (decades to centuries), deeper soils and the deep sea (centuries to millennia), and geological reservoirs, such as deep-sea carbonate sediments and the upper mantle (up to millions of years) as explained in Section 6.1. The amount of carbon involved into this chain of natural processes with increasing time scale, is very large compared to the atmospheric CO_2 storage. Emissions of anthropogenic carbon is now rapidly increasing atmospheric CO_2 content, but redistribution of this perturbation through slower reservoirs will take up to hundreds of thousand years. This extremely long relaxation timescale, of a large emission pulse of CO_2 , is supported by geological evidence from Paleocene-Eocene thermal maximum event ca. 55 million years ago (McInerney and Wing, 2011).

The main chemical reactions that remove anthropogenic CO_2 and their typical timescales are:

<i>Reaction</i>	<i>Relevant timescale (years)</i>
Photosynthesis (land uptake): $6\text{CO}_2 + 6\text{H}_2\text{O} + \text{photons} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$	10–102
Seawater buffer (ocean invasion): $\text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons 2 \text{HCO}_3^-$	10–103
Reaction with calcium carbonate: $\text{CO}_2 + \text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2 \text{HCO}_3^-$	103–104
Silicate weathering (reaction with igneous rocks): $\text{CO}_2 + \text{CaSiO}_3 \rightarrow \text{CaCO}_3 + \text{SiO}_2$	10^4 – 10^6

These reactions are active on all time scales, but the relative importance of their role in the CO_2 removal is changing with time. Accordingly, the response times of atmospheric CO_2 to anthropogenic carbon emissions can be divided into three phases associated with increasingly longer typical timescales.

Phase 1. Within a few years of CO_2 emissions, about a half of the anthropogenic C stays in the atmosphere, while the rest is absorbed in the land and ocean most active pools (Figure 1, top). Within a few centuries, most of the released anthropogenic CO_2 will end up in the form of additional dissolved inorganic carbon in

1 the ocean, decreasing ocean pH (the ocean invasion phase). Within a thousand years, the airborne fraction of
2 the CO₂ emissions (see Section 6.3.2.4) is expected to be between 15 and 40%, depending on the amount of
3 carbon released (Archer et al., 2009b). If emissions are large enough, the carbonate buffer system of the
4 ocean becomes depleted, so the larger the cumulative emissions, the higher the airborne fraction (Eby et al.,
5 2009).

6
7 Phase 2. In the second stage, the pH of the ocean will be restored by the CaCO₃ cycle, partly replenishing the
8 buffer capacity of the ocean and further drawing down atmospheric CO₂ as a new balance is re-established
9 between CaCO₃ sedimentation in the ocean and terrestrial weathering (Figure 1, bottom). This stage has a
10 time scale of 3–7 kyr, and pulls the cumulative airborne fraction (the fraction of an initial pulse of CO₂ that
11 stays in the atmosphere) down to 10–25% of the original CO₂ pulse after about 10 kyr (Archer and Brovkin,
12 2008; Lenton and Britton, 2006; Montenegro et al., 2007; Ridgwell and Hargreaves, 2007; Tyrrell et al.,
13 2007).

14
15 Phase 3. During the third phase, the rest of the anthropogenic CO₂ will be removed from the atmosphere by
16 silicate weathering, a very slow process of CO₂ reaction with CaO and other minerals of igneous rocks. This
17 geological process takes up to several hundred thousand years (e.g., Sundquist, 1990; Walker and Kasting,
18 1992).

19
20 Involvement of extremely long processes into the removal of anthropogenic CO₂ complicates comparison
21 with the cycling of the other greenhouse gases. This is why the concept of a single, characteristic
22 atmospheric lifetime is not applicable to CO₂ (Chapter 8).

23 24 **[INSERT BOX 6.2, FIGURE 1 HERE]**

25 **Box 6.2, Figure 1:** A fraction of a given amount of CO₂ emitted to the atmosphere remaining in the atmosphere in
26 response to an idealized instantaneous CO₂ pulse in year 0 as calculated by a range of coupled climate-carbon cycle
27 models. (Top) Multi-model mean (black line) and the uncertainty interval (± 2 standard deviations, grey shading)
28 simulated during 1,000 years following the instantaneous pulse of 100 PgC (Joos et al., submitted). (Bottom) A mean of
29 models with oceanic and terrestrial carbon components (solid lines) and a maximum range of these models (grey
30 shading) for instantaneous CO₂ pulse in year 0 of 100 PgC (black), 1,000 PgC (brown) and 5,000 PgC (red line) on a
31 time interval up to ten thousand years (Archer et al., 2009b). (Blue boxes) the dominant processes that remove the
32 excess of CO₂ emitted in the atmosphere on the successive timescales. Note that higher pulse of CO₂ emissions leads to
33 higher airborne CO₂ fraction (Section 6.3.2.4) due to reduced carbonate buffer capacity of the ocean and positive
34 climate-carbon cycle feedback (Section 6.3.2.6.6).

35 36 **[END BOX 6.2 HERE]**

37 38 **6.3.2 Global CO₂ Budget**

39
40 Since the AR4 (Denman et al., 2007), a number of new advancements on data availability and data-model
41 synthesis have allowed the establishment of a more constrained anthropogenic CO₂ budget and a better
42 attribution to its flux components. The advancements are: (1) revised data on the rates of land use change
43 conversion from country statistics processed by the Food and Agriculture Organization (FAO, 2010) now
44 providing an arguably more robust estimate of the land use change flux (Houghton et al., 2012; Section
45 6.3.2.2), (2) new global compilation of forest inventory data, based upon thousands of individual forest
46 measurements in the northern forests, providing an independent estimate of the amount of carbon that has
47 been gained by forests over the past two decades, albeit with very scarce measurements for tropical forest
48 (Pan et al., 2011), (3) over 2 million new observations of the partial pressure of CO₂ at the ocean surface
49 (pCO₂) have been taken, added to global databases (Pfeil et al., subm.; Takahashi et al., 2009), and used to
50 quantify ocean CO₂ sink variability and trends (Section 6.3.2.5.4) and to evaluate and constrain models
51 (Schuster et al., subm.; Wanninkhof et al., subm.), and (4) for both ocean and land regions, the use of
52 multiple constraints with atmospheric inversions and combined atmosphere-ocean inversions (so called top
53 down approaches) and the up-scaling of reservoir-based observations using models (so called bottom up
54 approaches) providing coarse scale consistency checks on CO₂ flux estimates for a number of large regions
55 of the globe (Ciais et al., 2010; McGuire et al., 2009; Piao et al., 2009a). The global anthropogenic CO₂
56 budget estimated from a range of observations and methods accounts for most of the trends in the CO₂ sinks,
57 and a large part of the observed variability (Le Quere et al., 2009; Sitch et al., 2008). The causes of the year-
58 to-year variability observed in the annual atmospheric CO₂ accumulation shown in Figure 6.8 are estimated

1 with a medium to high confidence to be largely driven by terrestrial processes occurring in tropical latitudes
2 as inferred from atmospheric CO₂ inversions and supported by ocean data and models (Figure 6.9; Section
3 6.3.2.5.1).

4 [INSERT FIGURE 6.9 HERE]

5 **Figure 6.9:** The interannual variability of surface CO₂ fluxes from inversions of the TRANSCOM project for the period
6 of 1981–2010. The ensemble of inversion results contains up to 17 atmospheric inversion models. The orange bars at
7 the bottom panel indicates the number of available inversion models for each time period. The ensemble mean is
8 bounded by the 1 sigma inter-model spread in ocean-atmosphere (blue) and land-atmosphere (green) CO₂ fluxes (PgC
9 yr⁻¹) grouped into large latitude bands, and the global. For each flux and each region, the CO₂ flux anomalies were
10 obtained by subtracting the long term mean flux from each inversion and removing the seasonal signal. Grey shaded
11 regions indicate El Niño episodes, and the back bars indicate the cooling period following the Mt. Pinatubo eruption. A
12 positive flux means a larger than normal source of CO₂ to the atmosphere (or a smaller CO₂ sink).
13

14 6.3.2.1 CO₂ Emissions from Fossil Fuel Combustion and Cement Production

15
16
17 Global CO₂ emissions from the combustion of fossil fuels used for this chapter are determined from national
18 energy consumption statistics and converted to emissions by fuel type (Marland and Rotty, 1984). Estimated
19 uncertainty for the annual global emissions are on the order of ± 8% (converted from ± 10% uncertainty for
20 95% confidence intervals in Andres et al. (2012) to the 90% confidence intervals used here). The uncertainty
21 has been increasing in recent decades because a larger fraction of the global emissions originate from
22 emerging economies where energy statistics and emission factors per fuel type are more uncertain (Gregg et
23 al., 2008). CO₂ emissions from cement production were 4% of the total emissions during 2000–2009,
24 compared to 3% in the 1990s. Additional emissions from gas flaring represent <1% of the global emissions.

25
26 Global CO₂ emissions from fossil fuel combustion and cement production were 7.7 ± 0.6 PgC yr⁻¹ on
27 average in the decade 2000–2009, 6.4 ± 0.5 PgC yr⁻¹ during 1990–1999, and 5.5 ± 0.4 PgC yr⁻¹ during
28 1980–1989 (Table 6.1; Figure 6.9). Global fossil fuel CO₂ emissions increased by 2.9% yr⁻¹ on average
29 during the decade 2000–2009 compared to 1.0% yr⁻¹ in the 1990s and 1.9% yr⁻¹ in the 1980s. The global
30 financial crisis in 2008–2009 induced only a short-lived drop in global emissions in 2009 (1.3%; Peters et al.,
31 2012), with the return to high annual growth rates of 5.9% and 3.2% in 2010 and 2011, respectively, and
32 fossil fuel CO₂ emissions of 9.4 ± 0.8 PgC in 2011.

33 6.3.2.2 CO₂ Fluxes from Deforestation and other Land Use Change

34
35
36 CO₂ is emitted to the atmosphere by land use and land use change processes, in particular deforestation, and
37 taken up from the atmosphere by other land use change processes such as afforestation and regrowth on
38 abandoned lands. A critical distinction in estimating land use change is the difference between gross and net
39 emissions. Gross emissions include all the emissions to the atmosphere from carbon loss in above ground
40 vegetation (instantaneous) and soils (longer-term), while net emissions include in addition carbon uptake by
41 forest regrowth and soil sequestration on abandoned agricultural lands, afforestation and long-term change of
42 storage in wood products. Here we report net emissions, one of the drivers of the atmospheric CO₂ increase
43 in the global budget assessment of Table 6.1. Land use change CO₂ emissions occur on different time scales
44 including instantaneous release of carbon to the atmosphere, e.g., through combustion, and longer-term
45 decomposition of dead plant material and soil organic matter. Logging and other forms of biomass removal
46 emit CO₂ to the atmosphere when slash left on the ground burns or decomposes and when wood products
47 (e.g., paper, timber) reach the end of their lifetime (e.g., through combustion or decaying in landfills).

48
49 Approaches to estimate net CO₂ fluxes from land use fall into three categories: (1) a ‘bookkeeping’ method
50 that tracks carbon in living vegetation, dead plant material, wood products and soils with cultivation,
51 harvesting and reforestation using country-level reports on changes in forest area and biome-averaged
52 biomass values (Houghton, 2003); (2) process-based terrestrial ecosystem models that simulate on a grid the
53 carbon stocks (biomass, soils) and exchange fluxes between vegetation, soil, and atmosphere using as input
54 spatially-explicit time varying maps of the area of each biome (see references in Table 6.2), and (3) detailed
55 regional (primarily tropical forests) analyses based on satellite data that estimate changes in forest area with
56 high spatial resolution (Achard et al., 2004; DeFries et al., 2002) combined with the above-mentioned type of
57 bookkeeping model (Achard et al., 2004; DeFries et al., 2002), and more recently combined with satellite
58 derived maps of tropical forest biomass (Harris et al., 2012; Baccini et al., 2012). Satellite-derived estimates

of CO₂ emissions to the atmosphere from so-called deforestation fires (van der Werf et al., 2010) provide additional constraints on the spatial attribution and variability of land use change gross emissions. Most global estimates ignore emissions from peat burning or decomposition after a land use change, which are estimated at 0.30 PgC yr⁻¹ over 1997–2006 (van der Werf et al., 2009) but can reach much higher values during extreme years when peat forest is affected (Ballhorn et al., 2009; Page et al., 2002) and emissions from the decomposition of drained peat which are estimated at 0.1 to 0.23 PgC yr⁻¹ for Southeast Asia alone (Hooijer et al., 2010). The processes and time scales captured by these methods to estimate net land use change CO₂ emissions are diverse, creating difficulties with comparison of different estimates (Houghton et al., 2012; Table 6.2). For example, methods that do not include long-term ‘legacy’ fluxes from soils caused by deforestation prior to the starting period underestimate net land use change CO₂ emissions by 13–62% depending on the starting year and decade (Ramankutty et al., 2006).

Table 6.2: Estimates of net land to atmosphere CO₂ flux from land use change (PgC yr⁻¹). Positive values indicate CO₂ losses to the atmosphere from land ecosystems and in some estimates from wood products generated by land use change as well. Processes included are I=initial biomass loss D=decomposition of slash and soil carbon during the year of initial loss, R=regrowth, S=change in storage in wood products pools and L=‘legacy’ long-term decomposition flux carried over from land use change transitions prior to start of time period used for reporting in the table. In the absence of data on L in the assessed estimates, the studies have either assumed I = instantaneous loss of all biomass and soil carbon (a committed future flux) or did not considered the legacy flux L.

	Data for Land Use Change Area ^a	Biomass Data	Processes Included	1980–1989 PgC yr ⁻¹	1990–1999 PgC yr ⁻¹	2000–2009 PgC yr ⁻¹
<i>Bookkeeping Method (global)</i>						
Houghton et al. (2012)	FAO-2010	observed ^b	All	1.4	1.5	1.1
<i>Satellite-based Methods (tropics only)</i>						
Achard et al. (2004)	Landsat	observed ^b	I, D, R, S		0.9 (0.5–1.4) ^c	
DeFries et al. (2002)	AVHRR	observed ^b	I, D, R, S ^d	0.6 (0.3–0.8)	0.9 (0.5–1.4)	
Van der Werf et al. (2010)	GFED	CASA ^e	I, D		1.2 (0.6–1.8) ^f	
Baccini et al. (2012)	FAO-2010	satellite data	All			1.0
<i>Process Models (global)</i>						
Shevliakova et al. (subm.)	HYDE	LM3V	All	1.6	1.3	1.0
van Minnen et al. (2009) ^g	HYDE	IMAGE 2 ^c	All	1.8	1.4	1.2
Strassmann et al. (2008)	HYDE	BernCC ^c	I, D, R, L	1.3	1.3	
Stocker et al. (2011) ^g	HYDE	BernCC ^c	I, D, R, L	1.4	0.9	0.6
Jain et al. (subm.)	SAGE	ISAM ^e	all	1.7	1.7	
Jain et al. (subm.)	FAO-2005	ISAM ^e	all	1.7	1.8	
Jain et al. (subm.)	HYDE	ISAM ^e	all	2.2	1.5	1.2
Arora and Boer (2010)	SAGE	CTEM ^e	all	1.1 ^h	1.1 ^h	
Arora and Boer (2010) ^g	HYDE	CTEM ^e	all	0.4 ^h	0.4 ^h	
Poulter et al. (2010) ^g	HYDE	LPGmL ^c	all	1.0	0.9	0.5
Kato et al. (2012) ^g	HYDE	VISIT ^c	all	1.2	1.0	0.5
Zaehle et al. (2011)	HYDE	O-CN	all	1.2	1.0	
Average of process models ⁱ				1.4 ± 0.8	1.2 ± 0.6	0.8 ± 0.6

Notes:

(a) References for the databases used: FAO (2010) as applied in Houghton et al. (2012); FAO (2005) as applied in Houghton (2003), updated; GFED (van der Werf et al., 2009); HYDE (Goldewijk et al., 2011), SAGE (Ramankutty and Foley, 1999). Landsat and AVHRR are satellite-based data and GFED is derived from satellite products as described in the references.

(b) Based on average estimates by biomes compiled from literature data (see details in corresponding references).

(c) 1990–1997 only.

- (d) Legacy fluxes for land cover change prior to 1980 are not included and are estimated to add about 0.2 PgC yr⁻¹ to the 1980s and 0.1 PgC yr⁻¹ to the 1990s estimates, based on (Ramankutty et al., 2006).
- (e) The vegetation and soil biomass is computed using a vegetation model described in the reference.
- (f) 1997–2006 average based on estimates of carbon emissions from deforestation and degradation fires, including peat carbon emissions. Estimates were doubled to account for emissions other than fire including respiration of leftover plant materials and soil carbon following deforestation following (Olivier et al., 2005). Estimates include peat fires and oxidation. If peat fires are excluded, estimate in tropical Asia is 0.23 and Pan-tropical total is 0.71
- (g) Method as described in the reference but updated to 2010 using the land cover change data listed in column 2.
- (h) The large variability produced by the calculation method is removed for comparison with other studies by averaging the flux over the two decades.
- (i) Average of estimates from all process models and 90% confidence uncertainty interval; note that the spread of the different estimates does not follow a Gaussian distribution.

Global net CO₂ emissions from land use change are estimated at 1.4, 1.5, and 1.1 PgC yr⁻¹ for the 1980s, 1990s and 2000s, respectively, by the bookkeeping method of Houghton et al. (2012) (Table 6.2; Figure 6.10). This estimate is consistent with global emissions from process-based terrestrial ecosystem models using mainly three land cover change data products as input for time-varying maps of land use change (Table 6.2). The bookkeeping method estimate is also generally consistent although higher than the satellite-based methods (tropics only). Part of the discrepancy can be accounted for by emissions from extratropical regions (~0.1 PgC yr⁻¹; Table 6.3) and by legacy fluxes for land cover change prior to 1980s (~0.2 PgC yr⁻¹) that are not covered by satellite based methods used in Table 6.2. We adopt an uncertainty of ± 0.8 PgC yr⁻¹ as representative of 90% uncertainty intervals. This is identical to the uncertainty of ± 0.5 PgC yr⁻¹ representing ± 1-sigma interval (68% if Gaussian distributed error) from Houghton et al. (2012). The uncertainty of ± 0.8 PgC yr⁻¹ on net land use change CO₂ fluxes is smaller than the one that was reported in AR4 of 0.5 to 2.7 PgC yr⁻¹ for the 1990s (68% confidence interval). In this chapter, uncertainty is estimated based on expert judgment of the available evidence, including improved accuracy of land cover change incorporating satellite data, the larger number of independent methods to quantify emissions and the consistency of the reported results (Table 6.2; Figure 6.10). In particular, the FAO forest area loss data were revised downwards in 2010 following improvements in data coverage, for instance, new data were introduced for Indonesia and higher resolution satellite data were used for the Amazon basin (FAO, 2010).

The lower land use change CO₂ emissions reported in the 2000s compared to the 1990s, by 0.4 PgC yr⁻¹ in the bookkeeping method based on FAO (2010), and by 0.3–0.5 PgC yr⁻¹ from five process-based ecosystem models based on the HYDE land cover change data updated to 2009 (Goldewijk et al., 2011), is within the error bar of the data and methods. Sixty one percent of the emissions originated from the tropics in the 1980s on average across methods, a share that increased to 67% in the 1990s and 73% in the 2000s. However the range of estimates is large and estimates from the bookkeeping method and process-based ecosystem models do not agree in the extra tropics (Table 6.3). Furthermore, the FAO (2010) forest report, based on country level reporting supported with satellite data for some countries, suggests decreasing forest loss between 2000 and 2005, while the FAO recent entirely satellite-based analysis suggests the contrary. These inconsistencies in the available land cover change data and in the modeling results prevent a firm assessment of recent trends and their partitioning among regions (see data in Table 6.3).

[INSERT FIGURE 6.10 HERE]

Figure 6.10: CO₂ emissions from land use change from a range of methods (PgC yr⁻¹). The estimate from Houghton et al. (2012) (thick black) is used in Table 6.1. The sources for the other estimates are shown in the legend and described in Table 6.2.

Table 6.3: Estimates of net land to atmosphere flux from land use change (PgC yr⁻¹; except where noted) for decadal periods from 1980s to 2000s by region. Positive values indicate net CO₂ losses from land ecosystems affected by land use change to the atmosphere. Uncertainties are reported as 90% confidence interval (unlike 68% in AR4). Numbers in parentheses are ranges in uncertainty provided in some studies. Tropical Asia includes the Middle East, India and surrounding countries, Indonesia and Papua New Guinea. East Asia includes China, Japan, Mongolia and Korea. N/A indicates not available from the study cited.

	Central and Africa South Americas	Tropical Asia	North America	Eurasia	East Asia	Oceania
--	---	------------------	------------------	---------	-----------	---------

<i>2000s</i>							
van der Werf et al. (2010) ^{a,b}	0.33	0.15	0.35	N/A	N/A	N/A	N/A
DeFries and Rosenzweig (2010) ^c	0.46	0.08	0.36	N/A	N/A	N/A	N/A
Houghton et al. (2012)	0.48	0.31 ^e	0.25	0.01	-0.07 ^d	0.01 ^e	N/A
van Minnen et al. (2009) ^a	0.45	0.21	0.20	0.09	0.08	0.10	0.03
Stocker et al. (2011) ^a	0.19	0.18	0.21	0.019	-0.067	0.12	0.011
Jain et al. (subm.) ^a	0.14	0.03	0.25	0.25	0.39	0.12	0.02
Poulter et al. (2010) ^a	0.09	0.13	0.14	0.01	0.03	0.05	0.00
Kato et al. (2012) ^a	0.36	-0.09	0.23	-0.05	-0.04	0.10	0.00
Average	0.31 ± 0.25	0.13 ± 0.20	0.25 ± 0.12	0.05 ± 0.17	0.12 ± 0.31	0.08 ± 0.07	0.01 ± 0.02
<i>1990s</i>							
DeFries et al. (2002)	0.5 (0.2–0.7)	0.1 (0.1–0.2)	0.4 (0.2–0.6)				
Achard et al. (2004)	0.3 (0.3–0.4)	0.2 (0.1–0.2)	0.4 (0.3–0.5)				
Houghton et al. (2012)	0.67	0.32 ^e	0.45	0.05	-0.04 ^d	0.05 ^e	
van Minnen et al. (2009) ^a	0.48	0.22	0.34	0.07	0.08	0.20	0.07
Stocker et al. (2011) ^a	0.30	0.14	0.19	-0.072	0.11	0.27	0.002
Jain et al. (subm.) ^a	0.20	0.04	0.31	0.27	0.47	0.19	0.00
Poulter et al. (2010) ^a	0.26	0.13	0.12	0.07	0.16	0.11	0.01
Kato et al. (2012) ^a	0.53	0.07	0.25	-0.04	-0.01	0.16	0.02
Average	0.41 ± 0.27	0.15 ± 0.15	0.31 ± 0.19	0.08 ± 0.19	0.16 ± 0.30	0.16 ± 0.13	0.02 ± 0.05
<i>1980s</i>							
DeFries et al. (2002)	0.4 (0.2–0.5)	0.1 (0.08–0.14)	0.2 (0.1–0.3)				
Houghton et al. (2012)	0.79	0.22 ^e	0.32	0.04	0.00 ^d	0.07 ^e	
van Minnen et al. (2009) ^a	0.70	0.18	0.43	0.07	0.06	0.37	0.04
Stocker et al. (2011) ^a	0.44	0.16	0.25	0.085	0.11	0.40	0.009
Jain et al. (subm.) ^a	0.26	0.01	0.34	0.30	0.71	0.59	0.00
Poulter et al. (2010) ^a	0.37	0.11	0.19	0.02	0.03	0.29	0.01
Kato et al. (2012) ^a	0.61	0.07	0.25	-0.04	-0.02	0.35	0.01
Average	0.51 ± 0.32	0.12 ± 0.12	0.28 ± 0.14	0.08 ± 0.19	0.15 ± 0.46	0.35 ± 0.28	0.01 ± 0.03

Notes:

(a) Method as described in the reference but updated to 2010 using the HYDE land cover change data.

(b) 1997–2006 average based on estimates of CO₂ emissions from deforestation and degradation fires, including peat carbon emissions. Estimates were doubled to account for emissions other than fire including respiration of leftover plant materials and soil carbon following deforestation following (Olivier et al., 2005). Estimates include peat fires and peat soil oxidation. If peat fires are excluded, estimate in tropical Asia is 0.23 and Pan-tropical total is 0.71.

(c) CO₂ estimates were summed for dry and humid tropical forests, converted to C and normalized to annual values. Estimates are based on satellite-derived deforestation area (Hansen et al., 2010), and assume 0.6 fraction of biomass emitted with deforestation. Estimates do not include carbon uptake by regrowth or legacy fluxes from historical deforestation. Estimates cover emissions from 2000 to 2005.

(d) Includes China only.

(e) East Asia and Oceania are averaged in one region. The flux is split in two equally for computing the average; North Africa and the Middle East are combined with Eurasia.

The estimates of net land use change CO₂ emissions are shown in Figure 6.10. Estimated gross emissions from tropical deforestation were 3.0 ± 0.5 PgC yr⁻¹ for the 1990s and 2.8 ± 0.5 PgC yr⁻¹ for the 2000s using forest inventory data, FAO (2010) reporting and the bookkeeping model method (Pan et al., 2011). The so called ‘gross emissions’ defined by all forest removal including both permanent deforestation and more temporary shifting cultivation and wood harvest cycles are about double the net emissions because of the presence of a large regrowth that compensates for about half of the gross emissions. A recent analysis estimated far lower gross deforestation of 0.6–1.2 PgC yr⁻¹ (Harris et al. 2012). However that study primarily

1 estimated permanent deforestation and excluded additional gross emissions from degraded forests, shifting
2 agriculture and some carbon pools (Houghton et al., 2012; House, subm.; van der Werf and Defries, subm.).
3 Understanding the different system boundary issues and what is and is not included in different analyses can
4 reconcile most of the difference between different 'gross emissions' published estimates (House, subm.).
5

6 Over the 1750–2011 time period, cumulative net CO₂ emissions from land use change of 180 ± 80 PgC are
7 estimated using the cumulative land use emissions of 150 PgC of Houghton et al. (2012) during 1850–2011
8 (Table 6.1) and an additional 30 PgC for 1750–1850 from the average of four publications (22 PgC by
9 Pongratz et al., 2009); 15 PgC by van Minnen et al. (2009); 64 PgC by Shevliakova et al. (2009b) and 24
10 PgC by Zaehle et al. (2011)). The uncertainty is based on the spread of the available estimates (Figure 6.10).
11 The CO₂ flux from land use has been dominated by deforestation and other land use change in the mid
12 northern latitudes prior to 1980s, and in the tropics since approximately 1980, largely from deforestation in
13 tropical America and Asia with smaller contributions from tropical Africa. Deforestation from 800 to 1750
14 has been estimated at 27 PgC using a process-based ecosystem model (Pongratz et al., 2009).
15

16 6.3.2.3 Atmospheric CO₂ Concentration Growth Rate

17
18 Since the beginning of the Industrial Era (1750), the concentration of CO₂ in the atmosphere increased by
19 40%, from 278 ± 5 ppm to 390.4 ppm in 2011 (Figure 6.11), updated from MacFarling-Meure et al. (2006),
20 corresponding to an increase in CO₂ of 240 ± 10 PgC in the atmosphere. Atmospheric CO₂ grew at a rate of
21 3.4 ± 0.2 PgC yr⁻¹ in the 1980s, 3.1 ± 0.2 PgC yr⁻¹ in the 1990s, and 4.0 ± 0.2 PgC yr⁻¹ in the 2000s (Conway
22 and Tans, 2011): data from NOAA/ESRL and Scripps Institution of Oceanography
23 (www.esrl.noaa.gov/gmd/ccgg/trends/). The rise of atmospheric CO₂ is established with a very small
24 uncertainty from measurements of CO₂ trapped in air bubbles in ice cores, between 1750 and 1957 e.g.,
25 Etheridge et al. (1996), and from highly precise continuous atmospheric CO₂ concentration measurements at
26 background stations after that date (Keeling et al., 1976).
27

28 [INSERT FIGURE 6.11 HERE]

29 **Figure 6.11:** Atmospheric CO₂, CH₄, and N₂O concentrations history over the last 260 years determined from air
30 enclosed in ice cores and firn air (color symbols) and from direct atmospheric measurements (blue lines, measurements
31 from the Cape Grim observatory) (MacFarling-Meure et al., 2006).
32

33 The ice core record of atmospheric CO₂ concentration during the past century exhibits some interesting
34 features, which can be related to climate induced-changes in the carbon cycle. Most conspicuous is the
35 interval from about 1940 until the early 1960s, during which the concentration increase of CO₂ (also CH₄
36 and N₂O) stalled (MacFarling-Meure et al., 2006), possibly caused by slightly decreasing temperatures over
37 land in the Northern Hemisphere (Rafelski et al., 2009).
38

39 There is substantial evidence (e.g., from ¹³C carbon isotopes in atmospheric CO₂, Keeling et al., 2005) that
40 source/sink processes on land generate most of the interannual variability in the atmospheric CO₂ growth
41 rate as shown in Figure 6.12 (Section 6.3.2.5). The data shown in this figure indicate that the strong positive
42 anomalies of the CO₂ growth rate in El Niño years (e.g., 1987/1988 and 1997/1998) originated in tropical
43 latitudes, while the anomalies in 2003 and 2005 originated in northern mid- latitudes, maybe reflecting the
44 European heat wave in 2003 (Ciais et al., 2010).
45

46 [INSERT FIGURE 6.12 HERE]

47 **Figure 6.12:** (Top) Global average atmospheric CO₂ growth rate, computed from the observations of the SIO network
48 (dark green curve; Keeling et al., 2005) and from the marine boundary layer air reference measurements of the NOAA-
49 GMD network (Conway et al., 1994; Keeling et al., 2005). (Bottom) Atmospheric growth rate of CO₂ as a function of
50 latitude determined from the GLOBALVIEW data product, representative of stations located in the marine boundary
51 layer at each given latitude (Masarie and Tans, 1995). Sufficient observations are available only since 1979.
52

53 6.3.2.4 CO₂ Airborne Fraction

54
55 The ratio of CO₂ annual growth rate in the atmosphere to total anthropogenic CO₂ emissions (fossil fuel and
56 cement, plus net land use change emissions), i.e., the fraction of total emissions remaining in the atmosphere,
57 is called the 'airborne fraction' (AF). This is an important diagnostic of the efficiency and variability of the
58 CO₂ sinks at absorbing excess CO₂ from total anthropogenic emissions. Several factors can influence the AF.

1 First and most importantly, the AF responds to the emissions trajectory through the effect of atmospheric
2 CO₂ on sinks. The AF is expected to be constant if emissions grow exponentially with a constant time scale
3 (e-folding) and if the sinks respond linearly to increasing CO₂ (Bacastow and Keeling, 1979; Gloor et al.,
4 2010). As emissions depart from exponential growth with constant time scale, the AF departs from
5 constancy. In addition, other factors can influence the AF, such as changes in the response of carbon sinks to
6 rising CO₂, nutrient availability, land management, and changes in physical climate and changes in terrestrial
7 and marine ecosystems (nonlinear effects of climate on carbon fluxes). Climate and CO₂ effects were
8 suggested to be important drivers of AF changes in future projections from coupled carbon-climate models
9 used in the AR4 (Friedlingstein et al., 2006), with a diagnosed increase in the AF of 0.07 (median of 11
10 models; range of 0.01–0.22; Canadell et al. (2007)) in 2100 under the SRES-A2 emission scenario.

11
12 Up to the date of publication of the AR4, no significant trend in AF had been identified over the period since
13 1959 (for which the most accurate atmospheric CO₂ data are available). Until recently, the uncertainty in
14 land use change emissions was too large to provide a meaningful measure of the trend in AF, and a definition
15 of the AF using fossil fuel emissions only was used, such as Figure 7.4 in AR4. Improved forest area loss
16 data from country statistics (FAO, 2010) and satellite data (Hansen et al., 2010; Regalado, 2010) have
17 contributed to reducing the uncertainty in tropical land use CO₂ emission estimates (Section 6.3.2.2). A
18 positive trend in AF of $\sim 0.3\% \text{yr}^{-1}$ relative to the mean was found by all recent studies using total
19 anthropogenic CO₂ emissions to define AF, over the ~ 1960 –2010 period, but there is no consensus on the
20 significance (Ballantyne et al., 2012; Knorr, 2009) and the cause of this trend (Canadell et al., 2007; Gloor et
21 al., 2010; Raupach et al., 2008). The significance of the AF positive trend is influenced by the specific
22 consideration of uncertainty and (in some studies) by the method used to filter out ‘known’ variability
23 associated with El Niño and volcanic major eruptions. The cause of the trend in the AF is also disputed, but
24 land and ocean carbon cycle model results attributing the trends to underlying processes suggest that climate
25 effects on ocean and land sinks could have a large influence (Le Quere et al., 2009), but that the role of
26 climate variability is important as well (Raupach et al., *subm.*) and could dominate the signal (Frölicher et
27 al., *subm.*).

28 29 6.3.2.5 Ocean Sinks

30 31 6.3.2.5.1 Global ocean sink

32 The estimate of the mean anthropogenic ocean CO₂ sink from AR4 of $2.2 \pm 0.7 \text{ PgC yr}^{-1}$ (uncertainty
33 converted from 68% in AR4 to 90% confidence intervals in this Chapter) is unchanged from the AR4 report
34 and confirmed by several contemporary estimates (see Chapter 3). The uptake of anthropogenic CO₂ by the
35 ocean is primarily a response to increasing CO₂ in the atmosphere and is limited mainly by the rate at which
36 anthropogenic CO₂ is transported from the surface waters into the deep waters (Gloor et al., 2010). However,
37 this anthropogenic ocean CO₂ sink occurs on top of a very active natural oceanic carbon cycle. Recent trends
38 in the climate system, such as ocean warming, changes in ocean circulation and changes in marine
39 ecosystems and biogeochemical cycles can have affected both the anthropogenic ocean CO₂ sink occurs as
40 well as natural CO₂ fluxes exchanged with the atmosphere. Since AR4, progress has been made to quantify
41 the rate of change of the net ocean CO₂ sink in the past decades, including the attribution to the response of
42 the ocean to increasing CO₂ in the atmosphere, and the response to climate and circulation trends and
43 variability, as explained below.

44
45 Observations of the partial pressure of CO₂ at the ocean surface (pCO₂) show that pCO₂ has been increasing
46 generally at about the same rate as CO₂ in the atmosphere when averaged over large ocean regions during the
47 past two to three decades (Inoue and Ishii, 2005; McKinley et al., 2011; Takahashi et al., 2009). However,
48 analyses of regional observations highlight substantial regional and temporal variations around this mean
49 trend of pCO₂, with surface ocean pCO₂ increasing regionally either at the same rate or faster than
50 atmospheric CO₂ between about 1990 and 2005 in the North Atlantic (Schuster et al., 2009; thus a constant,
51 or a decreasing sink for CO₂ in that region) and between 1981 and 2004 in the western equatorial Pacific
52 (Feely et al., 2006). A weakening sink in the Southern Ocean was also inferred from atmospheric CO₂
53 observations using one inversion model (Le Quere et al., 2007). By contrast, pCO₂ appears to have increased
54 at a slower rate than atmospheric CO₂ (thus a growing ocean CO₂ sink in that region) in the Northern North
55 Pacific Ocean (Takahashi et al., 2006).

The difference between decadal values of the ocean anthropogenic CO₂ sink is assessed in this Chapter with an ensemble of five studies using various methods, giving a decadal mean uptake of 2.0 ± 0.7 PgC yr⁻¹ for 1980–1989 and of 2.3 ± 0.7 PgC yr⁻¹ for 2000–2009 (Table 6.4). The methods used are: (1) an empirical Green’s function approach fitted to observations of transient ocean tracers (Khatiwala et al., 2009), (2) a model-based Green’s function approach fitted to anthropogenic carbon reconstructions (Mikaloff-Fletcher et al., 2006), (3) empirical relationships between ocean surface pCO₂ and temperature and salinity (Park et al., 2010), and (4) process-based global ocean biogeochemical models forced by observed meteorological fields (Assmann et al., 2010; Doney et al., 2009; LeQuere et al., 2010). All these different methods suggest that in the absence of recent climate change and climate variability, the ocean anthropogenic CO₂ sink should have increased by 0.23 ± 0.15 PgC yr⁻¹ between the 1980s and the 1990s, and by 0.33 ± 0.13 PgC yr⁻¹ between the 1990s and the 2000s (Figure 6.13). The decadal estimates in the ocean CO₂ sink reported in Table 6.4 as ‘CO₂ effects only’ are entirely explained by the faster rate of increase of atmospheric CO₂ in the later decade. On the other hand, ‘climate effects only’ in Table 6.4 are assessed to have no noticeable effect on the sink difference between the 1980s and the 1990s (0.02 ± 0.05 PgC yr⁻¹), but are estimated by process-based models to have reduced the ocean anthropogenic CO₂ sink by 0.19 ± 0.18 PgC yr⁻¹ between the 1990s and the 2000s (Table 6.4).

Table 6.4: Decadal change in the ocean CO₂ sink from models and from data-based methods (a positive change between two decades means an increasing sink with time). It is reminded that the total CO₂ sink for the 1990s is estimated at 2.2 ± 0.7 PgC yr⁻¹ based on observations.

	Method	1990s minus 1980s PgC yr ⁻¹ decade ⁻¹	2000s minus 1990s PgC yr ⁻¹
<i>CO₂ effects only</i>			
Khatiwala et al. (2009)	data based	0.24	0.20
Mikaloff-Fletcher et al. (2006) ^a	data inversion	0.40	0.44
Assmann et al. (2010) (to 2007 only)	model	0.28	0.35
Graven et al. (2012)	model	0.15	0.25
Doney et al. (2009)	model	0.15	0.39
Le Quere et al. (2010) NCEP	model	0.16	0.32
Le Quere et al. (2010) ECMWF	model	–	0.39
Le Quere et al. (2010) JPL	model	–	0.32
<i>Average^b</i>		0.23 ± 0.15	0.33 ± 0.13
<i>Climate effects only</i>			
Park et al. (2010)	data-based	–	–0.15
Assmann et al. (2010) (to 2007 only)	model	0.07	0.00
Graven et al. (2012)	model	0.02	–0.27
Doney et al. (2009)	model	–0.02	–0.21
Le Quere et al. (2010) NCEP	model	0.02	–0.27
Le Quere et al. (2010) ECMWF	model	–	–0.14
Le Quere et al. (2010) JPL	model	–	–0.36
<i>Average^b</i>		0.02 ± 0.05	-0.19 ± 0.18
<i>CO₂ and climate effects combined</i>		0.25 ± 0.16	0.14 ± 0.22

Notes:

(a) As published by Sarmiento et al. (2010).

(b) Average of all estimates \pm 90% confidence interval. The average includes results by Le Quere et al. (2010) – NCEP only because the other Le Quere et al. model versions do not differ sufficiently to be considered separately.

(c) The NCEP, ECMWF and JPL reproduce surface climate conditions as described in the reference.

[INSERT FIGURE 6.13 HERE]

Figure 6.13: Trends in the ocean-to-atmosphere flux of CO₂ in response to: (Top) variability and trends in surface climate, (middle) increasing atmospheric CO₂, and (Bottom) the sum of both effects (PgC yr⁻¹). All estimates are normalized to zero during 1990–2000 to highlight the trends. Estimates are updates from ocean models (in colours) and from indirect methods based on observations (Khatiwala et al., 2009; Park et al., 2010).

6.3.2.5.2 Regional air-sea CO₂ fluxes

Because of the superposition of an active natural cycle and the ocean anthropogenic CO₂ sink, a global map of net air-sea fluxes of CO₂ show regions in the ocean where CO₂ is absorbed from the atmosphere, and regions where CO₂ is released to the atmosphere, even though overall the ocean absorb about 2 PgC every year. The Equatorial Pacific (14°N–14°S) is a major net source for atmospheric CO₂ because deep waters rich in carbon are upwelled to the surface, losing about 0.5 PgC yr⁻¹ (Takahashi et al., 2009). The temperate oceans, between 14° and 50° in both hemispheres, are major sink zones. Altogether, the Atlantic and Arctic oceans act as a net CO₂ sink of 0.6 ± 0.2 PgC yr⁻¹ (Schuster et al., *subm.*). The North Atlantic is the most intense ocean CO₂ sink region on a per unit area basis, due to the combination of strong ocean mixing with strong biological productivity and cooling of surface waters. The Southern Ocean (<44°S) is estimated to be a CO₂ sink of ~0.3 PgC yr⁻¹ (Gruber et al., 2009). It is not as intense as the North Atlantic because of a partial cancellation of the summer CO₂ uptake by the winter release of CO₂ from the upwelling of CO₂-enriched deep water (Gruber et al., 2009). The North Pacific and Southern Ocean subtropics are also sinks for CO₂ (Takahashi et al., 2009).

6.3.2.5.3 Regional changes in ocean dissolved inorganic carbon storage

Data-based estimates for the global ocean inventory of anthropogenic carbon obtained from repeated shipboard hydrographic cross sections (Khatiwala et al., 2009; Sabine et al., 2004; Waugh et al., 2006) agree well among each other, with an average value of 155 ± 30 PgC for the period 1750–2011 (See Chapter 3). The uptake of anthropogenic carbon into the ocean is observed to be larger in the high latitudes than in the tropics and subtropics over the entire Industrial Era, because of the more vigorous ocean mixing in the high latitudes (Khatiwala et al., 2009). A number of ocean cross sections have been repeated over the last decade and the observed changes in carbon storage, assessed in Table 6.5, suggest that some locations see rates of carbon accumulation that are higher and others that are lower than the global average estimated by Khatiwala et al. (2009). No global synthesis of these observations exists at present. Model results suggest that there may be an effect of climate change and variability in the storage of total inorganic carbon in the ocean (Table 6.4), but that this effect is small (~2 PgC over the past 50 years; Figure 6.13) compared to the cumulative uptake of anthropogenic carbon during the same period.

Table 6.5: Regional rates of change in inorganic carbon storage from repeated hydrographic cross sections

Section	Time	Storage rate (mol C m ⁻² yr ⁻¹)	Data source
<i>Global average</i>	2008	0.53 ± 0.16	Khatiwala et al. (2009)
<i>Pacific Ocean</i>			
Section along 30°S	1992–2003	1.0 ± 0.4	Murata et al. (2007)
N of 50°S, 120°W–180°W	1974–1996	0.9 ± 0.3	Peng et al. (2003)
154°W, 20°–50°S	1991–2006	0.56 ± 0.04	Sabine et al. (2008)
140°E–170°W, 45°S–65°S	1968–1991/1996	0.40 ± 0.20	Matear and McNeil (2003)
149° W, 4°S–10°N	1993–2005	0.3 ± 0.1	Murata et al. (2009)
149° W, 24°N–30°N	1993–2005	0.6 ± 0.2	Murata et al. (2009)
Northeast Pacific	1973–1991	1.3 ± 0.5	Peng et al. (2003)
~160°E ~45°N	1997–2008	0.40 ± 0.08	Wakita et al. (2010)
North of 20°N	1994–2004/2005	0.39 ± 0.15	Sabine et al. (2008)
150°W, 20°S–20°N	1991/1992–2006	0.25 ± 0.09	Sabine et al. (2008)
<i>Indian Ocean</i>			
20°S–10°S	1978–1995	0.1	Peng et al. (1998)

10°S–5°N	1978–1995	0.65	Peng et al. (1998)
Section along 20°S <i>Atlantic Ocean</i>	1995–2003/2004	1.0 ± 0.1	Murata et al. (2010)
Section along 30°S ~30°W, 56°S–15°S	1992/1993–2003	0.6 ± 0.1	Murata et al. (2010)
20°W, 64°N–15°N	1989–2005	0.76	Wanninkhof et al. (2010)
~25°W, 15°N–15°S	1993–2003	0.57	Wanninkhof et al. (2010)
40°N–65°N	1993–2003	0.2	Wanninkhof et al. (2010)
20°N–40°N	1981–1997/1999	2.2 ± 0.7	Friis et al. (2005)
Nordic Seas	1981–2004	1.2 ± 0.3	Tanhua et al. (2007)
<i>Sub-decadal variations</i>	1981–2002/2003	0.9 ± 0.2	Olsen et al. (2006)
Irminger Sea	1981–1991	0.55 ± 0.39	Perez et al. (2008)
Irminger Sea	1991–1996	2.3 ± 0.6	Perez et al. (2008)
Irminger Sea	1997–2006	0.75 ± 0.16	Perez et al. (2008)

6.3.2.5.4 Interannual variability in air-sea CO₂ fluxes

The interannual variability in the global ocean CO₂ sink is estimated to be of about ± 0.2 PgC yr⁻¹ (Wanninkhof et al., *subm.*) which is small compared to the interannual variability of the terrestrial CO₂ sink. In general, the ocean takes up more CO₂ during El Niño episodes (Park et al., 2010) because of the temporary suppression of the natural source of CO₂ to the atmosphere over the eastern Pacific upwelling, during El Niño episodes. Interannual variability of ~0.3 PgC yr⁻¹ has been reported for the North Atlantic ocean region alone (Watson et al., 2009) but there is no agreement among estimates regarding the exact magnitude of driving factors of air-sea CO₂ flux variability in this region (Schuster et al., *subm.*). Interannual variability of 0.1–0.2 PgC yr⁻¹ was also estimated by models and one atmospheric inversion in the Southern Ocean (Le Quere et al., 2007), possibly driven by the Southern Annular Mode of climate variability (Lenton and Matear, 2007; Lourantou and Metzl, 2011; Lovenduski et al., 2007).

6.3.2.5.5 Processes driving variability and trends in air-sea CO₂ fluxes

Three type of processes are estimated to have an important effect on the air-sea fluxes of CO₂ on century time scales: (1) the dissolution of CO₂ at the ocean surface and its chemical equilibrium with other forms of carbon in the ocean (mainly carbonate and bicarbonate), (2) the transport of carbon between the surface and the intermediate and deep ocean, and 3) the cycling of carbon through marine ecosystem processes (see Section 6.1.1.1). The surface dissolution and equilibration of CO₂ with the atmosphere is well understood and quantified. It varies with the surface ocean conditions, in particular with temperature (solubility effect) and alkalinity (a measure of the capacity of an aqueous solution to neutralize acids). The capacity of the ocean to take up additional CO₂ for a given alkalinity decreases at higher temperature (4.23% per degree warming (Takahashi et al., 1993) and at elevated CO₂ concentrations (about 15% per 100 ppm, computed from the so called Revelle factor). These effects are well established and have been included in all previous IPCC Assessments Reports.

The recent increase in North Atlantic surface water pCO₂ values since about 1990 at rates faster than atmospheric CO₂ (causing a sink decrease) appear to be related to sea surface warming and its effect on solubility (Corbiere et al., 2007) and/or changes in ocean circulation (Schuster and Watson, 2007; Schuster et al., 2009). Recent changes have been associated with decadal variability in the North Atlantic Oscillation (NAO) and the Atlantic Multidecadal Variability (AMV) positive state (McKinley et al., 2011; Thomas et al., 2007; Tjiputra et al., 2012; Ullman et al., 2009), but a systematic analysis of estimates of trends in this region show no agreement regarding the drivers of change (Schuster et al., *subm.*). In addition, rapid increases of pCO₂ observed in winter 2003–2008 (observed pCO₂ increases between 5 to 7 μatm yr⁻¹) have been attributed to an increase of deep convection (import of rich-CO₂ subsurface and deep waters) that dominates the effect of recent cooling on pCO₂ (Metzl et al., 2010).

1 The weakening of the Southern Ocean CO₂ sink identified from atmospheric and oceanic CO₂ observations
2 (Le Quere et al., 2007; Metzl, 2009; Takahashi et al., 2009) is attributed by models as a response to an
3 increase in Southern Ocean winds driving increased upwards transport of carbon-rich deep waters (Lenton
4 and Matear, 2007; LeQuere et al., 2010; Lovenduski et al., 2007; Verdy et al., 2007). The increased
5 upwelling is in part compensated by increasing eddy fluxes outside the Southern Ocean and by increasing
6 export of carbon to depth from biological production (Lenton et al., 2009). The increase in winds has been
7 attributed to indirect human activities, mainly to the depletion of stratospheric ozone (Thompson and
8 Solomon, 2002) with a contribution from greenhouse gases (Fyfe and Saenko, 2006).

9
10 Large decadal variability has been observed in the Equatorial Pacific (Ishii et al., 2009) associated with
11 changes in the phasing of the Pacific Decadal Oscillation and its impact on gas transfer velocity (Feely et al.,
12 2006; Valsala et al., 2012). There is less evidence available to attribute the observed changes in other regions
13 to changes in underlying processes or climate change and variability.

14
15 Recent changes in nutrient supply in the ocean are also thought to have changed the export of organic carbon
16 from biological processes below the surface layer, and thus the ocean CO₂ sink. Anthropogenic reactive
17 nitrogen Nr (see Box 6.1) entering the ocean via atmospheric deposition or rivers acts as a fertilizer and is
18 enhancing carbon export to depth and hence the CO₂ sink. This Nr contribution has been estimated between
19 0.1 and 0.4 PgC yr⁻¹ in around year 2000 using models (Duce et al., 2008; Krishnamurthy et al., 2009; Reay
20 et al., 2008; Suntharalingam et al., 2012). Similarly, human-driven increase in iron deposition over the ocean
21 from land use change is estimated to have enhanced the ocean cumulative CO₂ uptake by 8 PgC during the
22 20th century (~3 percent) (Mahowald et al., 2010). Although changes in ocean circulation and in global
23 biogeochemical drivers have the potential to alter the ocean carbon fluxes through changes in marine
24 ecosystems, modelling studies show only small variability in ocean biological pump, which has not
25 significantly impacted the response of the ocean carbon cycle over the recent period (Bennington et al.,
26 2009). Therefore, there is no evidence that changes in marine ecosystems have had a large impact on the
27 ocean CO₂ sink in recent decades apart from those triggered by changes in nitrogen and iron supply.

28
29 Model studies suggest that the response of the air-sea CO₂ fluxes to climate change and variability in recent
30 decades has decreased the rate at which anthropogenic CO₂ is absorbed by the ocean (Sarmiento et al.
31 (2010), Sitch et al. (subm.); Table 6.4). This result is robust to the model or climate forcing used (Figure
32 6.13). The climate-induced weakening of the ocean CO₂ sink was attributed in one model to increases in
33 winds in the Southern Ocean and in the equatorial Pacific, with a ~20% contribution from warming and a
34 30% non-linear amplification of the response to climate change and variability due to surface ocean warming
35 (LeQuere et al., 2010). No formal attribution to anthropogenic climate change has been made outside the
36 Southern Ocean.

37 38 *6.3.2.5.6 Model evaluation of global and regional ocean carbon balance*

39 Ocean process-based carbon cycle models are capable to reproduce to a first order the mean air-sea fluxes of
40 CO₂ derived from pCO₂ observations (Takahashi et al., 2009) for at least ten years, including their general
41 patterns and amplitude (Sarmiento et al., 2000), the anthropogenic uptake of CO₂ (Orr et al., 2001;
42 Wanninkhof et al., subm.), and the regional distribution of air-sea fluxes (Gruber et al., 2009). The spread
43 between different model results for air-sea CO₂ fluxes is the largest in the Southern Ocean (Matsumoto et al.,
44 2004), where intense mixing occurs. Tracer observations (Schmittner et al., 2009) and water mass analysis
45 (Iudicone et al., 2011) have been used to reduce the model uncertainty associated with ocean mixing and
46 improve the simulation of carbon fluxes. The models reproduce the observed seasonal cycle of pCO₂ in the
47 sub-tropics but generally do poorly in sub-polar regions where the balance of processes is more difficult to
48 simulate well (McKinley et al., 2006; Schuster et al., subm.). Less information is available to evaluate
49 specifically the representation of biological fluxes in the models, outside from their reasonable representation
50 of surface ocean chlorophyll. Ocean process-based carbon cycle models used in AR5 reproduce the
51 relatively small interannual variability inferred from observations (Figure 6.11; Wanninkhof et al., subm.).
52 See also Chapter 9, Section 9.4.5.2.

53
54 *Sensitivity of modelled air-sea fluxes to CO₂*. The sensitivity of ocean models to the level and rate of change
55 of CO₂ in the atmosphere can be evaluated from several studies that have isolated the uptake of
56 anthropogenic CO₂ from changes in natural fluxes using combinations of observations. Data-based studies
57 have focused on three time-periods: 1750–1994, 1990–1999, and 1990–2009, and estimated a cumulative

1 uptake of carbon of $\sim 120 \pm 25$ PgC (Khaliwala et al., 2009; Sabine et al., 2004; Waugh et al., 2006), a mean
2 anthropogenic CO₂ sink of 2.2 ± 0.7 Pg C yr⁻¹, and decadal trends of 0.13 PgC yr⁻¹ per decade during the two
3 decades 1990–2009 (Wanninkhof et al., *subm.*; from atmospheric inversions), respectively. Models that have
4 estimated these quantities give a total ocean uptake of 130 ± 24 PgC for 1750–1994 and a mean ocean CO₂
5 sink of 2.3 ± 0.4 PgC yr⁻¹ for 1990–1999 (model ensemble from Orr et al., 2005), and a trend in uptake rate
6 of 0.12 PgC yr⁻¹ per decade for 1990–2009 (Wanninkhof et al., *subm.*). Therefore, although the ocean
7 models do not reproduce all the details of the regional structure and changes in air-sea CO₂ fluxes, their
8 globally integrated ocean CO₂ sink and decadal rate of change of this sink is in good agreement with the
9 available observations.

10
11 *Sensitivity of modelled air-sea fluxes to climate.* The relationship between air-sea CO₂ flux and climate is
12 strongly dependent on the oceanic region and on the time-scale. In general, the ocean takes up more CO₂
13 during El Niño events when the upwelling of carbon-rich waters in the Pacific decreases (see Section
14 6.3.6.4), and more CO₂ during glacial periods when the ocean temperature was cooler and the ocean
15 circulation modified (see Section 6.2.2.1.1). Yet, these time scales are not fully relevant to assess how
16 climate dynamics this century impacts air-sea CO₂ fluxes. Changes in atmospheric CO₂ by less than 25 ppm
17 during Dansgaard-Oeschger abrupt climate events during glacial periods may have been caused by the ocean
18 (Schmittner and Galbraith, 2008) on a millennial time scale see Section 6.2.1.2. Although these abrupt events
19 are relevant to gain insight on processes, they were associated with a re-organisation of the sea surface
20 temperature and ocean circulation, rather than with a GHG driven global mean temperature change as during
21 the Industrial Era. Ocean carbon cycle models used in AR5 estimate a reduction in cumulative ocean CO₂
22 uptake of 1.6–5.4 PgC over the period 1959–2008 (1.5–5.4%) in response to climate change and variability
23 (Figure 6.13), partly due to changes in the equatorial Pacific and to changes in the Southern Ocean. The only
24 observational-based estimate available to evaluate the climate response of the global air-sea CO₂ flux is from
25 Park et al. (2010), which is at the low end of the model estimate for the past two decades (Table 6.4).
26 However this estimate does not include the non-linear effects of changes in ocean circulation and warming
27 on the global air-sea CO₂ flux, which could amplify the response of the ocean CO₂ sink to climate by 20–
28 30% (LeQuere et al., 2010; Zickfeld et al., 2011). It is not yet possible to evaluate how much of this signal is
29 in response to climate trends and how much is caused by climate variability. From the model estimates
30 assessed in this chapter, the response of the ocean global CO₂ sink to climate trends and variability was
31 negative (weakening sink) and about half the magnitude of the positive response (increasing sink) to
32 atmospheric CO₂ in the past two decades (Table 6.4)

33
34 *Processes missing in ocean models.* The most important processes missing in current global ocean carbon
35 cycle models used in the AR5 are those representing small-scale physical circulation (e.g., eddies, brine
36 formation), which have an important influence on the vertical transport of water, heat and carbon (Loose and
37 Schlosser, 2011; Sallée et al., 2012). In particular, changes in vertical transport in the Southern Ocean is
38 thought to have caused most of the 80–100 ppm changes in atmospheric CO₂ between glacial and interglacial
39 conditions (Sigman et al., 2010), consistent with observed changes in deep stratification (Burke and
40 Robinson, 2012). This signal is not entirely reproduced by models (Section 6.2) and suggests that the
41 sensitivity of ocean models could be underestimated.

42
43 Processes related to marine ecosystems in global ocean models are also limited to the simulation of lower
44 trophic levels, with crude parameterizations for bacterial and other loss processes and their temperature-
45 dependence. Projected changes carbon fluxes from the response of marine ecosystems to changes in
46 temperature (Beaugrand et al., 2010), ocean acidification (Iglesias-Rodriguez et al., 2008), and pressure from
47 fisheries (Pershing et al., 2010) are all considered potentially important, though not yet quantified. Several
48 processes have been specifically identified that could lead to changes in the ocean CO₂ sink, in particular the
49 temperature effects on marine ecosystem processes (Riebesell et al., 2009; Taucher and Oschlies, 2011) and
50 the variable nutrient ratios induced by ocean acidification or ecosystem changes (Tagliabue et al., 2011).
51 Nevertheless, the fit of ocean model results to recent observations and trends suggest that, up to now,
52 changes in ecosystem processes have not had a dominant effect on ocean CO₂.

53 6.3.2.6 Land Sinks

6.3.2.6.1 Global land sink

The global budget of anthropogenic CO₂ constrained by observations of atmospheric CO₂ concentrations, estimates of fossil fuel emissions, land use change emissions and ocean observations and models provide an estimate of the so called ‘residual land sink’ necessary to satisfy mass conservation. This residual land sink of anthropogenic CO₂ is of 1.5 ± 1.1 , 2.6 ± 1.2 and 2.5 ± 1.2 PgC yr⁻¹ for the 1980s, 1990s, and 2000s, respectively (Table 6.1). The larger residual land sink in the early 1990s compared to the 1980s has been attributed to the response of terrestrial ecosystems to the eruption of Mount Pinatubo in June 1991, when a decrease in temperature and an increase in diffuse light fraction occurred, and were estimated using process-based terrestrial ecosystem models to have increased the residual land sink (Lucht et al., 2002; Mercado et al., 2009).

From an ensemble of several global process-based terrestrial ecosystem models forced by the same gridded weather and climate fields and observed atmospheric CO₂ concentrations, Sitch et al. (subm) estimate a global sink of anthropogenic CO₂ of 1.8 ± 0.7 PgC yr⁻¹ for the 1980s, 2.3 ± 0.9 PgC yr⁻¹ for the 1990s and 2.6 ± 1.4 PgC yr⁻¹ for the 2000s (Table 6.6; Sitch et al., subm). However, none of these models includes land use change effects or forest dynamics (i.e., mortality and recruitment rates affecting biomass and CO₂ fluxes).

The net land-to-atmosphere flux of anthropogenic CO₂ (including land use change emissions plus the residual land sink) assessed in Table 6.1 corresponds to a net sink of CO₂ by terrestrial ecosystems, which has intensified globally from a neutral CO₂ flux of 0.1 ± 0.8 PgC yr⁻¹ in the 1980s to a net CO₂ sink of 1.1 ± 0.9 PgC yr⁻¹ and 1.4 ± 0.9 PgC yr⁻¹ during the 1990s and 2000s, respectively (Table 6.1; Sarmiento et al., 2010). This increasing net land-to-atmosphere flux towards a larger sink is consistent with trends in the net atmosphere-to-land CO₂ flux from atmospheric inversion methods, which estimate an increasing trend in the atmosphere-to-land flux of -0.057 ± 0.01 PgC yr⁻² during 1980–2008 (Gurney and Eckels, 2011).

Table 6.6: Estimates of atmosphere-to-land CO₂ flux from process-based terrestrial ecosystem models driven by rising CO₂ and by changes in climate.

Model name	Nitrogen limitation (yes/no)	Natural Fire CO ₂ emissions (yes/no)	1980–1989 PgC yr ⁻¹	1990–1999 PgC yr ⁻¹	2000–2009 PgC yr ⁻¹
CLM4C ^{b,c}	No	Yes	1.98	2.11	2.64
CLM4CN ^{b,c}	Yes	Yes	1.27	1.25	1.67
Hyland ^d	No	No	3.28	4.07	5.23
LPJ ^e	No	Yes	1.14	1.90	2.60
LPJ_GUESS ^f	No	Yes	1.15	1.54	2.07
OCN ^g	Yes	No	1.75	2.18	2.36
ORC ^h	No	No	2.08	3.05	3.74
SDGVM ⁱ	Yes	Yes	1.25	1.95	2.30
TRIFFID ^j	Yes	No	1.85	2.52	3.00
VEGAS ^k	No	No	-0.05	0.22	0.57
Average ^a			1.57 ± 1.34	2.08 ± 1.61	2.62 ± 1.93

Notes:

(a) Average of all model. The uncertainty represents ± 1 Mean Absolute Deviation from the mean.

(b) Oleson et al. (2010)

(c) Lawrence et al. (2011)

(d) Levy et al. (2004)

(e) Sitch et al. (2003)

(f) (Smith et al., 2001a)

(g) Zaehle and Friend (2010)

(h) Krinner et al. (2005)

(i) Woodward and Lomas (2004)

1 (j) Cox (2001)

2 (k) Zeng (2003)

3 All these models run are forced by rising CO₂ concentration and time-varying historical reconstructed weather and
4 climate fields using the same protocol from the TRENDY project (Sitch et al., *subm*)
5 (<http://www.globalcarbonproject.org/global/pdf/DynamicVegetationModels.pdf>).
6
7

8 6.3.2.6.2 Regional atmosphere-land CO₂ fluxes

9 In this Chapter, the results from CO₂ inversions, terrestrial ecosystem models and forest inventories
10 (obviously restricted to forest biomes, with very sparse coverage in the tropics) consistently show that the
11 largest net terrestrial CO₂ sink is located in the northern extra-tropics (Gurney and Eckels, 2011; Jacobson et
12 al., 2007; Pan et al., 2011; Sitch et al., 2008; Figure 6.14). Inversion estimates of atmosphere-land CO₂
13 fluxes in the tropics remain highly unconstrained, given very few atmospheric CO₂ stations, and inversion
14 results show flux estimates ranging from neutral to a net tropical source of 0.5–1.0 PgC yr⁻¹ (Gurney and
15 Eckels, 2011; Jacobson et al., 2007). Stephens et al. (2007) selected from an ensemble of inversion models
16 those that were consistent with independent aircraft cross-validation data, and constrained a quasi neutral
17 tropical land CO₂ flux of 0.1 ± 0.8 PgC yr⁻¹ during the period 1992–1996, and a Northern Hemisphere net
18 land CO₂ sink of 1.5 ± 0.6.
19

20 [INSERT FIGURE 6.14 HERE]

21 **Figure 6.14:** Decadal average CO₂ fluxes for 22 partitions of the globe for (1) the 1990s (cyan) and 2000s (brown) as
22 estimated by atmospheric CO₂ inversions, (2) the dynamic vegetation models (DGVMs), and (3) pCO₂ measurements
23 based air-sea exchange climatology. The regional partitions are depicted as an inset and shaded by CO₂ flux density
24 (blue-green-brown: -ve flux, red-grey: +ve flux). The mean values are calculated from monthly-mean fluxes from 17
25 inverse models for the period of 1990–2008, and standard deviations shown as error bars are for model-to-model
26 differences within each decade. The DGVM fluxes are calculated using 14 climate-carbon model simulations (not true
27 values).
28

29 A number of studies since AR4 have compared and attempted to reconcile regional atmosphere-land CO₂
30 flux estimates from multiple approaches and so provided an important test for the degree of confidence of
31 regional land flux estimates. For North America, a net land CO₂ sink of 0.5 PgC yr⁻¹ with 95% certain that
32 the estimate is within 25% (SOCCR, 2007) and 0.3 ± 0.2 PgC yr⁻¹ (Hayes et al., 2012); Europe, a 0.3 ± 0.2
33 PgC yr⁻¹ sink (Schulze et al., 2009); for China, a 0.2 ± PgC yr⁻¹ sink (Piao et al., 2009a); Russia a 0.6 – 0.8
34 PgC csyr⁻¹ (Dolman et al., 2012); Arctic tundra, a 0.1 PgC yr⁻¹ sink with an uncertainty between a sink of
35 0.3 PgC yr⁻¹ and a source of 0.1 PgC yr⁻¹ (McGuire et al., 2009). A broader analysis of regional
36 contributions estimated a 1.7 PgC yr⁻¹ sink in the Northern Hemisphere regions above 20°N with consistent
37 estimates from terrestrial models and inventories (uncertainty: ±0.3 PgC yr⁻¹) and atmospheric CO₂
38 inversions (uncertainty: ±0.7 PgC yr⁻¹) (Ciais et al., 2010).
39

40 Pan et al. (2011) assessed the contribution of regional forests to the global land CO₂ sink during the past two
41 decades based on repeated forest biomass inventory data, completed with coarse estimates of soil carbon
42 change and by the bookkeeping model of Houghton (2003) estimates of the net land use change CO₂ flux to
43 the atmosphere. For the period 2000–2007, they estimated a global forest carbon accumulation of 0.5 PgCyr⁻¹
44 in boreal forests, and of 0.8 PgC yr⁻¹ in temperate forests. Tropical forests were found to be near neutral
45 with net emissions from land use change being compensated by sinks elsewhere in established tropical
46 forests, therefore consistent with the Stephens et al. inversion estimate of tropical land CO₂ fluxes.
47

48 6.3.2.6.3 Interannual variability in atmosphere-land CO₂ fluxes

49 The interannual variability of the residual CO₂ land sink shown in Figures 6.8 and 6.13 accounts for most of
50 the interannual variability of the atmospheric CO₂ growth rate. Atmospheric CO₂ inversion results suggest
51 that tropical land ecosystems dominate the global CO₂ variability, with positive anomalies during El Niño
52 episodes (Baker et al., 2006; Bousquet et al., 2000; Rodenbeck et al., 2003), which is consistent with the
53 results of one inversion of atmospheric ¹³C and CO₂ measurements (Rayner et al., 2008). A combined
54 ENSO-Volcanic index time series explains 75% of the observed variability (Raupach et al., 2008). A positive
55 phase of ENSO (El Niño) is associated with enhanced land CO₂ source, and a negative phase (La Niña) with
56 enhanced land CO₂ sink (Jones and Cox, 2001; Peylin et al., 2005). Observations from eddy covariance
57 networks suggest that interannual carbon flux variability in the tropics and temperate regions is dominated
58 by precipitation, while boreal ecosystem fluxes are more sensitive to temperature and shortwave radiation

1 variation (Jung et al., 2011), in agreement with the results from process-based terrestrial ecosystem models
2 (Piao et al., 2009b).

3 4 *6.3.2.6.4 Inland water fluxes*

5 Estimates of the transport of carbon from land ecosystems to the coastal ocean by rivers are $\sim 0.2 \text{ Pg yr}^{-1}$ for
6 Dissolved Organic Carbon (DOC), 0.3 Pg yr^{-1} for Dissolved Inorganic Carbon (DIC), and $0.1\text{--}0.4 \text{ Pg yr}^{-1}$ for
7 Particulate Organic Carbon (POC) (Mayorga et al., 2010; Seitzinger et al., 2005; Syvitski et al., 2005). For
8 the DIC fluxes, only $\sim 2/3$ of it originates from atmospheric CO_2 and the rest of the carbon is supplied by the
9 weathered carbonate rocks (Gaillardet et al., 1999; Hartmann et al., 2009; Oh and Raymond, 2006; Suchet
10 and Probst, 1995). Regional DIC fluxes transported by rivers are possibly increased in response to
11 agricultural practices (Hamilton et al., 2007; Oh and Raymond, 2006; Perrin et al., 2008) and coupled with
12 climate change can lead to large increases in regional scale DIC export in watersheds with a large
13 agricultural footprint (Raymond et al., 2008). Furthermore, regional urbanization also elevate DIC fluxes in
14 rivers (Baker et al., 2008; Barnes and Raymond, 2009) which suggest that anthropogenic activities could
15 contribute a significant portion of the annual global river transported DIC flux to the ocean.

16
17 Land clearing and management are thought to produce an acceleration of POC transport, much of which is
18 trapped in alluvial and colluvial deposition zones, lakes, reservoirs, and wetlands (Smith et al., 2001b;
19 Stallard, 1998; Syvitski et al., 2005). One study argues that due to its long residence time in these new
20 depositional environments, land clearing and management coupled to lateral transport by erosion is leading
21 to a net carbon accumulation on land of $\sim 0.1 \text{ PgC yr}^{-1}$ (Van Oost et al., 2007). Numerous studies have
22 demonstrated an increase in the concentration of DOC in rivers over the northeastern United States and
23 northern/central Europe over the past 2–4 decades (Evans et al., 2005; Findlay, 2005; Lepisto et al., 2008;
24 Monteith et al., 2007; Worrall et al., 2003). Due to the central role of wetlands on DOC export to rivers, the
25 loss of global wetlands is probably the largest human-induced cause of changes in global river DOC fluxes
26 to date (Seitzinger et al., 2005), although a global estimate of this alteration is not available. The robust
27 partitioning between natural and anthropogenic C flows in freshwater systems is not yet possible, nor a
28 quantification of its ultimate fate in the coastal and open oceans.

29 30 *6.3.2.6.5 Processes driving terrestrial atmosphere-land CO_2 fluxes*

31 Three type of processes are estimated to have an important effect on the net flux of CO_2 between the
32 atmosphere and the land: (1) processes driven by changes in atmospheric composition such as CO_2 and N
33 deposition inducing a ‘fertilisation effect’ on ecosystem productivity, (2) processes driven by changes in
34 climate that can affect net primary productivity (NPP) and respiration responses to changes in temperature,
35 radiation including radiation quality (diffuse fraction) and precipitation, and (3) processes driven by changes
36 in land use (e.g., deforestation, degradation, afforestation) and land management (agricultural and forestry
37 practices).

38
39 Assessment of experimental data (mostly local experiments), observations and model results suggest that the
40 main processes that have an effect on the land CO_2 sink include the CO_2 fertilisation effect on photosynthesis
41 (see Box 6.3), N fertilisation (Bonan and Levis, 2010; Gerber et al., 2010; Piao et al., 2009b; Thornton et al.,
42 2007), forest regrowth and afforestation (Bellassen et al., 2011; Houghton, 2010; Pacala et al., 2001;
43 Williams et al., 2012a), changes in forest management and reduced harvest rates (Nabuurs et al., 2008), and
44 possibly increased radiation in the tropics (Gloor et al., 2009; Nemani et al., 2003). The lengthening of the
45 growing season in northern latitude ecosystems is also estimated to contribute to explain at least partly the
46 current CO_2 sink.

47 48 **[START BOX 6.3 HERE]**

49 50 **Box 6.3: The CO_2 Fertilization Effect**

51
52 The CO_2 fertilisation as a process susceptible to increase terrestrial primary productivity has a dominant role
53 as a process to explain a global land CO_2 sink in terrestrial biogeochemical models (Sitch et al., 2008), yet it
54 remains one of the most unconstrained process.

55
56 Field experiments provide direct evidence of increased photosynthesis rates and water use efficiency in
57 plants growing under elevated CO_2 , which in turn translates into an broad range of higher plant carbon

1 accumulation in at least 2/3 of the experiments (Ainsworth and Long, 2004; Ainsworth et al., 2012; Canadell
2 et al., 2007; Denman et al., 2007; Luo et al., 2004; Norby et al., 2005; Nowak et al., 2004; Wang et al.,
3 2012).

4
5 Since the AR4, new evidence is available from decade-long Free-air CO₂ Enrichment (FACE) experiments
6 showing the capacity of ecosystems to sustain higher rates of carbon accumulation at elevated CO₂ over time
7 (Aranjuelo et al., 2011; Dawes et al., 2011; Lee et al., 2011; Liberloo et al., 2009; McCarthy et al., 2010; Zak
8 et al., 2011). The mean net primary production response for one decade-long tree FACE experiments is an
9 increase of 8% (non-significant), 26% and 26% at double CO₂ (McCarthy et al., 2010; Norby et al., 2010;
10 Zak et al., 2011). The FACE experiments also show the diminishing or lack of CO₂ fertilization effect in
11 some ecosystems and plant species (Adair et al., 2009; Bader et al., 2009; Norby et al., 2010) and tree ring
12 evidence suggests a lack of CO₂ fertilization in the sampled boreal and temperate forests (Gedalof and Berg,
13 2010; Peñuelas et al., 2011).

14
15 Nutrient limitation is the likely primary cause of a reduced or lack of CO₂ fertilization effect observed on
16 NPP in some experiments (Dukes et al., 2005; Finzi et al., 2007; Luo et al., 2004; Norby et al., 2010).
17 Nitrogen and phosphorus are very likely to play the most important role in this limitation of the CO₂
18 fertilization effect on NPP, and these nutrients are estimated to have an additive effect at the global scale,
19 with N limitation prevalent in temperate and boreal ecosystems, and P limitation in the tropics (Goll et al.,
20 2012b; Luo et al., 2004; Vitousek et al., 2010; Wang et al., 2010a). Although the enhancement of the CO₂
21 fertilization effect on the global terrestrial net primary productivity is very likely, the magnitude of such an
22 effect remains uncertain in view of the broad range of experimental responses, and the uncertainty stemming
23 from the lack of experiments outside of temperate climates.

24 25 **END BOX 6.3 HERE]**

26
27 Process attribution of the land sink of CO₂ at the global scale is difficult due to limited data, and because ,
28 global models do not represent yet the full range of processes thought to be important. Attribution of regional
29 sinks has been more successful. Legacies of past forest clearing and decreased harvest removal are key
30 processes very likely to explain a large fraction of the current forest carbon sink in the U.S.A. and Europe,
31 with additional contribution from CO₂ and N fertilization effect, and in some regions of warming induced
32 longer growing seasons (Bellassen et al., 2011; Ciais et al., 2008; Pacala et al., 2001; Schulze et al., 2010;
33 Williams et al., 2011). Afforestation and forest regrowth likely play a major role in the carbon sink of East
34 Asia, with a large uncertainty on the contribution of CO₂ fertilization (Fang et al., 2005; Piao et al., 2011). In
35 the tropics, there is evidence from forest inventories that increasing forest growth rates are not explained by
36 the natural recovery from disturbances, suggesting that increasing atmospheric CO₂ and climate change play
37 a role in the observed sink in established forests (Lewis et al., 2009; Pan et al., 2011). Nemani et al. (2003)
38 based on satellite greenness, estimated an increase in net primary productivity (NPP) in the region over the
39 the period 1982–1999 which they largely attributed to increased solar radiation from reduced cloud cover.
40 Although increased forest growth rates and NPP are not surrogates for net land sinks, they are components of
41 it and so provide information on the underlying processes.

42
43 Processes involving human induced / natural export of carbon from a land area, such as export of carbon
44 through river transport (see Section 6.3.2.6.4), wood harvest and net trade balance of food and wood are
45 significant components of the C balance for some regions (Pacala et al., 2001).

46
47 Disturbances such as fires, insect damage, storms, droughts and heat waves are significant processes driving
48 inter-annual variability and possibly trends of regional land carbon fluxes (Chambers et al., 2007; Ciais et al.,
49 2005; Clark et al., 2010; Lewis et al., 2011). It is not well understood to what degree disturbance caused
50 instantaneous losses of CO₂ are compensated by regrowth in the short term (e.g., savanna fires) or if they are
51 net long term losses (e.g., peat fires; Page et al., 2002; deforestation fires; van der Werf et al., 2010; see
52 Section 6.3.2.2). In the future, climate induced disturbances are expected to become more important in
53 driving trend dynamics of regional carbon fluxes, as it has already been observed with increased fire
54 frequency and insect damage in Canadian forests (Kurz et al., 2008b).

55
56 Warming (and possibly the CO₂ fertilization effect) has also been correlated with global trends in satellite
57 greenness observations, which resulted in an estimated 6% increase of global NPP, or the accumulation of

1 3.4 PgC on land over the period 1982–1999. This enhanced NPP was attributed to the relaxation of climatic
2 constraints to plant growth, particularly in high latitudes, as also seen by an increase in the net carbon sink
3 during the warmer 2000s compared to the 1990s in the Arctic tundra (McGuire et al., 2012). Concomitant to
4 the increased of NPP with warming, global soil respiration increased between 1989 and 2008 (Bond-
5 Lamberty and Thomson 2010) reducing the magnitude of the net land sink. More recent NPP trends
6 suggested a reduction of 55 PgC over 2000–2009 (Zhao and Running (2010) although the model used to
7 reconstruct NPP trends from satellite observation has not been widely accepted (Medlyn, 2011; Samanta et
8 al., 2011; Zhao and Running, 2011).

9
10 An additional contributor to the growing global land sink is the effect of increased diffused radiation on
11 photosynthesis, estimated to account for one quarter of the of the land sink during 1960–1999 (Mercado et
12 al., 2009). The effect is largely driven by the enhanced efficiency of photosynthesis under diffuse light
13 brought about by the increased in anthropogenic aerosols (Roderick et al., 2001; Romanou et al., 2007).

14 6.3.2.6.6 *Model evaluation of global and regional terrestrial carbon balance*

15 Evaluation of global process based ecosystem models was performed against ground and satellite
16 observations including: (1) measured CO₂ fluxes and carbon storage change at particular sites around the
17 world, in particular sites from the Fluxnet global network (Jung et al., 2007; Schwalm et al., 2010; Stockli et
18 al., 2008; Tan et al., 2010), (2) observed spatio-temporal change in leaf area index (LAI) (Lucht et al., 2002;
19 Piao et al., 2006), and (3) interannual and seasonal change in atmospheric CO₂ (Cadule et al., 2010;
20 Randerson et al., 2009).

21
22
23 Figure 6.15 compares the global land sink of CO₂ simulated by different process based carbon cycle models
24 (see Sitch et al., subm) without land use change, with the residual land sink (diagnosed as the sum of fossil
25 fuel and cement emissions and land use change emissions minus the sum of CO₂ growth rate and ocean sink)
26 from 1980 to 2009 (Friedlingstein and Prentice, 2010; Le Quere et al., 2009). The magnitude of the residual
27 land sink and its trend can be reproduced faithfully by the multi-model mean, despite the large discrepancies
28 among individual models, and the lack of land use change prescribed to models. Limited availability of in-
29 situ measurements, particularly in the tropics, limits the progress towards reducing uncertainty on model
30 parameterizations.

31 [INSERT FIGURE 6.15 HERE]

32 **Figure 6.15:** Time series for the land CO₂ sink showing the residual land sink deduced (1) from the global budget
33 (Figure 6.8) with the black line being obtained as the difference between emissions from fossil fuel and land use
34 change, minus the atmospheric growth rate and the ocean sink, and (2) from global process-based terrestrial ecosystem
35 models (Table 6.6 for references) shown as red lines. The red shading shows one standard deviation from the model
36 mean.
37

38
39 At the regional scale, the models of terrestrial carbon dynamics can be better constrained because of the
40 higher availability of data, at least in some regions. In Europe, forest inventory data show that the forest
41 carbon sink density over Europe is of $89 \pm 19 \text{ gC m}^{-2} \text{ yr}^{-1}$, which is comparable with model estimates with
42 afforestation ($-63 \text{ gC m}^{-2} \text{ yr}^{-1}$; Luyssaert et al., 2010), while modeled NPP was 43% larger than the
43 inventory estimate. In North America, the ability of 22 terrestrial carbon cycle models were evaluated to
44 simulate the seasonal cycle of land-atmosphere CO₂ exchange from 44 eddy covariance flux towers, and
45 found that the difference between observations and simulations was about 10 times the observational
46 uncertainty (Schwalm et al., 2010); key model shortcomings are the variability due to spring phenology, soil
47 thaw, and snow pack melting, as well as lag responses to extreme climate events (Keenan et al., 2012). In
48 China, the magnitude of the carbon sink estimated by five terrestrial ecosystem models (0.22 to 0.13 PgC yr^{-1})
49 was comparable to the observation-based estimate ($0.18 \pm 73 \text{ PgC yr}^{-1}$; Piao et al., 2009b), but modelled
50 interannual variation was weakly corrected to observed regional land-atmosphere CO₂ fluxes (Piao et al.,
51 2011).

52
53 *Sensitivity of the terrestrial carbon cycle to CO₂.* The sensitivity of the terrestrial carbon cycle to rising
54 atmospheric CO₂ concentration is one of the key metrics to inter-compare and evaluate terrestrial carbon
55 cycle models. Results from Free Air CO₂ experiments (FACE) on diverse ecosystems generally show a
56 higher net primary productivity (NPP) under elevated atmospheric CO₂ (see Box 6.3). The magnitude of the
57 NPP enhancement at the four temperate forest FACE experiments was reproduced correctly by the LPJ-
58 GUESS model (Hickler et al., 2008). Some experiments failed to show a CO₂ fertilisation effect on NPP, and

1 factorial experiments with elevated CO₂ and nitrogen additions inferred that nitrogen limitation was the
2 cause of the lack of CO₂ fertilization effect (see Box 6.3). This implies that carbon cycle models not
3 considering the limitation of nitrogen availability on vegetation growth are likely to overestimate the
4 response of plant productivity to rising atmospheric CO₂ concentration (Zaehle and Friend, 2010). The small
5 number of in situ measurements of the long-term response of CO₂ fluxes to elevated CO₂ limits the
6 evaluation of the models for the CO₂ fertilization effect. Phosphorus information to parameterize process
7 models, in addition to N, is also required to test the role of P in limiting the current and future land carbon
8 sink.

9
10 *Sensitivity of terrestrial carbon cycle to climate trends and variability.* Warming exerts a direct control on
11 the net land-atmosphere CO₂ exchange since both photosynthesis and respiration are sensitive to changes in
12 temperature. Warming is likely to increase vegetation productivity in temperate and boreal regions through
13 increasing growing season length (Lucht et al., 2002; Piao et al., 2006; Zhou et al., 2001). A meta-analysis of
14 field warming experiments from temperate and boreal regions suggests for instance an average 19% increase
15 in aboveground plant primary productivity (Rustad et al., 2001), along with an increase or no change in the
16 net atmosphere-land CO₂ flux (Luo, 2007; Marchand et al., 2004).

17
18 From estimates of the annual residual land CO₂ sink, it is assessed that a 1°C global temperature anomaly
19 leads to a decrease of 4 PgC yr⁻¹ of the global land CO₂ sink (Figure 6.16), a response close to the multi-
20 model estimated average of the interannual temperature sensitivity of the global land CO₂ sink (-3.5 PgC yr⁻¹
21 °C⁻¹ in Piao et al., *subm.*). Different models, however, showed different sensitivities of their global land CO₂
22 sink to interannual temperature variability, with values ranging from -0.5 PgC yr⁻¹ °C⁻¹ to -6.2 PgC yr⁻¹ °C⁻¹
23 (Piao et al., *subm.*). The sensitivity of the the global land CO₂ sink to climate is likely to vary with different
24 time scale as well. For instance, the sensitivity of atmospheric CO₂ concentration to century-scale
25 temperature change was estimated at about 3.6~45.6 PgC °C⁻¹ (or 1.7~21.4 ppm CO₂ °C⁻¹) using the ice core
26 observed CO₂ drop during the Little Ice Age, when human impacts on atmospheric CO₂ were assumed to be
27 negligible (Frank et al., 2010).

28
29 Carbon release in response to future drying in the Tropics is one of the dominant explanation of the positive
30 carbon cycle-climate feedback found in the coupled carbon-climate models used in AR4 (Cox, 2001;
31 Friedlingstein et al., 2006; Sitch et al., 2008). An artificial drought experiment in an east-central Amazonian
32 rainforest at Tapajos showed that a 50% reduction in precipitation led to a 25% reduction in aboveground
33 NPP during the first two years of prescribed drought (Nepstad et al., 2002), followed by a 38% increase in
34 tree mortality rates which further reduced NPP (Nepstad et al., 2007). A global estimate of GPP show that
35 30% of the spatial GPP variability in tropical forests was correlated with precipitation (Beer et al., 2010).
36 Carbon cycle models used in AR5 generally underestimate GPP in the water limited regions, implying that
37 these models do not correctly simulate soil moisture conditions, or that they are too sensitive to changes in
38 soil moisture (Jung et al., 2007). It is also suggested that the AR5 models overestimate the interannual
39 precipitation sensitivity of the land flux in the tropics (Wang et al., *subm.*). At the global scale, most of the
40 process-based terrestrial ecosystem models in Table 6.6 (eight of nine models) estimated that the interannual
41 precipitation sensitivity of the global land CO₂ sink to be higher than that of the observed residual land sink
42 (-0.01 PgC yr⁻¹ mm⁻¹; Figure 6.16).

43 44 **[INSERT FIGURE 6.16 HERE]**

45 **Figure 6.16:** The sensitivity of Net Ecosystem Production (NEP) to interannual variation in temperature and
46 interannual variation in precipitation at the global and regional scales. The global residual land sink is estimated as the
47 sum of fossil fuel and cement emissions and land use change emissions minus the sum of CO₂ growth rate and modelled
48 ocean sink (Friedlingstein and Prentice, 2010; Le Quere et al., 2009). The sensitivities of NEP to interannual variation
49 of temperature and precipitation are estimated by a multiple linear regression approach using detrended NEP as
50 dependent variable and detrended annual temperature and annual precipitation as independent variables (Piao et al.,
51 *subm.*). 10 carbon cycle models are Community Land Model 4C (CLM4C), Community Land Model 4CN (CLM4CN),
52 Hyland (HYL), Lund-Potsdam-Jena (LPJ), LPJ_GUESS, ORCHIDEE-CN (OCN), ORCHIDEE (ORC), Sheffield-
53 DGVM (SDGVM), TRIFFID (TRI), and VEGAS. Negative value indicates decrease in carbon sink.

54
55 *Processes missing in terrestrial models.* Currently, most global terrestrial ecosystem models used in AR5
56 only consider the effects of climate change and atmospheric CO₂ on land-atmosphere CO₂ fluxes, but still
57 miss several key processes governing the terrestrial carbon cycle. First, many of global models do not
58 explicitly take into account the various forms of disturbances: fire, logging, harvesting and the resulting

1 variation in forest age structure which is known to affect the net carbon exchange (Bellassen et al., 2010).
2 Eddy covariance flux observations show that the strength of net carbon uptake of forest ecosystem is locally
3 controlled by forest stand age (Amiro et al., 2010). Second, processes relevant to decomposition of carbon in
4 permafrost and wetlands, including tropical peatland are not dealt in the majority of models, despite these
5 pools hold large carbon stores and are vulnerable to warming and land use change (Hooijer et al., 2010;
6 Koven et al., 2011; Page et al., 2010; Tarnocai et al., 2009). However, progress is taking place as now some
7 models do include permafrost carbon (Koven et al., 2011; Schaefer et al., 2011). Third, despite several
8 studies demonstrating the important role of N limitation in regulating the terrestrial carbon cycle, and the
9 fertilizing effect of N-deposition on ecosystem productivity (Magnani et al., 2007), N dynamics is only taken
10 into account by few models. For instance, the global land carbon sink estimated by the model (CLM4CN)
11 with considering N limitation is lower than in that of the model (CLM4C) without considering N limitation
12 (Table 6.6). Phosphorus (P) availability is also observed to limit, or, with N, to co-limit, productivity in some
13 ecosystems (Elser et al., 2007; LeBauer and Treseder, 2008), but even fewer models represent P dynamics or
14 N-P interactions. Fourth, the effects of elevated tropospheric ozone have also not been taken into account for
15 most of current carbon cycle models. It was found that increased exposure of plants to elevated tropospheric
16 ozone would reduce vegetation productivity, and thus further decrease NEP (Sitch et al., 2007). Fifth,
17 transfer of radiation, water and heat in the vegetation-soil-atmosphere continuum are treated very simply in
18 the global ecosystem models used in this Chapter, which further limit credibility of model simulation.
19 Finally, lateral surface process (e.g., water and tillage erosion; Quinton et al., 2010) and human
20 managements including fertilisation and irrigation (Gervois et al., 2008) may also substantially influence C
21 cycle at regional scales, but it was not considered in most of current model studies.

22 23 **6.3.3 Global CH₄ Budget**

24
25 AR5 is the first IPCC assessment report providing a consistent synthesis of the CH₄ budget per decade, using
26 different approaches. A suite of different atmospheric CH₄ inversion models (top-down) and various process-
27 based models and inventories (bottom-up) are used to derive the main CH₄ emission sources and their
28 regional contributions, during the 1980s, the 1990s and 2000s (Table 6.7; Kirsche et al. *subm.*). In the table,
29 the uncertainties on emissions and sinks are listed using minimum and maximum of each published estimate
30 for each decade. Bottom-up approaches are used to attribute decadal budgets to different processes emitting
31 CH₄ (see Section 6.1.1.2 for a general overview). Top-down inversions provide an atmospheric-based
32 constraint for the total CH₄ source per region. Estimations of CH₄ sinks in the troposphere by reaction with
33 tropospheric-OH, in soils and in the stratosphere are also reported for the past three decades.

34 35 **6.3.3.1 Atmosphere Burden and Trend**

36
37 Since preindustrial times, the concentration of the global average surface CH₄ increased by a factor of 2.5
38 (from 730 ppb to 1803 ppb in 2011) and it is measured today by a network of more than 100 surface sites
39 (Cunnold et al., 2002; Dlugokencky et al., 2011; Langenfelds et al., 2002), aircraft profiles in the lower part
40 of the atmosphere, and before 1979 from analyses of firn air and ice cores (see Chapter 5 and Section 6.2),
41 Figure 6.11. The growth of CH₄ in the atmosphere is largely in response to increasing anthropogenic
42 emissions. Currently, the vertically averaged atmospheric CH₄ concentration field can be mapped by remote
43 sensing from the surface using Fourier Transform Infrared Spectroscopy (FTIR) instruments (Total Carbon
44 Column Observing Network, TCCON, <http://www.tcon.caltech.edu/>) and from space by several satellite
45 instruments: AIRS (since 2002), TES (since 2004), IASI (since 2006), SCIAMACHY (since 2003), and
46 GOSAT-TANSO-FTS (since 2009). As an example, SCIAMACHY (Frankenberg et al., 2008) clearly shows
47 the column CH₄ gradient between the two hemispheres as well as increased concentrations over South East
48 Asia, due to emissions from agriculture, wetlands, waste, and energy production (Figure 6.2).

49
50 The growth rate of CH₄ has declined since the mid 1980s and a near zero growth rate (quasi-stable
51 concentrations) was observed during 1999–2006 suggesting an approach to steady state where the sum of
52 emissions are in balance with the sum of sinks (Dlugokencky et al., 2003; Khalil et al., 2007; Figure 6.17).
53 The reasons for this growth rate change after the mid-1980s are still debated, and results from various studies
54 provide possible scenarios: (1) a reduction of emitting activities such as coal mining, gas industry and animal
55 husbandry in the countries of the former Soviet Union (Dlugokencky et al., 2003; Savolainen et al., 2009),
56 (2) a compensation between increasing anthropogenic emissions and decreasing wetland emissions
57 (Bousquet et al., 2006), (3) reduced emissions from rice paddies attributed to changes in agricultural

1 practices (Kai et al., 2011), (4) stable microbial and fossil fuel emissions in the early 2000s (Levin et al.,
2 2012), and/or (5) significant (Rigby et al., 2008) to small (Montzka et al., 2011) changes in OH
3 concentrations.

6 [INSERT TABLE 6.7 HERE]

7 **Table 6.7:** Global CH₄ budget for the past three decades (in Tg(CH₄)yr⁻¹). T-D stands for Top-Down inversions and B-
8 U for Bottom-Up approaches. Full references are given at the end of the chapter. Ranges represent minimum and
9 maximum values from the cited references. The sum of sources and sinks from B-U approaches does not automatically
10 balance the atmospheric changes. Only studies covering at least five years of each decade have been used. For B-U
11 studies, individual source types are also presented. For T-D inversions, the 1980s decade starts in 1984. As some
12 atmospheric inversions did not reference their global sink, balance with the atmosphere and the sum of the sources has
13 been assumed. One biomass burning estimate²² excludes biofuels (a). Stratospheric loss for B-U is the sum of the loss
14 by OH radicals, a 10 Tg yr⁻¹ loss due to O¹D radicals (Neef et al., 2010) and a 20–35% contribution due to Cl radicals²⁴.

17 Since 2007, the growth rate of CH₄ has been observed to increase again (Dlugokencky et al., 2009; Rigby et
18 al., 2008) with positive anomalies of emissions of 21 Tg(CH₄) yr⁻¹ and 18 Tg(CH₄) yr⁻¹ inverted for 2007
19 and 2008, respectively (Bousquet et al., 2011) as compared to the 1999–2006 period. The increase of
20 emissions in 2007–2008 was dominated by tropical regions (Bousquet et al., 2011) with a major role from
21 tropical wetlands, and some role from high latitude wetlands in the 2007 anomaly (Bousquet et al., 2011;
22 Dlugokencky et al., 2009) as suggested by the growth rate vs. latitude in Figure 6.17 (Dlugokencky et al.,
23 2009). The recent increase of CH₄ concentration since 2007 is also in line with the EDGAR4–v4.2
24 anthropogenic emission inventory, which shows rapidly increasing anthropogenic CH₄ emissions in the
25 period 2000–2008, related to increased energy production in growing Asian economies (EDGAR4,
26 edgar.jrc.ec.europa.eu). The atmospheric increase has continued after 2009, at a rate of 4–5 ppb per year
27 (Sussmann et al., 2012).

9 [INSERT FIGURE 6.17 HERE]

10 **Figure 6.17:** Upper panel: Globally averaged growth rate of atmospheric CH₄ in ppb yr⁻¹ determined from the
11 GLOBALVIEW data product, representative for the marine boundary layer (Masarie and Tans, 1995). Lower panel:
12 Atmospheric growth rate of CH₄ as a function of latitude determined from the GLOBALVIEW data product.

13 6.3.3.2 Emissions

14 The global atmospheric burden and trend of CH₄ results from the balance between emissions and sinks.
15 Methane emission sources around the globe are biogenic, thermogenic, or pyrogenic in origin (Neef et al.,
16 2010), and they can be the direct result of either human activities and/or natural processes (see Section
17 6.1.1.2 and Table 6.7). Biogenic sources are due to degradation of organic matter in anaerobic conditions
18 (natural wetlands, ruminants, waste, landfills, rice paddies, fresh waters, termites). Thermogenic sources
19 come from the slow transformation of organic matter into fossil fuels on geological timescales (natural gas,
20 coal, oil). Pyrogenic sources are due to incomplete combustion of organic matter (biomass and biofuel
21 burning). Some sources can eventually combine a biogenic and a thermogenic origin (e.g., natural geological
22 sources such as oceanic seeps, mud volcanoes or hydrates). Each of these three processes is characterized by
23 distinct ranges in the magnitude of isotopic fractionation against ¹³C-CH₄: –55 to –70‰ for biogenic, –25 to
24 –45‰ for thermogenic, and –13 to –25‰ for pyrogenic. These isotopic distinctions provide a basis to
25 separate the relative contribution of different methane sources using the top-down approach (Bousquet et al.,
26 2006; Monteil et al., 2011; Neef et al., 2010).

27 During the decade of the 2000s, natural sources of CH₄ are assessed to account for 35–55% of the decadal
28 mean global emissions (Table 6.7). The single most dominant CH₄ source of the global flux and inter-annual
29 variability is CH₄ emissions from wetlands from the tropics and high latitudes (177–284 Tg(CH₄) yr⁻¹). The
30 term ‘wetlands’ denotes here a variety of ecosystems emitting CH₄: wet soils, swamps, peatlands, fresh
31 waters from lakes and rivers. These emissions are highly sensitive to climate change and variability, as seen
32 for instance from the response to the recent 2007–2008 anomalies in precipitation and temperature. The
33 relatively dry conditions that prevailed in some regions of the Northern Hemisphere continents during the
34 late 1990s and early 2000s may have decreased wetland emissions at this period (Bousquet et al., 2006),
35 although ¹³C in CH₄ atmospheric observations seem to suggest stable microbial and fossil fuel emissions

1 during the early 2000s (Levin et al., 2012). Several process-based models of methane emissions from natural
2 wetlands have been developed since AR4, and these models are improving rapidly (Hodson et al., 2011;
3 Melton et al., *subm.*; Ringeval et al., 2011; Spahni et al., 2011). Nonetheless, the confidence in present-day
4 modelled spatial and temporal patterns of wetland CH₄ emissions remains low, in particular because of
5 limited observational datasets available for the models calibration and evaluation at the regional scale.
6 Likely, wetland CH₄ emissions increase in response to elevated atmospheric CO₂ concentrations, a
7 consequence of the CO₂ fertilization effect (see Box 6.3), while the sign and magnitude of the CH₄ emission
8 response to changes in temperature and precipitation vary among models (Melton et al., *subm.*). In addition
9 both wetland area and CH₄ flux density are sensitive to climate.

10
11 In AR4, natural geological sources were estimated between 4 and 19 Tg(CH₄)yr⁻¹. Since then, these sources
12 received more attention and have been re-evaluated (Etiopie et al., 2008). Emissions from terrestrial (13–29
13 Tg(CH₄)yr⁻¹) and marine (~20 Tg(CH₄)yr⁻¹) seepages, mud volcanoes (6–9 Tg(CH₄)yr⁻¹), hydrates (5–10
14 Tg(CH₄)yr⁻¹) and geothermal and volcanic areas (3–6 Tg(CH₄)yr⁻¹) are assessed to represent between 42 and
15 64 Tg(CH₄)yr⁻¹ (Etiopie et al., 2008). This larger than in AR4 contribution from natural, geological, and
16 partly fossil CH₄ is consistent with a recent ¹³CH₄ re-analysis showing natural and anthropogenic fossil
17 contributions to the global CH₄ budget to be around 30% (Lassey et al., 2007) and not around 20% as
18 previously thought.

19
20 Of the natural sources of CH₄, emissions from thawing permafrost and CH₄ hydrates in the northern
21 circumpolar region are potentially important in the next century because they could increase dramatically
22 due to the rapid climate warming of the Arctic and the large C pools stored there (Tarnocai et al., 2009).
23 Hydrates are however estimated in this Chapter to represent only a very small emission, between 5 to 10
24 Tg(CH₄) yr⁻¹ (Table 6.7). Super saturation of dissolved CH₄ at the bottom and surface waters in the East
25 Siberian Arctic Shelf indicate some CH₄ activity across the region, with a net sea-air flux of 10.5 Tg(CH₄)yr⁻¹
26 ¹ which is similar in magnitude to the flux for the entire ocean (Shakhova et al., 2010). The ebullition of CH₄
27 from decomposing, thawing lake sediments in north Siberia with an estimated flux of ~4 Tg(CH₄)yr⁻¹ is
28 another demonstration of the activity of this region and of its potential importance in the future (van
29 Huissteden et al., 2011; Walter et al., 2006). Over the past decades, however, there is no evidence for
30 significant emission of CH₄ from permafrost and hydrates (Dlugokencky et al., 2009).

31
32 Pyrogenic sources of CH₄ are assessed to have a small contribution in the global flux for the 2000s (16–20
33 Tg(CH₄)yr⁻¹) and play a role much smaller than wetlands in inter-annual variability, particularly from the
34 burning of tropical and boreal forests in response to regional droughts and deforestation. Tropical fire
35 emissions during the 1997–1998 record high El Niño, during which burning of forests and peatland took
36 place in Indonesia and Malaysia, released 12 Tg(CH₄) (Langenfelds et al., 2002; van der Werf et al., 2004),
37 with other smaller fire CH₄ emissions positive anomalies were suggested during the dry spell over the
38 northern mid-latitudes in 2002–2003, in particular over Eastern Siberia in 2003 (van der Werf et al., 2010)
39 and Russia in 2010. Traditional biofuel burning was estimated to be a source of 10 Tg(CH₄)yr⁻¹ (Yevich and
40 Logan, 2003) during the 1980s.

41
42 Keppler et al. (2006) reported that plants under aerobic conditions were able to emit CH₄, and thus
43 potentially could constitute a large additional emission that had not been previously considered in AR4 in the
44 global CH₄ budget. Later studies do not support plant emissions as a wide spread mechanism (Dueck et al.,
45 2007; Nisbet et al., 2009; Wang et al., 2008) or show negligible emissions in the context of the global CH₄
46 budget (Bloom et al., 2010; Nisbet et al., 2009; Vigano et al., 2008). Alternative mechanisms have been
47 suggested to explain the apparent aerobic CH₄ production involving adsorption and desorption, but not new
48 production (Kirschbaum and Walcroft, 2008; Nisbet et al., 2009), degradation of organic matter under strong
49 UV light (Dueck et al., 2007; Nisbet et al., 2009), and methane in the groundwater emitted through internal
50 air spaces in tree bodies (Terazawa et al., 2007). Therefore, we assessed that significant plant CH₄ emissions
51 are very unlikely, and this source was not reported in Table 6.7. Finally, CH₄ emissions from termites range
52 from 2 to 22 Tg(CH₄)yr⁻¹ (Table 6.7).

53
54 Anthropogenic CH₄ sources are estimated to range between 45% and 65% of the decadal-mean global
55 emissions for the 2000s (Table 6.7) and included rice-paddies agriculture, ruminant animals, sewage and
56 waste, landfills, and fossil fuel extraction, storage, transformation, transportation and use (coal mining, gas,
57 oil and industry). Anthropogenic sources are dominant over natural sources in top-down inversions but they

1 are of the same magnitude in bottom-up models and inventories (Table 6.7). Natural emissions are estimated
2 by different bottom-up models with no constrain on their sum, which might be overestimated considering the
3 large imbalance with the modelled chemical sink (Table 6.7). Rice paddies emit between 32 and 44
4 $\text{Tg}(\text{CH}_4)\text{yr}^{-1}$, continuously flooded paddies having much higher emissions per square metre than drought-
5 prone, rain-fed paddies, or irrigated paddies that are intermittently drained. Ninety per cent of emissions
6 come from Monsoon Asia, and more than 50% from China and India alone (Yan et al., 2009). Ruminant
7 livestock, such as cattle, sheep, goats and deer produce CH_4 by food fermentation in their anoxic rumens
8 with a total estimate of between 89 and 97 $\text{Tg}(\text{CH}_4)\text{yr}^{-1}$. Major regional contributions of this flux come from
9 India, China, Brazil, and the US (EPA, 2006). India, with the world's largest livestock population (485
10 millions in 2003, with no deer), emitted 11.8 $\text{Tg}(\text{CH}_4)\text{yr}^{-1}$ in 2003, including emission from enteric
11 fermentation (10.7 $\text{Tg}(\text{CH}_4)\text{yr}^{-1}$) and manure management (1.1 $\text{Tg}(\text{CH}_4)\text{yr}^{-1}$; Chhabra et al., 2009).
12 Methanogenesis in landfills, livestock manure and waste waters produce between 65 and 90 $\text{Tg}(\text{CH}_4)\text{yr}^{-1}$ due
13 to anoxic conditions and a high availability of acetate, CO_2 and H_2 . Loss of natural gas (~90% CH_4) is the
14 largest contributor to fossil fuel related emissions (52–69 $\text{Tg}(\text{CH}_4)\text{yr}^{-1}$). Unintended emissions from
15 industrial processes (fugitive emissions) are high in the Russian Federation, where they relate to older energy
16 infrastructure, and in the USA (EPA, 2006). Coal mining contributes between 18 and 35 $\text{Tg}(\text{CH}_4)\text{yr}^{-1}$ and
17 residual emissions are associated with oil industry (EPA, 2006).

18
19 Global CH_4 emissions, as estimated from the sum of bottom-up models and inventories, are very uncertain
20 (range 519–822 $\text{Tg}(\text{CH}_4)\text{yr}^{-1}$) for the 2000s (Kirschke et al., *subm.*). No constrain applies on the sum of
21 emissions in bottom-up models, unlike for top-down inversions which display a narrower range (526–569
22 $\text{Tg}(\text{CH}_4)\text{yr}^{-1}$), based on the assimilation of atmospheric observations of CH_4 , (Kirschke et al., *subm.*).
23 Therefore, top-down inversions can help close the global sum of sources in the global CH_4 budget, although
24 they do not provide as detailed of a budget as bottom-up approaches since they do not account for processes
25 (Table 6.7).

26 27 6.3.3.3 Sinks of Atmospheric CH_4

28
29 The main sink of atmospheric CH_4 is its oxidation by OH radicals, a process which takes place mostly in the
30 troposphere and stratosphere (Table 6.7). OH removes about 90% of atmospheric CH_4 , yielding a partial
31 atmospheric lifetime of about 9 years (7–11 years) for an atmospheric burden of 4800 $\text{Tg}(\text{CH}_4)$ (4700–4900
32 TgCH_4 ; see Chapter 8, Section 8.2.3.3). Oxidation in dry soils removes about 21–33 $\text{Tg}(\text{CH}_4)\text{yr}^{-1}$ (Kirschke
33 et al., *subm.*). A small sink is suspected, but still debated, in the marine boundary layer due to a reaction with
34 chlorine (Allan et al., 2007). Another minor sink is the reaction of CH_4 with Cl radicals and $\text{O}(^1\text{D})$ in the
35 stratosphere (Kirschke et al., *subm.*; Shallcross et al., 2007).

36
37 There have been a number of published estimates of global OH concentrations and variations over the past
38 decade (Bousquet et al., 2005; Dentener et al., 2003; Montzka et al., 2011; Prinn et al., 2001; Prinn et al.,
39 2005; Rigby et al., 2008). The very short lifetime of OH makes it almost impossible to estimate global OH
40 concentrations from the aggregation of sparse direct measurements. Either chemistry transport models
41 (CTMs), chemistry climate models (CCMs), or proxy methods have to be used to obtain a global mean value
42 and time variations. Global mean chemical loss is very uncertain between 509 and 794 $\text{Tg}(\text{CH}_4)\text{yr}^{-1}$ for the
43 2000s as estimated by CCMs and CTMs (Table 6.7), but top-down inversions using methyl-chloroform
44 (MCF) as a proxy provide a more narrow range of 510–540 $\text{Tg}(\text{CH}_4)\text{yr}^{-1}$ for the total chemical loss in the
45 2000s. CCMs and CTMs produce small variations of OH radicals, typically of 1–3% due to a high buffering
46 of this radical by the atmospheric photochemical reactions. Atmospheric inversions indicate much larger
47 variations for the 1980s and the 1990s (5–10%), likely because of an oversensitivity to uncertainties on
48 methyl-chloroform emissions of the methyl-chloroform proxy (Montzka et al., 2011), although reduced
49 variations are inferred after 1998 (Prinn et al., 2005). For the 2000s, the reduction of MCF in the atmosphere,
50 due to the Montreal protocol (1987), allows a consistent estimate of OH variations (<±3%) between
51 atmospheric inversions (within 5%) and CCMs/CTMs. However, the very low atmospheric values reached
52 by MCF (a few ppt in 2010) impose the need to find another OH proxy in the upcoming years. Finally,
53 evidence for the role of changes in OH concentrations in explaining the increase in atmospheric methane
54 since 2007 is variable, ranging from a significant contribution (Rigby et al., 2008) to only a small role
55 (Bousquet et al., 2011).

6.3.4 Global N₂O Budget

The atmospheric abundance of N₂O has been increasing mainly as a result of agricultural intensification and extensification to meet the food demand for a growing human population. Fertilizer use and manure excretion increase the production of N₂O in soils and sediments, via nitrification and denitrification pathways, leading to increased N₂O emissions. Increased emissions do not only occur in agricultural fields, but also in aquatic systems after N leaching and runoff, and in natural soils and ocean surface waters as a result of atmospheric deposition of N originating from agriculture and industrial activities. Food production is likely responsible for 80% of the increase in atmospheric N₂O (Davidson, 2009; Kroeze et al., 1999; Park et al., 2012; Syakila and Kroeze, 2011; Williams and Crutzen, 2010; Zaehle and Dalmonech, 2011). Global emissions of N₂O are difficult to estimate. Table 6.8 presents global emissions based on upscaling of flux measurements at the Earth's surface. Global and regional budgets are constrained by inverse modelling studies (Hirsch et al., 2006; Huang et al., 2008; Rhee et al., 2009; Thompson et al., *subm.*). However, the atmospheric life-time of N₂O is not well constrained due to uncertainty in the dominant loss term of N₂O, i.e., the destruction of N₂O by photolysis and reaction with O(1D) in the stratosphere, which causes considerable uncertainty in the top-down global N₂O budget. The long atmospheric lifetime of N₂O (122 years, Volk et al. 1997) implies that it will take decades before atmospheric abundances stabilize after the stabilization of global emissions. This is of concern not only because of its contribution to the global radiative forcing, but also because emissions of N₂O are currently the most important of any ozone depleting substance (Ravishankara et al., 2009).

Firstly, AR4 estimated total N₂O emissions in the 1990s (Table 6.8). Since then, a number of studies have been published that give reason to update some of the N₂O emission estimates. First and most importantly, the IPCC Guidelines have been revised in 2006 (DeKlein et al., 2007). In particular the emission factors for estimating agricultural emissions have been updated. Applying these 2006 emission factors to global agricultural statistics results in direct emissions from agriculture (from fertilized soils and animal production) that are higher than in AR4, but in indirect emissions (mainly from leaching and runoff) that are considerably lower (Table 6.8). It should be noted that emissions of N₂O show large spatial and temporal variability, resulting in large uncertainties from default emission factors when applied at the global scale (Crutzen et al., 2008). Recent top-down estimates, show that the emission factor approach still severely underestimates agricultural, and thus total emissions, in (sub)-tropical regions (Thompson et al., *subm.*).

[INSERT TABLE 6.8 HERE]

Table 6.8: Section 1 gives the Global N budget (TgN yr⁻¹): a) creation of reactive N, b) emissions of NO_x, NH₃ in 2000s to atmosphere, c) deposition of N to land and oceans and d) discharge of total N to coastal ocean. Section 2 gives the N₂O budget for the year 2005, and for the 1990s compared to AR4. Unit: Tg(N₂O-N) yr⁻¹.

Secondly, it has been recently recognized that the open ocean is an anthropogenic source of N₂O (Duce et al., 2008) because atmospheric deposition of anthropogenic reactive nitrogen Nr (nitrogen oxides and ammonia) increases N₂O emissions from the open ocean. This anthropogenic N₂O source was implicitly included in the natural ocean source estimate in AR4, but is now included as anthropogenic source in Table 6.8.

Third, a first estimate was published of global N₂O uptake at the Earth's surface (Syakila and Kroeze, 2011; Syakila et al., 2010), based on reviews of measurements of N₂O uptake in soils and sediments (Chapuis-Lardy et al., 2007; Kroeze et al., 2007). The uncertainty in this estimate is large. On the global scale, surface uptake may seem negligible, but at the local scale it may not be irrelevant. It was therefore included in Table 6.8.

6.3.4.1 Atmosphere Burden and Trends

The concentration of N₂O is currently 19% higher than pre-industrial levels (Figure 6.12; MacFarling-Meure et al., 2006) Figure 6.18 shows the concentration and annual growth rate of atmospheric N₂O estimated from direct measurements (NOAA/ESRL programme). On decadal time scales the concentration of N₂O has been rising steadily at a rate of 0.73 ± 0.03 ppb yr⁻¹. The inter-annual variability in mid to high latitudes in Northern and Southern hemispheric N₂O abundances has been shown to be correlated with the strength of the Brewer-Dobson circulation (Nevison, 2011). Variability in stratosphere to troposphere air mass exchange, coupled with the stratospheric N₂O sink is likely to be responsible for a fraction of the variability

1 in tropospheric N₂O, but the prognostic understanding of the seasonal and inter-annual variability of the
2 stratosphere-troposphere exchange is low (Huang et al., 2008). This removal process signal is obscured in
3 the southern hemisphere by the timing of oceanic thermal and biological ventilation signals (Nevison, 2011).
4 Quantitative understanding of the terrestrial source variability is low, although it may be driven by soil water
5 content variability in the Northern hemisphere, as inferred from correlations with the observed variability in
6 the N₂O atmospheric growth rate (Ishijima et al., 2009). A first process model-based estimate suggests that
7 the mainly climate-driven variability in the terrestrial source may account for only 0.07 ppb yr⁻¹ in
8 atmospheric N₂O, which would be difficult to detect in the observed growth rate (Zaehle et al., 2011).
9

10 [INSERT FIGURE 6.18 HERE]

11 **Figure 6.18:** Globally averaged growth rate of N₂O in ppb yr⁻¹ determined from the observations of the NOAA/ESRL
12 halocarbons program. Brown dots indicate annual values augmented by a smoothed line to guide the eye.
13

14 6.3.4.2 Emissions and Sinks

15
16 Most N₂O is produced by biological (microbial) processes such as nitrification and denitrification in
17 terrestrial and aquatic systems, including rivers, estuaries, coastal seas and the open ocean. In general, more
18 N₂O is formed when more reactive nitrogen is available. The production of N₂O shows a large spatial and
19 temporal variability. Experimental data are mostly available for terrestrial systems in temperate zones. As a
20 result emission estimates for tropical regions and for aquatic systems are relatively uncertain. Inverse
21 modelling studies add to our assessments of the N₂O budget by providing mostly independent constraints on
22 the global and regional emission estimates from bottom-up methods, and show that the errors in these are
23 large, especially in (sub)-tropical regions (e.g., Hirsch et al., 2006; Huang et al., 2008, Thompson et al.,
24 subm.). Emissions from rivers, estuaries and continental shelves have been subject of debate for several
25 decades (DeKlein et al., 2007; Seitzinger and Kroeze, 1998). A recent study in North America confirms that
26 rivers can be important sources of N₂O (Beaulieu et al., 2011b).
27

28 Table 6.8 does not include the formation of atmospheric N₂O from the abiotic decomposition of ammonium
29 nitrate in the presence of light, appropriate relative humidity and a surface, however it has been recently
30 proposed as a potentially important source of N₂O (Rubasinghege et al., 2011). A global estimate of the
31 source strength, however, does not yet exist. Table 6.8 indicates that the global N₂O emissions in the mid
32 1990s amount to 17.4 (8.5–27.7) Tg N yr⁻¹. This is essentially the same as the estimate in AR4 (17.7 TgN yr⁻¹
33 in AR4). The uncertainty range overlaps with that of inverse modelling studies (14.1–17.8) by Huang et al.
34 (2008). Anthropogenic emissions have steadily increased over the last two decades and in 2006 were 15%
35 higher than the value in the early 1990s. Overall, anthropogenic emissions are now a factor of 8 greater than
36 their estimated level in 1900. These trends are consistent with observed increases in atmospheric N₂O
37 (Syakila et al., 2010). Human activities strongly influence the source of N₂O, since N-fertilizer used in
38 agriculture is now the main source of N for nitrification and denitrification. Trends in nitrogen isotopes
39 confirm that agriculture is primarily responsible for historic increase in N₂O (Park et al., 2012; Sutka et al.,
40 2006).
41

42 6.3.4.3 Sensitivity of N₂O fluxes to Climate and Elevated CO₂

43
44 Early studies have suggested a considerable positive feedback between N₂O and climate (Khalil and
45 Rasmussen, 1989) supported by observed glacial-interglacial swings in atmospheric N₂O (Fluckiger et al.,
46 1999). Climate changes influence marine and terrestrial sources, but their individual contribution and even
47 the sign of their response to climate variations are difficult to estimate, and there appears to be no consensus
48 about the sources responsible for the long-term (glacial-interglacial) N₂O concentration changes. Simulations
49 of a terrestrial biosphere model suggest a moderate increase of global N₂O emissions with recent climatic
50 changes (Zaehle and Dalmonech, 2011). However, most of the change in atmospheric N₂O is attributed to
51 anthropogenic reactive nitrogen (Nr) and industrial emissions (Davidson, 2009; Holland et al., 2005; Zaehle
52 and Dalmonech, 2011). Significant uncertainty remains in the N₂O-climate feedback from land ecosystems,
53 as it is very sensitive to the changes in the seasonal and frequency distribution of precipitation, and also
54 because agricultural emissions themselves may also be sensitive to climate.
55

56 Methods to monitor ecosystem exchanges of N₂O have greatly improved in recent years, but technological
57 challenges persist and the network remains very sparse (Sutton et al., 2007). Climate change will directly

1 affect nitrification and denitrification processes, and thus N₂O production, due to its effect on temperature
2 and soil moisture regimes (Butterbach-Bahl and Dannenmann, 2011). N₂O emissions may also be influenced
3 indirectly by the effects of CO₂ fertilisation or by N deposition induced changes in soil moisture, plant
4 productivity, activity and composition of soil microbial and fungal communities, and nitrogen availability
5 due to plant-soil interactions (Barnard et al., 2005; Singh et al., 2010). Only a few long-term manipulation
6 experiments have been conducted to investigate the effect of global changes on terrestrial N₂O emissions,
7 and these have mostly focused on temperate and boreal ecosystems. Warming experiments show varying
8 N₂O emission responses, likely due to co-variations in soil moisture and temperature-related increase in N₂O
9 production (Brown et al., 2011; Chantarel et al., 2011; Lohila et al., 2010). N₂O emissions were estimated to
10 predominantly increase with elevated CO₂ (vanGroenigen et al., 2011), however, reductions have also been
11 observed (Billings et al., 2002; Mosier et al., 2002), depending mainly on changes in the microbial/fungal
12 community and the overall plant-soil nitrogen cycling (Kammann et al., 2008; Reich et al., 2006). In
13 ecosystems where N is not limiting, the N₂O response to temperature and atmospheric CO₂ increases will
14 likely be positive (Butterbach-Bahl and Dannenmann, 2011). The effect of interacting climate and
15 atmospheric CO₂ change modulates and potentially dampens the individual responses to each driver,
16 however, the global implications of these interactions remain poorly understood (Brown et al., 2011).
17 Thawing permafrost soils may under particular hydrological settings may liberate reactive nitrogen and turn
18 into significant sources of N₂O, however, the global significance of this source is not established (Elberling
19 et al., 2010).

20 21 6.3.4.4 Global N Budget

22
23 For base year 2005, anthropogenic activities created ~220 TgN of reactive nitrogen Nr from N₂, in contrast
24 to natural terrestrial sources totalling ~100 TgN (90–120 TgN yr⁻¹) – human actions amounted to a factor of
25 2 more reactive nitrogen than natural terrestrial processes (Table 6.8, Section 1a). This contrast might be
26 even larger. A recent analysis estimates that natural terrestrial process may only total ~58 TgN yr⁻¹ (40–100
27 TgN yr⁻¹; Vitousek et al., *subm.*). Of this created reactive nitrogen, NO_x and NH₃ emissions from
28 anthropogenic sources are ~4-fold greater than natural emissions (Table 6.8, Section 1b). The resulting
29 deposition of NH_x is more favored to the continents than the oceans relative to the NO_y deposition due to the
30 longer atmospheric residence time of the latter. These deposition estimates are lower limits, as they do not
31 include organic nitrogen species, which can increase deposition rates by up to 30% (Duce et al., 2008; Table
32 6.8, Section 1c). Discharge of reactive nitrogen to the coastal oceans is ~45 TgN yr⁻¹ (Table 6.8, Section 1c).
33 There are two broad findings in AR5 compared to AR4. First, human creation of reactive nitrogen is 2 to 4
34 times greater than creation by natural terrestrial systems, and second, the atmosphere is about twice as
35 important as riverine systems in distributing reactive nitrogen through the global environment.

36 37 6.4 Projections of Future Carbon and Other Biogeochemical Cycles

38 39 6.4.1 Introduction

40
41 In this section, we assess how accurately changes in the evolution of CO₂, CH₄ and N₂O concentration can be
42 projected using models, and hence the role of carbon and other biogeochemical cycles in future climate
43 under socio-economic emission scenarios. AR4 reported how climate change can affect the natural carbon
44 cycle in a way which could feed back onto climate itself. A comparison of 11 coupled climate-carbon cycle
45 models of different complexity (Coupled Climate-Carbon Cycle Model Intercomparison Project; C4MIP;
46 Friedlingstein et al., 2006) showed that all 11 models simulated a positive feedback. In other words, climate
47 change reduced natural carbon uptake in these models and amplified atmospheric CO₂ increases (see Box
48 6.4). However, there is substantial quantitative uncertainty in future CO₂ and temperature, both across
49 coupled carbon-climate models (Friedlingstein et al., 2006) and within each model parametrizations (Booth
50 et al., 2012). This uncertainty on the coupling between carbon cycle and climate is of comparable magnitude
51 to the uncertainty caused by physical climate processes discussed in Chapter 12 of this report (Denman et al.,
52 2007; Gregory et al., 2009; Huntingford et al., 2009), showing that carbon-climate interactions are key to
53 climate projections.

54
55 Very few coupled carbon-climate models include a representation of nutrient cycles in the terrestrial carbon
56 cycle, which are yet an important component of the terrestrial carbon cycle, affecting both its ability to take
57 up anthropogenic carbon and its response to future climate change (Section 6.4.6). Recent studies (Sokolov

1 et al., 2008; Thornton et al., 2009; Zaehle et al., 2010a) have found that representation of nitrogen in
2 terrestrial carbon cycle models substantially alters the response of future CO₂ projections and can even
3 change the sign of the climate-carbon feedback. Available nitrogen can both limit the natural uptake of
4 carbon by terrestrial ecosystems, and also reduce the potential sensitivity of land carbon sink to future
5 climate change. The availability of labile forms of phosphorus (P) is also known to limit ecosystem
6 productivity, with important interactions among carbon, nitrogen, and phosphorus cycles (Elser et al., 2007;
7 LeBauer and Treseder, 2008). Other important processes such as anthropogenic or natural disturbances
8 (Sections 6.4.3.2, 6.4.8.1), forest age distribution or interactions with atmospheric composition (Sections
9 6.4.8.3, 6.4.8.5) are often missing or treated simplistically in these models (see also Section 6.3.2.6.6).

10
11 Other biogeochemical cycles and feedbacks other than induced by the carbon cycle play an important role in
12 the future of the climate system, although the carbon cycle represents the strongest of these. Natural CH₄
13 emissions from wetland and fires are sensitive to climate change (Sections 6.4.7 and 6.3.3.2). The fertilizing
14 effects of nitrogen deposition and rising CO₂ also likely affect CH₄ emissions by wetlands through increased
15 productivity. Changes in the nitrogen cycle, in addition to interactions with CO₂ sources and sinks, are very
16 likely to affect the emissions of N₂O both on land and from the ocean (Section 6.4.6) and potentially on the
17 rate of CH₄ oxidation (Gardenas et al., 2011). A recent review highlighted the complexity of terrestrial
18 biogeochemical feedbacks (Arneeth et al., 2010). A model study including feedbacks from carbon storage,
19 and CH₄ and N₂O emissions from land estimated land-climate feedbacks contribute an additional 30–40% to
20 climate sensitivity (Stocker et al., *subm.*). Mahowald (2011) estimated that the radiative forcing from aerosol
21 effects on biogeochemical cycles is of comparable magnitude to the conventional aerosol direct and indirect
22 radiative forcing effects. A similar degree of complexity exists in the ocean and in interactions between land,
23 atmosphere and ocean cycles (Figure 6.19). Many of these processes are not yet represented in coupled
24 climate-biogeochemistry models and so their magnitudes have to be estimated in offline or simpler models,
25 which makes their quantitative assessment difficult. It is likely that there will be non-linear interactions
26 between many of these processes, but these are not yet quantified. Confidence in the magnitude, and
27 sometimes even the sign, of these feedbacks is low.

28 29 [INSERT FIGURE 6.19 HERE]

30 **Figure 6.19:** A summary of the magnitude of biogeochemical feedbacks. Gregory et al. (2009) proposed a framework
31 for expressing non-climate feedbacks in common units ($W\ m^{-2}\ K^{-1}$) with physical feedbacks, and Arneeth et al. (2010)
32 extended this beyond carbon cycle feedbacks to other terrestrial biogeochemical feedbacks. The figure shows the results
33 compiled by Arneeth et al. (2010), with ocean carbon feedbacks from the C4MIP coupled climate-carbon models used
34 for AR4 also added. Some further biogeochemical feedbacks from the HadGEM2-ES Earth System model (Collins et
35 al., 2011) are also shown. Black dots represent single estimates, and coloured bars denote the simple mean of the dots
36 with no weighting or assessment being made to likelihood of any single estimate. An indication of the confidence in the
37 magnitude of these estimates is shown in the right hand column and is low for feedbacks with only one, or few, dots.
38 The role of nitrogen limitation on terrestrial carbon sinks is also shown – this is not a separate feedback, but rather a
39 modulation to the climate-carbon and concentration-carbon feedbacks. This list is not exhaustive. These feedback
40 metrics are also likely to be state or scenario dependent and so cannot always be compared like-for-like (see Section
41 6.4.2.2). Results have been compiled from (a) Arneeth et al. (2010), (b) Friedlingstein et al. (2006), (c) HadGEM2-ES
42 (Collins et al., 2011) simulations, (d) Burke et al. (*subm.*), (e) von Deimling et al. (2012). Note the expanded x-axis
43 scale for the lower portion of the figure.

44
45 The response of land and ocean carbon storage to changes in climate, atmospheric CO₂ levels and
46 anthropogenic activity varies strongly on different timescales making it hard to simply use past changes to
47 make projections of future changes. This chapter has assessed carbon cycle changes across many timescales
48 from monthly to millennial, and these are summarised in Table 6.9. A common result is that an increase in
49 atmospheric CO₂ will *always* lead to an *increase* in land and ocean carbon storage. However, changes in
50 climate do not lead to a consistent sign of response in carbon storage change due to the very many different
51 mechanisms that operate. For example, land carbon increases on seasonal time scales in temperate and high
52 latitudes in northern spring-summer months due to higher temperatures and light levels; over glacial cycles,
53 land carbon also increases as climate warms due to reduced cover of ice sheets. However, on centennial
54 timescales land carbon is projected to reduce in a warmer climate due to faster decomposition of soil organic
55 matter. Thus changes in carbon cycling on different timescales cannot simply be extrapolated to make
56 projections on different timescales, but can provide valuable information on the processes at work and can be
57 used to evaluate and improve models.

[INSERT TABLE 6.9 HERE]

Table 6.9: Comparison of the magnitude of changes in carbon storage (PgC) by land and ocean over different timescales. These changes are shown as approximate numbers to allow a comparison across timescales. For more details see the indicated chapter section. An indication, where known, of what causes these changes (climate, CO₂, land use change) is also given with an indication of the sign: ‘+’ means that an increase in CO₂ or global-mean temperature is associated with an increase in carbon storage (positive β or γ), and a ‘-’ means an increase in CO₂ or global-mean temperature is associated with a decrease in carbon storage (negative β or γ). The processes which operate to drive these changes can vary markedly from seasonal phenology of vegetation to long-term changes in ice sheet cover or ocean circulation. Some of these processes are ‘reversible’ in the context that they can increase and decrease cyclically, whereas some are ‘irreversible’ in the context that changes in one sense might be much longer than in the opposite direction.

[START BOX 6.4 HERE]**Box 6.4: Climate-Carbon Cycle Models and Experimental Design***What are coupled climate-carbon cycle models and why do we need them?*

General circulation models (GCMs, generally referred to as ‘climate models’) have long been used for making climate projections, and have formed the core of previous IPCC climate projection chapters (e.g., Meehl et al. (2007)). For the 5th Coupled Model Intercomparison Project (CMIP5) many models now have an interactive carbon cycle. What exactly does this mean, how do they work and how does their use differ from previous climate models? Atmosphere-ocean GCMs typically represent the physical behaviour of the atmosphere and oceans but atmospheric composition, such as the amount of CO₂ in the atmosphere, is prescribed as an input to the model. This approach neglects the fact that changes in climate might affect the natural biogeochemical cycles, which control atmospheric composition, and so there is a need to represent these processes in climate projections.

Specifically there is growing recognition that interactions between climate change and the global carbon and other biogeochemical cycles can have profound influences on future climate. In 2006, the C4MIP project (Coupled climate-carbon cycle model intercomparison project; Friedlingstein et al., 2006) assembled results from 11 models, which explicitly represented these interactions and thus enabled the first multi-model quantification of the climate-carbon cycle feedback. At the core of coupled climate-carbon cycle models is the physical atmosphere-ocean GCM, but additional components of land and ocean biogeochemistry respond to the changes in the climate conditions to influence the atmospheric CO₂. Now, the atmospheric CO₂ becomes a part of the model and its evolution in time is simulated rather than being prescribed as an input. Instead, the input comes in the form of CO₂ emissions (such as from burning fossil fuel) which can increase the CO₂ and then the natural carbon cycle exchanges CO₂ between the atmosphere and land and ocean components. These ‘climate-carbon cycle models’ (also commonly referred to as ‘Earth System Models’ (ESMs) – see Glossary) provide a predictive link between fossil fuel CO₂ emissions and future CO₂ concentrations and are an important part of the CMIP5 experimental design (Hibbard et al., 2007). The phrase ‘earth system’ refers to more than just the carbon cycle, and some models (e.g., HadGEM2-ES; Collins et al., 2011) also represent atmospheric chemistry processes. In this box we focus specifically on the implementation and use of coupled climate-carbon cycle models within the CMIP5 experiments.

The Role of Land-Cover

Land cover is the term used to describe what occupies an area of land, be it trees, grasses, ice or urban areas. All models require some description of the physical properties of the land surface, but how this is represented differs between them. Conventional climate models would have prescribed land-cover: i.e., the land cover at every point is pre-defined, although it may be defined to change in time to represent a scenario of land use change. Land cover change includes deforestation and other land use change assessed in Section 6.3.2.2 for their effect on CO₂ emissions during the past decades. Some models used for coupled climate-biogeochemical cycles projections incorporate the ability to simulate changes in the natural land cover from biome migration, as different types of vegetation grow or die in response to environmental changes. So-called Dynamic Global Vegetation Models (DGVMs, e.g., Sitch et al. (2008)) can simulate such changes in the natural land-cover and hence additional biophysical effects through heat and moisture fluxes as well as changes in carbon storage.

How are these models used?

Earth System GCMs (ESMs) are the primary tool for making projections of climate change for the next century. The additional capability to simulate carbon cycle processes and feedbacks and in some models other biogeochemical cycles, allows for a greater range of quantities to be simulated such as changes in natural carbon stores, fluxes or ecosystem functioning. As described above, the ESM models have the capability of simulating the time variations in atmospheric CO₂ interactively with GCM simulated climate. But there may also be applications where it is desirable for the user to pre-define the pathway of atmospheric CO₂ and prescribe it as a forcing to the ESMs. Thus, numerical simulations with ESM models can be either ‘concentration driven’ or ‘emissions driven’ as described below. It should be noted that a model can be used in either configuration – this is not a distinction between different models, but a distinction between different ways of using them.

Concentration-driven simulations follow the ‘traditional’ approach of prescribing the time-evolution of atmospheric CO₂ as an input to the model used in IPCC AR1 to AR4 Assessment reports, although AR4 discussed in their Chapter 7 the emission-driven C4MIP results. This is shown schematically in Box 6.4 Figure 1 (left hand side). Atmospheric CO₂ concentration is prescribed as input to the model from a given scenario (e.g., RCP scenarios) and follows a pre-defined pathway regardless of changes in the climate or natural carbon cycle processes. The processes between the horizontal dashed lines in the figure represent the model components which are calculated during the concentration-driven simulation. Externally prescribed changes in atmospheric CO₂ concentration, and hence climate, can and will affect land and ocean carbon storage. By construction, changes in land and ocean storage, however, do not feedback on the atmospheric CO₂ concentration and hence wider climate. The changes in natural carbon fluxes and stores are output by the model and can be used to diagnose the sensitivity of the carbon cycle to (prescribed) CO₂ and (calculated) climate changes. Additionally in concentration driven simulations, externally prescribed human-caused changes in land use and land-cover may be applied from scenarios, which affect the terrestrial carbon storage, but this has no impact on the atmospheric CO₂, although the physical impact of land-cover change on the climate will be included.

[INSERT BOX 6.4, FIGURE 1 HERE]

Box 6.4, Figure 1: Schematic representation of carbon cycle numerical experimental design. Concentration-driven (left hand side) and emissions-driven (right hand side) simulation experiments make use of the same ESM models, but configured differently. Concentration-driven simulations prescribe atmospheric CO₂ as a pre-defined input to the climate and carbon cycle model components, but their output does not affect the CO₂. Emissions-driven simulations prescribe CO₂ emissions as the input and atmospheric CO₂ is now an internally calculated element of the earth system model.

Emissions-driven simulations allow the full range of interactions in the models to operate and determine the evolution of atmospheric CO₂ and climate as an internal part of the simulation itself (Box 6.4, Figure 1, right hand side). In this case external fossil fuel and cement emissions of CO₂ are the externally prescribed input to the model and the subsequent changes in atmospheric CO₂ concentration are simulated by it. The model simulates changes in land and ocean carbon storage, and associated carbon fluxes with the atmosphere and these affect the atmospheric CO₂ allowing the effects of feedbacks between climate and the carbon cycle to be quantified. If externally prescribed human caused land use or land cover changes are applied as a forcing scenario then in addition to the physical effects on the climate, changes in carbon storage from deforestation or other land use change (see Section 6.3.2.2) will influence the course of atmospheric CO₂.

The outputs from the two types of simulation experiment are different but closely related. In both cases natural land and ocean carbon fluxes and stores are simulated by the models. In *emissions-driven* experiments, the atmospheric CO₂ growth rate is calculated within the model due to the net effect of the anthropogenic emissions, E , and natural fluxes:

$$\frac{dCO_2}{dt}_{\text{simulated}} = E - (\text{land_carbon_uptake} + \text{ocean_carbon_uptake})$$

In *concentration-driven* simulation experiments, the so called ‘compatible fossil fuel emissions’, E , that can be diagnosed afterwards from mass conservation principle, from the prescribed atmospheric CO₂

concentration pathway by calculating the residual between the prescribed CO₂ pathway and the natural fluxes, i.e., as given by the following equation:

$$E = \frac{dCO_2}{dt}_{prescribed} + (land_carbon_uptake + ocean_carbon_uptake)$$

The effect of climate change on the natural carbon cycle will manifest itself either through changes in atmospheric CO₂ in the *emissions-driven* experiments or in the compatible emissions in the *concentration-driven* experiments.

Concentration-driven simulation experiments have the advantage that they can be performed by GCMs without an interactive carbon cycle. For this reason, most of the RCP simulations presented later in this Chapter with carbon cycle models and in Chapter 12 are performed this way. Emissions-driven simulations have the advantage of representing the full range of interactions in the coupled climate-carbon cycle models and may be seen as a more realistic experimental design. Hence the RCP8.5 pathway is repeated by many ESM models as an emissions-driven simulation to quantify the possible effects of the climate-carbon cycle feedback on climate change under this high-emissions scenario (Friedlingstein et al., *subm.*).

Feedback Analysis


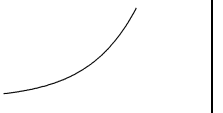




The Earth System models are made up of many ‘components’, corresponding to separate parts of the computer programme which perform calculations to represent different processes or aspects of the system. E.g., models may have components to represent clouds, rainfall, ocean currents, sea ice and land and ocean ecosystems. All these components interact in the full model – i.e., the output from one set of calculations may change the conditions, which affect another. For example if it rains in a dry place, the plants may grow more.

In order to understand the behaviour of the very complex ESM models a technique was developed to assess different aspects of the models' sensitivities (Arora et al., *subm.*; Friedlingstein et al., 2003; Friedlingstein et al., 2006). The two dominant interactions in the carbon cycle are the response of the carbon cycle to changes in CO₂ and its response to changes in climate. These can be measured using two metrics: ‘beta’ (β) measures the strength of changes in carbon fluxes by land or ocean in response to changes in atmospheric CO₂; ‘gamma’ (γ) measure the strength of changes in carbon fluxes by land or ocean in response to changes in climate. These metrics can be calculated as cumulative changes in carbon storage (as in Friedlingstein et al., 2006) or instantaneous rates of change (Arora et al., *subm.*). It is not possible to measure these sensitivities simultaneously in a single simulation because it is not possible to know whether carbon fluxes are responding to CO₂, climate or both. Hence it is necessary to perform ‘decoupled’ simulations where some processes in the models are artificially disabled in order to be able to evaluate the changes in other processes.

For climate-carbon cycle models, these decoupled experiments are summarised in Box 6.4 and in Table 1. In a fully coupled simulation, the carbon cycle components of the models experience both changes in atmospheric CO₂ and changes in climate. Additionally the models can perform two further simulations. In the first the atmospheric radiation experiences constant CO₂ while the carbon cycle model components experience increasing CO₂. This is known as ‘biogeochemically coupled’ referring to the fact that this experiment quantifies the strength of the effect of rising CO₂ concentration alone on the carbon cycle in the absence of climate change (referred to as CMIP5 experiments called ‘esmFixClim’). The role of this simulation is to allow quantification of the β metric (independently for land and ocean), defined as the change in carbon store per unit change in atmospheric CO₂ in the absence of climate change.

Box 6.4, Table 1: Configurations of simulations designed for feedback analysis by artificially allowing some processes to operate but holding others constant. The curves denote whether increasing or constant CO₂ values are input to the radiation and carbon cycle model components.

	CO ₂ input to radiation scheme	CO ₂ input to carbon-cycle scheme	Reason

Fully coupled			Simulates the fully coupled system
Biogeochemically coupled 'esmFixClim'			Isolates carbon-cycle response to CO ₂ (β)
Radiatively coupled 'esmFdbk'			Isolates carbon-cycle response to climate change (γ)

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The second decoupled experiment is the converse of the first one, and is known as ‘radiatively coupled’ (the CMIP5 experiments called ‘esmFdbk’). In this experiment, the climate model's radiation scheme experiences an increase in CO₂ (and hence produces a change in climate) while fixed CO₂ concentrations are input to the carbon cycle model components. The role of this simulation is to allow quantification of the effect of climate change alone on the carbon cycle: the γ metric, defined as the change in carbon store per degree of global temperature change.

A large positive value of β denotes that a model responds to increasing CO₂ by simulating large increases in natural carbon uptake, e.g., through a large modelled ‘CO₂ fertilization effect’ (see Box 6.3). Negative values of γ denote that a model response to climate warming is to reduce CO₂ uptake from the atmosphere, whilst a positive value means warming acts to increase CO₂ uptake. β and γ values are not specified in a model, but are properties that emerge from the suite of complex processes represented in the model. The values of the β and γ metrics diagnosed from simulations can vary from place to place within the same model (see Section 6.4.2.3) although it is the global aggregate that determines the global extent of the climate-carbon cycle feedback.

Other feedback analysis techniques exist than that of Friedlingstein et al. (2006) . Boer and Arora (2010) analysed the carbon cycle response to climate and CO₂ at a grid-point level and present maps of these metrics in a method analogous to that used for physical radiative feedback analyses. Yoshikawa et al. (2008) also presents geographical analysis of the feedback metrics. Goodwin and Lenton (2009) show that feedbacks can be expressed as an equivalent emission. Arora et al. (subm.) analyse CMIP5 models using both the Boer and Arora (2010) flux-based and Friedlingstein et al. (2006) cumulative-based methodologies to define the sensitivities. The metrics calculated for each approach vary in time during the simulations and would differ for different scenarios. Such analysis frameworks should be seen as techniques for assessing relative sensitivities of models and understanding their differences, rather than as absolute measures of invariant system properties.

Evaluation

The complex ESM models have new components and new processes beyond conventional atmosphere-ocean GCMs and thus require additional evaluation to assess their ability to make climate projections. Evaluation of the carbon cycle model components themselves is presented in Sections 6.3.2.5.6 for ocean carbon models and 6.3.2.6.6 for land carbon models, whilst evaluation of the fully coupled models is presented in Chapter 9.

[END BOX 6.4 HERE]

6.4.2 Carbon Cycle Feedbacks in CMIP5 Models

6.4.2.1 Global Analysis

The carbon cycle response to future climate and CO₂ changes can be viewed as two strong and opposing feedbacks (Gregory et al., 2009). The climate-carbon response γ determines changes in carbon storage due to changes in climate, and the concentration-carbon response β determines changes in storage due to elevated CO₂. Climate-carbon cycle feedback responses have been analysed for 8 CMIP5 models which performed idealized simulations involving atmospheric CO₂ increasing at a prescribed rate of 1% per year (Arora et al., subm.). Increased atmospheric CO₂ will lead to increased land and ocean carbon uptake (high confidence) but by an uncertain amount. Models agree on the sign of land and ocean response to rising CO₂ but show only medium and low agreement for the magnitude of ocean and land carbon uptake respectively (Figure 6.20). Future climate change will decrease land and ocean carbon uptake (medium confidence). Models agree on the sign, globally, of land and ocean response to climate change but show low agreement on the magnitude of this response. Land and ocean carbon uptake may differ in sign between different regions and between models (Section 6.4.2.3). Inclusion of N-cycle processes in 2 land carbon cycle model components out of these 8 reduces the magnitude of the sensitivity to both CO₂ and climate (Section 6.4.6.2).

[INSERT FIGURE 6.20 HERE]

Figure 6.20: Comparison of carbon cycle feedback metrics between the C4MIP ensemble of 7 GCMs and 4 EMICs under the SRES-A2 scenario (Friedlingstein et al., 2006) and 8 CMIP5 models (Arora et al., subm.) under the 1% increase per year CO₂ scenario. Black dots represent a single model simulation and coloured bars the mean of the multi-model results, grey dots are used for models with a coupled terrestrial nitrogen cycle. The comparison with C4MIP is for context, but these metrics are known to be variable across different scenarios and rates of change (see Section 6.4.2.2). Some of the CMIP5 models are derived from models that contributed to C4MIP and some are new to this analysis. Table 6.10 lists the main attributes of each CMIP5 model used in this analysis. The SRES A2 scenario is closer in rate of change to a 0.5% yr⁻¹ scenario and as such it should be expected that the CMIP5 gamma terms are comparable, but the beta terms are likely to be around 20% smaller for CMIP5 than for C4MIP. This high dependence on scenario (Section 6.4.2.2) reduces confidence in any quantitative statements of how CMIP5 carbon cycle feedbacks differ from C4MIP. Models used: MPI-ESM-LR, BCC-CSM1, HadGEM2-ES, IPSL-CM5A-LR, CanESM2, NorESM-ME, CESM1-BGC, MIROC-ESM.

[INSERT TABLE 6.10 HERE]

Table 6.10: CMIP5 model descriptions in terms of carbon cycle attributes and processes.

The role of the idealised experiment presented here is to study model processes and understand what causes the differences between models. Arora et al. (subm.) assess the global carbon budget from these idealized simulations and find across CMIP5 ESMs the contribution of land and ocean carbon-concentration feedback is typically 4–5 times larger than that of the carbon-climate feedback (Figure 6.21). The land carbon-climate feedback (γ) is larger than the ocean carbon-climate feedbacks in all models. Whilst land and ocean contribute equally to the total carbon-concentration feedback (β), model *spread* in the land response is greater than for the ocean.

[INSERT FIGURE 6.21 HERE]

Figure 6.21: Cumulative emissions across CMIP5 models broken down into the contributions of land and ocean response to CO₂ and climate. The contribution of the carbon-concentration feedback is larger than the climate-carbon feedback for all models and the land and ocean contributions to this are typically comparable. The exception is for NorESM-ME and CESM1-BGC which include nitrogen interactions in the terrestrial carbon cycle – these models with nitrogen included in the terrestrial carbon cycle model component simulate a smaller response to both climate and carbon than the other models, but still of the same sign as the other models. The contribution of the ocean to the climate-carbon response is small for all models. Models used: MPI-ESM-LR, BCC-CSM1, HadGEM2-ES, IPSL-CM5A-LR, CanESM2, NorESM-ME, CESM1-BGC, MIROC-ESM.

6.4.2.2 Scenario Dependence of Feedbacks

The values of carbon-cycle feedback metrics can vary markedly for different scenarios and as such cannot be used to compare model simulations with different time periods, nor inter-compare model simulations with different scenarios (Arora et al., subm.). Gregory et al. (2009) demonstrated how sensitive the feedback metrics are to the rate of change of CO₂ in the forcing scenario. For two models, β varied under different rates of increase of CO₂ (0.5% yr⁻¹, 1% yr⁻¹ and 2% yr⁻¹), decreasing by around 20% from 0.5% yr⁻¹ to 1% yr⁻¹ and from 1% yr⁻¹ to 2% yr⁻¹. Faster rates of CO₂ increase lead to reduced beta values as the carbon

1 uptake (especially in the ocean) lags further behind the forcing. γ is much less sensitive to the scenario,
2 especially between 0.5 % yr⁻¹ and 1% yr⁻¹, as both global temperature and carbon uptake lag the forcing.

3 4 6.4.2.3 Regional Feedback Analysis

5
6 The linear feedback analysis with the β and γ metrics of Friedlingstein et al. (2006) has been applied at the
7 regional scale to future carbon uptake by Roy et al. (2011), Yoshikawa et al. (2008). Figure 6.22 shows this
8 analysis extended to land and ocean points for the CMIP5 models.

9 10 [INSERT FIGURE 6.22 HERE]

11 **Figure 6.22:** The spatial distributions of multi model-mean land and ocean β and γ s for 7 CMIP5 models using the
12 *concentration-driven* idealised 1% per year CO₂ simulations. For land and ocean, β and γ are defined from changes in
13 terrestrial carbon storage and changes in air-sea accumulated fluxes respectively, from the beginning to the end of the
14 1% simulation relative to global (not local) CO₂ and temperature change. Stippling denotes areas where the magnitude
15 of the multi-model ensemble mean exceeds the 90% confidence level interval for β , and where at least 80% models
16 agree on the sign of change for γ . The solid lines show the multi-model mean and shaded areas denote ± 1 standard
17 deviation. Models used are: CanESM2, GFDL-ESM2M, HadGEM2-ES, IPSL-CM5A-LR, MPI-ESM-LR, NorESM1-
18 ME for all, CESM1-BGC for land β , and bcc-csm1-1 for ocean β and γ .

19 20 6.4.2.3.1 Regional ocean response

21 Increased CO₂ is projected by the CMIP5 models to increase oceanic CO₂ sinks almost everywhere (high
22 confidence) with the exception of some very limited areas. The spatial distribution of this ocean response to
23 CO₂, β_o , is consistent between the models and with Roy et al. (2011) analysis, with the largest β s in the high-
24 latitudes ocean regions of both the northern and southern Hemispheres in agreement with historical uptake of
25 anthropogenic carbon (Section 6.3.2.5.3). On average, the regions with the strongest increase of oceanic CO₂
26 sinks in response to higher atmospheric CO₂ are the North Atlantic and the Southern Ocean. The magnitude
27 and distribution of β_o in the ocean closely resemble the distribution of historical anthropogenic CO₂ flux
28 from inversion studies and forward modelling studies (Gruber et al., 2009), with the dominant anthropogenic
29 CO₂ uptake regions in the subpolar Southern Ocean.

30
31 Climate warming is projected by the CMIP5 models to reduce oceanic carbon uptake in most oceanic regions
32 (medium confidence) consistent with the Roy et al. (2011) analysis. This sensitivity of ocean CO₂ sinks to
33 climate, γ_o , is mostly negative (i.e., a reduced regional ocean CO₂ sink in response to climate change) but
34 with regions of positive values in the Arctic, the Antarctic and in the equatorial Pacific (i.e., climate change
35 increases ocean CO₂ sink in these regions). The North Atlantic ocean and the mid-latitude Southern Ocean
36 have the largest negative γ_o values. Reduced CO₂ uptake in response to climate change in the sub-polar
37 Southern Ocean and the tropical regions has been attributed to warming induced decreased CO₂ solubility,
38 reduced CO₂ uptake in the mid-latitudes to decreased CO₂ solubility and decreased vertical mixing which
39 decreases the absorption of anthropogenic CO₂ in intermediate and deep waters (Roy et al., 2011). Increased
40 uptake in the Arctic and the polar Southern Ocean is partly associated with a reduction in the fractional sea
41 ice coverage (Roy et al., 2011). The North Atlantic ocean may exhibit a peak and subsequent reduction in
42 carbon uptake as a combined response to CO₂ and climate feedbacks occurring through carbonate system
43 CO₂ buffering and a slowdown in the Atlantic Meridional Overturning Circulation respectively (Halloran et
44 al., subm.).

45 46 6.4.2.3.2 Regional land response

47 Increased CO₂ is projected by the CMIP5 models to increase land CO₂ sinks everywhere (high confidence).
48 This response, β_L , has largest values over tropical land, in humid rather than arid regions, associated with
49 enhanced carbon uptake in forested areas of already high biomass. In the zonal totals, there is a secondary
50 peak of high β_L values over Northern Hemisphere temperate and boreal ecosystems partly due to a greater
51 land area there but also coincident with large areas of forest. Models agree on the sign of response but have
52 low agreement on the magnitude.

53
54 Climate warming is projected by the CMIP5 models to reduce land CO₂ sinks in tropics and mid-latitudes
55 (high confidence). CMIP5 models show medium agreement that warming may increase land carbon uptake
56 in high latitudes but none of these models include representation of permafrost carbon which is projected to
57 decrease in warmer conditions (Section 6.4.3.3), therefore confidence is low regarding the sign and
58 magnitude of future high-latitude land carbon response to climate change. Jones and Falloon (2009) showed

1 that changes in soil organic matter were the most important driver of the climate-carbon cycle feedback
 2 across C4MIP models, but these changes are not necessarily driven by soil processes. Matthews et al. (2005)
 3 have previously shown that vegetation productivity is a larger cause of model spread than modelled soil
 4 carbon decomposition processes.

6.4.3 Implications of the Future Projections for the Carbon Cycle

8 The CMIP5 simulations include 4 future scenarios referred to as ‘Representative Concentration Pathways’ or
 9 RCPs (Moss et al., 2010): RCP2.6, RCP4.5, RCP6.0, RCP8.5 (see Chapter 1). These future scenarios include
 10 CO₂ concentration and emissions, and have been generated by four Integrated Assessment Models (IAMs)
 11 and are labelled according to the approximate global radiative forcing level at 2100.

6.4.3.1 Climate and Carbon Cycle Model Components Used in the Integrated Assessment Models for the RCP Future CO₂ Concentration and Emissions Scenarios

16 van Vuuren (2011) have shown that the basic climate and carbon cycle responses of IAMs is generally
 17 consistent with the spread of climate and carbon cycle responses from ESMs. Some of the IAMs which were
 18 run to create the RCPs are more complex than others in terms of their carbon cycle model component and
 19 some use common climate and carbon cycle components. For the RCPs, three of the four IAMs (GCAM,
 20 RCP4.5; AIM, RCP6.0; MESSAGE, RCP8.5) use a version of the MAGICC simple climate and carbon
 21 cycle model that has been commonly used in IPCC Assessment reports. Hence, for the physical and
 22 biogeochemical components of the RCP scenarios 4.5, 6.0 and 8.5, the underlying IAMs are closely related.
 23 Only the IMAGE IAM, which created RCP2.6 differs markedly by using a newer version of MAGICC
 24 climate and a more sophisticated carbon cycle components for land and ocean carbon cycle (see Table 6.11).
 25 The same version of MAGICC was subsequently used to generate the CO₂ pathway for all 4 RCP scenarios
 26 using the CO₂ emissions output by the 4 IAMs (Meinshausen et al., 2011).

27
 28
 29 **Table 6.11:** Description of carbon cycle parameterizations in integrated assessment models.

IAM Model Name	Scenario	Climate	Terrestrial Carbon Cycle Model Component	Resolution	Vegetation Dynamics	Ocean Carbon
IMAGE	2.6	MAGICC6	Detailed description	0.5 x 0.5 degree	Biome model	Bern model
GCAM	4.5	MAGICC5.3	GCAM submodel	Regional/land use type	N	MAGICC
AIM	6	MAGICC4	MAGICC	Regional	N	MAGICC
MESSAGE	8.5	MAGICC4.1 ^a	Explicit for forests (DIMA), otherwise via MAGICC	Regional	N	MAGICC

30 Notes:

31 (a) Some parameters have been adjusted.

6.4.3.2 Land Use Changes in Future Scenarios

36 ESMs and IAMs use a diversity of approaches for representing land use changes (Table 6.12), including
 37 different land use classifications, parameter settings, and geographical scales. To implement land use change
 38 in a consistent manner across ESMs, a ‘harmonized’ set of annual gridded land use change during the period
 39 (1500–2100) covering the historical period based on land use reconstructions, and the future based on socio-
 40 economic projections by IAMs were developed for input to the CMIP5 ESMs (Hurt et al., 2011).

41 Not all the ESMs models used for CMIP5 used the full range of information available from the land use
 42 change scenarios, such as wood harvest projections, sub-grid scale shifting cultivation or representation of
 43 primary and secondary forests. This has implications for their ability to simulate carbon fluxes associated
 44 with land use change because sensitivity studies indicated that shifting cultivation, wood harvesting and
 45 simulation start date all strongly affect secondary land area and age, and estimated carbon fluxes (Section
 46 6.3.2.2; Hurt et al., 2011). The choice of RCP had a smaller impact on CO₂ emissions from land use change
 47 than the effects of wood harvest, shifting cultivation and choice of start date.
 48
 49

Table 6.12: Processes of land use incorporated in IAMs and ESMs.

Model	Deforestation	Wood Harvest	Explicit Age Classes	Crop Management	Explicit Biofuels
IAMs					
IMAGE	Y	Y	N	Y	Y
GCAM	Y	Y	N	Y	Y
AIM	Y	Y	N	Y	Y
MESSAGE	Y	Y	N	Y	Y
ESMs					
CanESM2	Y	N	N	Y	N
CCSM4	Y	Y	N	N	N
CESM1-BGC	Y	Y	N	N	N
GFDL-ESM2G	Y	Y	Y	Y (harvest)	N
HadGEM2-ES	Y	Y	N	N	N
INM-CM4	Y	Y	N	?	N
IPSL-CM5A	Y	Y	N	N	N
MIROC-ESM	Y	Y	Y	Y	N
MPI-ESM	Y	Y	N	N	N
NorESM1	Y	Y	N	N	N

Land use has been in the past and will be in the future a significant driver of forest land cover change and terrestrial carbon storage. Land use trajectories in the RCPs show very distinct trends and cover a wide-range of projections. These land use trajectories are very sensitive to assumptions made by each individual IAMs regarding the amount of land needed for food production (Figure 6.23). Wise et al. (2009) and Thomson et al. (2010) use the GCAM IAM model to highlight the large sensitivity of future land use requirements to modelling assumptions, such as increases in crop yield technology. Tilman et al. (2011) using empirical projection of cropland need for food production by 2050 also showed the sensitivity of future demand for cropland to assumptions about how agricultural technology and intensification is applied. The area of cropland and pasture increases in RCP8.5 with the MESSAGE IAM model, mostly driven by an increasing global population, but cropland area also increases in the RCP2.6 with the IMAGE IAM model, despite a smaller population increase, as a result of bio-energy production necessary to maintain low CO₂ concentration pathway. RCP6 with the AIM IAM model shows an expansion of cropland but a decline in pasture land. RCP4.5 with the GCAM IAM is the only scenario to show a decrease in global cropland. It should not be assumed that there is a monotonic progression from ‘low’ to ‘high’ land use through the scenarios related to the radiative forcing of each scenario.

Within the IAMs, land use change is translated into land use change CO₂ emissions as shown in Figure 6.23(b). The degree of process detail strongly depends on the IAM model and hence differs between the RCP scenarios. IAMs typically model the demand and supply of land use related commodities (food crops, feed, animal products and timber) at the level of world regions. In the IAMs, land is used for mitigation in the future in ways that have no equivalent in the historical period, using for instance bio-energy and forms of capture and storage (BECCS), which strongly affects land use projections in the IAM. The CO₂ emissions from land use change are then estimated from the calculated land use patterns using the terrestrial carbon cycle model component specific to each IAM (see Table 6.11). Depending on the IAM, this may be done at an aggregated, regional, level – or using a detailed representation of vegetation and carbon flows at the grid level. The CO₂ emissions from land use change calculated by IAM models in the RCPs tend to decline over time due to a slow down (or even reversal) of agricultural land expansion. As most scenarios expect the population level to stabilise (or even decline), agricultural production levels are expected to stabilize as well. Cumulative emissions for the 21st century (Figure 6.23c) vary markedly across RCPs, with increasing cropland and pastureland areas in RCP2.6 and RCP8.5 giving rise to the highest emissions from land use change, RCP4.5 to intermediate emissions, and RCP6.0 to close to zero net emissions. All scenarios suggest that 21st century land use emissions will be less than half of those from 1850 to present day, which has important consequences for projections of CO₂ and climate in the AR5 IPCC Assessment Report.

1 The adoption of widely differing approaches among ESMS for the treatment of land use and land cover
2 change (LULCC) processes in terrestrial carbon cycle models leads to substantial between-model variation
3 in predicted LULCC fluxes and associated carbon stocks. Present-day fluxes associated with anthropogenic
4 land cover transitions (sources to the atmosphere) vary by more than a factor of 10 among models, as do
5 model predictions of present-day wood product pools. The highest present-day fluxes are predicted by
6 models which include representation of rotational harvest on managed forest lands (Lawrence et al., 2012;
7 Shevliakova et al., 2009a), while variation in the size of wood product pools depends on differing rates of
8 harvest as well as differing rates of wood product decomposition. Differences among IAMs in the treatment
9 of LULCC processes compounds the variability in LULCC fluxes and pools among ESMS for predictions
10 over the 21st century. The harmonization process applied to LULCC datasets for CMIP5 has been an
11 important step toward consistency among IAMs. However, among ESMS, and between IAMs and ESMS,
12 assignment of meaningful uncertainty ranges to present-day and future LULCC fluxes and states remains a
13 critical knowledge gap with implications for compatible emissions to achieve CO₂ pathways (Section
14 6.4.3.3; Jones et al., *subm.*).

15 [INSERT FIGURE 6.23 HERE]

16 **Figure 6.23:** Land use trends and emissions according to the four different integrated assessment models (IAM) used to
17 define the RCP scenarios. Global changes in croplands and pasture from the historical record and the RCP scenarios
18 (top left), and associated annual land use emissions of CO₂ (bottom left). Bars (right panel) show cumulative land use
19 emissions for the historical period (defined here as 1850–2005) and the 4 RCP scenarios from 2006 to 2100.
20

21 6.4.3.3 Projections of Future Carbon Cycle Response Under the RCP Scenarios

22 Future projections with Earth system models can be either *emissions-driven* or *concentration-driven* (see
23 Box 6.4). Simulated changes in land and ocean carbon uptake and storage under the four RCP scenarios are
24 presented here using results from CMIP5 ESMS concentration-driven simulations. The implications of these
25 changes on atmospheric CO₂ and climate as simulated by CMIP5 emissions-driven simulations are presented
26 in Chapter 12.
27

28 The results of the CMIP5 ESMS show medium agreement on the magnitude of cumulative ocean carbon
29 uptake from 1850 to 2005 (Figure 6.24a): average 128 PgC, range: 95–198 PgC. The models show low
30 agreement on the sign and magnitude of changes in land carbon storage (Figure 6.24b): average –8 PgC,
31 range –124 to +134 PgC. These central estimates are very close to observational estimates of 125 ± 25 PgC
32 for the ocean and -5 ± 40 PgC for the land respectively (Table 6.1), but show wide spread across models.
33 For the four RCP scenarios all the concentration-driven ESMS models project an increase in ocean uptake
34 over the 21st century. For RCP4.5 and RCP6, all the models also project an increase in land carbon uptake,
35 but for RCP2.6 and RCP8.5 some models (CanESM2 for RCP2.6, MIROC-ESM for RCP2.6 and 8.5,
36 CESM1-BGC for RCP8.5) project a decrease in land carbon storage at 2100 relative to 2005. Model spread
37 in land carbon projections is much greater than model spread in ocean carbon projections. Cox et al. (*subm.*)
38 find a relationship between short term variability and long-term land carbon cycle sensitivity which may
39 offer an observational constraint on the climate-carbon cycle response over the next century.
40

41 Representation of land use processes in ESMS is an advance since the AR4 (C4MIP models) which
42 considered no land use processes in terrestrial carbon cycle models, but the range of processes included
43 differs greatly between ESMS making comparison with historical land use CO₂ emissions trends (Tables 6.2
44 and 6.3) and RCP scenarios difficult (Section 6.4.3.1). Quantifying the carbon emissions from those land use
45 processes included is not straightforward due to their far-reaching influence on land carbon, atmospheric
46 CO₂ and climate. Simulated land use emissions cannot be deduced by the same method as for compatible
47 fossil fuel emissions as they leave no net effect on the total carbon in the system (Jones et al., *subm.*). The
48 net effect of a time-varying land use scenario on the carbon balance can be understood by comparison with a
49 second simulation without land use changes (Arora and Boer, 2010). It remains a challenge to diagnose land
50 use carbon emissions consistently across the CMIP5 models, and this is not tackled in the assessment
51 presented in this Chapter.
52

53 [INSERT FIGURE 6.24 HERE]

54 **Figure 6.24:** Changes in land and ocean carbon uptake simulated for the four RCP scenarios. Total ocean and land
55 reservoirs cumulative changes in carbon content are shown in the top two panels respectively for the whole period from
56 1850 to 2100. The lower four panels show the 21st century changes in carbon uptake for land (dashed) and ocean
57
58

(solid) separately for each scenario. Models used: CanESM2, GFDL-ESM2G, GFDL-ESM2M, HadGEM2-CC, HadGEM2-ES, IPSL-CM5A-LR, IPSL-CM5A-MR, IPSL-CM5B-LR, MIROC-ESM-CHEM, MIROC-ESM, MPI-ESM-LR, NorESM1-ME, Inmcm4, CESM1-BGC.

The *concentration-driven* ESM simulations can be used to quantify the compatible fossil fuel emissions required to follow the four RCP CO₂ pathways (Jones et al., *subm.*; see Box 6.4, Figure 6.25, Table 6.13). There is significant spread between ESMs, but no systematic inconsistency between the ESMs compatible fossil fuel emissions and the ‘original’ emissions themselves estimated by IAMs to define each RCP scenario. By the end of RCP8.5 on average, the CMIP5 models project lower compatible emissions than the MESSAGE IAM. The IMAGE IAM predicts that global negative emissions are required to achieve the RCP2.6 decline in radiative forcing from 3 W m⁻² to 2.6 W m⁻² by 2100. There is disagreement between the complex ESMs over the necessity for global emissions to become negative to achieve this, with 4 ESM models simulating negative compatible emissions and 4 ESM models simulating positive emissions from 2080 to 2100. The RCP2.6 scenario achieves this negative emission rate through use of large-scale bio-energy with carbon-capture and storage (BECCS). This would be classed as a carbon dioxide removal (CDR) form of geoengineering under the definition used in this IPCC report, and is discussed further in Section 6.5. Rogelj et al. (2011) also demonstrate the importance of BECCS to achieve a 2°C climate target, but any such negative emissions should be offset against existing forest carbon sinks which may be displaced (Hudiburg et al., 2011). The ESMs themselves make no assumptions about how the compatible emissions could or would be achieved, but merely compute the global total emission that is required to follow the CO₂ concentration pathway.

Table 6.13: The range of compatible fossil fuel emissions (PgC) simulated by the CMIP5 models for the historical period and the 4 RCP scenarios, expressed as cumulative fossil fuel emission from 2006 to 2100.

	Compatible fossil fuel emissions diagnosed from <i>concentration-driven</i> CMIP5 simulations			Land carbon changes			Ocean carbon changes		
	Historical / RCP scenario	CMIP5 ESM mean	CMIP5 ESM range	Historical / RCP scenario	CMIP5 ESM mean	CMIP5 ESM range	Historical / RCP scenario	CMIP5 ESM mean	CMIP5 ESM range
1850–2005	315 ^a	300	195–395	–5 ± 40 ^b	–10	–125–135	125 ± 20 ^b	130	95–200
RCP2.6	325	330	190–470	^c	80	–40–215	^c	160	120–200
RCP4.5	785	840	640–1070		235	60–470		265	200–425
RCP6.0	1215	1145	995–1310		225	100–340		305	275–350
RCP8.5	1905	1760	1450–1960		190	–90–370		415	330–660

Notes:

(a) Historical estimates of fossil fuel are as prescribed to all CMIP5 ESM models (Andres et al., 2011).

(b) Estimate of historical net land and ocean carbon uptake from Table 6.1.

(c) IAM breakdown of future carbon changes by land and ocean are not available.

(d) Consistent with Table 6.1 budgets values are rounded to the nearest 5 PgC.

[INSERT FIGURE 6.25 HERE]

Figure 6.25: Compatible fossil fuel emissions simulated by the CMIP5 models for the 4 RCP scenarios. Top: timeseries of instantaneous emission rate. Thick lines represent the historical estimates and emissions calculated by the integrated assessment models (IAM) used to define the RCP scenarios, thin lines show results from CMIP5 ESMs. Bottom: cumulative emissions for the historical period (1860–2005) and 21st century (defined in CMIP5 as 2006–2100) for historical estimates and RCP scenarios (bars) and ESMs (symbols). In the CMIP5 model results, total carbon in the land-atmosphere-ocean system can be tracked and changes in this total must equal fossil fuel emissions to the system (see also Table 6.13). Other sources and sinks of CO₂ such as from volcanism, sedimentation or rock weathering, which are very small on centennial time scales are not considered here. Hence the compatible emissions are given by cumulative-Emissions = ΔC_A + ΔC_L + ΔC_O or emission rate = d/dt [C_A + C_L + C_O], where C_A, C_L, C_O are carbon stored in atmosphere, land and ocean respectively. Models used: CanESM2, GFDL-ESM2G, GFDL-ESM2M, HadGEM2-CC, HadGEM2-ES, IPSL-CM5A-LR, IPSL-CM5A-MR, IPSL-CM5B-LR, MIROC-ESM-CHEM, MIROC-ESM, MPI-ESM-LR, NorESM1-ME, Inmcm4, CESM1-BGC.

The dominant cause of future changes in the airborne fraction (AF) is the emissions scenario and not carbon cycle feedbacks (Figure 6.26). Models show high agreement that 21st century cumulative AF will increase under rapidly increasing CO₂ in RCP8.5 and decreases under the peak-and-decline RCP2.6 scenarios. AF declines slightly under RCP4.5 and remains of similar magnitude in the RCP6.0 scenario. Inter-model spread in changes in the land-fraction is greater than inter-scenarios spread. Models show high agreement that the ocean fraction will increase under RCP2.6 and remain of similar magnitude in the other RCP scenarios.

[INSERT FIGURE 6.26 HERE]

Figure 6.26: changes in airborne, land and ocean fraction of fossil fuel carbon emissions. The fractions are defined as the changes in storage in each component (atmosphere, land, ocean) divided by the compatible fossil fuel emissions derived from each CMIP5 simulation for the 4 RCP scenarios. Solid circles show the observed estimate based on Table 6.11 for the 1990s. The coloured lines and symbols denote the change in uptake fractions under the different RCP scenarios for each model, calculated using the cumulative change in carbon from 2005 to 2100. Multi-model mean values are shown as star symbols and the multi-model range (min-to-max) is shown by the vertical coloured lines. Due to the difficulty of estimating fossil and land use emissions from the ESMs this figure uses a fossil fuel definition of airborne fraction, rather than the preferred definition of fossil + land use emissions discussed in Section 6.3. 21st century cumulative airborne, land and ocean fractions are shown here in preference to the more commonly shown instantaneous fractions because for RCP2.6 emissions reach and cross zero and so an instantaneous definition of AF becomes singular at that point. Models used: CanESM2, GFDL-ESM2G, GFDL-ESM2M, HadGEM2-CC, HadGEM2-ES, IPSL-CM5A-LR, IPSL-CM5A-MR, IPSL-CM5B-LR, MIROC-ESM-CHEM, MIROC-ESM, MPI-ESM-LR, NorESM1-ME, Inmcm4, CESM1-BGC.

Several studies (Jones et al., 2006; Matthews, 2006; Miyama and Kawamiya, 2009; Plattner et al., 2008) have shown that climate-carbon cycle feedbacks affect the compatible fossil fuel CO₂ emissions that are consistent with a given CO₂ concentration pathways. Five CMIP5 ESMs from decoupled simulations (see ESM_BOX) agree for RCP4.5 that the climate impact on carbon uptake by both land and oceans will reduce the compatible fossil fuel CO₂ emissions for that scenario by between 6% and 29% between 2006 and 2100 respectively (Figure 6.27) equating to an average of 157 PgC (range 61–262 PgC) less carbon that can be emitted from fossil fuel use. Such uncoupled simulations have not been performed for the other RCP scenarios, but previous work has shown that compatible emissions are reduced by a greater degree under higher CO₂ scenarios which exhibit a greater degree of climate change (Jones et al., 2006).

[INSERT FIGURE 6.27 HERE]

Figure 6.27: Diagnosed compatible fossil fuel emissions (top panel) in the presence (red lines) and absence (blue lines) of the climate impact on the carbon cycle for the RCP4.5 scenario, and the difference between them (bottom panel). Thin lines show annual values and thick lines 10-year smoothed values. This shows the impact of climate change on the compatible fossil fuel CO₂ emissions to achieve the RCP4.5 CO₂ concentration pathway. Models used: CanESM2, GFDL-ESM2M, HadGEM2-ES, IPSL-CM5A-LR and MIROC-ESM.

6.4.3.4 Permafrost Carbon

Current estimates of permafrost soil carbon stocks are 1670 PgC (Tarnocai et al., 2009), the single largest component of the terrestrial carbon pool and higher than previously thought. Terrestrial carbon models show a land CO₂ sink with warming at high northern latitudes, however none of the models participating in C4MIP or CMIP5 included explicit representation of permafrost soil carbon decomposition, which at a minimum requires sufficient vertical resolution in modelled soil carbon distribution and processes to separate surface pools from very old (Pleistocene) permafrost carbon pools. Including permafrost carbon processes into an ESM can change the sign of this C response to warming from a sink to a source in northern high latitudes (Koven et al., 2011). The magnitude of this source of CO₂ to the atmosphere from decomposition of permafrost carbon varies widely by 2100 according to different model estimates: process-model estimates include 7–17 Pg (Zhuang et al., 2006), 55–69 Pg (Koven et al., 2011), and 126–254 Pg (Schaefer et al., 2011); estimates of uncertainty ranges suggest the source could range from 33 to 114 Pg C (68% range) under RCP8.5 warming (von Deimling et al., 2012), or 50–270 PgC (5th–95th percentile range; Burke et al., subm.). Combining observed vertical soil C profiles with modelled thaw rates estimate that the total quantity of newly-thawed soil C by 2100 will be 246 Pg for RCP4.5 and 436 Pg for RCP8.5 (Harden et al., 2012 in press). Sources of uncertainty for the permafrost C feedback include the physical thawing rates, the fraction of C that is release after being thawed and the timescales of release, possible mitigating nutrient feedbacks, and the role of fine-scale processes in determining the terrestrial response.

6.4.4 Future Ocean Acidification

A fraction of CO₂ emitted into the atmosphere dissolves in the ocean, reducing surface ocean pH and carbonate ion concentrations. The associated chemistry is not debated by the scientific community (very high confidence) and expected changes are in line with what is measured at ocean time series stations (see Chapter 3). Multi-model projections using ocean process-based carbon cycle models discussed in AR4 demonstrate large decreases in pH and carbonate ion concentration [CO₃²⁻] during the 21st century throughout the world oceans (Orr et al., 2005). The largest decrease in surface [CO₃²⁻] occur in the warmer low and mid-latitudes, which are naturally rich in this ion (Feely et al., 2009). However, it is the colder high-latitude oceans that first become undersaturated with respect to aragonite (i.e., $\Omega_A < 1$, where $\Omega_A = [\text{Ca}^{+2}][\text{CO}_3^{2-}]/K_{sp}$, where K_{sp} is the solubility product for the metastable form of CaCO₃ known as aragonite). This undersaturation in surface waters is reached within decades in the Southern Ocean as highlighted in AR4, but occurs sooner and is more intense in the Arctic (Steinacher et al., 2009). Ten percent of Arctic surface waters are projected to become undersaturated when atmospheric CO₂ reaches 428 ppm (by 2025 under all IPCC SRES scenarios). That proportion increases to 50% when atmospheric CO₂ reaches 534 ppm (Steinacher et al., 2009). By 2100 under the A2 scenario, much of the Arctic surface is projected to become undersaturated with respect to calcite (Feely et al., 2009). Surface waters would then be corrosive to all CaCO₃ minerals. These general trends are confirmed by the latest projections from the CMIP5 earth system models (Christian et al., *subm.*), Figure 6.28).

[INSERT FIGURE 6.28 HERE]

Figure 6.28: Projected ocean acidification from 12 CMIP5 earth system models under the RCP8.5 scenario: time series of surface (a) carbonate ion concentration and (b) pH shown as the mean (solid line) and range of models (filled), given as area-weighted averages over the Arctic Ocean (green), the tropical oceans (red), and the Southern Ocean (blue); maps of the median model's (c) change in surface pH from 1850 to 2100 and its surface Ω_A in (d) 2013, (e) 2050, and (f) 2100; and zonal mean sections (latitude vs. depth) of Ω_A in 2100 over the (g) Atlantic and (h) Pacific, while the ASH is shown in 2013 (dotted line) as well as 2100 (solid line). Panels (a) and (b) also include mean model results from three other scenarios: RCP2.6, RCP4.5, and RCP6.0 (dashed lines). Over most of the ocean, gridded data products of carbonate system variables (Key et al., 2004) are used to correct each model for its present-day bias by subtracting the model-data difference at each grid cell following (Orr et al., 2005). Where gridded data products are unavailable (Arctic Ocean, all marginal seas, and the ocean near Indonesia), results are shown without bias correction. The bias correction reduces the range of model projections by up to a factor of 4, e.g., in panels (a) and (b) compare the large range of model projections for the Arctic (without bias correction) to the smaller range in the Southern Ocean (with bias correction).

Regional ocean carbon cycle models project that some nearshore systems are highly vulnerable to future pH decrease. In the California Current System, an eastern boundary upwelling system, strong seasonal upwelling of carbon-rich waters (Feely et al. 2008) renders surface waters as vulnerable to future ocean acidification as those in the Southern Ocean (Gruber et al., 2012). In the Northwestern European Shelf Seas, large spatiotemporal variability is enhanced by local effects from river input and organic matter degradation, exacerbating acidification from anthropogenic CO₂ invasion (Artioli et al., 2012). In the Gulf of Mexico and East China Sea, coastal eutrophication, another anthropogenic perturbation, has been shown to enhance subsurface acidification as additional respired carbon accumulates at depth (Cai et al., 2011).

In the open ocean, future reductions in surface ocean pH and CaCO₃ saturation states are controlled mostly by the invasion of anthropogenic carbon. Other effects due to future climate change counteract less than 10% of the CO₂-induced reductions in CaCO₃ saturation (Cao et al., 2007; McNeil and Matear, 2006; Orr et al., 2005). Warming dominates other effects from climate-change by reducing CO₂ solubility and thus by enhancing [CO₃²⁻]. An exception is the Arctic Ocean where reductions in pH and CaCO₃ saturation states (for both aragonite and calcite, the stable form of calcium carbonate) are projected to be exacerbated by effects from increased freshwater input due to enhanced sea ice melt, more precipitation, and greater air-sea CO₂ fluxes due to less sea ice cover (Steinacher et al., 2009; Yamamoto et al., 2012). The projected effect of freshening is consistent with current observations of lower saturation states and lower pH values near river mouths and in areas under substantial fresh-water influence (Chierici and Fransson, 2009; Salisbury et al., 2008; Yamamoto-Kawai et al., 2009).

Surface CaCO₃ saturation also varies seasonally, particularly in the high latitudes, where observed saturation is higher in summer and lower in winter (Feely et al., 1988; Findlay et al., 2008; Merico et al., 2006). Future

1 projections using ocean carbon cycle models indicate that undersaturated conditions will be reached first in
 2 winter (Orr et al., 2005). In the Southern Ocean, it is projected that wintertime undersaturation with respect
 3 to aragonite will begin when atmospheric CO₂ will reach 450 ppm, which is about 100 ppm sooner (~30
 4 years under the IS92a scenario) than for the annual mean undersaturation (McNeil and Matear, 2008).

5
 6 Although projected changes are generally largest at the surface, the greatest pH changes in the subtropics
 7 occur between 200–300 m where subsurface changes in anthropogenic CO₂ are similar to surface changes
 8 but the carbonate buffering capacity is lower (Orr, 2011). This more intense projected subsurface pH
 9 reduction is consistent with the observed subsurface changes in pH in the subtropical North Pacific (Byrne et
 10 al., 2010; Dore et al., 2009; Ishii et al., 2011). As subsurface saturation states decline, the horizon separating
 11 undersaturated waters below from supersaturated waters above is projected to move upward (shoal). By 2100
 12 under the RCP8.5 scenario, the median projection from 12 CMIP5 models is that this interface (aragonite
 13 saturation horizon) will shoal from 197 m up to 36 m in the subarctic Pacific, from 965 m up to the surface
 14 in the Southern Ocean, and from 2870 m to 151 m in the North Atlantic, consistent with results from
 15 previous model comparison (Orr, 2011; Orr et al., 2005). Under the SRES A2 scenario, the volume of ocean
 16 with supersaturated waters is projected to decline from 42% in the preindustrial era to 25% in 2100
 17 (Steinacher et al., 2009). Yet even if atmospheric CO₂ does not go over 450 ppm, most of the deep ocean
 18 volume is projected to become undersaturated with respect to both aragonite and calcite after several
 19 centuries (Caldeira and Wickett, 2005). Nonetheless, the most recent projections under RCPs mitigation
 20 scenarios illustrate that limiting atmospheric CO₂ will greatly influence the level of ocean acidification that
 21 will be experienced (Joos et al., 2011).

22 23 **6.4.5 Future Ocean Oxygen Depletion**

24
 25 It is likely that global warming will lead to declines in dissolved O₂ in the ocean interior through warming-
 26 induced reduction in O₂ solubility and increased ocean stratification (see Box 6.5). This would have
 27 implications for nutrient and carbon cycling, ocean productivity and marine habitats (Keeling et al., 2010).

28
 29 **[START BOX 6.5 HERE]**

30 31 **Box 6.5: IPCC AR5 Ocean Deoxygenation**

32
 33 A general decrease in the dissolved oxygen concentration of the ocean has been observed across much of the
 34 coastal and open ocean over the latter decades of the 20th century (Gilbert et al., 2010; Helm et al., 2011;
 35 Keeling et al., 2010). These changes in oceanic oxygen (ΔO_2^{tot}) can be related to climate forcing, both
 36 directly through the reduced solubility of oxygen in warm waters (ΔO_2^{sol}), and indirectly through changes in
 37 ocean mixing and ventilation processes (ΔO_2^{vent}) and changes in biological activity (ΔO_2^{bio}). These processes
 38 are highlighted in Figure 1 and combine simply as follows:

$$39 \quad \Delta O_2^{\text{tot}} = \Delta O_2^{\text{sol}} + \Delta O_2^{\text{vent}} + \Delta O_2^{\text{bio}} \quad (6.3.1)$$

40
 41
 42 The processes that influence ocean oxygen also affect the ocean carbon cycle, albeit in different proportions.
 43 Thus, climate signatures of ocean deoxygenation provide an important insight into the functioning of the
 44 oceans and their capacity to take up CO₂. Models consistently estimate that changes in ocean ventilation
 45 explain most of the observed ‘deoxygenation’ of the ocean, causing oxygen decreases about four times
 46 greater than those expected from ocean warming alone, and exceeding any oxygen increases that may be
 47 caused by decreases in biological productivity at low latitudes. However, although the observed
 48 deoxygenation is consistent with the impact expected from climate change, formal attribution has not been
 49 made and the observed deoxygenation signal could be mainly caused by natural variability in the ocean
 50 carbon cycle system. Ocean deoxygenation leads to increases in the oceanic emissions of N₂O, and has
 51 impacts on marine ecosystems.

52
 53 **[INSERT BOX 6.5, FIGURE 1 HERE]**

54 **Box 6.5, Figure 1: The ocean O₂ cycle.** The oceanic reservoir of oxygen communicates with the atmosphere via air-sea
 55 gas exchange (F_{O_2}). In the ocean interior, a change in dissolved O₂ concentration over time can be driven by changes in:
 56 (1) surface ocean O₂ solubility ΔO_2^{sol} , (2) the ventilation age of a water parcel advected into the subsurface (ΔO_2^{vent}) (3)
 57 biological utilisation of oxygen in remineralization of Dissolved Organic Carbon (DOC; ΔO_2^{bio}).

[END BOX 6.5 HERE]

Future changes in dissolved O₂ have been investigated using intermediate complexity ocean models (EMIC) (Oschlies et al., 2008; Plattner et al., 2001; Schmittner et al., 2008; Shaffer et al., 2009) and 3D ocean carbon cycle models (Bopp et al., 2002; Frolicher et al., 2009; Matear and Hirst, 2003; Matear et al., 2000; Sarmiento et al., 1998). There is broad consensus that the global oceanic oxygen inventory will decline significantly under future scenarios (Cocco et al., *subm.*). Simulated declines in mean dissolved O₂ concentration for the global ocean range from 6 to 12 μmol kg⁻¹ by the year 2100 (Table 6.14), with a projection of 3–4 μmol kg⁻¹ in one model with low climate sensitivity (Frolicher et al., 2009). This general trend is confirmed by the latest projections from the CMIP5 earth system models, with reductions in mean dissolved O₂ concentrations from 3 to 6% (5 to 10 μmol kg⁻¹) in 2100 for RCP8.5 (Figure 6.29b).

The global decline in oxygen concentration is explained in models by enhanced surface ocean stratification leading to reductions in convective mixing and deep water formation with a contribution of 18–50% from ocean warming-induced reduction in solubility, in part compensated by a small increase in O₂ concentration from projected reductions in biological export production (Bopp et al., 2001; Steinacher et al., 2010) or changes in ventilation age of the tropical thermocline (Gnanadesikan et al., 2007). The largest regional decreases in oxygen concentration (~20–100 μmol kg⁻¹) are projected for the intermediate (200–400 m) to deep waters of the North Atlantic, North Pacific and Southern Ocean for 2100 (Cocco et al., *subm.*; Frolicher et al., 2009; Matear and Hirst, 2003; Matear et al., 2010; Plattner et al., 2002; Figure 6.29a).

Table 6.14 Model configuration and predictions for marine O₂ depletion by 2100 (adapted from Keeling et al. (2010))

Study	Ocean carbon cycle model	Forcing	Mean [O ₂] Decrease (μmol kg ⁻¹) ^{a,b}	Solubility Contribution (%)
Sarmiento et al. (1998)	GFDL		7 ^c	
Matear et al. (2000)	CSIRO	IS92a		18
(Plattner et al., 2002)	Bern 2D	SRES A1	12	35
Bopp et al. (2002)	IPSL	SRES A2 ^d	4	25
Matear and Hirst (2003)	CSIRO	IS92a	9	26
Schmittner et al. (2008)	UVic	SRES A2	9	
Oschlies et al. (2008), Shaffer et al. (2009)	UVic	SRES A2	9 ^e	
	UVic-variable C:N	SRES A2	12 ^e	
Frolicher et al. (2009)	NCAR CSM1.4-CCCM	SRES A2	4	50
		SRES B1	3	
Shaffer et al. (2009)	DCESS	SRES A2	10 ^e	

Notes:

(a) Assuming a total ocean mass of 1.48 x 10²¹ kg⁻¹

(b) Relative to pre-industrial baseline in 1750

(c) Model simulation ends at 2065

(d) Radiative forcing of non-CO₂ GHGs is excluded from this simulation(e) For simulations with reduced ocean exchange, assuming modern average ocean O₂ concentration of 178 μmol kg⁻¹ (Sarmiento and Gruber, 2006)

There is not such a broad consensus on the evolution of the extent of hypoxic (dissolved oxygen <60–80 μmol kg⁻¹) and suboxic (dissolved oxygen <5 μmol kg⁻¹) waters. Most models show even some increase in oxygen in most O₂-poor waters and thus a slight decrease in the extent of suboxic waters under the SRES-A2 scenario (Cocco et al., *subm.*), as well as under RCP8.5 scenario (Figure 6.29b). This rise in oxygen in most suboxic waters has been shown to be caused in one model study by an increased supply of oxygen due to lateral diffusion (Gnanadesikan et al., 2011). Given the limitations of global ocean models in simulating

1 today's O₂ distribution (Cocco et al., *subm.*), as well as simulating the changes detected in O₂ concentrations
2 over the past 50 years (Andrews et al., *subm.*; Stramma et al., 2012), the model predictions are speculative,
3 especially concerning the evolution of O₂ in and around oxygen minimum zones.

4
5 A number of biogeochemical ocean carbon cycle feedbacks, not yet included in most EMICs or ESMs, could
6 also impact future trends of ocean deoxygenation. For example, model experiments which include a pCO₂-
7 sensitive C:N drawdown in primary production, as suggested by some mesocosm experiments (Riebesell et
8 al., 2007), project future increases of up to 50% in the volume of the suboxic waters by 2100 (Oschlies et al.,
9 2008; Tagliabue et al., 2011). In addition, future marine hypoxia could be amplified by changes in the
10 CaCO₃ to organic matter 'rain ratio' in response to rising pCO₂ (Hofmann and Schellnhuber, 2009).
11 Reduction in biogenic calcification due to ocean acidification would weaken the strength of CaCO₃ mineral
12 ballasting effect which would lead organic material to be remineralised at a shallower depth exacerbating the
13 future expansion of shallow hypoxic waters.

14
15 These estimates do not take into account processes that are specific of the coastal ocean and may amplify
16 deoxygenation. Recent observations for the period 1976–2000 have shown that dissolved O₂ concentrations
17 have declined at a faster rate in the coastal ocean (–0.28 μmol kg^{–1} yr^{–1}) than the open ocean (–0.02 μmol kg^{–1}
18 y^{–1}; Gilbert et al., 2010). Hypoxia in the shallow coastal ocean (apart from continental shelves in Eastern
19 Boundary Upwelling Systems) is largely eutrophication-driven and is controlled by the anthropogenic flux of
20 nutrients (N and P) and organic matter from rivers. If continued industrialisation and intensification of
21 agriculture yield larger nutrient loads in the future, eutrophication should intensify (Rabalais et al., 2010),
22 and further increase the coastal ocean deoxygenation.

23
24 On longer time scales, ocean deoxygenation is projected to keep increasing after 2100, with some models
25 simulating a tripling in the volume of suboxic waters by 2500 (Schmittner et al., 2008). Ocean
26 deoxygenation and further expansion of suboxic waters could persist on millennial timescales, with average
27 dissolved O₂ concentrations projected to reach minima of up to 56 μmol kg^{–1} below pre-industrial levels in
28 experiments with high CO₂ emissions and high climate sensitivity (Shaffer et al., 2009).

29
30 The potential expansion of hypoxic or suboxic water over large parts of the future is also likely to impact the
31 marine cycling of important nutrients, particularly nitrogen. In particular, the marine flux of N₂O depends
32 critically upon the volume of low-O₂ waters since denitrification, which provide an important pathway for
33 N₂O production, is inhibited by oxic conditions (Nevison et al., 2003). The intensification of low oxygen
34 waters will likely lead to significant increases in global N₂O emissions (e.g., Codispoti, 2010; Naqvi et al.,
35 2009). A tripling in the volume of suboxic waters would lead to a quadrupling in global water column
36 denitrification and a doubling in marine N₂O production by the year 4000 (Schmittner et al., 2008). Changes
37 in denitrification and nitrogen fixation in a deoxygenated ocean are also likely to impact upon the marine
38 inventory of fixed nitrogen, however the sign and magnitude of this feedback is uncertain (e.g., Codispoti et
39 al., 2001; Deutsch et al., 2007; Lam and Kuypers, 2010).

40 41 [INSERT FIGURE 6.29 HERE]

42 **Figure 6.29:** (a) Multi-model mean projected changes in dissolved O₂ (μmol kg^{–1} in the main thermocline (100–600 m
43 depth average) from 1995–2005 to 2090–2100 under the RCP8.5 scenario. To indicate consistency in the sign of
44 change, regions are stippled where at least 80% of models agree on the sign of the mean change. (b) Modelled evolution
45 from 1850 to 2100 (under RCP8.5 scenario) of the relative change in global mean O₂ concentration, as well as of
46 volume anomalies of hypoxic (O₂ <80 μmol kg^{–1}) and suboxic (O₂ <5 μmol kg^{–1}) waters. These diagnostics are detailed
47 in Cocco et al. (*subm.*) in a previous model intercomparison using the SRES-A2 scenario and have been applied to
48 CMIP5 models under RCP8.5 here. Models used: GFDL-ESM2G, GFDL-ESM2M, HadGEM2-ES, IPSL-CM5A-LR,
49 IPSL-CM5A-MR, MPI-ESM-LR, MPI-ESM-MR.

50 51 **6.4.6 Future Trends in the Nitrogen Cycle and Impact on Carbon Fluxes**

52 53 **6.4.6.1 Projections for Formation of Reactive N by Human Activity**

54
55 Since 1970s, human activities of food production, industrial activity and fossil fuel combustion have
56 introduced more reactive nitrogen (Nr) into the biosphere than natural processes (Section 6.1; Box 6.1,
57 Figure 1). A simple conceptual model of the future global use of nitrogen fertilizer was derived from the
58 current use and the expected developments of drivers that influence this use (Winiwarter et al., *subm.*). Five

1 driving parameters (population growth, biofuels use, food equity, increased N-use efficiency and diet
2 optimization) are used to project future N demands (Figure 6.30). During the 21st century, the projections
3 are expected to change from just a slight increase to roughly doubling with respect to the year 2005 situation.
4 Despite the uncertainties and the non-inclusion of many important drivers, all scenarios generated by the
5 (Winiwarter et al., subm.) model point towards an increase in future production of reactive nitrogen. The
6 actual amounts of Nr released to the environment in the future will depend on the demand for food (and its
7 type), and the demand for energy (and its type).

8
9 **[INSERT FIGURE 6.30 HERE]**

10 **Figure 6.30:** Global fertilizer Nr fixation (TgN yr^{-1}) derived as fertilizer demand, projected till 2100. Lines in the left
11 panel reflect trends based on drivers from the RCP scenarios, dots different independent assessment. The asterisks
12 report the ranges of two different interpretations of the SRES scenarios, with Erisman et al. (2008) using a methodology
13 very similar to the one used for RCPs (Winiwarter et al., subm.).

14
15 With the continuing increases in the formation of Nr from anthropogenic activities will come increased
16 injection into environmental reservoirs, especially soils, terrestrial vegetation, the atmosphere, groundwater
17 and the coastal ocean.

18
19 The main driver of future global N deposition is the emission trajectories of NO_y and NH_3 . For the
20 atmosphere, in some RCP scenarios, deposition of NO_y and NH_x is projected to remain relatively constant
21 globally although there is a balance between increases in NH_x deposition and decreases in NO_y deposition.
22 On a regional basis, there are future projected decreases in North America and Northern Europe, and
23 generally increases in Asia. The regional impacts (spatial patterns) for deposition are more complex and
24 sensitive to, apart from its sources, climate change and corresponding changes in precipitation, temperature
25 and atmospheric circulation. Large uncertainties remain in our understanding of atmospheric NO_y and NH_x
26 removal mechanisms, which also depend on atmospheric physical state and hence is sensitive to climate
27 change. These changes in both emissions, and atmospheric transport and deposition processes lead to major
28 uncertainties in the projection of future Nr deposition fluxes, particularly in regions remote from
29 anthropogenic emissions (Dentener et al., 2006). The large spread between atmospheric GCM models
30 associated with precipitation projections confounds extraction of an anthropogenic-forced climate signal in
31 deposition projections (Hedegaard et al., 2008; Langner et al., 2005).

32
33 The area of natural vegetation exposed to critical loads of nitrogen deposition in excess of $1000 \text{ mg N m}^2 \text{ yr}^{-1}$
34 is projected to increase under future emissions scenarios for 2050. Under all RCP scenarios except RCP4.5,
35 Nr deposition is expected to increase in many land regions, following projected increases in NH_3 emissions
36 but overall decreases in anthropogenic NO_x emissions (Lamarque et al., 2011). By 2100, emission-driven
37 change could more than double atmospheric Nr deposition to some world biodiversity hotspots (under a
38 IS92a scenario) with half of these hotspots subjected to nitrogen deposition rates over at least 10% of their
39 total area higher than $15 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, thus exceeding critical loads set for sensitive ecosystems (Bleeker et
40 al., 2011; Phoenix et al., 2006).

41
42 Given the tight coupling between the atmospheric N and S cycles, and the impact of both on climate, e.g.,
43 through aerosols, this Chapter also presents scenarios for sulphur. Deposition of SO_x is also projected to
44 decrease (Figure 6.31). Estimates for sulfur deposition in 2100, based on scenarios prior to RCPs, strongly
45 depend on regional projections for SO_2 emissions, with all scenarios projecting decreases in North America
46 and Europe, but potential for large growth (or reductions) in regions such as South America, Africa, South
47 and East Asia (Dentener et al., 2006; Tagaris et al., 2008; Figure 6.33). Under the RCP scenarios, SO_x
48 deposition is projected to ultimately decreases strongly throughout the globe by 2100 (Lamarque et al., 2011)
49 but in some regions SO_2 emission increases will very likely lead to higher sulfate deposition in the near-term
50 under some of the RCPs.

51
52 With increasing introduction of Nr into terrestrial ecosystems will come increased flux from rivers into
53 coastal systems. As illustrated by the Global NEWS 2 model, by the base year 2000, the discharge of
54 dissolved inorganic nitrogen (DIN) to marine coastal waters was $>500 \text{ kg N km}^{-2}$ of watershed area for most
55 watershed systems downstream of either high population or extensive agricultural activity (Figure 6.34a)
56 (Mayorga et al., 2010; Seitzinger et al., 2010). The change in DIN discharge under the Global Orchestration
57 (GO) scenario of the Millennium Ecosystem Assessment (MEA) (the scenario with the most extreme
58 pressures) was assessed by taking the change between the base year 2000, and the projection year, in this

1 case 2050 (Figure 6.34b). Manure is the most important contributor as a result of assumed high per capita
2 meat consumption, although there are considerable regional variations (Seitzinger et al., 2010). At the other
3 extreme is the projected change in the riverine flux between 2000 and 2050 for the Adapting Mosaic
4 scenario, the most ambitious in terms of nutrient managements of the MEA scenarios. These two scenarios
5 provide a range of projections for future DIN riverine fluxes by the year 2050.

6
7 **[INSERT FIGURE 6.31 HERE]**

8 **Figure 6.31:** Deposition of SO_x (left panel, TgS yr⁻¹), NH_x (middle panel, TgN yr⁻¹) and NO_y (right panel, TgN yr⁻¹)
9 from 1850 to 2000 and projections of deposition to 2100 under the four RCP emission scenarios (Lamarque et al., 2011;
10 van Vuuren et al., 2011). Also shown are the 2030 scenarios using the SRES B1/A2 energy scenario with assumed
11 current legislation and maximum technically feasible air pollutant reduction controls (Dentener et al., 2006).

12
13 **[INSERT FIGURE 6.32 HERE]**

14 **Figure 6.32:** Spatial variability of N deposition in 2000 with projections for 2100, using the 2.6, 4.5, 6.0 and 8.5 RCP
15 scenarios, kg N ha⁻¹ yr⁻¹ adapted from (Lamarque et al., 2011).

16
17 **[INSERT FIGURE 6.33 HERE]**

18 **Figure 6.33:** Spatial variability of S deposition in 2000 with projections for 2100, using the 2.6, 4.5, 6.0 and 8.5 RCP
19 scenarios, kg S ha⁻¹ yr⁻¹ (Lamarque et al., 2011).

20
21 **[INSERT FIGURE 6.34 HERE]**

22 **Figure 6.34:** (a) Dissolved inorganic nitrogen river discharge to coastal zone (mouth of rivers) in 2000, based up on
23 Global NEWS 2 model, (b) change in DIN discharge from 2000 to 2050, based upon Global Orchestration and the
24 Adapting Mosaic scenarios, Millennium Ecosystem Assessment (Mayorga et al., 2010; Seitzinger et al., 2010). Units
25 are kg N per km² watershed per year, as an average for each watershed.

26
27 In addition to these future changes in the atmospheric and riverine fluxes of short-lived Nr, there are also
28 projected to be increases in N₂O emissions. This is illustrated by the comparison of emissions from 1850 to
29 those in 2000 and 2050, using the IMAGE model (Figure 6.35). This spatially explicit soil nutrient budget
30 and N gas emission scenario was elaborated by Bouwman et al. (2011b) on the basis of the International
31 Assessment of Agricultural Knowledge, Science and Technology for Development (IAASTD) baseline
32 scenario (McIntyre et al., 2009). A comprehensive spatially explicit inventory of N budgets in livestock and
33 crop production systems (Bouwman et al., 2011a) shows that between 1900 and 1950, the global soil Nr
34 surplus almost doubled to 36 TgN yr⁻¹ and between 1950 and 2000 to 138 TgN yr⁻¹. The IMAGE model
35 scenario shown in Figure 6.35 portrays a world with a further increasing global crop production (+82% for
36 2000–2050) and livestock production (+115%). Despite rapidly assumed increasing Nr recovery in crop
37 (+35%) and livestock (+35%) production, global Nr surpluses are projected to continue to increase (+23%).
38 Associated agricultural emission of N₂O (soil emission from agricultural fields) are consequently projected
39 to increase from 2.5 Tg in 1900 to 7.0 Tg of N₂O-N yr⁻¹ in 2000, with a continued increase to 9.3 Tg yr⁻¹,
40 reflecting the above developments.

41
42 Regional to global scale model applications suggest a strong effect of climate variability on inter-annual
43 variability of land N₂O emissions (Tian et al., 2010; Zaehle and Dalmonech, 2011). Kesik et al. (2006) found
44 that higher temperatures and lower soil moisture could in the future the European average of forest soil N₂O
45 emissions under scenarios of climate change, despite local increases of emission rates by up to 20%. Other
46 modelling studies have shown no significant effect of climate change on terrestrial net emissions (Abdalla et
47 al., 2010). Two independent global modelling studies (Stocker et al., *subm.*; Zaehle, *subm.*) have suggested
48 an increase of terrestrial N₂O emissions by 0.5 to 5 TgN yr⁻¹ due to climate and atmospheric CO₂ abundance
49 changes under different future global change scenarios between the years 2005 and 2100, partly due to the
50 amplification of agricultural emissions under altered climate regimes. These changes provide a small but
51 long-lasting positive feedback mechanism between terrestrial biogeochemistry and the climate system.
52 However, due to the limited observational constraint and modelling evidence, there is little confidence in the
53 overall magnitude of this feedback.

54
55 On a related matter concerning actions that would need to be taken to decrease N₂O emission, Davidson
56 (2012), in a model-based analysis, shows that the magnitude of changes that would be required to stabilize
57 atmospheric N₂O by 2050, consistent with the most aggressive of the RCP mitigation scenarios, would have

1 to be about 50% reductions in emission factors in all sectors and about a 50% reduction in mean per capita
2 meat consumption in the developed world.

3
4 **[INSERT FIGURE 6.35 HERE]**

5 **Figure 6.35:** N₂O emissions in 1900, 2000 and projected to 2050 (Bouwman et al., 2011a).

6 7 *6.4.6.2 Impact of Future Changes in Reactive Nitrogen on Carbon Uptake and Storage*

8
9 Anthropogenic Nr addition and natural N-cycle responses to global changes will have an important impact
10 on the global carbon cycle. As a principal nutrient for plant growth, nitrogen can both limit future carbon
11 uptake and stimulate it depending on changes in Nr availability. A range of global terrestrial carbon cycle
12 models have been developed since AR4 that integrate nitrogen dynamics into the simulation of land carbon
13 cycling (Churkina et al., 2009; Esser et al., 2011; Gerber et al., 2010; Jain et al., 2009; Sokolov et al., 2008;
14 Thornton et al., 2007; Zaehle and Friend, 2010).

15
16 In response to climate warming, increased decomposition of soil organic matter increases N mineralisation,
17 (high confidence) which can enhance Nr uptake and growth of vegetation. Generally, higher C:N ratio in
18 woody vegetation causes increased Nr uptake and hence ecosystem carbon storage (Melillo et al., 2011). In
19 two models (Sokolov et al., 2008; Thornton et al., 2009), this effect is strong enough to turn the carbon-
20 climate interaction into a small negative feedback, i.e., an increased land CO₂ uptake in response to climate
21 warming (positive γ_L values in Figure 6.19), whereas in other (Zaehle et al., 2010b) CMIP5 models that
22 describe C, N interactions, (Arora et al., subm.) the carbon-climate interaction remains positive, i.e.,
23 decreased land CO₂ uptake in response to climate change (negative γ_L values in Figures 6.19, 6.20). Sokolov
24 et al. (2008) note, however, that the land biosphere eventually becomes a net CO₂ source despite nitrogen
25 feedbacks and γ_L would eventually change sign.

26
27 Consistent with the observational evidence (Finzi et al., 2006; Norby et al., 2010; Palmroth et al., 2006),
28 modelling studies have shown a strong effect of Nr availability on the response of plant growth and land
29 carbon sequestration to elevated atmospheric CO₂ (Sokolov et al., 2008; Thornton et al., 2009; Zaehle and
30 Friend, 2010). These analyses are affected by the projected future trajectories of anthropogenic Nr
31 deposition. The effects of N availability interact synergistically with the N constraints on CO₂ fertilisation
32 and climate (Churkina et al., 2009; Zaehle et al., 2010a). Estimates of the total net C storage on land due to
33 Nr deposition between 1860 and 2100 range between 27 and 66 PgC (Thornton et al., 2009; Zaehle et al.,
34 2010a), based on diverging assumptions about the future evolution of N deposition.

35
36 There is high confidence that at the global scale, nutrient limitation will reduce the global land carbon
37 sequestration projected by carbon-cycle only models (Figure 6.36). Only two of the current CMIP5 ESM
38 models explicitly consider C, N interactions (CESM1-BGC and NorESM1-ME) in the AR5. The effect of
39 the N limitations on terrestrial carbon sequestration in the results of the other CMIP5 models may be
40 approximated by comparing the implicit N requirement given plausible ranges of terrestrial C:N
41 stoichiometry (Wang and Houlton, 2009) to plausible increase in terrestrial N supply due increased
42 biological nitrogen fixation (Wang and Houlton, 2009) and anthropogenic Nr deposition (Lamarque et al.,
43 2011). For the ensemble of CMIP5 projections under the RCP 8.5 scenario, this implies a lack of available
44 nitrogen of 1.9–18.8 PgN which would reduce terrestrial C sequestration by 92–400 PgC. Assuming an
45 average 21st century airborne fraction of 0.6 in the RCP 8.5 scenarios (Section 6.4.3.3; Jones et al., subm.),
46 this lack of available nitrogen would cause an increase in atmospheric CO₂ of 26–113 ppm by the year 2100,
47 implying an additional radiative forcing of 0.15–0.61 W m⁻². The inferred geographic pattern suggests that N
48 limitation will be stronger in temperate/boreal ecosystems and tropical ecosystems and in pristine areas than
49 highly polluted areas (Section 6.3), but this varies widely between models.

50
51 The different magnitude and spatial distribution of N limitation across the two CMIP5 terrestrial carbon
52 cycle model components inclusive of these processes is caused by uncertainty about key mechanisms
53 controlling C-N couplings (Zaehle and Dalmonech, 2011). Alternative mechanisms to represent N limitation,
54 loss and stoichiometry, have important consequences for determining the N requirement associated with an
55 increase in land carbon stocks (Sokolov et al., 2008). Zaehle et al. (2010b) demonstrated the potential use of
56 ecosystem manipulation experiments to constrain model responses. However, the observational data to
57 evaluate carbon-nitrogen coupling in these models remains vague.

1
2 The effect on land C storage due to climate-induced N release from soils is of comparable magnitude to the
3 C storage associated with increased anthropogenic Nr. Models disagree, however, which of the two factors is
4 more important, with both effects dependent on the choice of scenario. Crucially, the effect of N limitation
5 on vegetation growth and ecosystem carbon storage under elevated CO₂ is the strongest effect of the natural
6 and disturbed N cycle on terrestrial C dynamics (Bonan and Levis, 2010; Zaehle et al., 2010a). In
7 consequence, the projected atmospheric CO₂ concentrations (and thus degree of climate change) in 2100 are
8 higher in projections with models describing C, N interactions than in those projected by traditional carbon-
9 cycle-only climate models. The influence of current and future nitrogen deposition on the ocean sink for
10 anthropogenic carbon is estimated to be rather small, with less than 5% of the ocean carbon sink in 2100
11 attributable to fertilization from anthropogenic nitrogen deposition over the oceans (Reay et al., 2008).

12 [INSERT FIGURE 6.36 HERE]

13 **Figure 6.36:** (a) Implied global terrestrial nitrogen deficit of the RCP8.5 carbon sequestration projections; (b) implied
14 overestimation of terrestrial C sequestration due to neglecting N limitations; (c) Additional radiative forcing resulting
15 from the nitrogen limitation of terrestrial C sequestration. The N deficit was calculated as follows: The simulated
16 increase in terrestrial C stocks were converted into N requirements as described by Wang and Houlton (2009). The
17 yearly evolution of the nitrogen requirements were compared on a model grid-cell bases against the newly available
18 nitrogen due to changes in biological nitrogen fixation and atmospheric deposition. The error bars represent the range of
19 results obtained using alternative assumption about terrestrial C:N stoichimetry, N retention from N deposition and
20 changes in fixation. Values are presented for the year 2005 and 2100 and displaced in time for clearer visibility.
21 Radiative forcing was calculated using the formulation of Ramaswamy et al. (2001), assuming an air-borne fraction of
22 0.6, and are evaluated as change in atmospheric CO₂ burden against the RCP8.5 scenario abundances in 2005 (377
23 ppm) and 2100 (935 ppm). The panels also show simulations of the IPSL-CM4-A2-OC model (Zaehle et al., 2010a),
24 driven with the SRES-A2 scenario projections of the IPSL-CM4 model for which both a C-cycle only and dynamically
25 coupled C-N cycle simulation are available, and for which the N deficit of the C-cycle model can therefore be
26 determined explicitly.
27

28 6.4.7 Future Changes in CH₄ Emissions

29 Future atmospheric CH₄ concentrations are sensitive to future changes in both emissions and subsequent
30 oxidation. Atmospheric chemistry is not covered in this chapter and we assess here future changes in natural
31 CH₄ emissions, which may change in response to climate change (e.g., O'Connor et al., 2010). Methane
32 sources most likely to be affected by climate change are wetlands (Section 6.4.7.1) and natural fires (Section
33 6.4.7.4). In high latitudes, where future temperature changes are likely to be highest, wetlands may be
34 influenced by permafrost (Section 6.4.7.2). Methane hydrate deposits, both in permafrost soils and in subsea
35 sediments, may become unstable and escape to the atmosphere, though the quantities stored in hydrates are
36 not well known (Section 6.4.7.3). Future changes in anthropogenic emissions may also be important but are
37 not assessed here. Potential future changes in CH₄ emissions are assessed in the following Sections and
38 summarised in Figure 6.37.
39

40 [INSERT FIGURE 6.37 HERE]

41 **Figure 6.37:** Summary of the sizes and time scales associated with future CH₄ emissions (adapted from O'Connor et
42 al., 2010). Uncertainty in these future changes is large, and so this figure demonstrates the relative magnitude of
43 possible future changes. Anthropogenic emissions continuing at a present day level of 300 Tg(CH₄) yr⁻¹ (consistent
44 with Table 6.7) are shown for reference. Wetland emissions are taken as 140–280 Tg(CH₄) yr⁻¹ present day values
45 (Table 6.7) and increasing by between 0–100% (Section 6.4.7.1; Figure 6.38). Permafrost emissions may become
46 important during the 21st century. Large CH₄ hydrate release to the atmosphere is not expected during the 21st century.
47 No quantitative estimates of future changes in CH₄ emissions from wildfires exist, so plotted here are continued present
48 day emissions of 1–4 Tg(CH₄) yr⁻¹ (Table 6.7).
49

50 6.4.7.1 Future CH₄ Emissions from Global Wetlands

51 Wetlands exist most commonly in the tropics and high latitudes, and emit CH₄ due to anaerobic
52 decomposition (methanogenesis) of organic matter in water-logged soils. Wetland extent is determined by
53 geomorphology and soil moisture, which depends on precipitation, evapotranspiration, drainage and runoff.
54 All of these may change in the future. Increasing temperature can lead to higher rates of evapotranspiration,
55 reducing soil moisture and therefore reduced wetland extent. Regional projections of precipitation changes
56 are especially uncertain (see Chapter 12). These hydrological processes operate on fine spatial scales and are
57 thus particularly difficult to include in ESMs. Those ESMs that do include wetland dynamics predict wetland
58
59

1 extent increasing in some areas due to increased water availability either through more precipitation and/or
2 lower evapotranspiration due to the CO₂ effect on stomatal closure, and decreasing in other areas due to
3 increased evapotranspiration and drainage, or earlier snowmelt (Koven et al., 2011; Ringeval et al., 2011).
4 The UVic ESCM has projected for instance a loss of wetland area north of 45°N in the 21st century from
5 6.6% for RCP2.6 to 19.8% for RCP8.5 (Avis et al., 2011).
6

7 Since AR4, several modelling studies attempted to quantify the sensitivity of global wetland CH₄ emissions
8 to environmental changes, and these are summarised in Figure 6.38. The studies cover a wide range of
9 simulation experiments but there is high agreement between model results that the combined effect of CO₂
10 increase and climate change by the end of the 21st century will increase wetland CH₄ emissions. Using a
11 common experimental protocol (Melton et al., *subm.*) seven models indicate that under increased
12 temperature alone (red bars in Figure 6.38) CH₄ emissions may increase or decrease, while the effect of
13 increased precipitation alone (green bars in Figure 6.38) there was always an increase in wetland CH₄
14 emissions, although generally small. The effect of increased atmospheric CO₂ concentration (blue bars)
15 always resulted in an increase of wetland CH₄ emissions: between 22 and 162%. Other studies assessed
16 different environmental changes such as temperature and precipitation together (orange bars in Figure 6.38)
17 and often found an increase in wetland CH₄ emissions (Eliseev et al., 2008; Gedney et al., 2004; Shindell
18 et al. 2004; Volodin, 2008), although Ringeval et al. (2011) found a net decrease. One reason for this current
19 disagreement between models on the sign of the temperature sensitivity of emissions is that some models
20 simulate a reduction of wetland area followed by a reduction of CH₄ emissions under higher temperatures,
21 whereas other models that use fixed wetland areas show an increase in CH₄ emissions under higher
22 temperatures. The combined effect of climate and CO₂ results in an increase of CH₄ emissions of 40%
23 (Volodin, 2008; fixed wetland area) and 68% (Ringeval et al., 2011; variable wetland area).
24

25 The mechanisms that cause the simulated changes of wetland CH₄ emissions shown in Figure 6.38 are: (1)
26 decreased wetland area caused by (a) reduced soil moisture due to higher temperatures and (b) decreased
27 precipitation, and (2) increased wetland area caused by (a) thawing permafrost due to higher temperatures
28 and (b) a reduction of evapotranspiration due to the CO₂ effect on stomatal closure. Depending on which
29 effects prevail in a model, wetland area will either decrease and reduce CH₄ emissions or increase and
30 enhance CH₄ emissions. Direct effects on CH₄ emissions are caused by (1) higher NPP under higher
31 temperature and higher atmospheric CO₂ concentrations, (2) higher CH₄ production rates under higher
32 temperature, and (3) reduction of CH₄ oxidation through increased precipitation that increases water table
33 position (Melton et al., *subm.*). In most models, enhanced CO₂ concentration has the strongest enhancement
34 effect on CH₄ emissions. However, large uncertainties exist concerning the lack of wetland specific plant
35 functional types in most models and the lack of understanding how wetland plants will react to CO₂
36 fertilization (e.g., Berendse et al., 2001; Boardman et al., 2011; Heijmans et al., 2001; Heijmans et al.,
37 2002a, 2002b).
38

39 Small-scale studies show that simulated CH₄ emissions from a bog in western Siberia approximately doubled
40 when temperature (+3–5°C) and precipitation (+10–15%) were increased at the same time (Bohn et al.,
41 2007). However, in the same study, an increase in only temperature led to such a big decrease in emissions
42 that methane oxidation became larger than the emissions and the simulated site became a CH₄ sink. This
43 extreme sensitivity to fine-scale conditions is typical of methane models, and implies large uncertainty to
44 their current predictive capability (Riley et al., 2011). Field-based experiments in Alaska showed a weaker
45 response to water table manipulations and warming experiments: warming and flooding increased CH₄
46 fluxes on average by 79%, while lowering the water table reduced the flux by up to 36% (Turetsky et al.,
47 2008).
48

49 [INSERT FIGURE 6.38 HERE]

50 **Figure 6.38:** Relative changes of global CH₄ emissions from either pre-industrial or present day conditions and
51 environmental changes that reflect potential conditions in 2100. The first seven models took part in the WETCHIMP
52 intercomparison project and were run under a common protocol (Melton et al., *subm.*) . Other studies used different
53 future conditions as listed in the figure: Eliseev et al. (2008), Gedney et al. (2004), Ringeval et al. (2011), Shindell et al.
54 (2004), Volodin (2008).
55

56 The effect of climate change on methane emissions from tropical wetlands (Section 6.3; Bergamaschi et al.,
57 2007; Chen and Prinn, 2006) received little attention but tropical wetlands are likely to experience multiple
58 disturbances such as alterations to the thermal and hydrological regime and changes in the freshwater-

1 seawater gradient (Hamilton, 2010; Mitsch et al., 2010). A separation between wetlands that are inundated
2 for long periods and wet mineral soils that are defined as mineral soils that are not inundated but whose soil
3 moisture can intermittently reach a level that facilitates CH₄ emissions was introduced by (Spahni et al.,
4 2011). There is still a large uncertainty around the magnitude of CH₄ emissions from these wet mineral soils
5 but Spahni et al. (2011) allocated 63 Tg(CH₄) yr⁻¹ to wet mineral soils and 80 Tg(CH₄) yr⁻¹ to inundated
6 wetlands for the present day. Regional changes in soil moisture will affect heterotrophic respiration in
7 mineral soils (Falloon et al., 2011) and could also lead to a change in CH₄ emissions from wet soils, but the
8 sign of such a change is uncertain.

9
10 Soil CH₄ oxidation of about 30 Tg(CH₄) yr⁻¹ (Table 6.7) represents the smallest of the three sinks for
11 atmospheric methane (see Table 6.7) but is also sensitive to future environmental changes. Soil CH₄
12 oxidation is projected to increase by up to 23% under the SRES A1B due to rising atmospheric CH₄
13 concentrations, higher soil temperature and lower soil moisture (Curry, 2009).

14 6.4.7.2 Future CH₄ Emissions from Permafrost Areas

15
16 Permafrost thaw may lead to increased drainage and a net reduction in wetlands, a process that has already
17 begun to be seen in lakes in the discontinuous permafrost zone (Smith et al., 2005), or alternatively to lake
18 growth in continuous permafrost areas underlain by ice-rich material subject to thermokarst (Christensen et
19 al., 2004; Plug and West, 2009). There is high agreement between land surface models that permafrost extent
20 is expected to reduce during the 21st century, accompanying particularly rapid warming at high latitudes
21 (Chapter 12). However, estimates vary widely as to the pace of degradation. Lawrence and Slater (2005),
22 using the NCAR CCSM3, climate model predicted widespread loss (60–90%) of permafrost within the upper
23 3 m of soils during the 21st century. Burn and Nelson (2006) argue that this is an overestimate, as it does not
24 include many of the known stabilizing effects for permafrost; however, subsequent improvements to this
25 model to include some of these mechanisms still show large permafrost losses (Lawrence et al., 2008). The
26 LPJ-WHyMe model projected permafrost area loss of 30% (SRES B1) and 47% (SRES A2) by 2100
27 (Wania, 2007). Marchenko et al. (2008) calculate that by 2100, 57% of Alaska will lose permafrost within
28 the top 2 m. For the RCP scenarios, the CMIP5 multi-model ensemble show a wide range of predictions for
29 permafrost loss: 15–87% under RCP4.5 and 30–99% under RCP8.5 (Koven et al., *subm.*). Hydrological
30 changes to wetland systems may lead to tradeoffs between the CO₂ and CH₄ balance of these ecosystems,
31 with anoxic methane production rates being roughly an order of magnitude less than rates of oxic
32 decomposition to CO₂, but the global warming potential of CH₄ is an order of magnitude greater than CO₂.
33 The extent of permafrost thaw simulated by climate models has been used to estimate possible subsequent
34 carbon release (Burke et al., *subm.*; Harden et al., 2012 in press; Section 6.4.3.4) but few studies explicitly
35 partition this into CO₂ or CH₄ release to the atmosphere. Schneider von Deimling et al. (2012) estimate
36 cumulative CH₄ emissions by 2100 between 131 and 533 Tg(CH₄) across the 4 RCPs.

37
38 Thawing of deeper unsaturated Yedoma deposits (large amounts of organic carbon located in permafrost in
39 northeast Siberia) was postulated to produce significant CH₄ emissions (Khvorostyanov et al., 2008),
40 however more recent estimates with Yedoma carbon lability constrained by incubation observations (Dutta
41 et al., 2006) argue for smaller emissions at 2100 (Koven et al., 2011). Other significant sources of
42 uncertainty are the fraction of thawed carbon that becomes available as a substrate for methanogenesis and
43 the impact of vegetation shifts on soil gas transport and substrate supply.

44 6.4.7.3 Future CH₄ Hydrate Emissions and in Response to Climate Warming

45
46 Substantial quantities of methane are believed to be stored within submarine hydrate deposits at continental
47 margins (see also Section 6.1, FAQ 6.2). Estimates of the hydrate pool remain poorly constrained by limited
48 observations and uncertain model boundary conditions. There is concern that warming of overlying waters
49 may melt these deposits, releasing CH₄ into the ocean and atmosphere systems.

50
51 Considering a potential warming of bottom waters by 1, 3 and 5 K during the next 100 years, (Reagan and
52 Moridis, 2007), hereafter RM07, found that hydrates residing in a typical deep ocean setting (4°C and 1000
53 m depth) would be stable during this timeframe. Within a typical shallow low-latitude setting (6°C and 560
54 m) sea-floor CH₄ fluxes did not exceed calculated ranges of CH₄ oxidation and consumption within the
55 sediments, but in a typical cold-shallow Arctic setting (0.4°C and 320 m) these scenarios resulted in CH₄
56
57

1 fluxes that exceeded rates of benthic sediment oxidation. Observations of gas venting along the Svalbard
2 margin seafloor (Westbrook et al., 2009) suggest observed regional warming of 1°C during the last 30 years
3 is driving hydrate disassociation, an idea supported by modelling (Reagan and Moridis, 2009). Elliott et al.
4 (2011), incorporating the Arctic CH₄ fluxes of RM07 into an ocean biogeochemistry model, demonstrated
5 significant impacts on marine hypoxia and acidity, although atmospheric CH₄ release was small. These
6 findings are supported by the modelling study of (Biastoch et al., 2011). Using the multi-model response to
7 AR4 1% yr⁻¹ CO₂ increase (Lamarque, 2008), predicted an upper-estimate of the global sea-floor flux of
8 between 560–2140 Tg(CH₄)yr⁻¹, mostly in the high-latitudes.

9
10 Simulations of heat penetration through the sediment by Fyke and Weaver (2006) suggest that only small
11 changes in the gas hydrate stability zone will result on century timescales except in high-latitude regions of
12 shallow ocean shelves. In the study of Hunter et al. (subm.), pre-2100 hydrate dissociation was similarly
13 focussed in shallow Arctic waters and comparable in magnitude to Biastoch et al. (2011) although maximum
14 CH₄ sea floor fluxes at 2100 were smaller than Lamarque (2008), peaking at 270 to 420 Tg(CH₄)yr⁻¹ for RCP
15 4.5 to 8.5. Most of the sea-floor flux of CH₄ would be expected to be oxidised in the water column. Mau et
16 al. (2007) suggest only 1% might be released to the atmosphere but this fraction depends on the depth of
17 water and ocean conditions. These studies do not consider subsea-permafrost hydrates suggested recently to
18 be regionally significant sources of atmospheric CH₄ (Shakhova et al., 2010).

19
20 Large methane hydrate release due to marine landslides is unlikely as any given landslide could only release
21 a tiny fraction of the global inventory (Archer, 2007). There was no positive excursion in the methane
22 concentration recorded in ice cores from the largest known submarine landslide, the Storegga slide off
23 Norway 8,200 years ago.

24
25 Overall, chronic methane release from hydrates could lead to climate impacts over the next century of
26 potentially similar magnitude to other CH₄ sources such as thawing permafrost peats (Archer, 2007). In the
27 longer term (Archer et al., 2009a) estimated that between 35 and 940 PgC, up to half the inventory assumed
28 in that study, could be released over several thousand years in the future following a sustained 3 K seafloor
29 warming, but confidence is higher in modelling abilities to simulate equilibrium hydrate inventories than
30 transient changes in them.

31 32 *6.4.7.4 Fire CH₄ Emissions and Climate*

33
34 Fire is a source of CH₄, both from natural but mainly anthropogenic fires (see Table 6.7). Projected increases
35 in future fire activity (Section 6.4.8.1) imply that CH₄ from fires will also increase, but there are no
36 quantitative projections published on future fire CH₄ sources. Interactions with other processes, such as
37 thawing of permafrost may also cause fire occurrence and CH₄ emissions to increase (Turetsky et al., 2011).

38 39 **6.4.8 How Future Trends in Other Biogeochemical Cycles Will Affect the Carbon Cycle**

40 41 *6.4.8.1 Changes in Fire Under Climate Change / Scenarios of Anthropogenic Fire Changes*

42
43 Fire is a disturbance process that affects the net landscape carbon balance. Regional studies for boreal
44 regions suggest an increase in future fire activity (e.g., Amiro et al., 2009; Balshi et al., 2009; Flannigan et
45 al., 2009a; Spracklen et al., 2009; Tymstra et al., 2007; Westerling et al., 2011; Wotton et al., 2010; Kurz et
46 al., 2008b) indicated that increased fire activity has the potential to turn the Canadian forest from a sink to a
47 source of atmospheric CO₂. Research on future changes in fire activity and CO₂ emissions has so far focused
48 mainly on boreal North America. Models predict spatially variable responses in fire activity, including strong
49 increases and decreases, due to regional variations in the climate – fire relationship, and anthropogenic
50 interference (Flannigan et al., 2009b; Kloster et al., 2011; Krawchuk et al., 2009; Pechony and Shindell,
51 2010; Scholze et al., 2006). The response of future fire frequency and severity and CO₂ emissions in response
52 to climate change will depend on the prevalent fire regime, which can be limited by fuel availability or by
53 fuel moisture content. Wetter conditions can reduce fire activity, but increased biomass availability can
54 promote fires (Scholze et al., 2006).

55
56 Using a land-surface model and future climate projections from two GCMs, Kloster et al. (2011) projected
57 fire carbon emissions in 2075–2099 that exceed present day emissions by 17–62% depending on scenario.

1 The amount of CO₂ released from fires depends critically on the burn severity. Increasing burned area and
2 more late season burning in the future will enhance ground-layer combustion and carbon emissions, which
3 will become even more dramatic if climate change continues to affect thawing of permafrost (Turetsky et al.,
4 2011; Section 6.4.7).

5
6 Future fire activity will also depend on anthropogenic factors. Land use change, resulting in landscape
7 fragmentation, reduced biomass and a less flammable landscape, might explain the observed decreasing
8 trend in fire activity following 1870 (Kloster et al., 2010; Marlon et al., 2008; Pechony and Shindell, 2010) ,
9 although declines in rate of deforestation in the Amazon do not seem to be accompanied by reduced
10 incidence of fire (Davidson, 2012). Fire management efforts to protect life and property will try to adapt to
11 changes in fire activity, but might reach their limits with projected increases (Flannigan et al., 2009a). For
12 the Amazon it is estimated that at present 58% of the area is too humid to allow deforestation fires. Climate
13 change might reduce this area to 37% by 2050 (LePage et al., 2010). Golding and Betts (2008) estimated that
14 future Amazon forest vulnerability to fire may depend non-linearly on combined pressure from climate
15 change and deforestation.

16
17 Fire modelling in the CMIP5 ESMs does not adequately represent the complex fire-climate relationship and
18 possible anthropogenic interferences for a quantitative assessment of projections of future fire carbon
19 emissions.

20 21 *6.4.8.2 Impacts of Phosphorus Limitations on the Land Carbon Cycle*

22
23 In contrast to N, which can be obtained from the atmosphere by N-fixing microorganisms, P enters land
24 ecosystems almost exclusively through weathering of bedrock (Vitousek et al., 2010). On centennial time
25 scales, the P limitation of terrestrial carbon uptake could become more severe than the N limitation because
26 of limited P sources. In model simulations, elevated temperatures and high CO₂ concentrations cause a shift
27 after 2100 from N to P limitation at high latitudes, induced by a strong increase in NPP and the low P
28 sorption capacity of soils (Goll et al., 2012a). The confidence in this shift is low as processes of soil P
29 sorption and biochemical mineralization are poorly constrained from observations. Recent synthesis efforts
30 are leading toward global-scale datasets needed to drive coupled C-N-P models (Yang and Post, 2011).

31 32 *6.4.8.3 Impacts of Tropospheric Ozone on the Land Carbon Cycle*

33
34 Plants are known to suffer damage due to exposure to high levels of ozone (O₃) (Ashmore, 2005) and are
35 likely to respond to water limitation by reducing stomatal aperture, restricting leaf uptake of both CO₂ and
36 O₃. Using a 2030 current legislation scenario, van Dingenen (2009) estimated future reductions in global
37 crop yields of 2–6% and 1–2% for wheat and rice, respectively. Felzer et al. (2005) presented global
38 simulations of plant O₃ damage on the carbon cycle and showed a reduction in cumulative net terrestrial
39 carbon storage between 2005 and 2100 ranging from 4 to 140 PgC depending strongly on degree of ozone
40 increase, use of fertilizers and levels of CO₂. Sitch et al. (2007) found a significant suppression of the global
41 land CO₂ sink due to O₃ damage to vegetation by up to 260 PgC by 2100 using one terrestrial carbon cycle
42 model based on the SRES A2 emission scenarios. The indirect radiative forcing from the resulting increased
43 CO₂ concentration in response to O₃-induced decreased CO₂ sinks reported by Sitch et al. (2007) could
44 exceed that of direct radiative effect of tropospheric O₃ increases.

45 46 *6.4.8.4 Iron-Deposition to Ocean*

47
48 Desert dust carries iron, which is an essential micronutrient for marine biogeochemistry and thus can
49 modulate ocean carbon storage. Future projections of desert dust deposition over the ocean are still largely
50 uncertain, even about the sign of changes (Mahowald et al., 2009; Tegen et al., 2004). Tagliabue et al. (2008)
51 present results showing relatively little impact of varying aeolian Fe input on cumulative ocean CO₂ fluxes
52 and atmospheric pCO₂ over 2000–2100, but Mahowald et al. (2011) show projected changes in ocean
53 productivity as large as the changes in productivity due to CO₂ increases and climate change.

54 55 *6.4.8.5 Impacts of Changes in Radiation Quality on the Land Carbon Cycle*

1 Mercado et al. (2009) estimated that variations in the diffuse fraction, associated largely with the 'global
2 dimming' period (Stanhill and Cohen, 2001), enhanced the land carbon sink by approximately 25% between
3 1960 and 1999. This more than offsets the negative effect of reduced surface radiation on the land carbon
4 sink. However Mercado et al. (2009) also showed local site optima in the relationship between
5 photosynthesis and diffuse light conditions. Under heavily polluted or dark cloudy skies, plant productivity
6 will decline as the diffuse effect is insufficient to offset decreased surface irradiance (UNEP, 2011). Under a
7 future scenario involving rapid reductions in sulphate and black carbon aerosols, the 'diffuse-radiation'
8 fertilisation declines to near zero by 2100. This implies that steeper GHG emission cuts are required to
9 stabilize climate if anthropogenic aerosols decline as expected.

11 **6.4.9 The Long Term Carbon Cycle and Commitments**

13 Long term changes in vegetation structure and induced carbon storage potentially show larger changes
14 beyond 2100 than during the 21st century as the long timescale response of tree growth and ecosystem
15 migrations means that by 2100 only a part of the eventual committed change will be realised (Jones et al.,
16 2009). Long-term 'commitments' to ecosystems migration also carry long-term committed effects to changes
17 in terrestrial carbon storage (Jones et al., 2010; Liddicoat et al., *subm.*) and permafrost (O'Connor et al.,
18 2010; Section 6.4.7). The short and long term response of terrestrial carbon storage may vary in sign over
19 different time horizons (Jones et al., 2010; Smith and Shugart, 1993). Rapid response of tropical ecosystems
20 may lead to early loss of carbon which could be later offset due to a larger, but slower, uptake in enhanced
21 high latitude forests.

23 Northward expansion of boreal forest may be considered likely because warming of high latitudes is
24 common to most climate models (Chapter 12) and will enable forest ecosystems to extend north into present
25 tundra regions (Kurz et al., 2008a; MacDonald et al., 2008). The CMIP5 simulations forced by extended
26 RCP scenarios to 2300 (Meinshausen et al., 2011) allow analysis of this longer term response of the carbon
27 cycle. Two ESMs with dynamic vegetation that have performed these extended scenarios using the
28 *concentration-driven* approach both simulate increases in tree cover and terrestrial carbon storage north of
29 60°N (Figure 6.39). Changes in temperate forests and the southern boundary of the boreal forest vary across
30 climate scenarios with models showing either an increase or decrease in tree cover depending on scenario.
31 Increases in fire disturbance or insect damage may drive loss of forest in these regions (Kurz et al., 2008a)
32 however, but this process is poorly represented or not accounted at all in these models. Large scale loss of
33 tropical forest has been found to be uncertain (Scholze et al., 2006) and depends strongly on the predicted
34 future changes in precipitation (Good et al., 2011), although both models here simulate reduced tree cover
35 and carbon storage for the RCP8.5 scenario. Earth System models also poorly simulate resilience of
36 ecosystems to climate changes and usually do not account for possible existence of alternative ecosystem
37 states such as tropical forest or savannah (Hirota et al., 2011).

39 Regional specific changes in ecosystem composition and carbon storage are uncertain but it is very likely
40 that ecosystems will continue to change for decades to centuries following stabilisation of greenhouse gases
41 and climate change.

43 **[INSERT FIGURE 6.39 HERE]**

44 **Figure 6.39:** Maps of changes in woody cover fraction, %, (left) and terrestrial carbon storage, kg C m⁻², (right) for
45 three RCP extension scenarios 2.6 (top), 4.5 (middle), and 8.5 (bottom) between years 2100 and 2300 averaged for two
46 models, HadGEM2-ES and MPI-ESM, which simulate vegetation dynamics. Model results were interpolated on 1° x 1°
47 grid; white colour indicate areas where models disagree in sign of changes. Note the RCP6.0 extension was not a
48 CMIP5 required simulation. Anthropogenic land use in these extension scenarios is kept constant at 2100 levels, so
49 these results show the response of natural ecosystems to the climate change.

51 **6.5 Potential Effects of Carbon Dioxide Removal Methods and Solar Radiation Management on the Carbon Cycle**

54 **6.5.1 Introduction to Carbon Dioxide Removal Methods**

56 To slow or perhaps reverse projected increases in the future atmospheric CO₂ concentrations (Section 6.4),
57 several methods have been proposed to augment the removal of atmospheric CO₂ and enhance the storage of
58 carbon in land, ocean and geological reservoirs. These methods have been categorized as 'Carbon Dioxide

Removal (CDR) methods and fall under a broad class of ‘climate intervention’ proposals. Another category of methods involves the intentional manipulation of planetary solar absorption to counter climate change, and is called the ‘Solar Radiation Management (SRM)’ (discussed in Chapter 7). In this Section, CDR methods are discussed from the point of view of their effects on carbon and other biogeochemical cycles, and a brief discussion on the indirect carbon cycle effects of SRM methods are also provided. Most of the currently proposed CDR methods are summarized in Table 6.15 and some are illustrated schematically in Chapter 7 (FAQ 7.3 Figure 2). Since a subset of these CDR methods concepts are designed for operating on large spatial scales in order to remove significant amounts of CO₂ from the atmosphere, these CDR methods could cause a large scale modification to the global climate and carbon cycle, and hence they are also called ‘Geoengineering’ proposals (Keith, 2001). Removal of non-CO₂ greenhouse gases such as CH₄ and N₂O has been also proposed to slow down climate change.

Table 6.15: Main examples of proposed CDR methods and their implications for carbon cycle and climate. The list is non-exhaustive. The ‘Rebound’ effect and thermal inertia of climate system are associated with all CDR methods.

Carbon Cycle Process to be Manipulated	CDR Method Name	Nature of CDR Removal Process	Storage Location	Storage Form	Some Carbon Cycle and Climate Implications
Enhanced biological production on land	Afforestation/reforestation ^a Improved forest management ^b Sequestration of wood in buildings ^c Biomass burial ^d No till agriculture ^e Biochar ^f Conservation agriculture ^g Fertilisation of land plants ^h Creation of wetlands ⁱ Biomass Energy with Carbon Capture and Storage (BECCS) ^j	Biological	^a Land (biomass, soils) ^b Land (biomass, soils) ^c Land (urban) ^d Land/ocean floor ^e Land (soils) ^f Land (soils) ^g Land (soils) ^h Land (biomass, soils) ⁱ Land (wetland soils) ^j Ocean/geological formations	^a Organic ^b Organic ^c Organic ^d Organic ^e Organic ^f Organic ^g Organic ^h Organic ⁱ Organic ^j Inorganic	^{a,b,c,e,f,g,h,i} Lack of permanence alters surface albedo and evapotranspiration Lack of permanence ^d Potentially permanent if buried on the ocean floor ^j Permanent if stored in geological reservoir
Enhanced biological production in ocean	Ocean iron fertilisation ^k Algae farming and burial ^l Blue carbon (mangrove, kelp farming) ^m Modifying ocean upwelling to bring nutrients from deep ocean to surface ocean ⁿ	Biological	Ocean	^k Inorganic ^l Organic ^m Organic ⁿ Inorganic	^k May lead to expanded regions with low oxygen concentration, altered production of DMS and non-CO ₂ greenhouse gases, possible pH change and disruptions to marine ecosystems and regional carbon cycle ⁿ Disruptions to regional carbon cycle
Accelerated weathering	Enhanced weathering over land ^o Enhanced weathering over ocean ^p	Chemical	^o Soils and oceans ^p Ocean	^o Inorganic ^p Inorganic	^o Permanent removal; likely to change pH of soils, rivers, and ocean ^p Permanent removal; likely to change pH of ocean
Enhanced solubility pump	Modifying ocean downwelling	Chemical	Ocean	Inorganic	Likely to alter regional carbon cycle and the thermal structure of the ocean
Others	Direct-air capture with storage	Chemical	Ocean/geological formations	Inorganic	Permanent removal if stored in geological reservoirs

Notes:

Superscripts in column 2 refer to the corresponding superscripts in column 4, 5 and 6.

By definition, in so-called carbon dioxide removal (CDR) methods, humans *remove* atmospheric CO₂ and store the amount of removed carbon in the land, ocean or geological reservoirs. Large scale industrial methods such as carbon capture and storage (CCS), biofuel energy production for substitution to fossil fuels (without CCS) and reducing emissions from deforestation and degradation (REDD) are not CDR methods

1 since they *reduce fossil fuel or land use change CO₂ emissions* to the atmosphere or provide alternatives to
2 fossil fuels but they do not involve a net removal of CO₂ that is already in the atmosphere. However, direct
3 air capture of CO₂ which uses industrial methods instead of natural carbon cycle processes (Table 6.15; and
4 Chapter 7 FAQ 7.3 Figure 2) will remove CO₂ from the atmosphere and is considered as a CDR method,
5 hence included in Table 6.15. According to the IPCC definition of mitigation, most CDR methods can be
6 considered as climate change mitigation options.

7
8 Most CDR methods are believed to be relatively less risky in terms of unintended side effects on the climate
9 system than are most solar radiation management (SRM) methods. This is because CDR methods remove
10 atmospheric carbon dioxide, thus reducing the associated radiative forcing and climate warming. CDR
11 methods also reduce direct consequences of high CO₂ levels including ocean acidification (see Section 6.4.4)
12 whereas SRM methods are thought to have little impact on the consequences of high CO₂ levels (Matthews
13 et al., 2009). The effects of CDR methods that propose to manipulate natural carbon cycle processes (see
14 Table 6.15) are slow, due to the long time scales (centennial to millennial timescales) required for example
15 to accumulate soil carbon, to transport CO₂ from surface waters to deep ocean or to remove CO₂ by
16 weathering of silicate and carbonate rocks (see Box 6.2). Modeling studies (see Box 6.2) show that the
17 climate system begins to respond with a <5-year relaxation (e-folding) time scale for an assumed
18 instantaneous reduction in radiative forcing to preindustrial levels (Held et al., 2010) but the approach to
19 climate equilibrium would take many decades (MacMynowski et al., 2011). At present, there is no known
20 CDR method, including industrial direct air capture of CO₂ that can feasibly reduce the atmospheric CO₂ to
21 pre-industrial levels within a few decades. Therefore, CDR methods do not present an option for rapid
22 mitigation of climate change. However, if implemented on large scales and for long enough, typically during
23 several consecutive decades, these methods could potentially make a contribution to slow-down or even
24 decrease atmospheric CO₂ concentrations. The level of confidence of the quantitative effects of potential
25 CDR methods on carbon and other biogeochemical cycles is based upon few model studies only, and can be
26 assessed as low.

27 28 *6.5.1.1 Permanence vs. Non Permanence of Carbon Sequestered by CDR Methods*

29
30 Important scientific considerations for evaluating CDR methods from the point of view of carbon and other
31 biogeochemical cycles include the associated carbon storage capacity, the permanence of the carbon storage
32 and potential adverse side effects (Shepherd et al., 2009). Geological reservoirs could store several thousand
33 PgC (House et al., 2006; Metz et al., 2005; Orr, 2009). For pulse CO₂ emissions of a few thousand PgC, 75–
34 90% of the released CO₂ will end up in the oceans after about 10,000 years (see Box 6.2; Archer et al.,
35 2009b). Hence, the ocean may be able to store a few thousand PgC of anthropogenic carbon in the long-term.
36 The terrestrial biosphere may have the potential to store carbon equivalent to the cumulative historical land
37 use flux of 180 ± 80 PgC (Table 6.1; Section 6.5.2.1).

38
39 CDR methods associated with either permanent or non-permanent carbon sequestration (see Table 6.15)
40 have very different climate implications (Kirschbaum, 2003). Permanent sequestration methods have the
41 potential to reduce the radiative forcing of CO₂ over time, and consequently to mitigate climate change. By
42 contrast, non-permanent sequestration methods will release back the temporarily sequestered carbon as CO₂
43 to the atmosphere, thus increasing radiative forcing in the future, after some delayed time interval (Herzog et
44 al., 2003). The interval of delayed time depends on the lifetime of stored carbon, and hence on the specific
45 CDR method (Matthews, 2010; Shaffer, 2010). As a consequence, elevated levels of atmospheric CO₂ and
46 climate warming will only be delayed and not avoided by non-permanent sequestration CDR methods
47 (Figure 6.40). Nevertheless, CDR methods that could create a temporary CO₂ sink in terrestrial ecosystems
48 (Table 6.15) may still have value (Dornburg and Marland, 2008) because they can decrease the cumulative
49 impact of higher temperature. Temporary sinks allow to ‘buy time’, i.e., they mitigate climate change in the
50 short term while allowing time for existing options to improve and/or new mitigation options to emerge in
51 the long term.

52 53 **[INSERT FIGURE 6.40 HERE]**

54 **Figure 6.40:** Idealized model simulations (Matthews, 2010) to illustrate the effects of CDR methods associated
55 respectively with either permanent or non-permanent carbon sequestration after CO₂ is removed from the atmosphere.
56 There is an emission of 1000 PgC in the reference case (black line) between 1800 and 2100. Permanent sequestration of
57 the additional emitted CO₂ of 380 PgC, assuming no leakage of sequestered carbon, has the potential to reduce the
58 radiative forcing of CO₂ and to mitigate climate change (blue line, compared to black line). By contrast, the green line

1 shows an idealized case of a non permanent sequestration CDR method where, after CO₂ removal from the atmosphere,
2 carbon will be sequestered in a non-permanent reservoir, in such a manner that all of the sequestered carbon will get
3 returned as CO₂ back to the atmosphere over three centuries. In this non-permanent sequestration case, climate change
4 would only be only delayed whereas the eventual magnitude of climate change will be equivalent to the no-
5 sequestration case (green line, compared to black). Figure adapted from Figure 5 of Matthews (2010).

6
7 Depending on the details of the specific CDR method considered, carbon stored in the terrestrial biosphere or
8 in the ocean is susceptible to be released back as CO₂ to the atmosphere during the time in the future when
9 fossil fuel will continue to be used, although some forms of storage may last for several centuries. In
10 contrast, carefully selected geological storage places are less subject to future human actions and interference
11 with the ecological processes (Caldeira et al., 2005). Carbon stored in the ocean in conjunction with alkaline
12 minerals also appears to be close to permanent on centennial timescales (Caldeira et al., 2005; Caldeira and
13 Rau, 2000; Kheshgi, 1995). Furthermore, for many of the CDR methods listed in Table 6.15, long-term
14 storage effectiveness could be affected by feedbacks involving climate and carbon cycle processes. Hence,
15 any CDR related sink permanence or non-permanence issues should be considered in the context of climate
16 change, of changes in nitrogen, phosphorus availability (see Section 6.4.6) and in atmospheric CO₂, of
17 changes in and in land use (see Section 6.4.1), and not only in the context of present-day conditions.

18 19 6.5.1.2 The Rebound Effect

20
21 In addition to permanence vs. non permanence of sequestration from CDR methods, another important
22 scientific consideration for CDR methods is the so called ‘rebound effect’. In the Industrial Era (since 1750)
23 about half of the CO₂ emitted into the atmosphere from fossil fuel emissions has been so far taken up and
24 sequestered by land and ocean carbon reservoirs (see Section 6.3 and Table 6.1). As for CO₂ emissions and
25 the consequent CO₂ rise which are *opposed* by natural reservoirs, any removal of CO₂ from the atmosphere
26 by CDR will be also *opposed* by natural reservoirs. Therefore, if CO₂ is removed from the atmosphere, the
27 subsequent inherent rate of removal of CO₂ from the atmosphere by natural carbon reservoirs on land and
28 ocean will be reduced or could be even reversed. Simple models have shown that when carbon is removed
29 from the atmosphere and stored permanently, the reduction in the atmospheric carbon is less than 50% of the
30 sequestered carbon (Kirschbaum, 2003). A recent climate-carbon modelling study (Cao and Caldeira, 2010b)
31 has shown the re-release of carbon from the land and ocean and the consequent increase in atmospheric CO₂
32 after an idealized complete instantaneous removal of all CO₂ in excess to pre-industrial period, i.e., the
33 opposite model simulation to the CO₂ pulse addition described in Box 6.2. Ultimately, returning to pre-
34 industrial CO₂ levels would require permanently sequestering an amount of carbon equal to total
35 anthropogenic CO₂ emissions that have been released before the time of CDR (Cao and Caldeira, 2010b;
36 Lenton and Vaughan, 2009; Matthews, 2010). Therefore, if the goal of CDR would be to return and maintain
37 atmospheric CO₂ near pre-industrial concentrations, not only will anthropogenic CO₂ in the atmosphere need
38 to be removed, but anthropogenic CO₂ currently stored in ocean and land carbon reservoirs will also need to
39 be removed when it will eventually outgas to the atmosphere (Figure 6.41).

40 41 [INSERT FIGURE 6.41 HERE]

42 **Figure 6.41:** Idealized simulations with a simple global carbon cycle model (Cao and Caldeira, 2010b) to illustrate the
43 ‘rebound effect’. Effects of an instantaneous cessation of CO₂ emissions (amber line), one-time removal of excess
44 atmospheric CO₂ (blue line) and removal of excess atmospheric CO₂ followed by continued removal of CO₂ that
45 degasses from the atmosphere and ocean (green line). To a first approximation, a cessation of emissions prevents
46 further warming but does not lead to significant cooling on the century time scale. A one-time removal of excess
47 atmospheric CO₂ eliminates approximately half of the warming experienced at the time of the removal. To cool the
48 planet back to pre-industrial levels would require the removal of all previously emitted CO₂, i.e., an amount equivalent
49 to approximately twice the amount of excess CO₂ in the atmosphere above pre-industrial level. Simulations were started
50 in 1800 but results are shown from 1850. Figure adapted from Cao and Caldeira (2010b).

51 52 6.5.2 Carbon Cycle Processes Involved in CDR Methods

53
54 The CDR methods listed in Table 6.15 rely primarily on human caused ‘improvement’ of natural carbon
55 cycle processes to accelerate the removal of atmospheric CO₂: (1) enhanced net biological uptake and
56 subsequent sequestration by land ecosystems, (2) enhanced biological production in ocean and subsequent
57 sequestration by the ocean, (3) accelerated chemical weathering reactions over land and ocean and (4)
58 enhanced solubility pump (see Sections 6.1.1.1 for a definition of this process) in the ocean. The exception is

1 industrial direct air capture of CO₂, which relies on chemistry-based methods to remove CO₂ directly from
2 air. The CO₂ removed from atmosphere by CDR methods would be stored in organic form on land, against
3 inorganic form in ocean and geological reservoirs (Table 6.15). The principle of these various CDR methods
4 is briefly described below and the characteristics of some CDR methods with peer-reviewed literature are
5 summarized in Table 6.16.

6
7 **[INSERT TABLE 6.16 HERE]**

8 **Table 6.16:** Characteristics of some CDR methods which have peer-reviewed literature. It should be noted that a
9 variety of economic, environmental, and other constraints could also limit deployment.

10
11 *6.5.2.1 Enhanced Net Biological Uptake of CO₂ and Carbon Sequestration by Land Ecosystems*

12
13 The key driver in these CDR methods (Table 6.15) is the net primary productivity by terrestrial plants which
14 produces biomass at a rate of approximately 50–60 PgC yr⁻¹ (Nemani et al., 2003). The common strategy of
15 many of these CDR methods is to increase net primary productivity and/or store a fraction of the biomass
16 produced under the form of wood in forests, or organic matter in soils or elsewhere (e.g.,
17 afforestation/reforestation, biochar, biomass burial, sequestration of construction wood in buildings) or the
18 use of biomass for energy production and subsequent sequestration of emitted CO₂ (BECCS).

19
20 Estimates of the global potential for enhanced primary productivity over land and for specific methods are
21 uncertain because the achievable sequestration by any specific method is severely constrained by competing
22 land needs (e.g., agriculture, biofuels, urbanization and conservation) and sociocultural considerations. A
23 first approximation of the potential of afforestation/reforestation is the cumulative historical (1750–2011)
24 deforestation flux from forest conversion to cropland and pasturelands which is estimated as 180 ± 80 PgC
25 (Table 6.1; Section 6.3.2.2; Canadell and Raupach, 2008; DeFries et al., 1999; Houghton, 2008). However,
26 House et al., (2002), using a simple global carbon cycle model estimated that the atmospheric CO₂
27 concentration by 2100 would be less by only about 40–70 (~80–140 PgC) ppm if all of the carbon released
28 by land use changes could be restored to the terrestrial biosphere.

29
30 The capacity for enhancing the soil carbon content on agricultural and degraded lands was estimated by one
31 study at 50–60% of the historical soil carbon loss of 42–78 PgC (Lal, 2004a). The sequestration of carbon in
32 soil will saturate as the soil carbon storage potential is realized. Recent estimates suggest a cumulative
33 potential of 30–60 PgC of additional storage over 25–50 years (Lal, 2004b). Soil sequestration is
34 clearly a non-permanent CDR method, since the sequestered carbon can be lost quickly with a change in soil
35 and agricultural management.

36
37 Finally, there is little peer-reviewed literature for CDR methods such as biochar and biomass burial methods
38 whose principle is to store organic carbon into very long turnover time pools of terrestrial ecosystems, since
39 none of these methods is implemented today at large scale. The maximum sustainable technical potential of
40 biochar cumulative sequestration is estimated at 130 PgC over a century by one study (Woolf et al., 2010).
41 The residence time of carbon converted to biochar in soils, and the effect on soil productivity of adding large
42 loadings of char is uncertain and further research is required to assess the potential of this CDR method
43 (Shepherd et al., 2009).

44
45
46 *6.5.2.2 Enhanced Biological Production in the Ocean*

47
48 Ocean fertilization, algae farming and enhanced storage in coastal plants are CDR methods that rely
49 primarily on enhanced primary productivity in the ocean. The carbon cycle principle here is to enhance
50 primary productivity of phytoplankton (the marine biological pump; Section 6.1.1) so that a fraction of the
51 extra organic carbon produced by plankton is transported to the deep ocean where another fraction could be
52 sequestered. Some of the inorganic carbon in the surface layers of ocean that is removed by the export of net
53 primary productivity below the surface layer can be subsequently replaced by CO₂ pumped from the
54 atmosphere. Ocean primary productivity is limited by the supply of nutrients. The principle behind enhanced
55 biological production in ocean CDR methods in Table 6.15 is to add nutrients that are otherwise limiting
56 (e.g., iron, nitrogen and phosphate) to the surface ocean to stimulate productivity and thereby pump
57 atmospheric CO₂ into the ocean. The expected result is an increase in the downward flux of carbon exported

1 below the surface layer (Martin, 1990), that can be partly sequestered as Dissolved Inorganic Carbon after
2 mineralization in the intermediate and deep waters. In other CDR methods like algae and kelp farming and
3 burial, the organic carbon would be rather stored in organic form.

4
5 Ocean-fertilisation by added iron has been tested in more than a dozen experiments (Boyd et al., 2007) on
6 small spatial scales (~10 km² scale). These experiments demonstrated only limited transient effects in
7 removing atmospheric CO₂: the addition of iron effectively led to increased productivity (phytoplankton
8 blooms), but this effect was moderated either by other limiting elements, or by compensatory respiration
9 from increased zooplankton grazing. There are some indications that sustained natural iron fertilization may
10 have a higher efficiency in exporting carbon from surface to intermediate and deep ocean (Pollard et al.,
11 2009). The effectiveness of ocean fertilization by iron addition depends both on the amount of increased
12 productivity in the ocean surface layers and on the ultimate fate of this carbon. Most of the carbon that
13 produced by primary productivity in the surface layers is oxidized (rematerialized into DIC) in the same
14 layer, and only a small fraction is ultimately exported to the intermediate and deep layers (Lampitt et al.,
15 2008). Increases in carbon export below the surface layer were measured in one experiment in the Southern
16 Ocean, but the amount of increased export of carbon was small relative to both natural phytoplankton
17 blooms occurring in that area, and to the scale of anthropogenic carbon dioxide emissions (Buesseler et al.,
18 2004).

19
20 Global or regional ocean carbon cycle model studies have assessed the potential carbon sink that could be
21 generated by widespread iron fertilization as a CDR method (Aumont and Bopp, 2006b; Jin et al., 2008;
22 Zeebe and Archer, 2005). Maximum potential drawdown of atmospheric CO₂ have been estimated from 15
23 ppm (Zeebe and Archer, 2005) to 33 ppm (Aumont and Bopp, 2006b) for a high-end future CO₂
24 concentration level of 700–800 ppm in 2100. In idealized model-based studies of ocean fertilization in global
25 ocean or only the Southern Ocean (Cao and Caldeira, 2010a; Joos et al., 1991; Peng and Broecker, 1991;
26 Watson et al., 1994), the maximum potential atmospheric CO₂ reduction was estimated at less than 100 ppm
27 for ideal conditions. Jin and Gruber (2003) obtained an atmospheric drawdown of more than 60 ppm over
28 100 years in modeling an idealized iron fertilization over the entire Southern Ocean.

29
30 Biological production in the surface water could also be enhanced if the supply of nutrients to surface layers
31 could be artificially increased in upwelling areas (Karl and Letelier, 2008; Lovelock and Rapley, 2007). The
32 amount of carbon sequestered by CDR methods that rely on enhanced upwelling depends critically on the
33 location and may well be negative (Yool et al., 2009). Human induced increased upwellings, under most
34 optimistic assumptions, has been estimated by models to sequester atmospheric CO₂ at a rate of about 0.9
35 PgC yr⁻¹ (Oschlies et al., 2010b) but under realistic conditions, this rate could be an order of magnitude lower
36 or even negative.

37 38 6.5.2.3 Accelerated Weathering

39
40 The removal of CO₂ involving the weathering or dissolution of silicate and carbonate minerals (Archer et al.,
41 2009b; Berner et al., 1983) occurs on time scales from thousands to tens of thousands of years (see Box 6.2).
42 The weathering reactions take place at a rate that is very slow and small relative to the rate at which fossil
43 fuel CO₂ is being emitted. Natural chemical weathering of minerals consumes about 0.2 PgCyr⁻¹ of CO₂ from
44 the atmosphere (Figure 6.1; Gaillardet et al., 1999; Hartmann et al., 2009). Carbonate mineral weathering
45 fluxes are small and over a time scale of thousands of years, transfers CO₂ from the atmosphere to the ocean.
46 Silicate mineral weathering operates on a time scale of hundreds of thousands of years. It is silicate-
47 weathering time scale that ultimately governs the removal of excess CO₂ from Earth's surface carbon
48 reservoirs (Archer et al., 2009b; Berner et al., 1983; see Box 6.2).

49
50 Fossil fuel CO₂ released to the atmosphere leads to chemical disequilibrium in the ocean, and geochemical
51 equilibrium will be eventually reset by the dissolution of ocean carbonate sediments (Archer et al., 1997).
52 The principle of CDR methods based upon accelerated weathering is to dissolve the carbonate mineral in
53 advance so the approach to the geochemical equilibrium can be accelerated. It has been proposed that large
54 amounts of silicate minerals such as olivine ((Mg,Fe)₂SiO₄) could be mined, crushed, transported to, and
55 distributed on agricultural land, with the intent that atmospheric CO₂ will react with olivine and be
56 immobilized partly as carbonate minerals and partly as bicarbonate ions in solution which would be
57 transported to the ocean (Schuiling and Krijgsman, 2006). Alternatively, the weathering reaction rate might

1 be enhanced by exposing minerals such as basalt or olivine to elevated CO₂ levels (Kelemen and Matter,
2 2008). In these land-based enhanced weathering CDR methods, some carbon would be stored in soils and the
3 remaining would be transported to the ocean by rivers. A recent study using a model estimated a potential
4 removal rate of up to 1 PgC yr⁻¹ from the atmosphere, in the idealized case where olivine could be
5 distributed as fine powder over land areas of the humid tropics, but the removal rate will be limited by the
6 saturation concentration of silicic acid (Köhler et al., 2010), and the feasibility of applying such a CDR
7 method approach at this scale has not been assessed.

8
9 In ocean based increased weathering CDR methods, carbonate rocks could be crushed and reacted with CO₂
10 captured at power plants to produce bicarbonate solution which would be released to the ocean (Caldeira and
11 Rau, 2000; Rau, 2008; Rau and Caldeira, 1999). Alternatively, carbonate minerals could be directly released
12 into the ocean (Harvey, 2008; Kheshgi, 1995). It has also been proposed that strong bases, derived from
13 silicate rocks, could be released to ocean (House et al., 2007), which would cause the ocean to absorb
14 additional CO₂. Carbonate minerals such as limestone could be heated to produce lime (Ca(OH)₂); this lime
15 could be added to the ocean to increase the ocean's alkalinity and thereby promote ocean uptake of
16 atmospheric CO₂ (Kheshgi, 1995). While there is sufficient level of scientific understanding of the
17 weathering processes, uncertainties are large in assessments of feasibility and effectiveness.

18 19 *6.5.2.4 Enhanced Solubility Pump*

20
21 It has been proposed that increasing artificially the overturning circulation of the ocean will cause increased
22 transport of DIC from the surface ocean to the deep ocean in high latitudes (Zhou and Flynn, 2005) and this
23 remove CO₂ from the atmosphere. This proposal is motivated by the fact that most of the carbon in the deep
24 sea is transported there by the overturning circulation (the 'solubility pump') and not by the 'marine
25 biological pump' pump (see Section 6.1.1; Sarmiento and Gruber, 2006; Volk and Hoffert, 1985). Therefore,
26 the principle of 'enhanced solubility pump' CDR methods listed in Table 6.15 is to increase the rate of
27 downwelling in high latitudes. In this process, carbon would be stored in the deep ocean in inorganic form
28 (DIC). However, deep ocean waters typically have higher concentrations of DIC than do surface waters
29 (Sarmiento and Gruber, 2006; Volk and Hoffert, 1985), thus such proposals risk transporting carbon from the
30 deep ocean to the atmosphere. Realistic enhancement of downwelling by 1 million m³ s⁻¹ (one Sverdrup
31 (Sv)) is estimated to increase ocean uptake of carbon by only ~0.01–0.02 PgC yr⁻¹ (Zhou and Flynn, 2005).
32 The proposed enhancement in downwelling of one Sv is much smaller than the projected slowdown in
33 Atlantic meridional overturning circulation of up to 5 to 10 Sv by 2100 because of climate change (Meehl et
34 al., 2007). The overall level of scientific knowledge on the effectiveness and feasibility of this CDR method
35 is low and uncertainties are very large.

36 37 *6.5.2.5 Other CDR Methods*

38 39 *6.5.2.5.1 Direct air capture*

40 Direct Air Capture (DAC) refers to the chemical process by which a pure CO₂ stream is produced by
41 capturing CO₂ from the ambient air. The captured CO₂ would be transported and used for commercial
42 purposes such as manufacturing carbonated drinks or sequestered in inorganic form in geological reservoirs
43 or the deep ocean. At least three methods have been proposed to capture CO₂ from the atmosphere: (1)
44 adsorption on solids (Gray et al., 2008; Lackner, 2009; Lackner, 2010); (2) absorption into highly alkaline
45 solutions (Mahmoudkhani and Keith, 2009; Stolaroff et al., 2008); (3) absorption into moderate alkaline
46 solution with a catalyst (Bao and Trachtenberg, 2006). The main scientific limitation to DAC is the
47 thermodynamic barrier due to the lower concentration of CO₂ in air (CO₂ content of the air is only about
48 0.039%) and hence there is large uncertainty on the effectiveness of this method.

49 50 *6.5.3. Impacts of CDR Methods on Carbon Cycle and Climate*

51
52 One impact that is common to all CDR methods is related to the thermal inertia of the climate system. Many
53 components of the Earth System will continue to respond for decades or centuries to the original increases in
54 CO₂ even after CDR is applied (see Section 6.4.9). Therefore, these components of the Earth System will lag
55 CDR-induced decreases in atmospheric CO₂ concentrations and surface temperature (Boucher et al., 2012).
56 Modelling the impacts of CDR method on the climate system is still in its infancy. Some of the first
57 modelling studies (Cao et al., 2011; Wu et al., 2010) have shown that there could be a temporary

1 intensification of the global hydrological cycle in response to a reduction in atmospheric CO₂ concentrations
2 (Figure 6.42). Another effect that is common to all CDR methods is the potential ‘loss of CO₂ fertilization’
3 (see Box 6.3) induced by lower CO₂ levels, that could decrease the terrestrial and the ocean CO₂ sink.
4

5 **[INSERT FIGURE 6.42 HERE]**

6 **Figure 6.42:** HadCM3L results from an idealized simulation (Cao et al., 2011) with 2% annual change in atmospheric
7 CO₂: (a) global and annual mean changes in precipitation as a function of atmospheric CO₂; (b) global and annual mean
8 changes in precipitation as a function of global and annual mean changes in surface temperature. Red dots represent the
9 first 70-year simulation phase with 2% annual CO₂ increase (ramp_up) and time moves forward from the lower left to
10 the upper right. Blue dots represent the subsequent 70-year period with 2% annual CO₂ decrease (ramp_down) and time
11 moves forward from the upper right to the lower left. Black dots represent the following 150-years with the constant
12 control CO₂ concentration and time moves forward from the upper right to the lower left. The simulation states when
13 atmospheric CO₂ reaches 1 × CO₂ and 4 × CO₂ concentrations are marked with pink circles. Due to the ocean thermal
14 inertia one atmospheric CO₂ state corresponds to two different states of temperature and precipitation, and due to the
15 precipitation sensitivity to atmospheric CO₂ content changes (Bala et al., 2009), one temperature state corresponds to
16 two different precipitation states. Figure adopted from Cao et al. (2011).
17

18 *6.5.3.1 Enhanced Net Biological Uptake by Land*

19
20 CDR methods aiming at increasing biomass in forests are non permanent and carry the risk that stored
21 carbon may return to the atmosphere by disturbances such as fire and insect outbreaks, exacerbated by
22 climate extremes and climate change, or by future human induced deforestation. When considering
23 afforestation/reforestation, it is also important to account for biophysical effects on climate in addition to
24 carbon sequestration because afforestation/reforestation changes surface characteristic such as albedo,
25 evapotranspiration and surface roughness (Bernier et al., 2011; Bonan, 2008). Modeling studies have shown
26 that afforestation in seasonally snow covered boreal and temperate regions is likely to decrease the land
27 surface albedo and have a net (biophysical plus biogeochemical) warming effect, whereas afforestation in
28 low latitudes (Tropics) is likely to enhance latent heat flux from evapotranspiration and have a net cooling
29 effect (Bala et al., 2007; Bathiany et al., 2010; Betts, 2000; Bonan et al., 1992; Montenegro et al., 2009).
30 Consequently, the location of biomass enhancement CDR methods needs to be considered carefully when
31 evaluating their net effects on climate (Bala et al., 2007; Lee et al., 2011). For instance, in idealized coupled
32 climate carbon model experiments, Bala et al., (2007) showed that global land mean temperature would
33 increase by 0.9 K for tropical deforestation but decreases by 0.2 and 1.4 K for mid- and high-latitude
34 deforestation, respectively. This result is confirmed in a recent study which estimated the warming
35 reductions per unit afforested area as three times higher in the tropics than in the boreal and northern
36 temperate regions, suggesting that afforestation in the tropics are effective forest management strategies from
37 a climate perspective (Arora and Montenegro, 2011). However, many of these studies examine average
38 conditions in a region, ignoring some of the local conditions that may produce results of opposite sign. For
39 example, reforestation in boreal regions may produce a net cooling effect because land that was actually
40 converted tended to be less snow-covered and have higher carbon stocks than average land in this region
41 (Pongratz et al., 2011b). CDR methods to increase forest biomass may require production of nutrients
42 (fertilizers) which is likely to be associated with negative consequences such as indirect CO₂ emission from
43 industrial fertilizer production and excess nitrogen runoff. Regarding biochar, there are some indications that
44 biochar addition could promote rapid loss of forest humus and background carbon in some ecosystems in the
45 first decade of application (Wardle et al., 2008).
46

47 *6.5.3.2 Enhanced Biological Production in the Ocean*

48
49 In the case of ocean fertilization, the utilization of macronutrients such as nitrogen and phosphate in the
50 fertilized region could lead to a decrease in production ‘downstream’ of the fertilized region (Gnanadesikan
51 and Marinov, 2008; Gnanadesikan et al., 2003; Watson et al., 2008). This effect can occur, for example, if
52 nutrients such as nitrogen and phosphate are depleted in the fertilized region. In a worst case scenario,
53 (Gnanadesikan et al., 2003) simulated a decline in export production of 30 tons of carbon for every ton
54 removed from the atmosphere. A sustained global-ocean iron fertilization for IPCC A2 CO₂ emission
55 scenario was also found to acidify the deep ocean by storing more DIC there (pH decrease of about 0.1–0.2
56 units) while mitigating the surface pH change by only 0.06 units (Cao and Caldeira, 2010a). Other
57 environmental risks associated with ocean fertilization include expanded regions with low oxygen
58 concentration (Oschlies et al., 2010a), increased production of dimethyl sulphide (DMS), Isoprene, CO, N₂O,

1 CH₄ and other non-CO₂ greenhouse gases (Jin and Gruber, 2003; Oeschler et al., 2010a) and possible
2 disruptions to marine ecosystems (Denman, 2008).

3
4 In the case of CDR methods relying on increased ocean upwelling to bring nutrients from deep ocean to the
5 surface ocean (or downwelling as discussed in Section 6.5.2.4), there could be disturbance to the regional
6 carbon balances, since the upwelling (downwelling) must be balanced by downwelling (upwelling) at
7 another location. Along with growth-supporting nutrients, enhanced concentrations of DIC are also brought
8 to surface waters which could degas to the atmosphere and partially offset carbon sequestration. Further,
9 whenever artificial upwelling is stopped, atmospheric CO₂ concentrations could rise rapidly because carbon
10 removed from the atmosphere and stored in soils could be suddenly released (Oeschler et al., 2010b). The
11 overall level of scientific knowledge on the impacts of the enhanced upwelling or downwelling is low.

12 6.5.3.3 *Enhanced Weathering*

13
14 The pH and carbonate mineral saturation of soils, rivers and ocean surface waters would be raised by
15 enhanced terrestrial weathering, which could alleviate some of the ocean acidification trend. In a modelling
16 study, Köhler et al. (2010) showed that the pH of the Amazon river would rise to 8.7 from its current mean
17 value of 6.2 if dissolution of olivine in entire Amazon basin was used to remove 0.5 PgC yr⁻¹ from the
18 atmosphere. In the marine environment, the elevated pH and increased alkalinity could potentially counteract
19 the effects of ocean acidification, which is beneficial. Change in alkalinity could also disturb existing
20 ecosystems. There is uncertainty in our understanding of the net effect on ocean CO₂ uptake but most likely
21 there will be a partial offset of the abiotic effect by calcifying species. As for other CDR methods, the overall
22 level of scientific knowledge on the impacts of accelerated weathering is low.

23 6.5.4 *Impacts of Solar Radiation Management on Carbon Cycle*

24
25 Solar radiation management (SRM) methods aim to reduce the amount of incoming solar radiation to the
26 Earth's surface (Chapter 7). Balancing reduced outgoing radiation by reduced incoming radiation may be
27 able to counter global mean temperature changes but may lead to a less intense global hydrological cycle
28 (Bala et al., 2008) and may not completely cancel regional changes in temperature and precipitation
29 (Govindasamy et al., 2003; Irvine et al., 2010; Matthews and Caldeira, 2007; Ricke et al., 2010) or may
30 create new ones (Robock et al., 2008). Therefore, effects of climate change on the carbon and other
31 biogeochemical cycles budgets may not be mitigated by SRM methods.

32
33 Whilst SRM techniques may avoid climate warming, they do not interfere with the direct biogeochemical
34 effects of CO₂ on ocean and land carbon cycle processes. For example, ocean acidification caused by
35 elevated CO₂ (Section 6.4.5) is not prevented by SRM. On land, enhanced vegetation productivity associated
36 with elevated CO₂ (see Box 6.3) is affected only marginally by SRM (Govindasamy et al., 2002; Matthews
37 and Caldeira, 2007; Naik et al., 2003). Similarly, SRM should not alter the stomatal response of plants to
38 elevated CO₂ that leads to a decline in evapotranspiration, causing land temperatures to warm and runoff to
39 increase (Betts et al., 2007; Cao et al., 2010; Gedney et al., 2006; Piao et al., 2007).

40
41 However, due to the strong coupling between climate and the carbon cycle, SRM could indirectly affect the
42 carbon cycle. In a coupled climate-carbon model, Matthews and Caldeira (2007) showed that carbon uptake
43 by land and ocean increased in response to SRM because there is a direct CO₂-driven increase in carbon
44 uptake without an offsetting temperature-driven suppression of carbon sinks. Consequently, for the SRES A2
45 scenario with SRM geoengineering, they simulated a lower CO₂ concentration of 110 ppm in year 2100
46 relative to the case without SRM. Further, land carbon sinks may be additionally enhanced by increasing the
47 amount of diffuse relative to direct radiation (Mercado et al., 2009) in case SRM is accompanied by an
48 increased fraction of diffuse light (e.g., injection of aerosols into the stratosphere). However, a parallel
49 reduction in the direct component of radiation available for plants by SRM methods could decrease terrestrial
50 CO₂ sinks. Information is lacking to ascertain whether the net effect of changes in diffuse versus direct
51 radiation on the carbon cycle would enhance or reduce the terrestrial carbon sink. Further, SRM may
52 negatively affect the efficiency of the southern ocean sink, for example, by altering the winds in the Southern
53 Ocean, although the magnitude or duration of this effect is uncertain (Vaughan and Lenton, 2011).

54
55 [START FAQ 6.1 HERE]

FAQ 6.1: What Happens to Carbon Dioxide After it is Emitted into the Atmosphere?

First, the emitted excess CO₂ is rapidly distributed between atmosphere, the upper ocean and vegetation. Then, the carbon further circulates among the different reservoirs of the global carbon cycle—such as soils, the deeper ocean, and rocks—on a multitude of time scales. Depending on the amount of CO₂ released, between 15% and 40% will remain in the atmosphere for up to 2000 years, after which a new balance is established between the atmosphere, the land biosphere and the ocean. Geological processes will take anything from tens to hundreds of thousand of years—perhaps longer—to reduce that carbon further. Enhanced atmospheric CO₂, and associated climate impacts of present emissions, will, therefore, persist for a very long time into the future.

Carbon dioxide is a largely non-reactive gas, which is rapidly mixed throughout the entire troposphere in less than a year. Unlike chemical compounds in the atmosphere such as methane, which are removed and broken down by sink processes, carbon is instead redistributed among the different reservoirs of the global carbon cycle. FAQ 6.1, Figure 1 shows a simplified diagram of the global carbon cycle. The open arrows indicate typical timeframes for carbon atoms to be transferred through the different reservoirs, and recycled back into the atmosphere.

[INSERT FAQ 6.1, FIGURE 1 HERE]

FAQ 6.1, Figure 1: Simplified schematic of the global carbon cycle showing the typical turnover time scales for carbon transfers through the major reservoirs.

Before the industrial era, the global carbon cycle was roughly balanced: carbon inflows closely matched the outflows of each carbon pool. Anthropogenic emissions of carbon dioxide into the atmosphere, however, disturbed that equilibrium. As global CO₂ concentrations rise, the exchange processes between CO₂ and the surface ocean and vegetation are altered, as are subsequent exchanges within and among further carbon reservoirs on land, in the ocean and eventually, the earth crust. In this way, the excess carbon is redistributed within the global carbon cycle, until the exchange fluxes between the different carbon pools have reached a new, approximate balance.

Over the ocean, CO₂ molecules pass through the air-sea interface by gas exchange. In sea water, CO₂ reacts with water to form carbonic acid, which exchanges very quickly with the large pool of dissolved inorganic carbon—bi-carbonate and carbonate ions—in the ocean. Currents and mixing processes transport the carbon between the surface layer and the middle depths of the ocean. The marine biota also redistributes carbon: marine organisms grow organic tissue and calcareous shells in surface waters, which, after their death, sink to deeper waters, where they are returned to the dissolved inorganic carbon pool by dissolution and microbial decomposition. A small fraction reach the sea floor, and are incorporated into the sediments. The extra carbon from anthropogenic emissions has the effect of increasing the atmospheric partial pressure of CO₂, which in turn increases the air-to-sea flux of CO₂ molecules. In the surface ocean, the carbonate chemistry quickly accommodates that extra CO₂. As a result, shallow surface ocean waters reach quickly balance with the atmosphere—within one or two years. Further circulation takes longer—between decades and many centuries—as CO₂ is transported from the surface into middle depths and deeper waters by ocean circulation and ventilation. On still longer time scales, acidification by the invading CO₂ dissolves carbonate sediments on the sea floor, which further enhances ocean uptake. However, it is believed that, unless substantial ocean circulation changes occur, plankton biomass remains roughly unchanged, since plankton growth is limited mostly by environmental factors, such as nutrients and light, and not by the abundant inorganic carbon. Therefore, it does not contribute to the ocean uptake of CO₂.

On land, vegetation absorbs CO₂ by photosynthesis and converts it into organic matter. A fraction of this carbon is immediately returned to the atmosphere as CO₂ by plant respiration. Plants use the remainder for growth. Dead plant material is incorporated into soils, eventually to be decomposed by microorganisms, then respired back into the atmosphere as CO₂. In addition, carbon in vegetation and soils is also converted back into CO₂ by disturbance processes such as fires, insects, herbivores and harvesting. Some organic carbon is also transferred through freshwater bodies into the ocean. An increase in atmospheric CO₂ stimulates photosynthesis, and thus carbon uptake. This in turn increases the biomass in vegetation and soils and so

1 fosters a carbon sink on land. The magnitude of this sink, however, also depends critically on other factors,
2 such as water and nutrient availability.

3
4 Modeling indicates that, overall, the warmer the climate, the less carbon is taken up by the ocean and land.
5 This implies that atmospheric CO₂ levels will increase, constituting a positive climate feedback on the global
6 carbon cycle. Many different factors contribute to this effect: warmer seawater, for instance, has a lower CO₂
7 solubility, so altered chemical carbon reactions result in less oceanic uptake of excess atmospheric CO₂. On
8 land, higher temperatures foster longer seasonal growth periods in temperate and higher latitudes, but also
9 faster respiration of soil carbon.

10
11 The time it takes to reach a new carbon distribution balance depends on the transfer times of carbon through
12 the different reservoirs, and takes place over a multitude of time scales. Carbon is first exchanged among the
13 'fast' carbon reservoirs, such as the atmosphere, oceans, land vegetation and soils, over time scales up to a
14 few thousand years. Over longer time scales, very slow secondary geological processes—dissolution of
15 carbonate sediments and sediment burial into the earth crust—become important.

16
17 FAQ 6.1, Figure 2 illustrates the decay of an excess amount of CO₂ initially emitted into the atmosphere, and
18 how it is redistributed among land and the ocean over time. Because of ocean chemistry the size of the initial
19 input is important: higher emissions imply that a larger fraction of CO₂ will remain in the atmosphere. After
20 2000 years, the atmosphere will still contain between 15% and 40% of those initial CO₂ emissions. A further
21 reduction by carbonate sediment dissolution, and reactions with igneous rocks, such as silicate weathering
22 and sediment burial, will take anything from tens to hundreds of thousands of years, or even longer.

23
24 **[INSERT FAQ 6.1, FIGURE 2 HERE]**

25 **FAQ 6.1, Figure 2:** Decay of a CO₂ excess amount of 5000 PgC emitted at time zero into the atmosphere, and its
26 subsequent redistribution into land and ocean as a function of time, computed by coupled carbon–cycle climate models.
27 The size of the colour bands indicate the carbon uptake by the respective reservoir. The first two panels show the multi-
28 model mean from a model intercomparison project (Joos et al., submitted). The last panel shows the longer term
29 redistribution including ocean dissolution of carbonaceous sediments as computed by the CLIMBER-2 model (after
30 Archer et al, 2009b).

31
32 **[END FAQ 6.1 HERE]**

33
34 **[START FAQ 6.2 HERE]**

35 36 **FAQ 6.2: Could Rapid Release of Methane and Carbon Dioxide from Thawing Permafrost or Ocean 37 Warming Substantially Increase Warming?**

38
39 *Permafrost is permanently frozen ground, mainly found in the high latitudes of the Arctic. Permafrost,
40 including the sub-sea permafrost on the shallow shelves of the Arctic Ocean, contains old organic carbon
41 deposits. Some are relicts from the last glaciation, and hold at least twice the amount of carbon currently
42 present in the atmosphere as carbon dioxide. Should a sizeable fraction of this carbon be released as
43 methane and carbon dioxide, it would increase atmospheric concentrations, which would lead to higher
44 atmospheric temperatures. That in turn would cause yet more methane and carbon dioxide to be released,
45 creating a positive feedback which would further amplify global warming.*

46
47 *The Arctic domain presently represents a net sink of carbon dioxide—sequestering around $0.4 \pm 0.4 \text{ PgCyr}^{-1}$
48 in growing vegetation—and a modest source of methane: between $15 \text{ and } 50 \text{ Tg}(\text{CH}_4) \text{ yr}^{-1}$, mostly from
49 seasonally unfrozen wetlands. There is no evidence yet that thawing contributes significantly to the current
50 global budgets of these two greenhouse gases. However, under sustained Arctic warming, modelling studies
51 and expert judgments indicate with medium agreement that a potential combined release of up to 200 PgC
52 as carbon dioxide equivalent could occur until the year 2100.*

53
54 **[INSERT FAQ 6.2, FIGURE 1 HERE]**

55 **FAQ 6.2, Figure 1:** A simplified graph of current major carbon pools and flows in the Arctic domain, including
56 permafrost on land, continental shelves and ocean (adapted from McGuire et al. (2009) and Tarnocai et al. (2009)). TgC
57 $= 10^{12} \text{ gC}$, and $\text{PgC} = 10^{15} \text{ gC}$.

1 Permafrost soils on land, and in ocean shelves, contain large pools of organic carbon, which must be thawed
2 and decomposed by microbes before it can be released—mostly as carbon dioxide. Where oxygen is limited,
3 as in waterlogged soils, some microbes also produce methane, which can escape to the atmosphere.
4

5 On land, permafrost is overlain by a surface 'active layer', which thaws during summer and forms part of the
6 tundra ecosystem. When warming spring and summer air temperatures thaw that active layer, it thickens,
7 making more organic carbon available for microbial decomposition. However, during summer, growing
8 Arctic vegetation increases its carbon dioxide uptake through photosynthesis. That means the net Arctic
9 carbon balance is delicate one between enhanced uptake and enhanced release of carbon.
10

11 Hydrological conditions during the summer thaw are also important. In standing water, lack of oxygen will
12 induce methane production. The complexity of Arctic landscapes under climate warming means we have low
13 confidence around which of these different processes might dominate on a regional scale. Heat diffusion and
14 permafrost melting takes time—in fact, the deeper Arctic permafrost can be seen as a relict of the last
15 glaciation, which is still slowly eroding—so any significant loss of permafrost soil carbon will happen over
16 similarly long time scales.
17

18 Given enough oxygen, mineralisation of organic soil carbon is accompanied by the release of heat by
19 microbes (similar to compost), which, during summer, might stimulate further permafrost thaw. Depending
20 on the amount of carbon and ice content of the permafrost, and the hydrological regime, this mechanism
21 could, under warming, trigger relatively fast local permafrost degradation.
22

23 Modelling studies of permafrost dynamics and greenhouse gas emissions indicate a relatively slow positive
24 feedback, on time scales of hundreds of years. Until the year 2100, up to 100 PgC could be released as
25 carbon dioxide, and up to five Pg as methane. Given methane's stronger greenhouse warming potential, that
26 corresponds to a further 100 PgC of equivalent carbon dioxide. These amounts are similar in magnitude to
27 other biogeochemical feedbacks, e.g., the additional carbon dioxide released by the global warming of
28 terrestrial soils.
29

30 Methane hydrates are another form of frozen carbon, occurring in deep permafrost soils, ocean shelves, shelf
31 slopes and deeper ocean bottom sediments. They consist of methane and water molecule clusters, which are
32 only stable in a specific window of low temperatures and high pressures. On land and in the ocean, most of
33 these hydrates originate from marine or terrestrial biogenic carbon, decomposed in the absence of oxygen
34 and trapped in an aquatic environment under suitable temperature-pressure conditions.
35

36 Any warming of permafrost soils, ocean waters and sediments and/or changes in pressure could destabilise
37 those hydrates, releasing their methane to the ocean. During larger, more sporadic releases, a fraction of that
38 methane might also be outgassed to the atmosphere. There is a large pool of these hydrates: in the Arctic
39 alone, the amount of methane stored as hydrates could be more than 10 times greater than the methane
40 presently in the global atmosphere.
41

42 Like permafrost thawing, liberating hydrates on land is a slow process, taking decades to centuries. The
43 deeper ocean regions and bottom sediments will take still longer—between centuries and millennia to warm
44 enough to destabilise the hydrates within them. Furthermore, methane released in deeper waters has to reach
45 the surface and atmosphere before it can become climatically active, but most is expected to be consumed by
46 microorganisms before it gets there. Only the methane from hydrates in shallow shelves, such as in the
47 Arctic Ocean north of Eastern Siberia, may actually reach the atmosphere to have a climate impact.
48

49 Several recent studies have documented locally significant methane emissions over the Arctic Siberian shelf
50 and from Siberian lakes. How much of this methane originates from decomposing organic carbon or from
51 destabilizing hydrates is not known. There is also no evidence available to determine whether these sources
52 have been stimulated by recent regional warming, or whether they have always existed—it may be possible
53 that these methane seepages have been present since the last deglaciation. In any event, these sources make a
54 very small contribution to the global methane budget—less than 5%. This is also confirmed by atmospheric
55 methane concentration observations, which do not show any substantial increases over the Arctic.
56

1 However modelling studies and expert judgment indicate that methane and carbon dioxide emissions will
2 increase under Arctic warming, and that they will provide a positive climate feedback. Over centuries, this
3 feedback will be moderate: of a magnitude similar to other climate-terrestrial ecosystem feedbacks. Over
4 millennia and longer, however, carbon dioxide and methane releases from permafrost and shelves/shelf
5 slopes are much more important, because of the large carbon and methane hydrate pools involved.

6
7 **[END FAQ 6.2 HERE]**

8
9

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1 **Tables**

2

3 **Table 6.7:** Global CH₄ budget for the past three decades (in Tg(CH₄) yr⁻¹). T-D stands for Top-Down inversions and B-U for Bottom-Up approaches. Full references are given at the
 4 end of the chapter. Ranges represent minimum and maximum values from the cited references. The sum of sources and sinks from B-U approaches does not automatically balance
 5 the atmospheric changes. Only studies covering at least five years of each decade have been used. For B-U studies, individual source types are also presented. For T-D inversions, the
 6 1980s decade starts in 1984. As some atmospheric inversions did not reference their global sink, balance with the atmosphere and the sum of the sources has been assumed. One
 7 biomass burning estimate²² excludes biofuels (a). Stratospheric loss for B-U is the sum of the loss by OH radicals, a 10 Tg yr⁻¹ loss due to O¹D radicals (Neef et al., 2010) and a 20–
 8 35% contribution due to Cl radicals²⁴.

Tg(CH ₄) yr ⁻¹	1980–1989		1990–1999		2000–2009	
	Top-Down	Bottom-Up	Top-Down	Bottom-Up	Top-Down	Bottom-Up
Natural Sources	203 [150–267]	355 [229–451]	182 [167–197]	336 [215–450]	218 [179–273]	347 [223–469]
Natural Wetlands	167 [115–231] ^{1,2,3}	225 [183–266] ^{4,5}	150 [144–160] ^{1,28,29}	206 [169–265] ^{4,5,27}	175 [142–208] ^{1,29,33,34,35,36}	217 [177–284] ^{4,5,27}
Other Sources	36 [35–36] ^{1,2}	130 [46–185]	32 [23–37] ^{1,28,29}	130 [46–185]	43 [37–65] ^{1,29,33,34,35,36}	130 [46–185]
Freshwater (Lakes & Rivers)		40 [8–73] ^{6,7,8}		40 [8–73] ^{6,7,8}		40 [8–73] ^{6,7,8}
Wild Animals		15 [-] ⁹		15 [-] ⁹		15 [-] ⁹
Wildfires		3 [1–5] ^{9,10,11,12,13}		3 [1–5] ^{9,10,11,12,13}		3 [1–5] ^{9,10,11,12,13}
Termites		11 [2–22] ^{9,10,14,15,x}		11 [2–22] ^{9,10,14,15,x}		11 [2–22] ^{9,10,14,15,x}
Geological (Incl. Oceans)		54 [33–75] ^{10,16,17}		54 [33–75] ^{10,16,17}		54 [33–75] ^{10,16,17}
Hydrates		6 [2–9] ^{9,18,19}		6 [2–9] ^{9,18,19}		6 [2–9] ^{9,18,19}
Permafrost (Excl. lakes & wetlands)		1 [0–1] ¹⁰		1 [0–1] ¹⁰		1 [0–1] ¹⁰
Anthropogenic Sources	349 [305–383]	307 [304–310]	372 [290–453]	300 [267–330]	331 [273–409]	318 [289–353]
Agriculture & Waste	208 [187–220] ^{1,2,3}	185 [178–197] ²⁰	239 [180–301] ^{1,28,29}	187 [180–193] ^{20,30,31}	209 [180–241] ^{1,29,33,34,35,36}	200 [188–217] ^{20,30,31}
Rice		43 [41–47] ²⁰		37 [32–44] ^{20,27,30,31}		38 [32–44] ^{20,27,30,31}
Ruminants		85 [81–90] ²⁰		86 [82–92] ^{20,30,31}		89 [87–97] ^{20,30,31}
Landfills & Waste		56 [50–60] ²⁰		65 [61–68] ^{20,30,31}		75 [65–90] ^{20,30,31}
Biomass Burning (Incl. Biofuels)	47 [43–55] ^{1,2,3}	20 [17–23] ^{21,22a}	38 [26–45] ^{1,28,29}	25 [21–28] ^{13,21,22a,32}	26 [16–45] ^{1,29,33,34,35,36}	18 [16–20] ^{13,21,32,37}
Fossil Fuels	94 [75–108] ^{1,2,3}	102 [-] ²⁰	95 [84–107] ^{1,28,29}	88 [66–109] ^{20,30,31}	96 [77–123] ^{1,29,33,34,35,36}	100 [85–116] ^{20,30,31}
Sinks						
Total Chemical Loss	490 [450–533] ^{1,2,3}	539 [411–671] ^{23,24,25,26}	525 [491–554] ^{1,28,29}	571 [546–646] ^{23,24,25,26}	518 [510–538] ^{1,29,33,34,36}	604 [509–764] ^{23,24,25,26}
Tropospheric OH		468 [382–567] ²⁶		479 [457–501] ²⁶		528 [454–617] ^{25,26}
Stratospheric OH		46 [16–67] ^{23,25,26}		67 [51–83] ^{23,25,26}		51 [16–84] ^{23,25,26}
Tropospheric Cl		25 [13–37] ²⁴		25 [13–37] ²⁴		25 [13–37] ²⁴
Soils	21 [10–27] ^{1,2,3}	25 [-] ²⁷	27 [-] ¹	25 [-] ²⁷	33 [26–42] ^{1,33,34,35,36}	26 [-] ²⁷

Global						
Sum of Sources	552 [500–592]	662	554 [529–596]	636	549 [526–569]	665
Sum of Sinks	511 [460–559]	539 [411–671]	542 [518–579]	596 [546–646]	540 [514–560]	630 [509–764]
Imbalance (Sources–Sinks)	30 [16–40]		12 [7–17]		9 [–4–19]	
Atmospheric Growth Rate	34		17		6	

- 1 ¹ Bousquet et al. (2011)
2 ² Fung et al. (1991)
3 ³ Hein et al. (1997)
4 ⁴ Hodson et al. (2011)
5 ⁵ Ringeval et al. (2011)
6 ⁶ Bastviken et al. (2004)
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8 ⁸ Walter et al. (2007)
9 ⁹ Denman et al. (2007)
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20 ²⁰ EDGAR4-database (2009)
21 ²¹ Mieville et al. (2010)
22 ²² Schultz et al. (2007) (a excluding biofuels)
23 ²³ Neef et al. (2010)
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25 ²⁵ Williams et al. (2012b)
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27 ²⁷ Spahni et al. (2011)
28 ²⁸ Chen and Prinn (2006)
29 ²⁹ Pison et al. (2009)
30 ³⁰ Dentener et al. (2005)
31 ³¹ EPA (2011)
32 ³² van der Werf (2004)
33 ³³ Bergamaschi et al. (2009)
34 ³⁴, ³⁵, ³⁶ Kirschke et al. (subm.)
35 ³⁷ Wiedinmyer et al. (2011)

1 **Table 6.8:** Section 1 gives the Global N budget (TgN yr^{-1}): a) creation of reactive N, b) emissions of NO_x , NH_3 in
 2 2000s to atmosphere, c) deposition of N to land and oceans and d) discharge of total N to coastal ocean. Section 2 gives
 3 the N_2O budget for the year 2005, and for the 1990s compared to AR4. Unit: $\text{Tg}(\text{N}_2\text{O-N}) \text{ yr}^{-1}$.

SECTION 1 (NO_y and NH_x)

<i>a. Conversion of N₂ to Nr</i>	2005		References
Anthropogenic sources			
Fossil Fuel Combustion	24.5		Galloway et al. (2008)
Haber-Bosch Process			
Fertilizer	100		Galloway et al. (2008)
Industrial Feedstock	24		Galloway et al. (2008)
BNF	70 (60–80)		Herridge et al. (2008)
Anthropogenic total	219		
Natural sources			
BNF, terrestrial	100 (90–120)		Galloway et al. (2004)
BNF, marine	100 (60–200)		Duce et al. (2008)
Lightning	4 (3–5)		AR4
Natural total	204		
Total Conversion of N₂ to reactive N	423		
b. Emissions to atmosphere			
	NO_x	NH₃	
Fossil Fuel Combustion & industrial processes	28.3	0.5	Dentener et al. (2006)
Agriculture	3.7	30.4	Dentener et al. (2006)
Biomass and biofuel burning	5.5	9.2	Dentener et al. (2006)
Anthropogenic total	37.5	40.1	
Natural Sources			
Soils under natural vegetation	7.3 (5–8)	2.4 (1–10)	AR4
Oceans	-	8.2 (3.6)	AR4
Lightning	4 (3–5)	-	AR4
Natural total	11.3	10.6	AR4
Total Sources	48.8	50.7	
c. Deposition from the atmosphere			
	NO_y	NH_x	
Continents	27.1	36.1	Lamarque et al. (2010)
Oceans	19.8	17.0	Lamarque et al. (2010)
Total	46.9	53.1	
d. Discharge to coastal ocean			
Surface water N flux	45		Mayorga et al. (2010)

SECTION 2 (N₂O)

	AR5 (2006)	AR5 (mid-1990s)	AR4 (1990s)
Anthropogenic sources			
Fossil fuel combustion & industrial processes	0.7 (0.2–1.8) ^a	0.7 (0.2–1.8) ^a	0.7 (0.2–1.8)
Agriculture	4.1 (1.7–4.8) ^b	3.7 (1.7–4.8) ^b	2.8(1.7–4.8)
Biomass and biofuel burning	0.7(0.2–1.0) ^a	0.7(0.2–1.0) ^a	0.7(0.2–1.0)
Human excreta	0.3 (0.1–0.4) ^a	0.3 (0.1–0.4) ^a	0.2 (0.1–0.3)
Rivers, estuaries, coastal zones	0.6 (0.1–2.9) ^c	0.6 (0.1–2.9) ^c	1.7(0.5–2.9)
Atmospheric deposition on land	0.4 (0.3–0.9) ^d	0.4 (0.3–0.9) ^d	0.6 (0.3–0.9)
Atmospheric deposition on ocean	0.2 (0.1–0.4) ^e	0.9 (0.5–1.4) ^e	-
Surface sink	-0.01 (0–1) ^f	-0.01 (0–1) ^f	-

Anthropogenic total	6.9	6.5	6.7
Natural sources^a			
Soils under natural vegetation	6.6 (3.3–9.0)	6.6 (3.3–9.0)	6.6 (3.3–9.0)
Oceans	3.8(1.8–5.8)	3.8(1.8–5.8)	3.8(1.8–5.8)
Lightning	–	–	–
Atmospheric chemistry	0.6 (0.3–1.2)	0.6 (0.3–1.2)	0.6 (0.3–1.2)
Natural total	10.8	10.8	11.0
Total sources	17.8 (8.5–27.7)	17.4 (8.5–27.7)	17.7 (8.5–27.7)

1 Notes:

2 (a) As in AR4 (not based on 2006 IPCC Guidelines); lower end of range in the natural ocean from Rhee et al. (2009).

3 (b) Direct soil emissions and emissions from animal production; calculated following 2006 IPCC Guidelines (Syakila
4 and Kroeze, 2011); Range from AR4.

5 (c) Following 2006 IPCC Guidelines (Kroeze et al., 2010; Syakila and Kroeze, 2011); Higher end of range from AR4;
6 lower end of range from 1996 IPCC Guidelines (Mosier et al., 1998). Note that a recent studies indicates that IPCC may
7 underestimate emissions from rivers (Beaulieu et al., 2011a).

8 (d) Following 2006 IPCC Guidelines (Syakila and Kroeze, 2011).

9 (e) Suntharalingam et al. (2012).

10 (f) Syakila et al. (2010).

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Table 6.9: Comparison of the magnitude of changes in carbon storage (PgC) by land and ocean over different timescales. These changes are shown as approximate numbers to allow a comparison across timescales. For more details see the indicated chapter section. An indication, where known, of what causes these changes (climate, CO₂, land-use change) is also given with an indication of the sign: ‘+’ means that an increase in CO₂ or global-mean temperature is associated with an increase in carbon storage (positive β or γ), and a ‘-’ means an increase in CO₂ or global-mean temperature is associated with a decrease in carbon storage (negative β or γ). The processes which operate to drive these changes can vary markedly from seasonal phenology of vegetation to long-term changes in ice sheet cover or ocean circulation. Some of these processes are ‘reversible’ in the context that they can increase and decrease cyclically, whereas some are ‘irreversible’ in the context that changes in one sense might be much longer than in the opposite direction.

Time Period	Duration	Land			Ocean		Section
		Climate	CO ₂	Land Use	Climate	CO ₂	
Seasonal Cycle	Weeks-Months	3–8 ^a			2	1	6.3.2.5.1
		+				+	
Interannual Variability	Months-Years	2–4 ^b			1	0.2	6.3.2.5.4
		-			+	+	
Historical (1750–Present)	Decades-Centuries	150 ^c		-180	2	155	6.3.2.5.3, Table 6.1
		-	+		?	+	
21st Century	Decades-Centuries	100–400 ^d		-100 to +100 ^e	100–600 ^d		6.4.3
		-	+		-	+	
Little Ice Age (LIA) ^f	Century	+5		+2 to +30			6.2.3
		-	+				
Holocene	10 kyr	+300		-50 to -150	+270 to -220 ^g		6.2.2
		+	+				
LGM / Glacial Cycles	>10 kyr	+300 to +1000 ^h			-500 to -1200 ^h		6.2.1
		+	+		-	+	
Pulse ⁱ , 100 PgC	1 kyr	+0 to +35		n/a	+48 to +75		6.2.2
			+		-	+	

7 Notes:

8 (a) Dominated by northern mid- to high-latitudes.

9 (b) Dominated by the tropics.

10 (c) ‘Residual terrestrial sink’, Table 6.1.

11 (d) Varies widely according to scenario. Climate effect estimated separately for RCP4.5 as -157 PgC (combined land and ocean), but not for other scenarios.

12 (e) Future scenarios may increase or decrease area of anthropogenic land use.

13 (f) Little Ice Age, 1500–1750.

14 (g) Shown here are two competing drivers of Holocene ocean carbon changes: carbonate accumulation on shelves (coral growth) and carbonate compensation to pre-Holocene changes. These are discussed in Section 6.2.2.

15 (h) Defined as positive if increasing from LGM to present, negative if decreasing.

16 (i) Idealised simulations with models to assess the response of the global carbon cycle to a sudden release of 100 PgC.

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1 **Table 6.10:** CMIP5 model descriptions in terms of carbon cycle attributes and processes.

Model	Modelling Centre	Atmos Resolution	Ocean Resolution	Land-Carbon						Ocean Carbon			Reference
				Model Name	Dynamic Vegetation Cover?	#PFTs	Incl. LUC?	N-cycle	Fire	Model Name	#Plankton Types	Micro-nutrients?	
BCC-CSM1.1	BCC	≈2.8°, L26	0.3–1°, L40	BCC_AVIM1.0	N	15		N	N	OCMIP2	n/a	n/a	Wu et al. (subm.)
CanESM2	CCCma	T63, L35	1.41° × 0.94°, L40	CTEM	N	9	Y	N	N	CMOC	1	N	Arora et al. (2011)
CESM1-BGC	NSF-DOE-NCAR	FV 0.9 × 1.25	1°	CLM4	N	15	Y	Y	Y	BEC	4	Y	Lindsay et al. (subm.)
GFDL-ESM2G	NOAA GFDL	2x2.5°, L24	1°, tri-polar, 1/3° at equator, L63.	LM3	Y	5	Y	N	Y	TOPAZ2	6	y	Dunne et al. (2012); Dunne et al. (subm.)
GFDL-ESM2M	NOAA GFDL	2x2.5°, L24	1°, tri-polar, 1/3° at equator, L50.	LM3	Y	5	Y	N	Y	TOPAZ2	6	y	Dunne et al. (2012); Dunne et al. (subm.)
HadGEM2-ES	MOHC	N96 (ca. 1.6°), L38	1°, 1/3° at equator, L40	JULES	Y	5	Y	N	N	Diat-HadOCC	3	Y	Collins et al. (2011); Jones et al. (2011)
INMCM4	INM												
IPSL-CM5A-LR	IPSL	3.75x1.9, L39	Zonal 2°, Meridional 2°–0.5° L31	ORCHIDEE	N	13	Y	N	Y	PISCES	2	Y	Dufresne et al. (subm.)
MIROC-ESM	MIROC	T42, L80	Zonal: 1.4°, Meridional: 0.5–1.7°, Vertical: L43+BBL1	SEIB-DGVM	Y	13	Y	N	N	NPZD (Oschlies, 2001)	2 (Phytoplankton and Zooplankton)	N	Watanabe et al. (2011)
MPI-ESM-LR	MPI-M	T63 (ca. 1.9°), L47	ca.1.5°, L47	JSBACH	Y	12 (8 natural)	Y	N	Y	HAMOCC	2	Y	Raddatz et al. (2007), Brovkin et al. (2009), Maier-Reimer et al. (2005)
NorESM-ME	NCC	1.9x2.5°, L26	1°, L53	CLM4	N	16	Y	Y	Y	HAMOCC	2	N	Bentsen et al. (subm.), Iversen et al. (subm.)

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1 **Table 6.16:** Characteristics of some CDR methods which have peer-reviewed literature. It should be noted that a variety of economic, environmental, and other constraints could also
2 limit deployment.

Carbon Dioxide Removal Method	Means of Removing CO ₂ from Atmosphere	Carbon Storage /Form	Time Scale of Carbon Storage	Physical Potential of CO ₂ Removed in a Century*	Reference	Unintended Side Effects
Afforestation and reforestation	Biological	Land /Organic	Decades to centuries	80–140 PgC ^a , 48 PgC ^b	^a Canadell and Raupach (2008) ^b Sitch et al. (2005)	Alters surface energy budget; depending on location, climate change is increased or decreased
Biomass energy with carbon capture and storage	Biological	Geological or ocean /Inorganic	Effectively permanent for geologic, centuries for ocean	100 PgC	[‡] See the footnote	Same as above
Biochar	Biological	Land /Organic	Decades to centuries	130 PgC	Woolf et al. (2010)	Same as above
Ocean fertilisation	Biological	Ocean /Inorganic	Centuries to millennia	30–66 PgC ^c 200Pg C ^d	^c Aumont and Bopp (2006), Zeebe and Archer (2005) ^d Cao and Caldeira (2010a)	Expanded regions with low oxygen concentration; Altered production of DMS and non-CO ₂ greenhouse gases; possible disruptions to marine ecosystems and regional carbon cycles
Accelerated weathering over land	Geo-chemical	Ocean (and some soils) /Inorganic	Centuries to millennia for carbonates, permanent for silicate weathering	^e No determined limit ^f 100 PgC	^e Kelemen and Matter (2008), Schuiling and Krijgsman (2006) ^f Köhler et al. (2010)	pH of soils and rivers could be increased locally causing disturbance to existing ecosystems
Ocean-based weathering	Geo-chemical	Ocean /Inorganic	Centuries to millennia for carbonates, permanent for silicate weathering	No determined limit	Rau (2008), Kheshgi (1995)	Increased alkalinity could disturb existing marine ecosystems
Direct air capture	Chemical	Geological or ocean /Inorganic	Effectively permanent for geologic, centuries for ocean	No determined limit	Keith et al. (2006), Shaffer (2010)	Not known
Modification of upwelling/down welling	Biological/chemical	Ocean /Inorganic	Centuries to millennia	^g 90 PgC ^h 1–2 PgC	^g Oschlies et al. (2010a); ^h Lenton and Vaughan (2009), Zhou and Flynn (2005)	Likely to cause changes to regional carbon cycle

3 Notes:

4 * Physical potential does not account for economic or environmental constraints of CDR methods, for example the value of the physical constraint for afforestation and reforestation
5 does not consider the conflicts with land needed for agricultural production. Potentials for BECCS and biochar are highly speculative.

6 [‡] If 2.5 tC per year per hectare can be harvested on a sustainable basis Kraxner et al. (2003) on ~4% (~500 million hectares, about one tenth of global agricultural land area) of global
7 land (13.4 billion hectares) for BECCS, approximately 1.25 PgC per year could be removed or about 125 PgC in this century.

Chapter 6: Carbon and Other Biogeochemical Cycles

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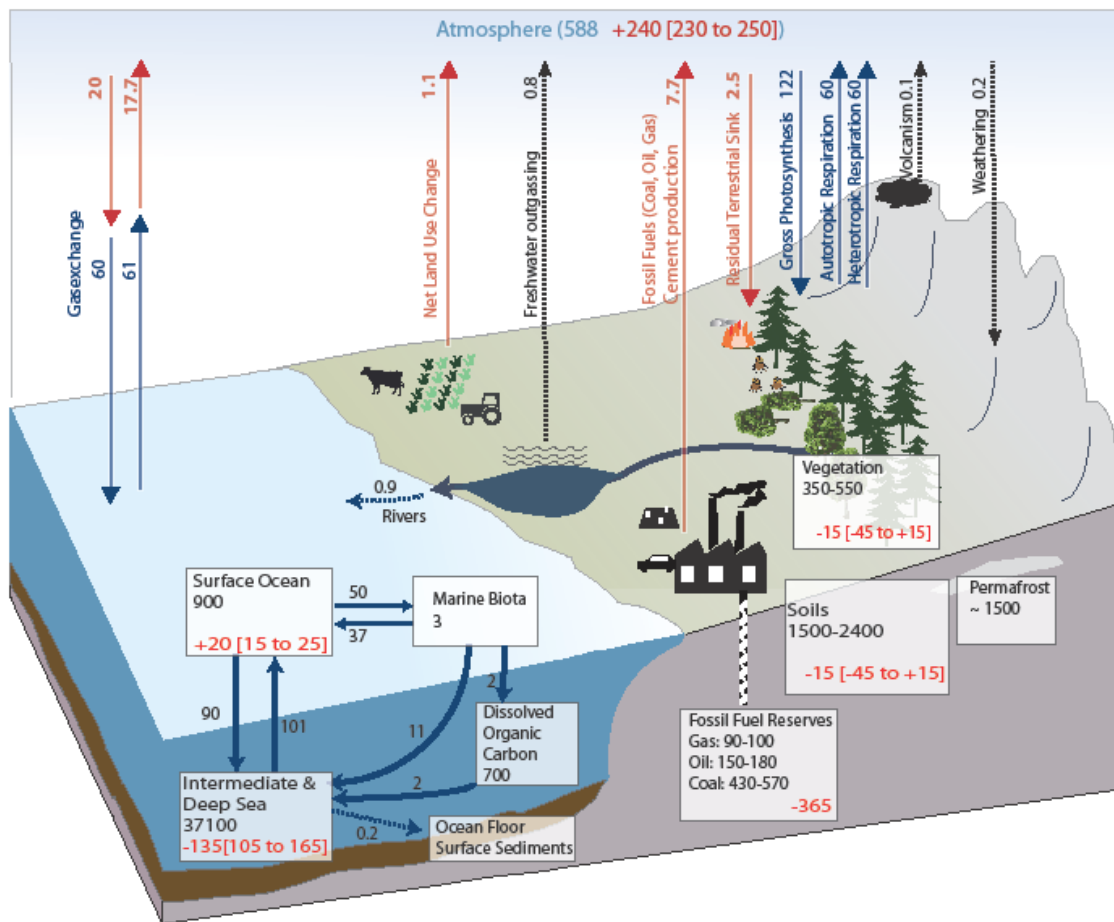
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Notes: TSU Compiled Version

1 **Figures**

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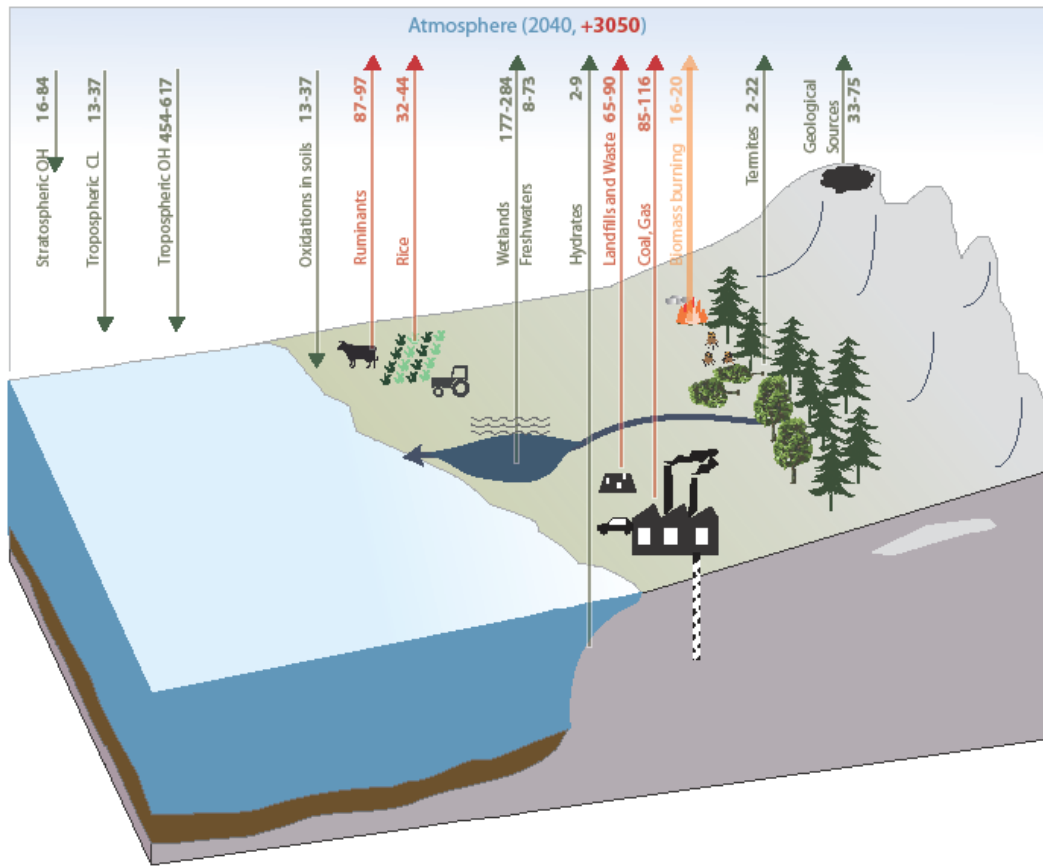
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5 **Figure 6.1:** Simplified schematic of the global carbon cycle. Numbers represent reservoir sizes (in PgC), and carbon
 6 exchange fluxes (in PgC yr⁻¹). Dotted arrow lines denote carbon fluxes between the fast and the slow carbon cycle
 7 domain (see text). Darkblue numbers and arrows indicate reservoir sizes and natural exchange fluxes estimated for the
 8 time prior to the Industrial Era. Red arrows and numbers indicate fluxes averaged over 2000–2009 time period resulting
 9 from the emissions of CO₂ from fossil fuel combustion, cement production, and changes in land use, and their
 10 partitioning among atmosphere, ocean and terrestrial reservoirs (see Section 6.3). Red numbers in the reservoirs denote
 11 cumulative changes over the Industrial Period 1750–2011.

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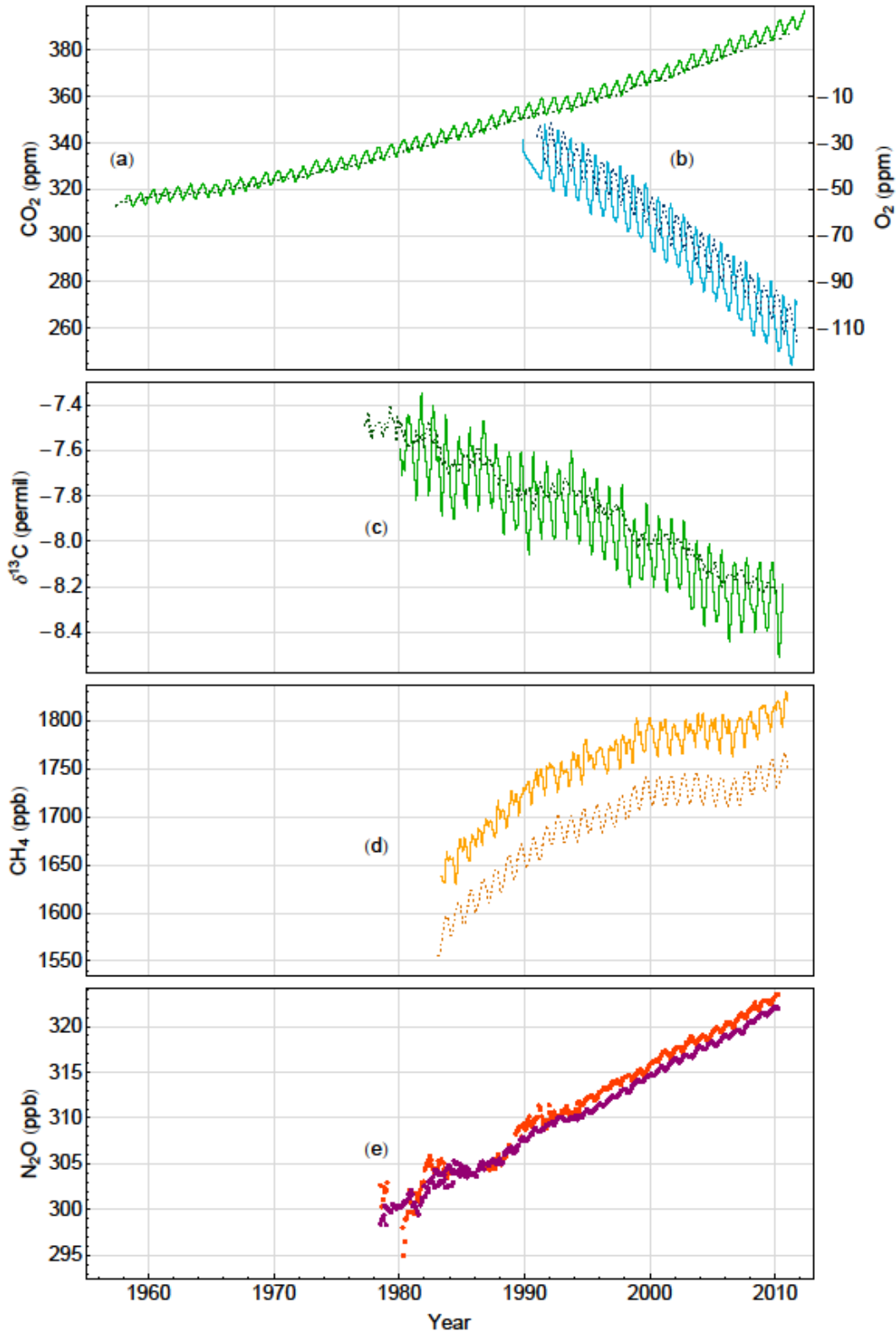
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Figure 6.2: Schematic of the global cycle of CH₄. Numbers represent fluxes in Tg (CH₄) yr⁻¹ estimated for the time period 2000–2009 (see Section 6.3). Green arrows denote natural fluxes, red arrows anthropogenic fluxes, and orange arrow denotes a combined natural+anthropogenic flux.

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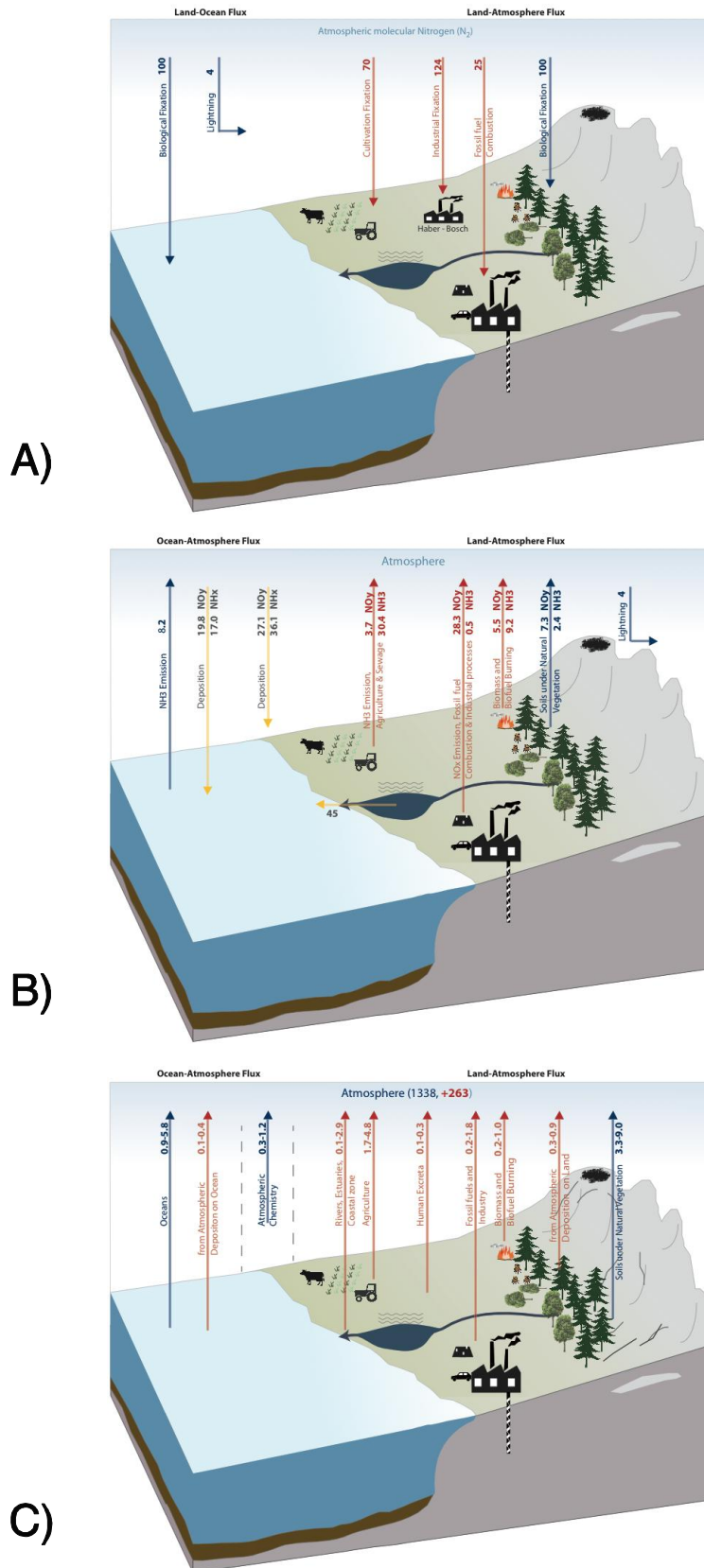
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Figure 6.3: Atmospheric concentration of CO₂, oxygen, ¹³C/¹²C stable isotope ratio in CO₂, CH₄ and N₂O recorded over the last decades at representative stations in the northern (solid lines) and the southern (dashed lines) hemisphere. (a: CO₂ from Mauna Loa and South Pole atmospheric stations (Keeling et al., 2005), O₂ from Alert and Cape Grim stations (<http://scrippsco2.ucsd.edu/> right axes), b: ¹³C/¹²C: Mauna Loa, South Pole (Keeling et al., 2005), c: CH₄ from Mauna Loa and South Pole stations (Dlugokencky et al., 2010), d: N₂O from Adrigole and Cape Grim stations (Prinn et al., 2000).

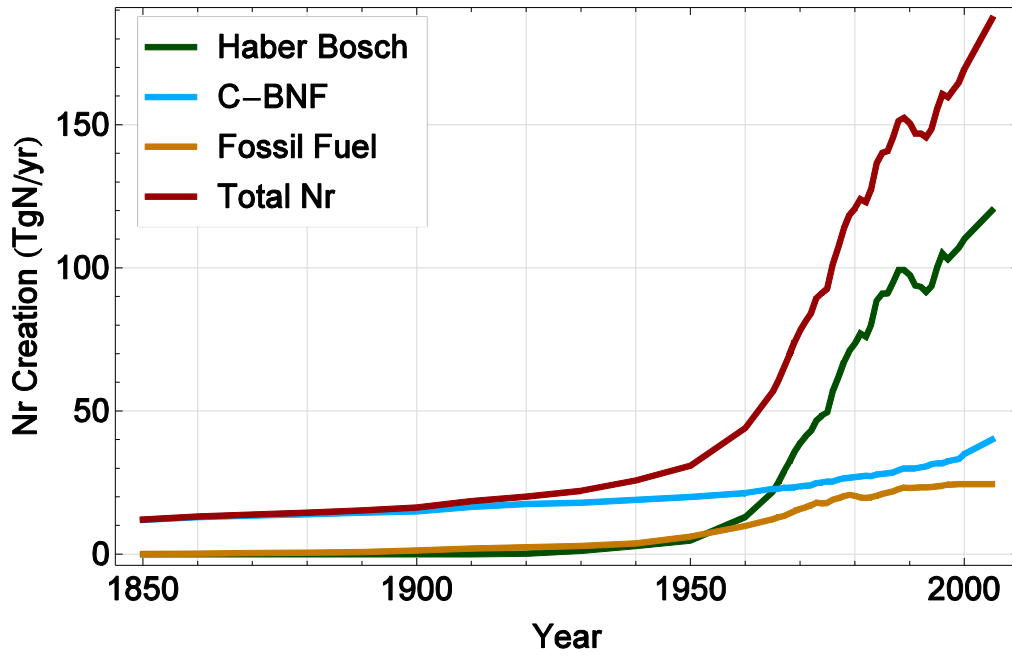
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Figure 6.4: Global nitrogen cycle. The upper panel (A) shows natural and anthropogenic process that create reactive nitrogen Nr. The middle panel (B) shows the flows of reactive Nitrogen species. The bottom panel (C) shows a schematic of the global cycle of N_2O . Blue arrows are natural, red arrows anthropogenic fluxes, and yellow arrows represent fluxes with an anthropogenic and natural component. Units: $TgN\ yr^{-1}$.

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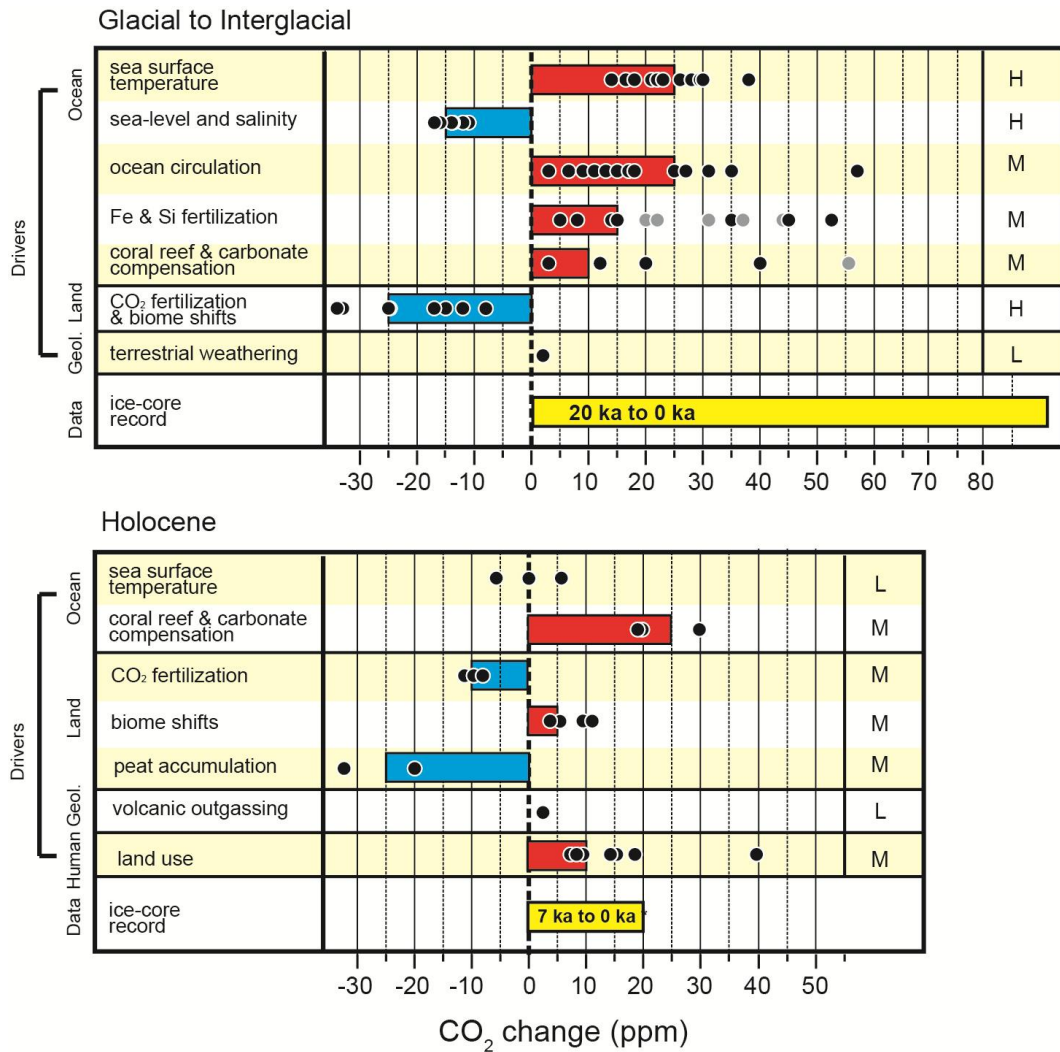
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Box 6.1, Figure 1: Reactive nitrogen (Nr) creation fluxes (in TgN yr⁻¹) from fossil fuel burning (green line), cultivation-induced BNF, C-BNF (red line), Haber-Bosch process (blue line), and total creation (purple line). Source: Galloway et al. (2003), Galloway et al. (2008).

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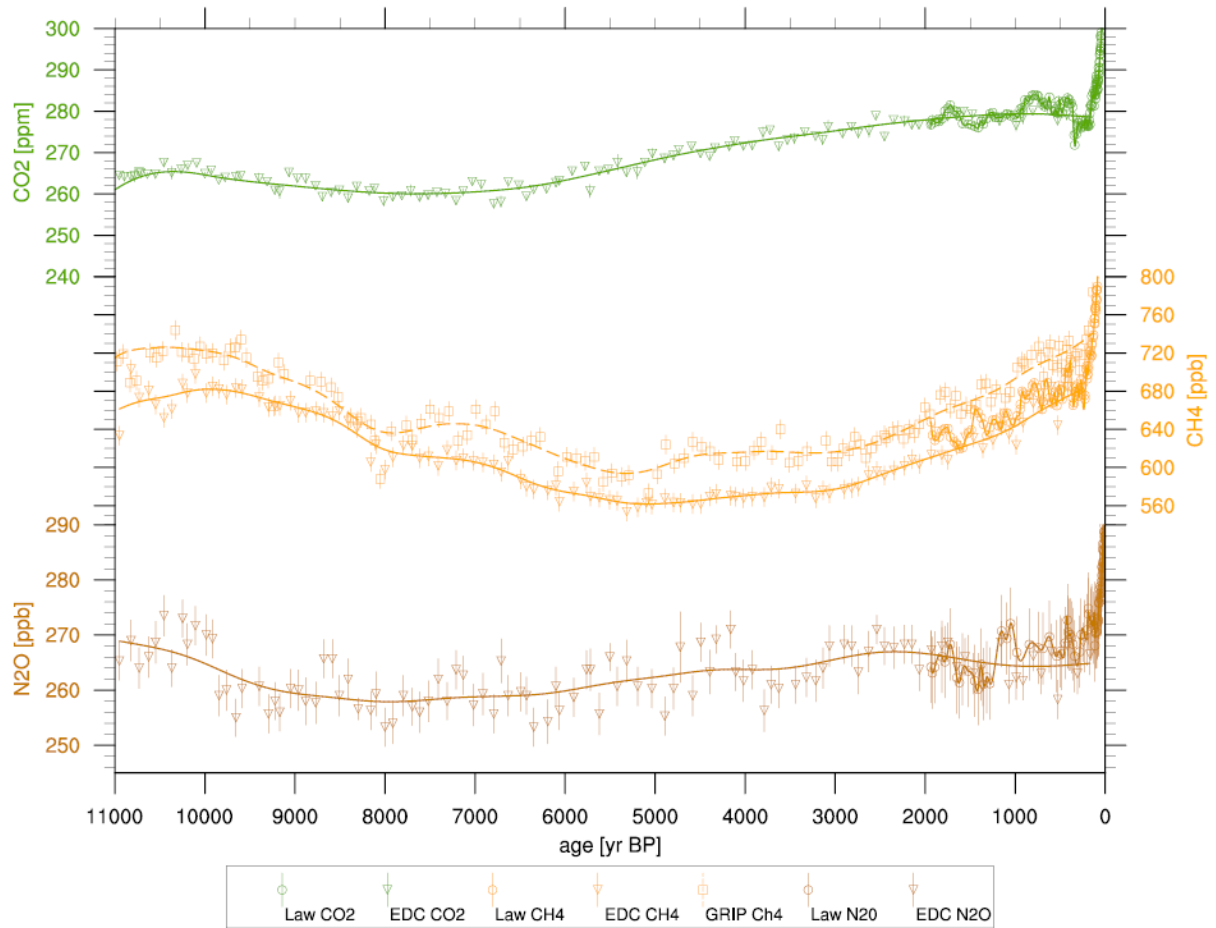
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Figure 6.5: Carbon dioxide concentrations changes from LGM to late Holocene (top) and from early/mid Holocene (7 ka) to late Holocene (bottom). Filled black circles represent individual model-based estimates for individual ocean, land, geological or human drivers. Solid color bars represent expert judgment (to the nearest 5 ppm) rather than a formal statistical average. References for the different model assessment used for the glacial drivers are as per Kohfeld and Ridgwell (2009) with excluded model projections in grey. References for the different model assessment used for the Holocene drivers are Joos et al. (2004), Brovkin et al. (2008), Kleinen et al. (2010), Broecker et al. (1999), Ridgwell et al. (2003), Brovkin et al. (2002), Schurgers et al. (2006), Yu (2011), Kleinen et al. (2011), Ruddiman (2003, 2007), Strassmann et al. (2008), Olofsson and Hickler (2008), Pongratz et al. (2009), Kaplan et al. (2011), Lemmen (2009), Stocker et al. (2011) and Roth and Joos (2012).

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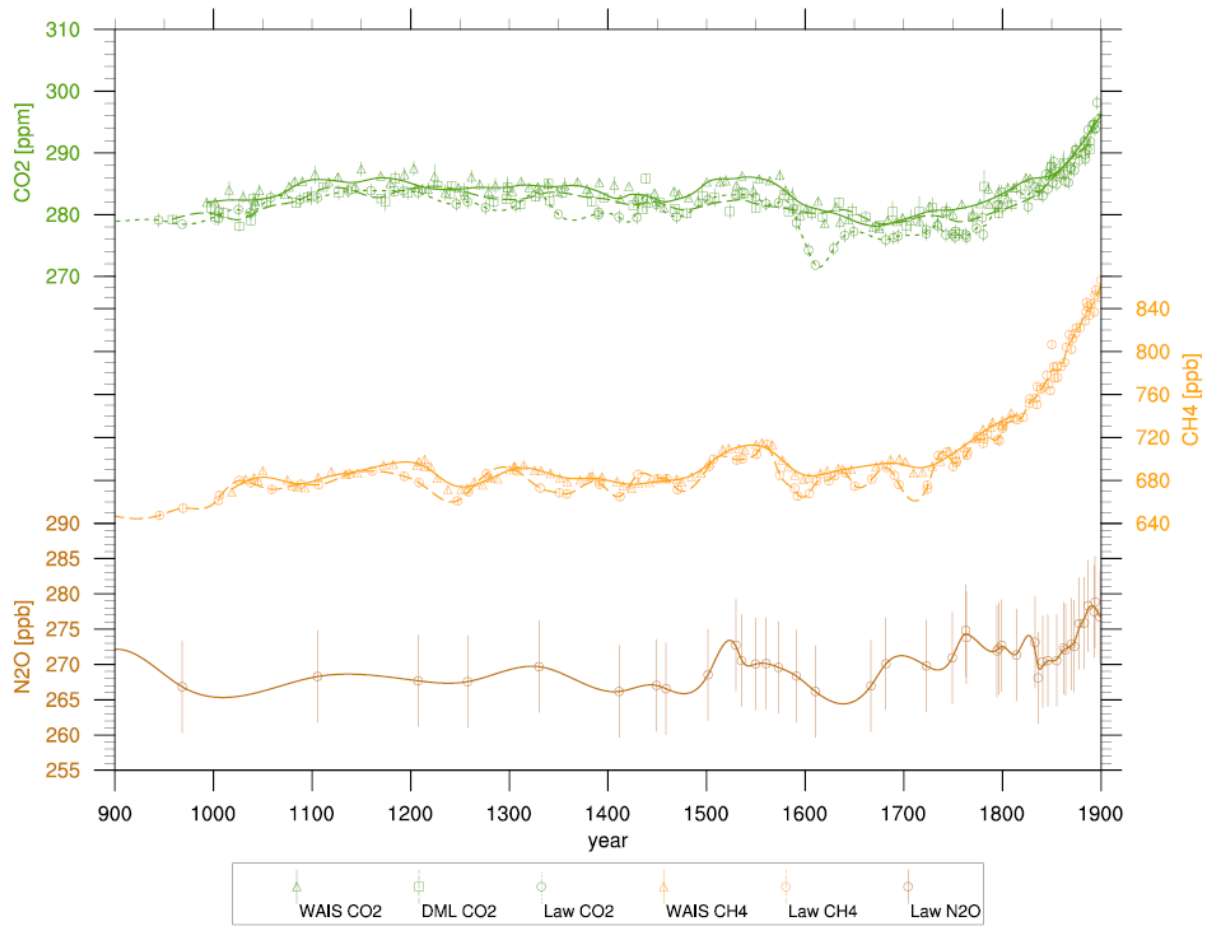
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Figure 6.6: Variations of CO₂, CH₄, and N₂O concentrations during the Holocene. The data are for Antarctic ice cores: EPICA Dome C (Fluckiger et al., 2002; Monnin et al., 2004), triangles; Law Dome (MacFarling-Meure et al., 2006), circles, and for Greenland ice core GRIP (Blunier et al., 1995), squares. Lines are for spline fits.

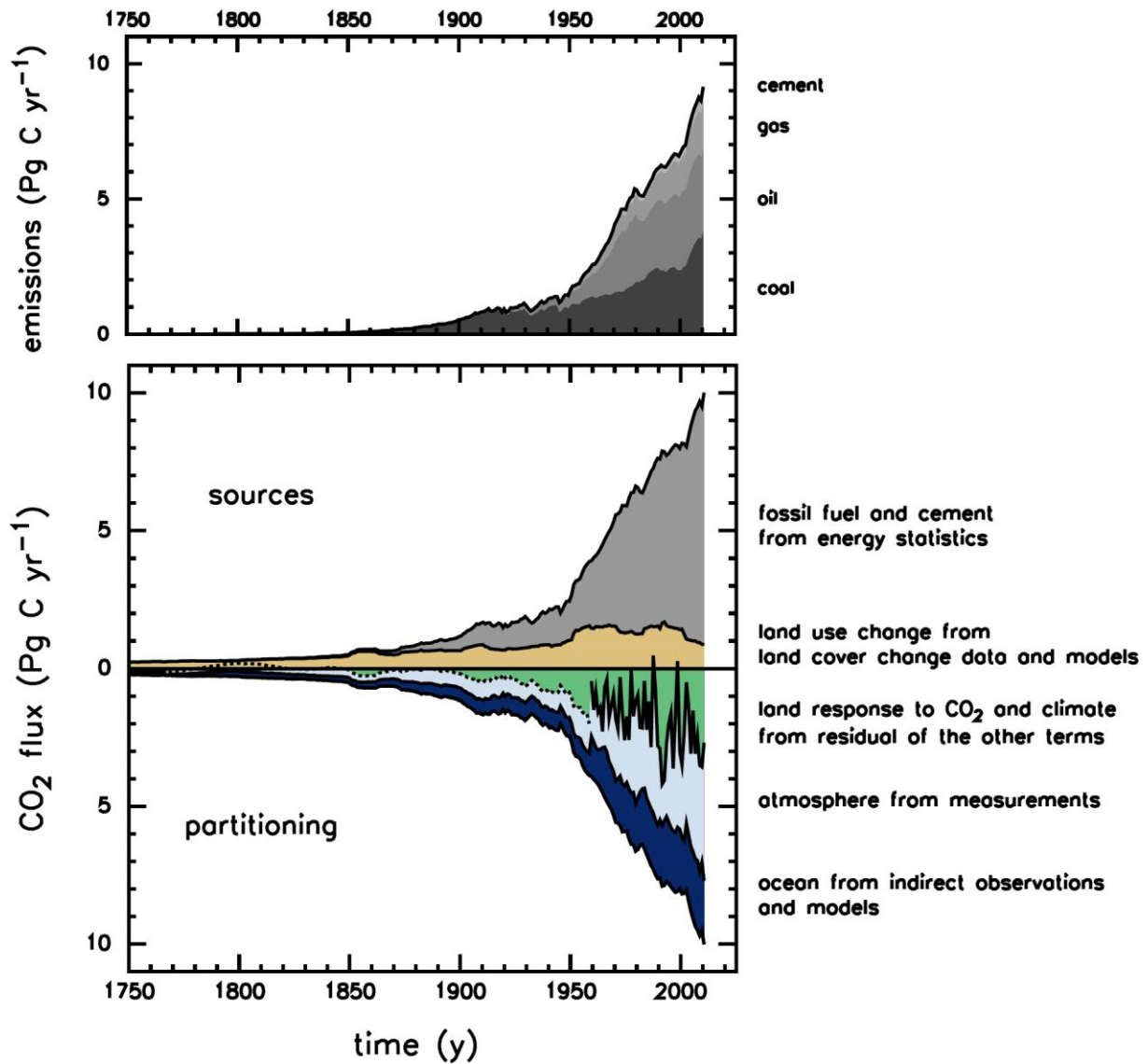
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Figure 6.7: Variations of CO₂, CH₄, and N₂O during 900–1900 AD from ice cores. The data are for Antarctic ice cores: Law Dome (Etheridge et al., 1996; MacFarling-Meure et al., 2006), circles; West Antarctic Ice Sheet (Ahn et al., 2012; Mitchell et al., 2011), triangles; Dronning Maud Land (Siegenthaler et al., 2005a), squares. Lines are spline fits to individual measurements.

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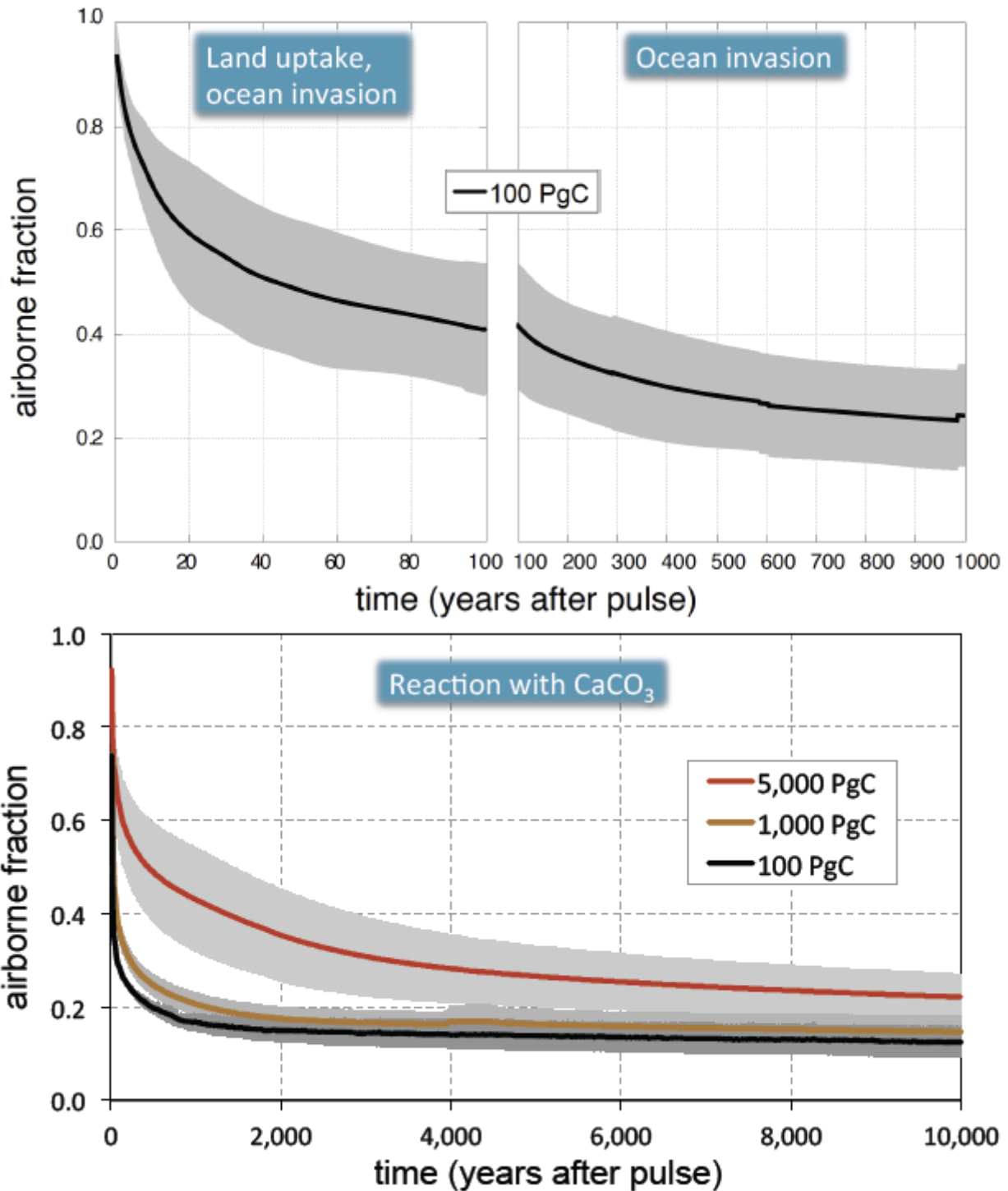
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Figure 6.8: Sources and sinks fluxes (PgC yr^{-1}) for the component of the global anthropogenic CO_2 budget from 1750 to 2010. (Top) Fossil fuel and cement CO_2 emissions by category, estimated by the Carbon Dioxide Information Analysis Center (CDIAC) based on UN energy statistics for fossil fuel combustion and US Geological Survey for cement production (Boden et al., 2011). (Bottom) Fossil fuel and cement CO_2 emissions as above. CO_2 emissions from net land use change, mainly deforestation for 1750–1850 are from the average of estimates (Pongratz et al., 2009; Shevliakova et al., 2009b; vanMinnen et al., 2009; Zaehle et al., 2011) and from Houghton et al. (2012) after 1850. The atmospheric CO_2 growth rate prior to 1960 is based on a spline fit to ice core observations (Etheridge et al., 1996; Friedli et al., 1986; Neftel et al., 1982) and a synthesis of atmospheric observations from 1960 (Conway and Tans, 2011). The fit to ice core observations does not capture the large interannual variability in atmospheric CO_2 and is represented with a dashed line on the figure. The ocean CO_2 sink prior to 1960 is from Khatiwala et al. (2009) and from a combination of model and observations from 1960 updated from (LeQuere et al., 2009). The residual land sink is computed from the residual of the other terms. The sources and sinks only include the fluxes that have changed since 1750, and not the natural CO_2 fluxes (e.g., atmospheric CO_2 uptake from weathering, natural river transport of carbon from land to ocean, and compensatory CO_2 outgassing by the ocean) between the atmosphere, and ocean reservoirs that existed before that date and still exist today. The uncertainties in the various terms are discussed in the text and reported in Table 6.1.

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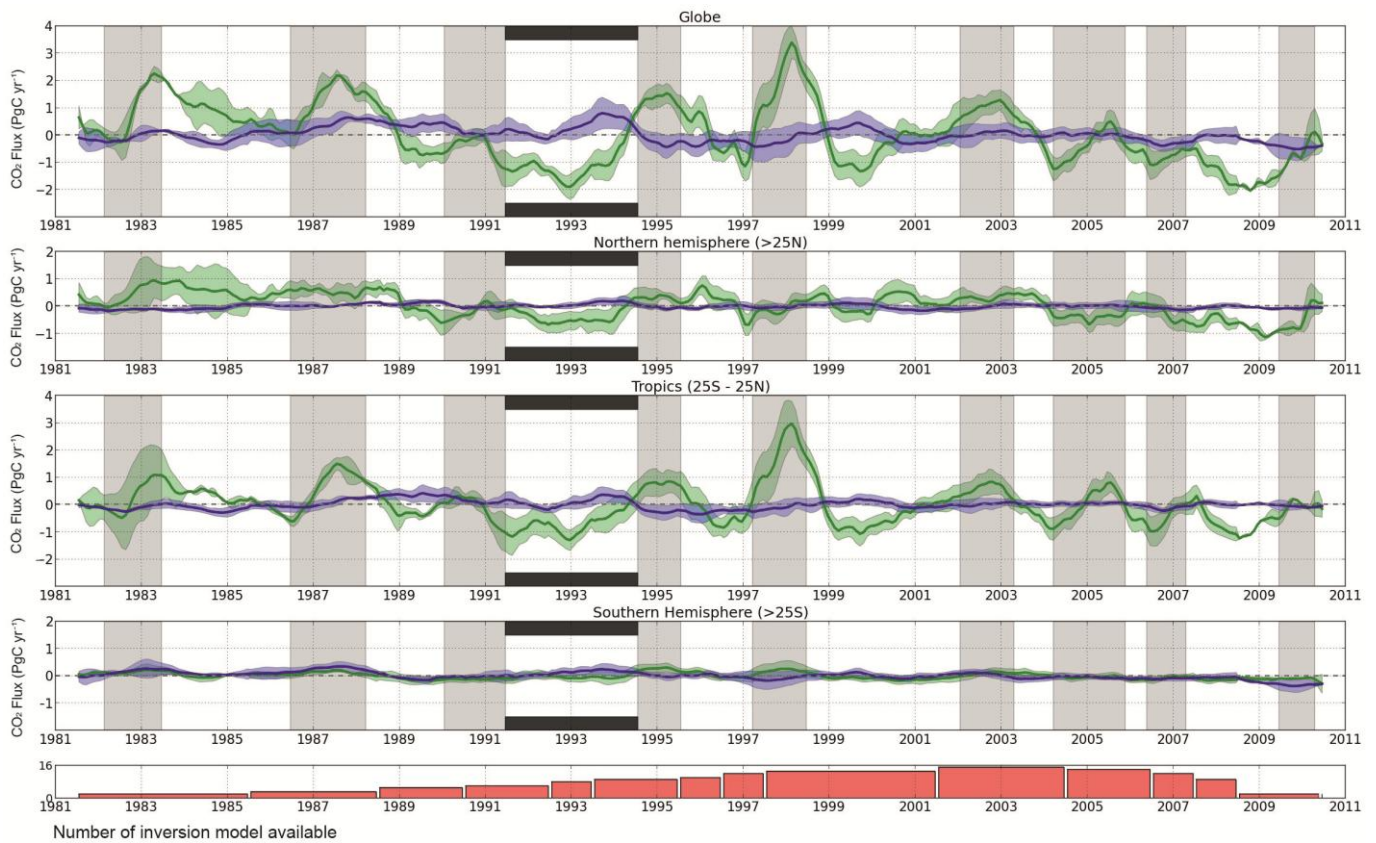
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Box 6.2, Figure 1: A fraction of a given amount of CO₂ emitted to the atmosphere remaining in the atmosphere in response to an idealized instantaneous CO₂ pulse in year 0 as calculated by a range of coupled climate-carbon cycle models. (Top) Multi-model mean (black line) and the uncertainty interval (± 2 standard deviations, grey shading) simulated during 1,000 years following the instantaneous pulse of 100 PgC (Joos et al., submitted). (Bottom) A mean of models with oceanic and terrestrial carbon components (solid lines) and a maximum range of these models (grey shading) for instantaneous CO₂ pulse in year 0 of 100 PgC (black), 1,000 PgC (brown) and 5,000 PgC (red line) on a time interval up to ten thousand years (Archer et al., 2009b). (Blue boxes) the dominant processes that remove the excess of CO₂ emitted in the atmosphere on the successive timescales. Note that higher pulse of CO₂ emissions leads to higher airborne CO₂ fraction (Section 6.3.2.4) due to reduced carbonate buffer capacity of the ocean and positive climate-carbon cycle feedback (Section 6.3.2.6.6).

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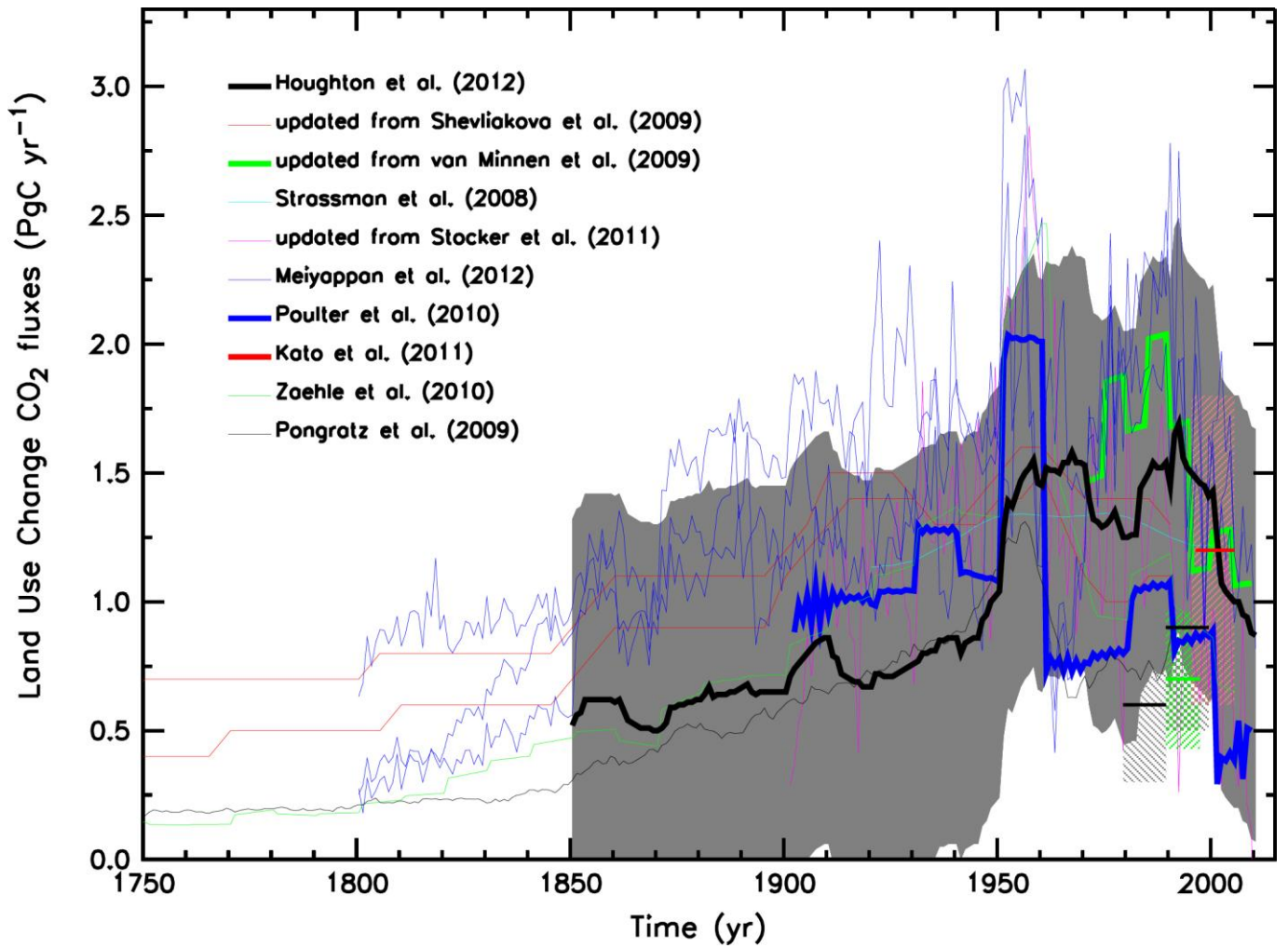
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4 **Figure 6.9:** The interannual variability of surface CO₂ fluxes from inversions of the TRANSCOM project for the period
 5 of 1981–2010. The ensemble of inversion results contains up to 17 atmospheric inversion models. The orange bars at
 6 the bottom panel indicates the number of available inversion models for each time period. The ensemble mean is
 7 bounded by the 1 sigma inter-model spread in ocean-atmosphere (blue) and land-atmosphere (green) CO₂ fluxes (PgC
 8 yr⁻¹) grouped into large latitude bands, and the globe. For each flux and each region, the CO₂ flux anomalies were
 9 obtained by subtracting the long term mean flux from each inversion and removing the seasonal signal. Grey shaded
 10 regions indicate El Niño episodes, and the back bars indicate the cooling period following the Mt. Pinatubo eruption. A
 11 positive flux means a larger than normal source of CO₂ to the atmosphere (or a smaller CO₂ sink).

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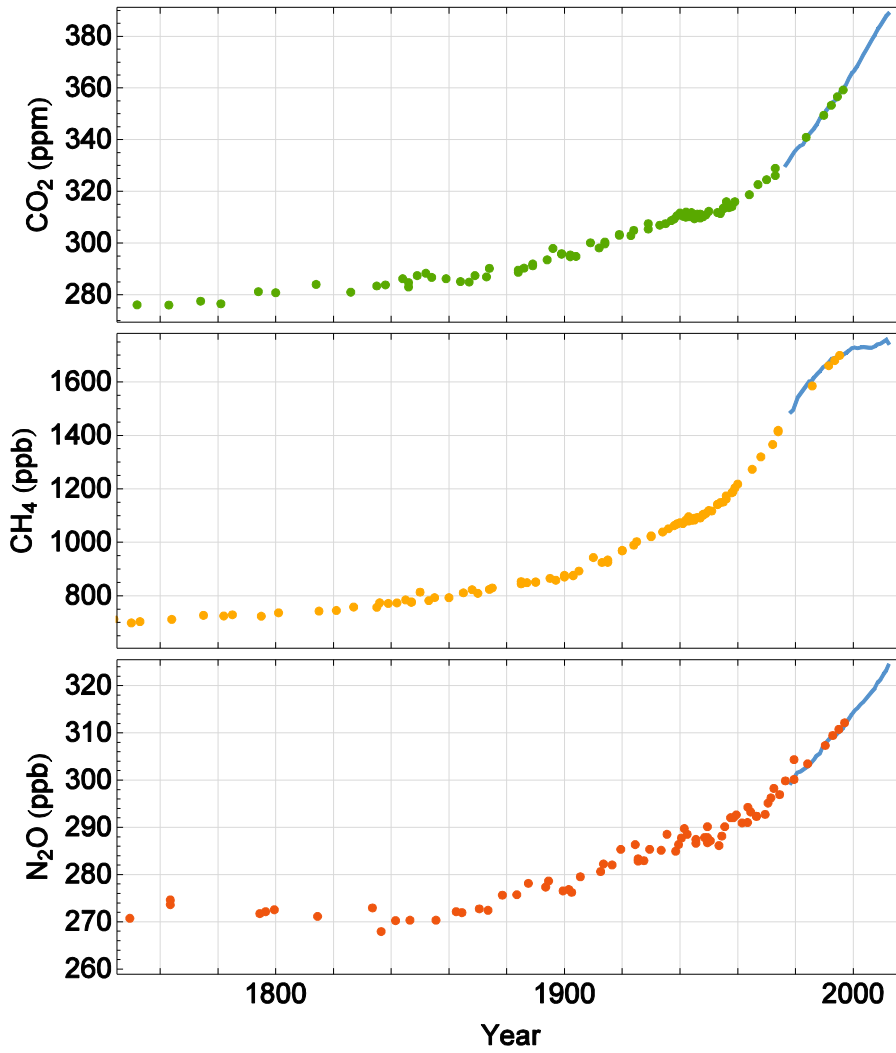
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4 **Figure 6.10:** CO₂ emissions from land use change from a range of methods (PgC yr⁻¹). The estimate from Houghton et
 5 al. (2012) (thick black) is used in Table 6.1. The sources for the other estimates are shown in the legend and described
 6 in Table 6.2.

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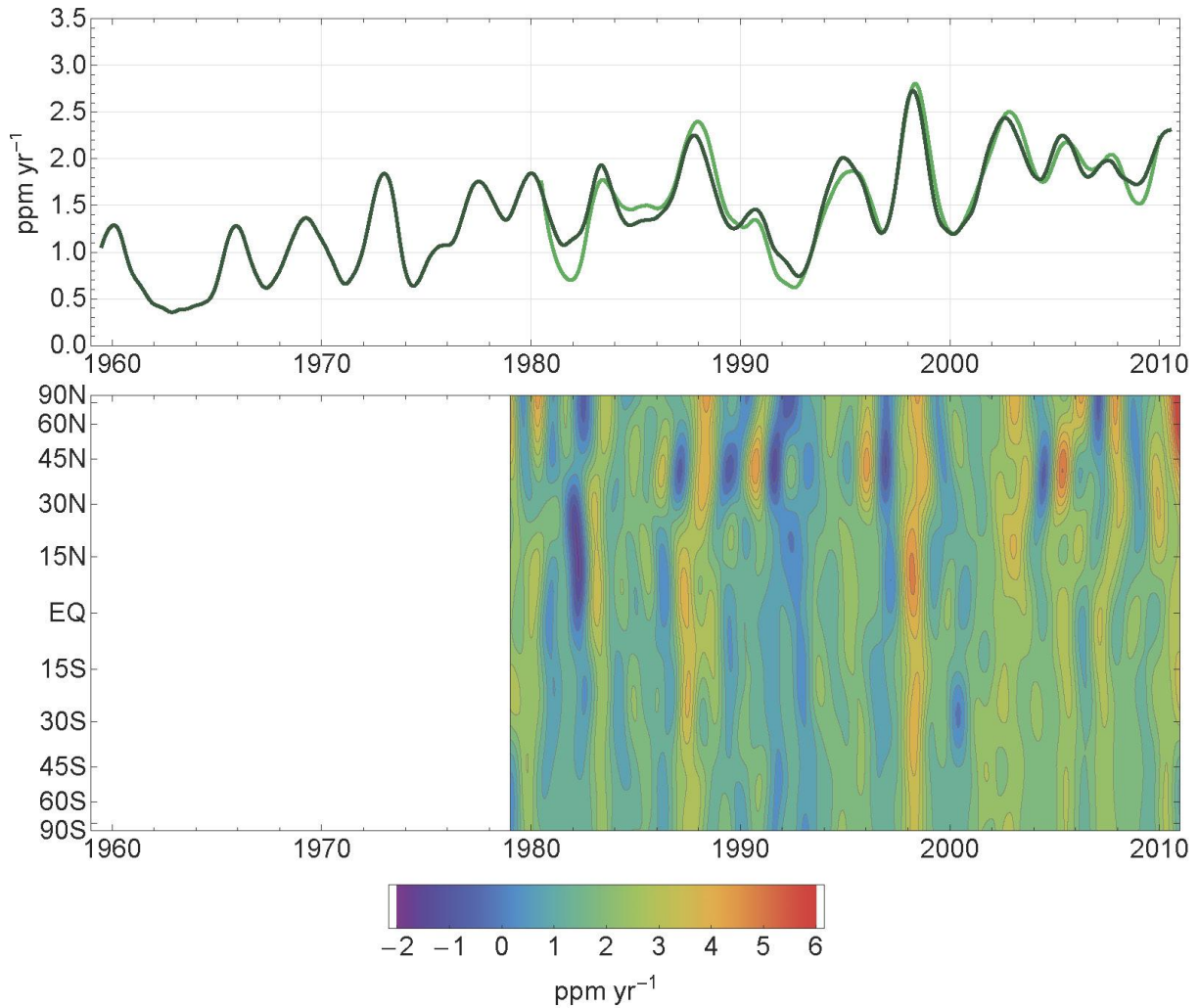
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Figure 6.11: Atmospheric CO₂, CH₄, and N₂O concentrations history over the last 260 years determined from air enclosed in ice cores and firn air (color symbols) and from direct atmospheric measurements (blue lines, measurements from the Cape Grim observatory) (MacFarling-Meure et al., 2006).

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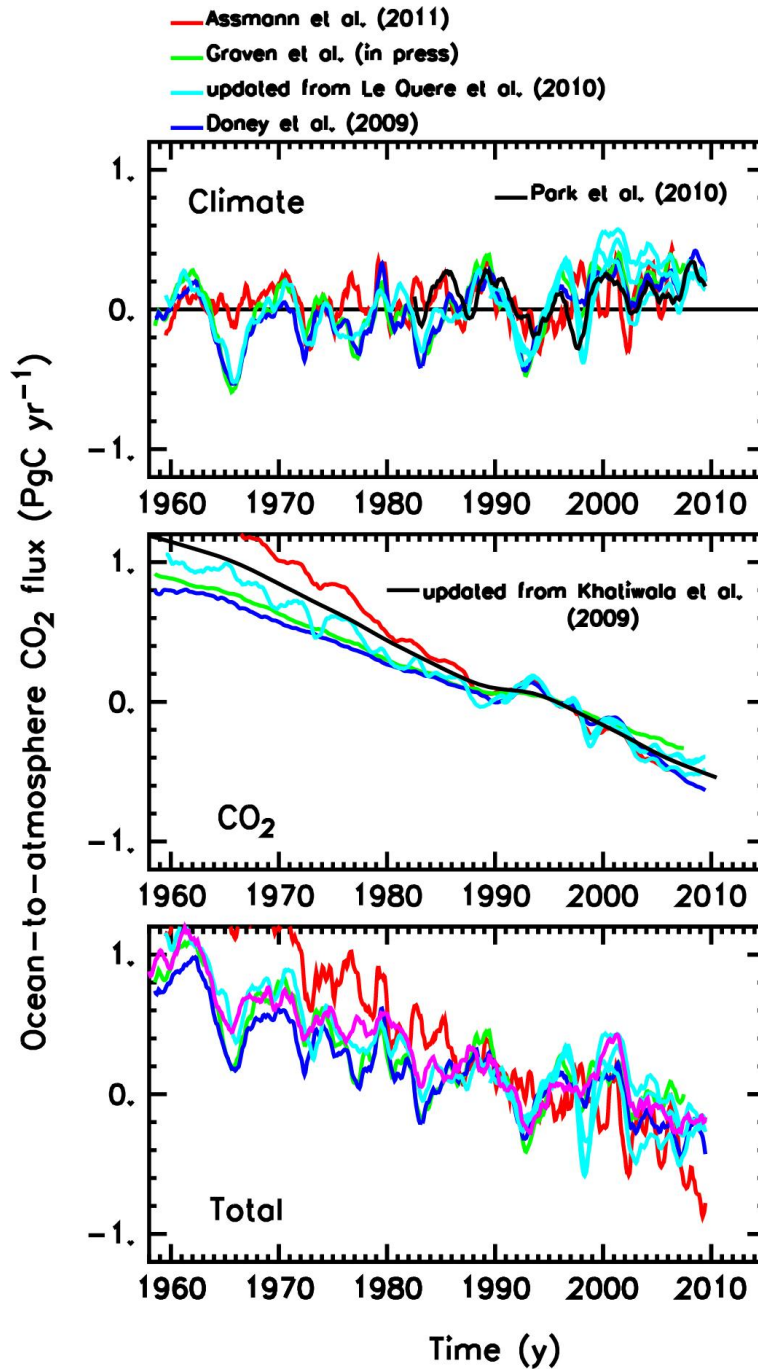
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Figure 6.12: (Top) Global average atmospheric CO₂ growth rate, computed from the observations of the SIO network (dark green curve; Keeling et al., 2005) and from the marine boundary layer air reference measurements of the NOAA-GMD network (Conway et al., 1994; Keeling et al., 2005). (Bottom) Atmospheric growth rate of CO₂ as a function of latitude determined from the GLOBALVIEW data product, representative of stations located in the marine boundary layer at each given latitude (Masarie and Tans, 1995). Sufficient observations are available only since 1979.

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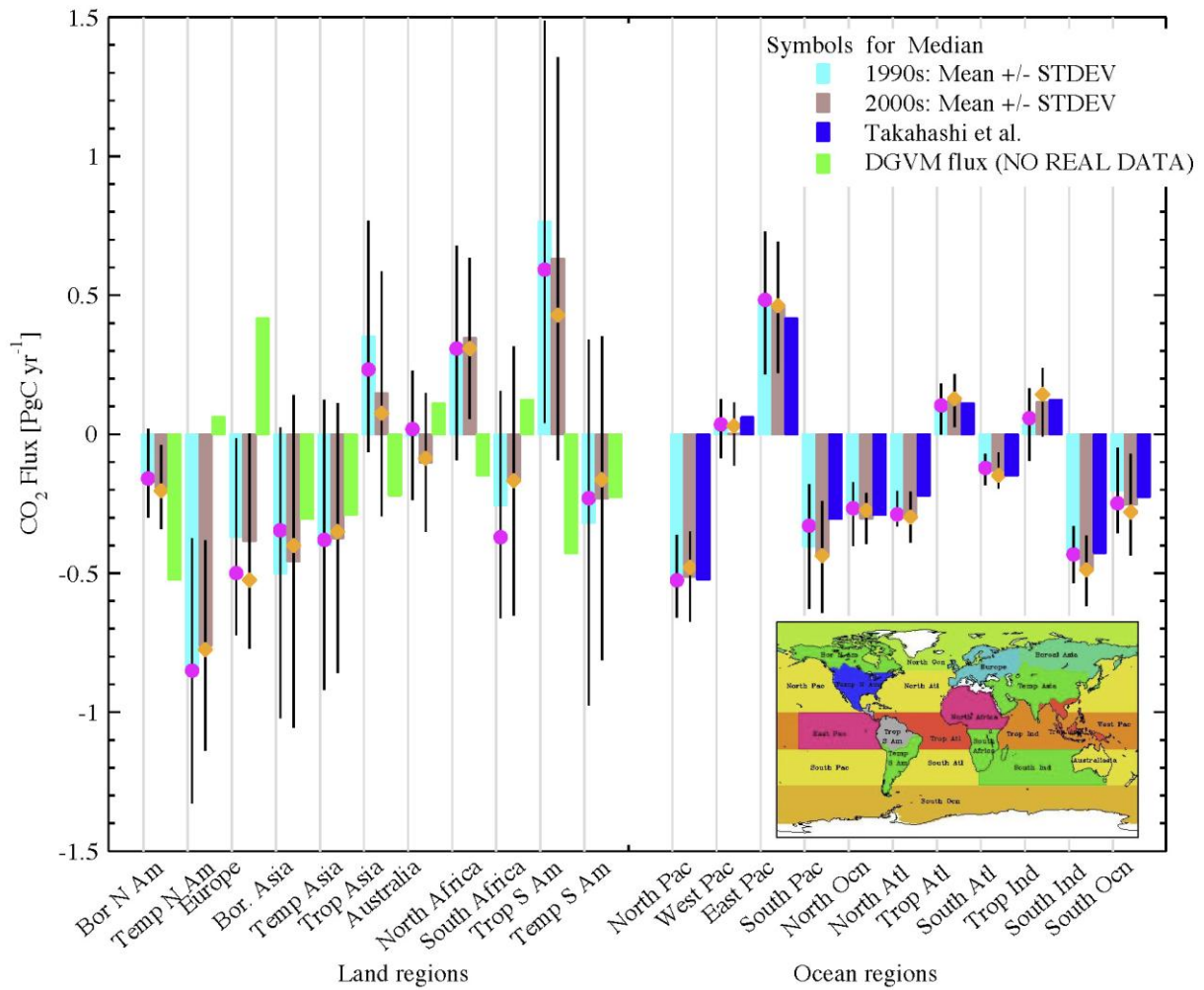
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Figure 6.13: Trends in the ocean-to-atmosphere flux of CO₂ in response to: (Top) variability and trends in surface climate, (middle) increasing atmospheric CO₂, and (Bottom) the sum of both effects (PgC yr⁻¹). All estimates are normalized to zero during 1990–2000 to highlight the trends. Estimates are updates from ocean models (in colours) and from indirect methods based on observations (Khatiwala et al., 2009; Park et al., 2010).

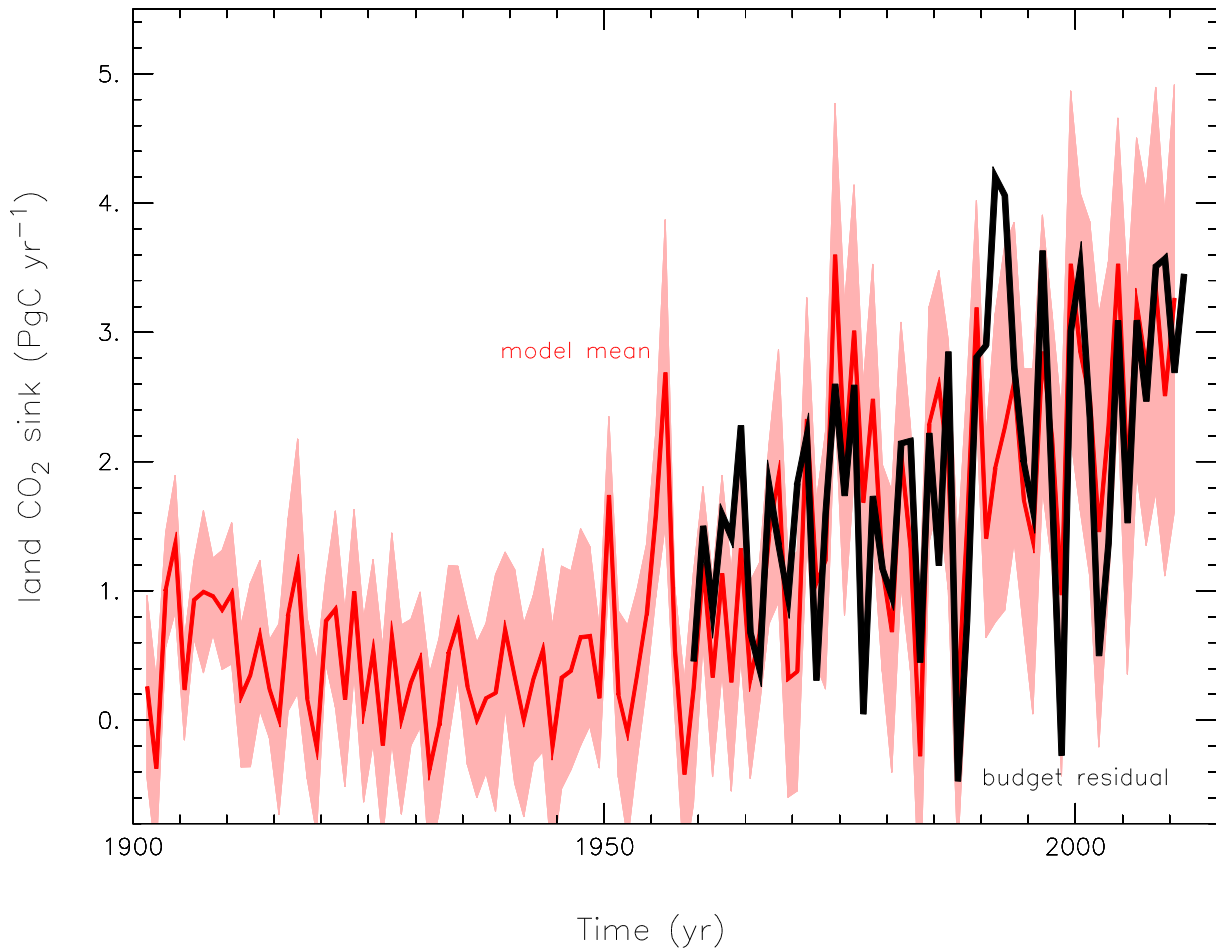
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Figure 6.14: Decadal average CO₂ fluxes for 22 partitions of the globe for (1) the 1990s (cyan) and 2000s (brown) as estimated by atmospheric CO₂ inversions, (2) the dynamic vegetation models (DGVMs), and (3) pCO₂ measurements based air-sea exchange climatology. The regional partitions are depicted as an inset and shaded by CO₂ flux density (blue-green-brown: -ve flux, red-grey: +ve flux). The mean values are calculated from monthly-mean fluxes from 17 inverse models for the period of 1990–2008, and standard deviations shown as error bars are for model-to-model differences within each decade. The DGVM fluxes are calculated using 14 climate-carbon model simulations (not true values).

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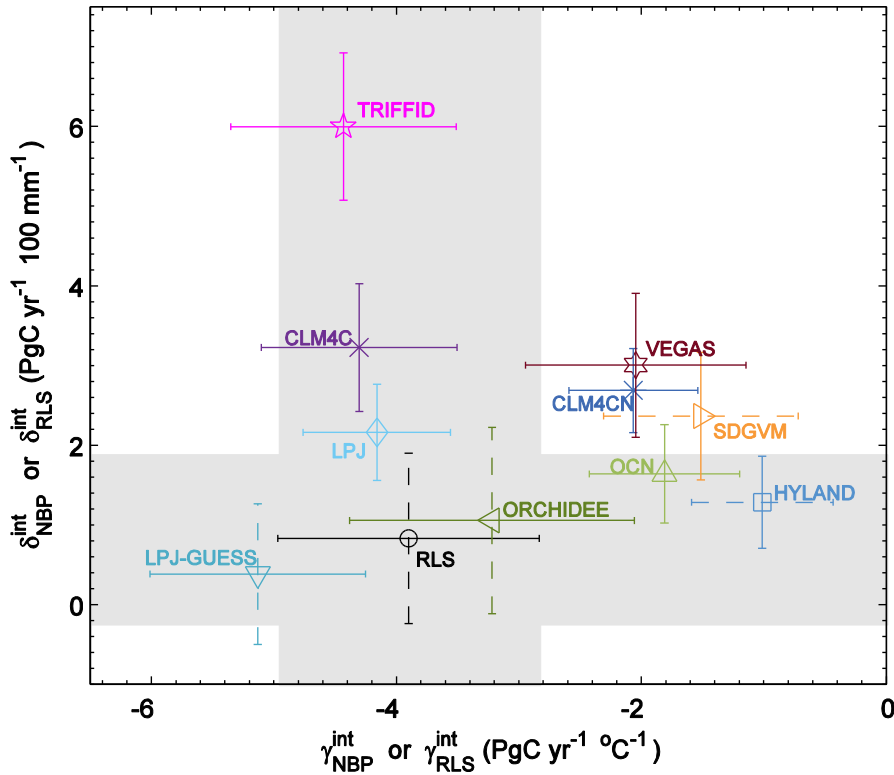
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Figure 6.15: Time series for the land CO₂ sink showing the residual land sink deduced (1) from the global budget (Figure 6.8) with the black line being obtained as the difference between emissions from fossil fuel and land use change, minus the atmospheric growth rate and the ocean sink, and (2) from global process-based terrestrial ecosystem models (Table 6.6 for references) shown as red lines. The red shading shows one standard deviation from the model mean.

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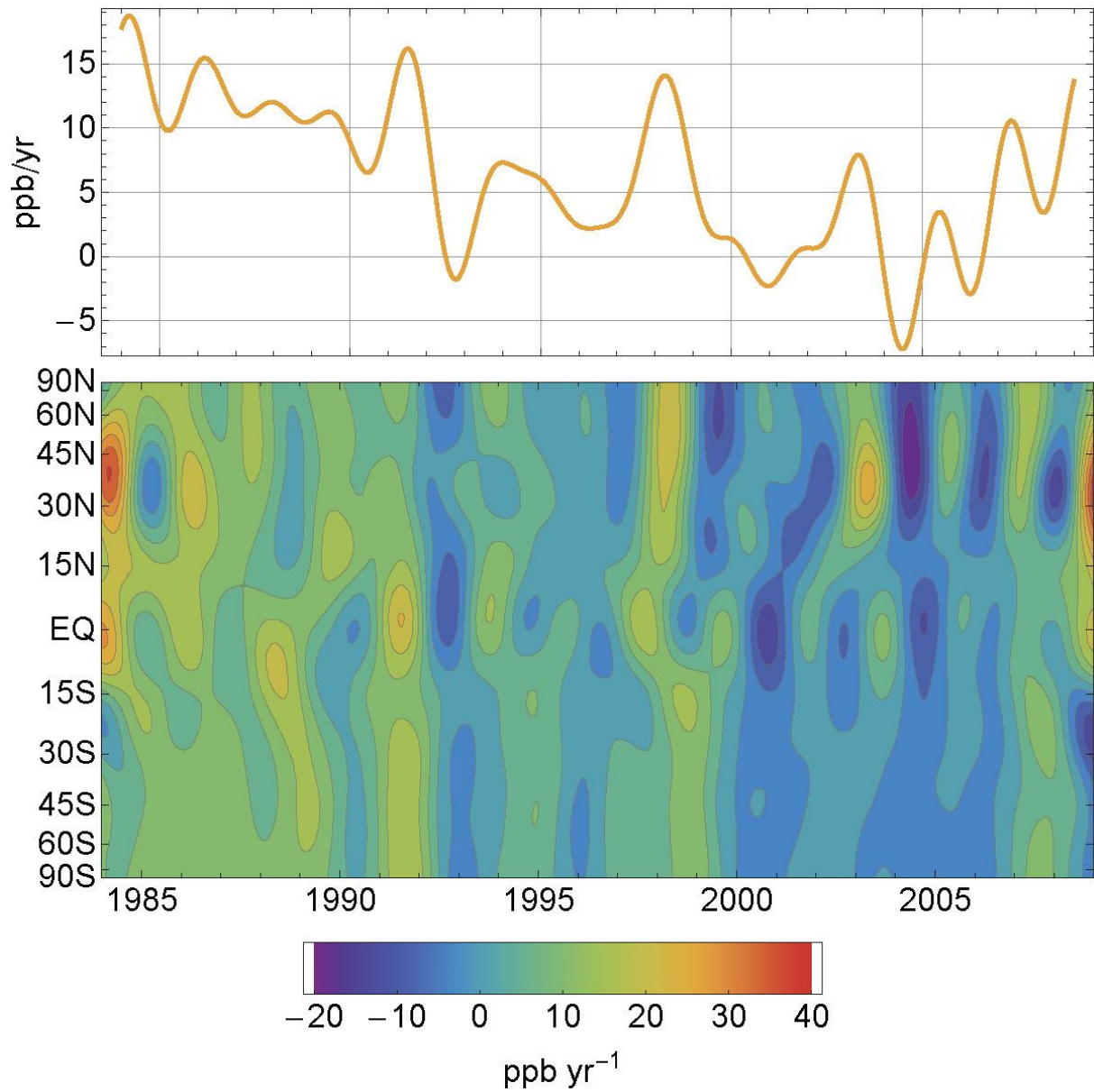
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Figure 6.16: The sensitivity of Net Ecosystem Production (NEP) to interannual variation in temperature and interannual variation in precipitation at the global and regional scales. The global residual land sink is estimated as the sum of fossil fuel and cement emissions and land use change emissions minus the sum of CO₂ growth rate and modelled ocean sink (Friedlingstein and Prentice, 2010; Le Quere et al., 2009). The sensitivities of NEP to interannual variation of temperature and precipitation are estimated by a multiple linear regression approach using detrended NEP as dependent variable and detrended annual temperature and annual precipitation as independent variables (Piao et al., subm.). 10 carbon cycle models are Community Land Model 4C (CLM4C), Community Land Model 4CN (CLM4CN), Hyland (HYL), Lund-Potsdam-Jena (LPJ), LPJ_GUESS, ORCHIDEE-CN (OCN), ORCHIDEE (ORC), Sheffield-DGVM (SDGVM), TRIFFID (TRI), and VEGAS. Negative value indicates decrease in carbon sink.

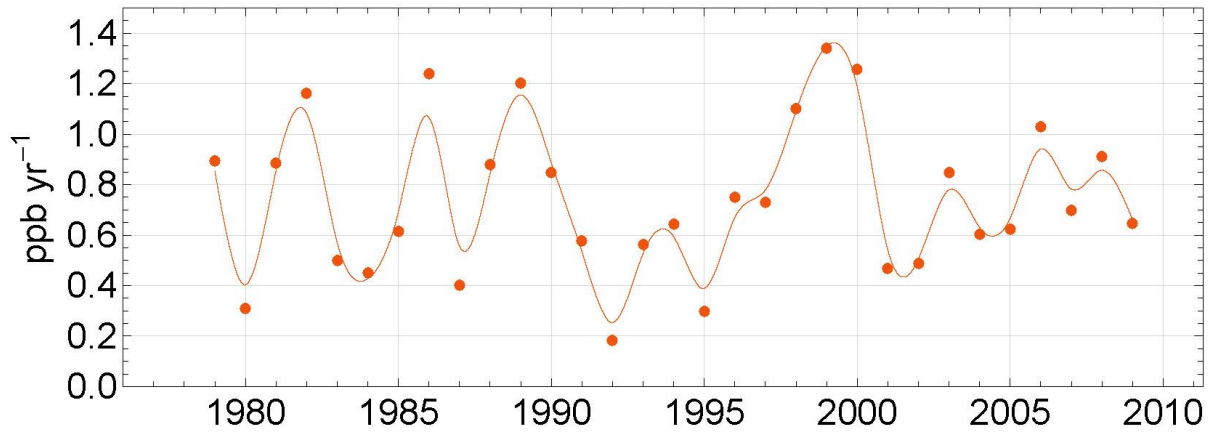
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Figure 6.17: Upper panel: Globally averaged growth rate of atmospheric CH₄ in ppb yr⁻¹ determined from the GLOBALVIEW data product, representative for the marine boundary layer (Masarie and Tans, 1995). Lower panel: Atmospheric growth rate of CH₄ as a function of latitude determined from the GLOBALVIEW data product.

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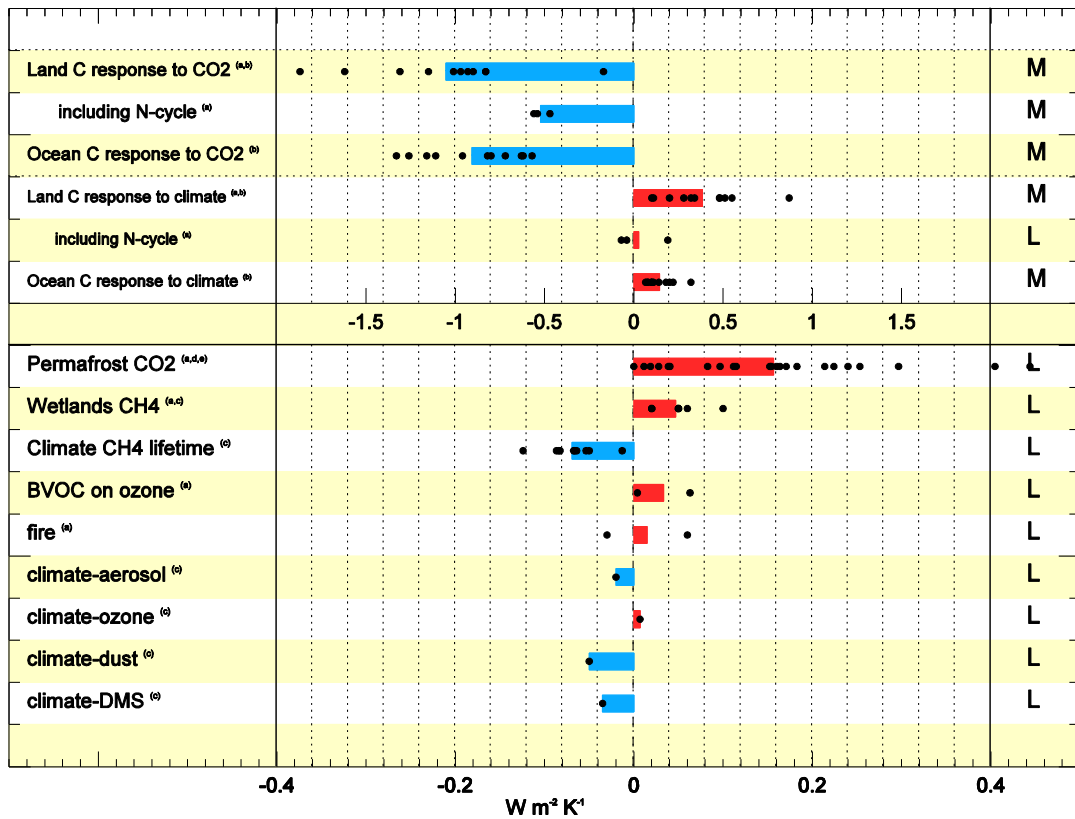
Figure 6.18: Globally averaged growth rate of N₂O in ppb yr⁻¹ determined from the observations of the NOAA/ESRL halocarbons program. Brown dots indicate annual values augmented by a smoothed line to guide the eye.

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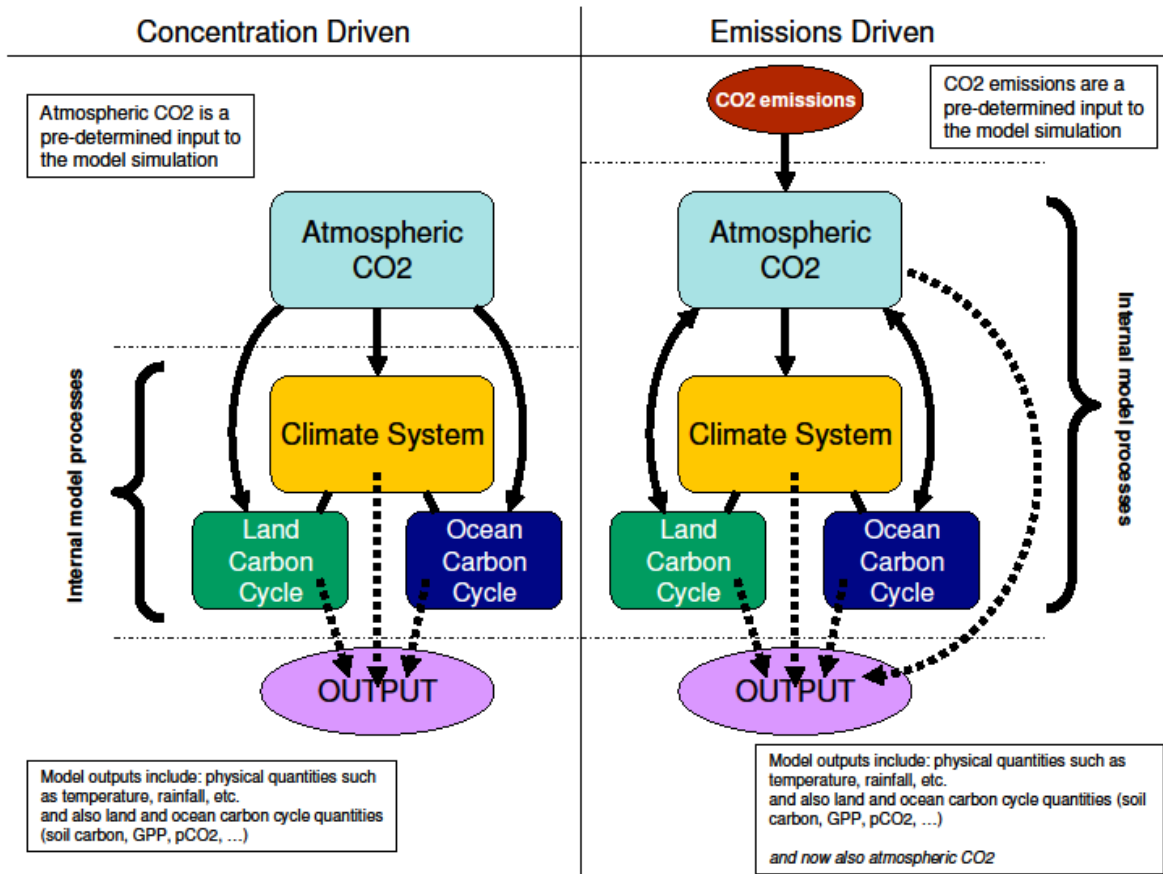
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4 **Figure 6.19:** A summary of the magnitude of biogeochemical feedbacks. Gregory et al. (2009) proposed a framework
 5 for expressing non-climate feedbacks in common units ($W m^{-2} K^{-1}$) with physical feedbacks, and Arneth et al. (2010)
 6 extended this beyond carbon cycle feedbacks to other terrestrial biogeochemical feedbacks. The figure shows the results
 7 compiled by Arneth et al. (2010), with ocean carbon feedbacks from the C4MIP coupled climate-carbon models used
 8 for AR4 also added. Some further biogeochemical feedbacks from the HadGEM2-ES Earth System model (Collins et
 9 al., 2011) are also shown. Black dots represent single estimates, and coloured bars denote the simple mean of the dots
 10 with no weighting or assessment being made to likelihood of any single estimate. An indication of the confidence in
 11 the magnitude of these estimates is shown in the right hand column and is low for feedbacks with only one, or few, dots.
 12 The role of nitrogen limitation on terrestrial carbon sinks is also shown – this is not a separate feedback, but rather a
 13 modulation to the climate-carbon and concentration-carbon feedbacks. This list is not exhaustive. These feedback
 14 metrics are also likely to be state or scenario dependent and so cannot always be compared like-for-like (see Section
 15 6.4.2.2). Results have been compiled from (a) Arneth et al. (2010), (b) Friedlingstein et al. (2006), (c) HadGEM2-ES
 16 (Collins et al., 2011) simulations, (d) Burke et al. (subm.), (e) von Deimling et al. (2012). Note the expanded x-axis
 17 scale for the lower portion of the figure.

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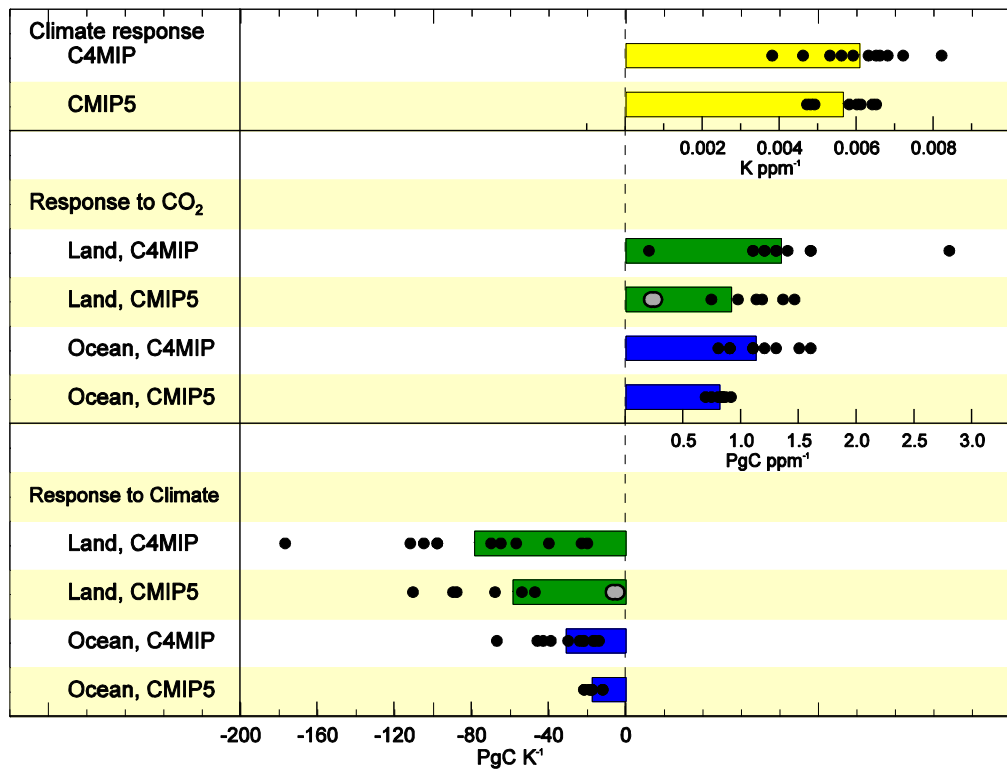
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Box 6.4, Figure 1: Schematic representation of carbon cycle numerical experimental design. Concentration-driven (left hand side) and emissions-driven (right hand side) simulation experiments make use of the same ESM models, but configured differently. Concentration-driven simulations prescribe atmospheric CO₂ as a pre-defined input to the climate and carbon cycle model components, but their output does not affect the CO₂. Emissions-driven simulations prescribe CO₂ emissions as the input and atmospheric CO₂ is now an internally calculated element of the earth system model.

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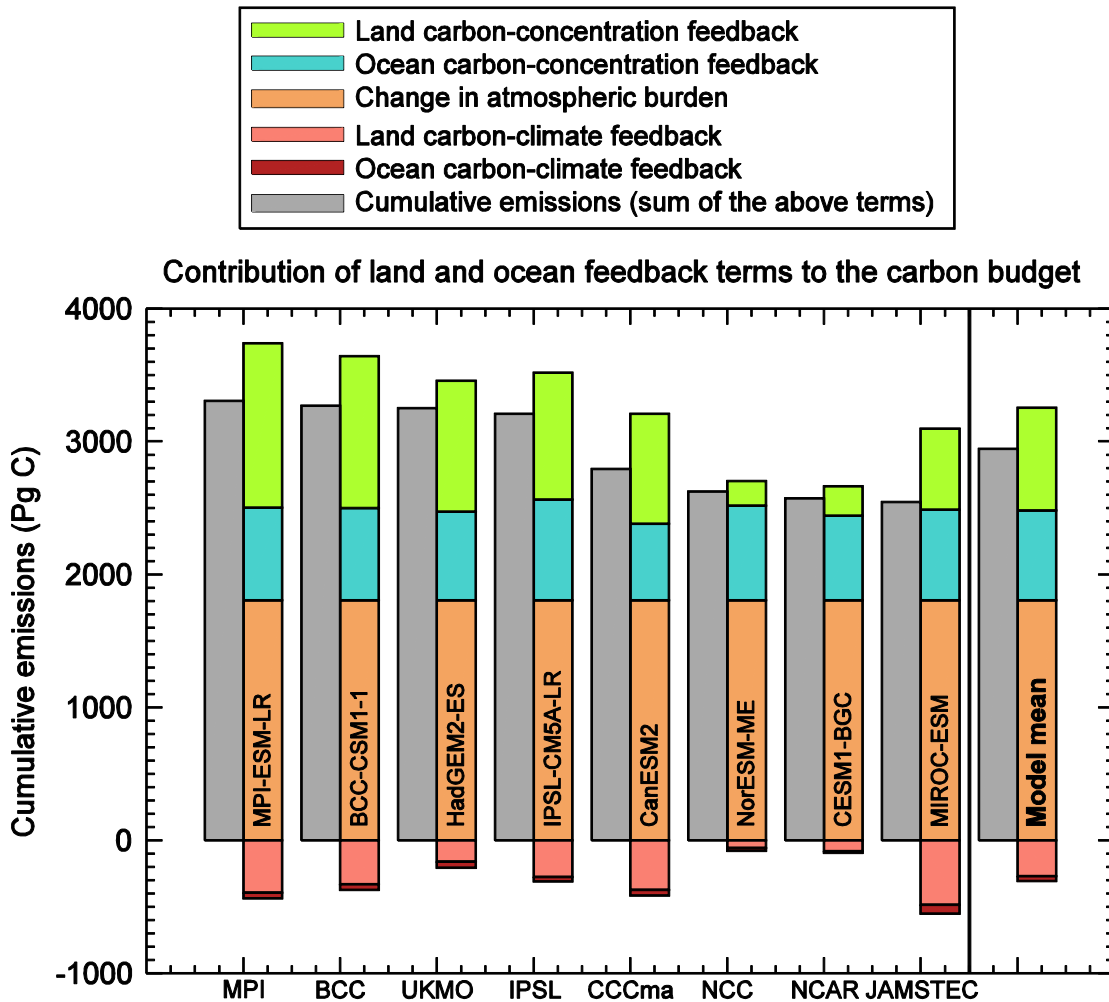
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Figure 6.20: Comparison of carbon cycle feedback metrics between the C4MIP ensemble of 7 GCMs and 4 EMICs under the SRES-A2 scenario (Friedlingstein et al., 2006) and 8 CMIP5 models (Arora et al., *subm.*) under the 1% increase per year CO₂ scenario. Black dots represent a single model simulation and coloured bars the mean of the multi-model results, grey dots are used for models with a coupled terrestrial nitrogen cycle. The comparison with C4MIP is for context, but these metrics are known to be variable across different scenarios and rates of change (see Section 6.4.2.2). Some of the CMIP5 models are derived from models that contributed to C4MIP and some are new to this analysis. Table 6.10 lists the main attributes of each CMIP5 model used in this analysis. The SRES A2 scenario is closer in rate of change to a 0.5% yr⁻¹ scenario and as such it should be expected that the CMIP5 gamma terms are comparable, but the beta terms are likely to be around 20% smaller for CMIP5 than for C4MIP. This high dependence on scenario (Section 6.4.2.2) reduces confidence in any quantitative statements of how CMIP5 carbon cycle feedbacks differ from C4MIP. Models used: MPI-ESM-LR, BCC-CSM1, HadGEM2-ES, IPSL-CM5A-LR, CanESM2, NorESM-ME, CESM1-BGC, MIROC-ESM.

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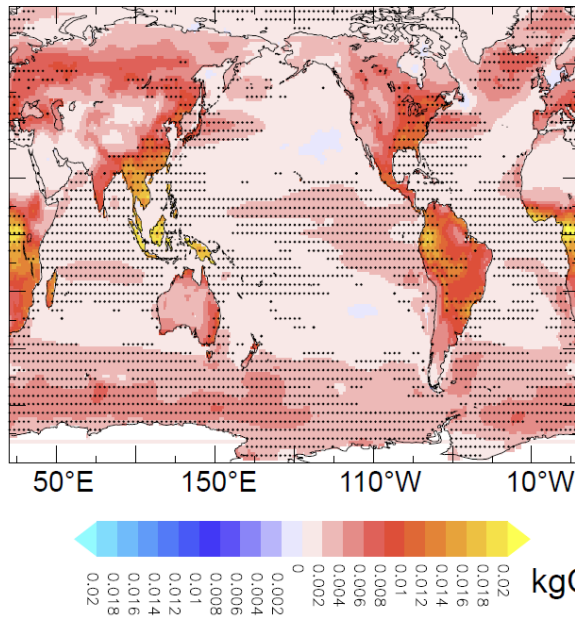
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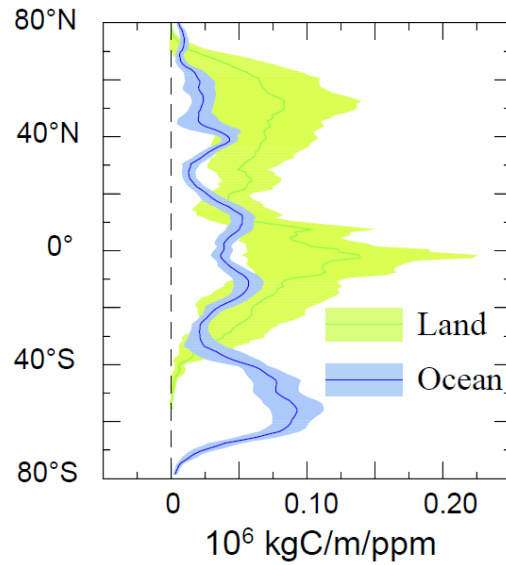
Figure 6.21: Cumulative emissions across CMIP5 models broken down into the contributions of land and ocean response to CO₂ and climate. The contribution of the carbon-concentration feedback is larger than the climate-carbon feedback for all models and the land and ocean contributions to this are typically comparable. The exception is for NorESM-ME and CESM1-BGC which include nitrogen interactions in the terrestrial carbon cycle – these models with nitrogen included in the terrestrial carbon cycle model component simulate a smaller response to both climate and carbon than the other models, but still of the same sign as the other models. The contribution of the ocean to the climate-carbon response is small for all models. Models used: MPI-ESM-LR, BCC-CSM1-1, HadGEM2-ES, IPSL-CM5A-LR, CanESM2, NorESM-ME, CESM1-BGC, MIROC-ESM.

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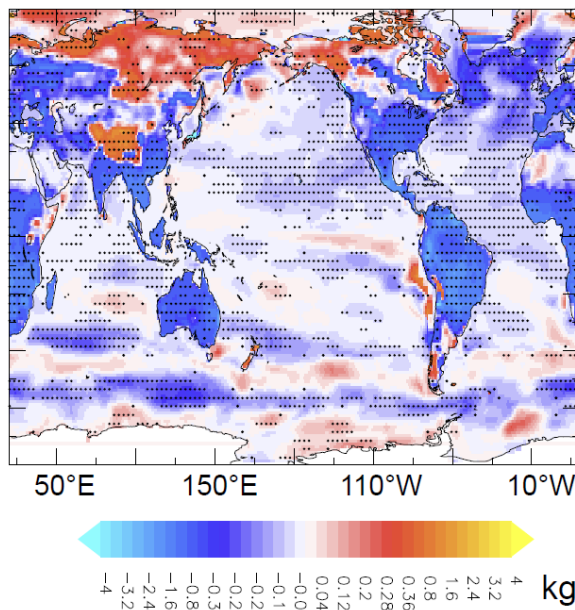
a. Regional β s



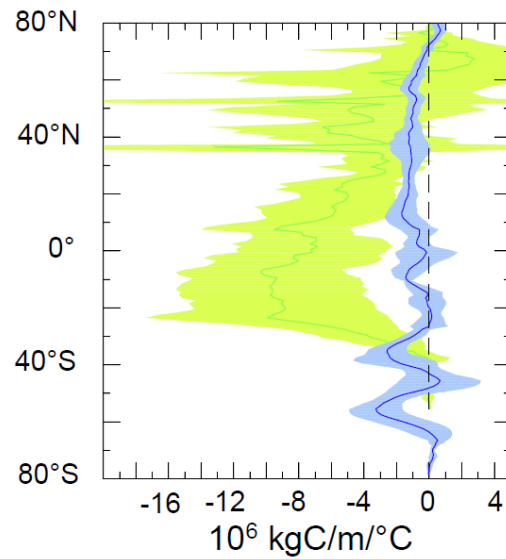
c. Zonal β s



b. Regional γ s



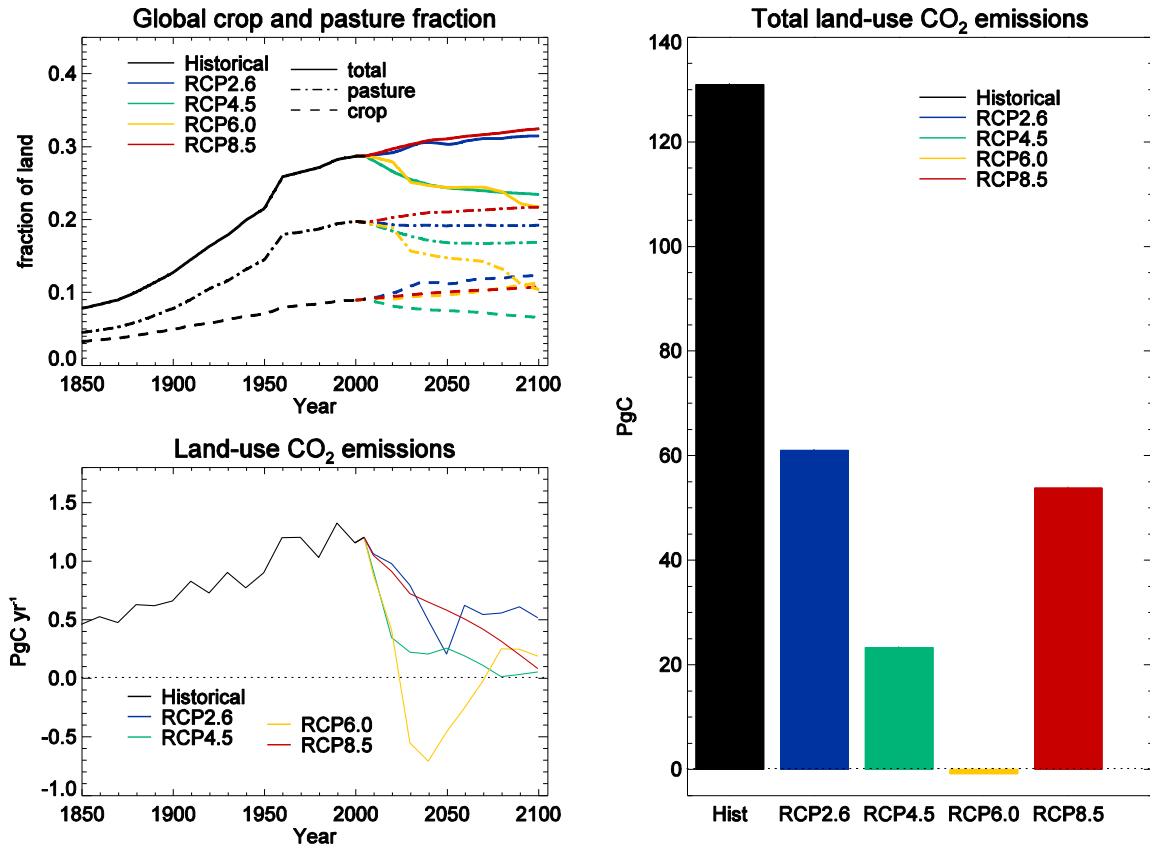
d. Zonal γ s



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Figure 6.22: The spatial distributions of multi model-mean land and ocean β and γ s for 7 CMIP5 models using the *concentration-driven* idealised 1% per year CO_2 simulations. For land and ocean, β and γ are defined from changes in terrestrial carbon storage and changes in air-sea accumulated fluxes respectively, from the beginning to the end of the 1% simulation relative to global (not local) CO_2 and temperature change. Stippling denotes areas where the magnitude of the multi-model ensemble mean exceeds the 90% confidence level interval for β , and where at least 80% models agree on the sign of change for γ . The solid lines show the multi-model mean and shaded areas denote ± 1 standard deviation. Models used are: CanESM2, GFDL-ESM2M, HadGEM2-ES, IPSL-CM5A-LR, MPI-ESM-LR, NorESM1-ME for all, CESM1-BGC for land β , and bcc-csm1-1 for ocean β and γ .

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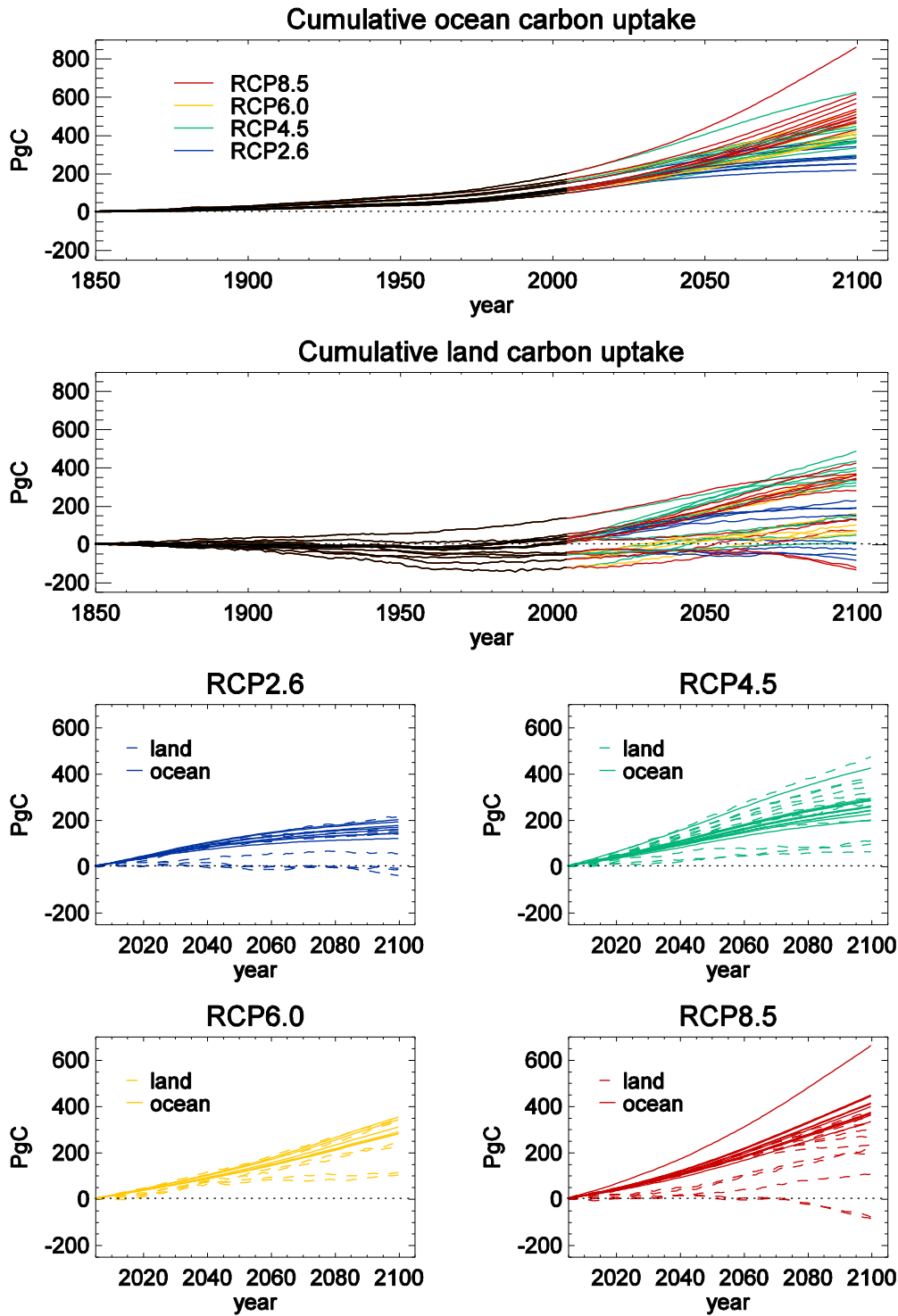
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4 **Figure 6.23:** Land use trends and emissions according to the four different integrated assessment models (IAM) used to
 5 define the RCP scenarios. Global changes in croplands and pasture from the historical record and the RCP scenarios
 6 (top left), and associated annual land use emissions of CO₂ (bottom left). Bars (right panel) show cumulative land use
 7 emissions for the historical period (defined here as 1850–2005) and the 4 RCP scenarios from 2006 to 2100.

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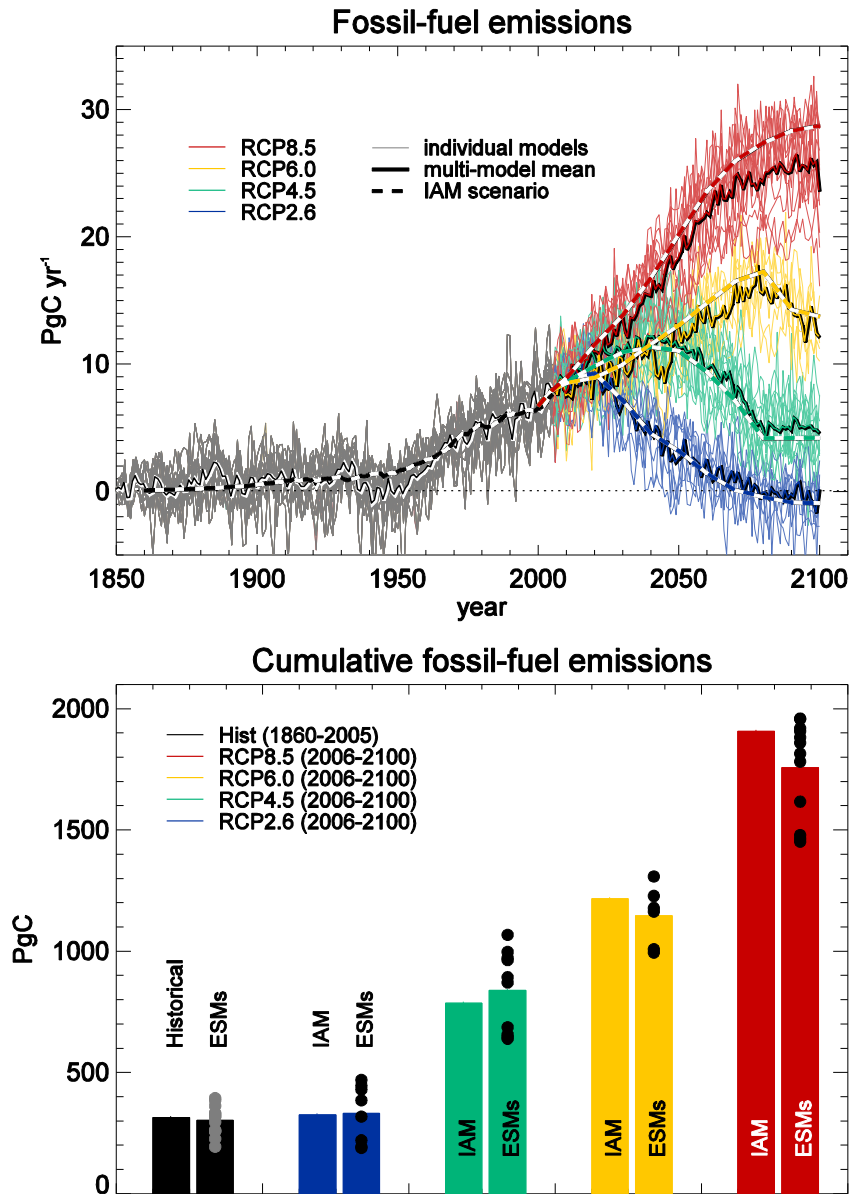
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Figure 6.24: Changes in land and ocean carbon uptake simulated for the four RCP scenarios. Total ocean and land reservoirs cumulative changes in carbon content are shown in the top two panels respectively for the whole period from 1850 to 2100. The lower four panels show the 21st century changes in carbon uptake for land (dashed) and ocean (solid) separately for each scenario. Models used: CanESM2, GFDL-ESM2G, GFDL-ESM2M, HadGEM2-CC, HadGEM2-ES, IPSL-CM5A-LR, IPSL-CM5A-MR, IPSL-CM5B-LR, MIROC-ESM-CHEM, MIROC-ESM, MPI-ESM-LR, NorESM1-ME, Inmcm4, CESM1-BGC.

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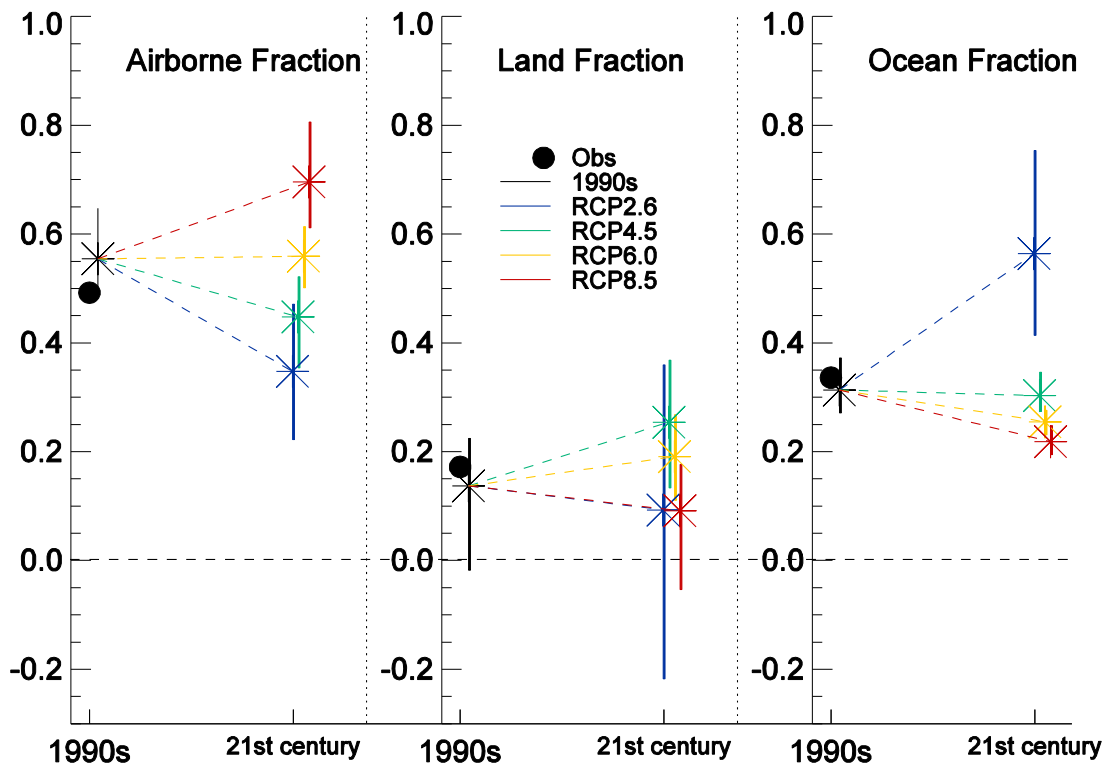
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Figure 6.25: Compatible fossil fuel emissions simulated by the CMIP5 models for the 4 RCP scenarios. Top: timeseries of instantaneous emission rate. Thick lines represent the historical estimates and emissions calculated by the integrated assessment models (IAM) used to define the RCP scenarios, thin lines show results from CMIP5 ESMs. Bottom: cumulative emissions for the historical period (1860–2005) and 21st century (defined in CMIP5 as 2006–2100) for historical estimates and RCP scenarios (bars) and ESMs (symbols). In the CMIP5 model results, total carbon in the land-atmosphere-ocean system can be tracked and changes in this total must equal fossil fuel emissions to the system (see also Table 6.13). Other sources and sinks of CO₂ such as from volcanism, sedimentation or rock weathering, which are very small on centennial time scales are not considered here. Hence the compatible emissions are given by cumulative-Emissions = ΔC_A + ΔC_L + ΔC_O or emission rate = d/dt [C_A + C_L + C_O], where C_A, C_L, C_O are carbon stored in atmosphere, land and ocean respectively. Models used: CanESM2, GFDL-ESM2G, GFDL-ESM2M, HadGEM2-CC, HadGEM2-ES, IPSL-CM5A-LR, IPSL-CM5A-MR, IPSL-CM5B-LR, MIROC-ESM-CHEM, MIROC-ESM, MPI-ESM-LR, NorESM1-ME, Inmcm4, CESM1-BGC.

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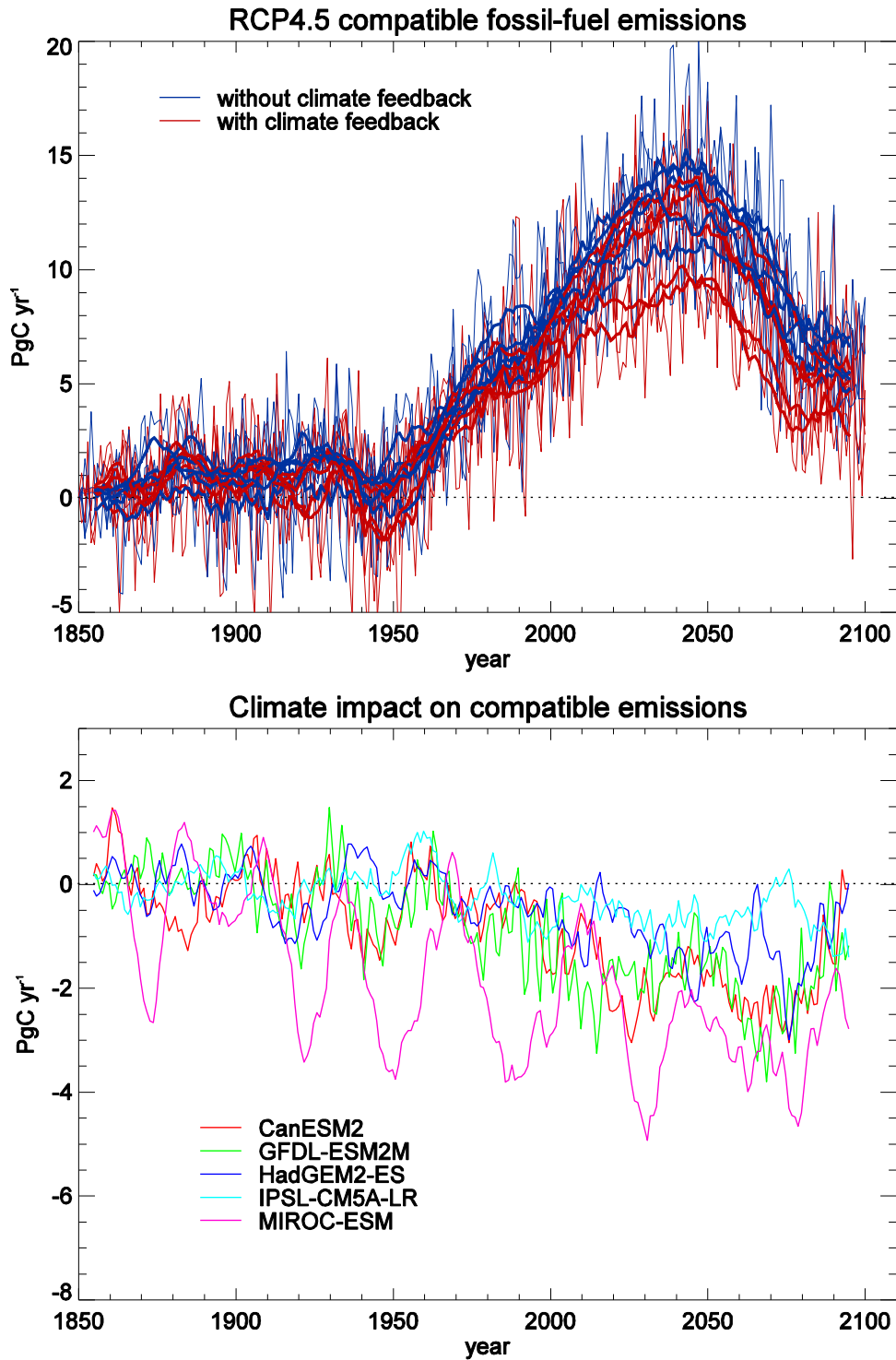
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Figure 6.26: changes in airborne, land and ocean fraction of fossil fuel carbon emissions. The fractions are defined as the changes in storage in each component (atmosphere, land, ocean) divided by the compatible fossil fuel emissions derived from each CMIP5 simulation for the 4 RCP scenarios. Solid circles show the observed estimate based on Table 6.11 for the 1990s. The coloured lines and symbols denote the change in uptake fractions under the different RCP scenarios for each model, calculated using the cumulative change in carbon from 2005 to 2100. Multi-model mean values are shown as star symbols and the multi-model range (min-to-max) is shown by the vertical coloured lines. Due to the difficulty of estimating fossil and land use emissions from the ESMs this figure uses a fossil fuel definition of airborne fraction, rather than the preferred definition of fossil + land use emissions discussed in Section 6.3. 21st century cumulative airborne, land and ocean fractions are shown here in preference to the more commonly shown instantaneous fractions because for RCP2.6 emissions reach and cross zero and so an instantaneous definition of AF becomes singular at that point. Models used: CanESM2, GFDL-ESM2G, GFDL-ESM2M, HadGEM2-CC, HadGEM2-ES, IPSL-CM5A-LR, IPSL-CM5A-MR, IPSL-CM5B-LR, MIROC-ESM-CHEM, MIROC-ESM, MPI-ESM-LR, NorESM1-ME, Inmcm4, CESM1-BGC.

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Figure 6.27: Diagnosed compatible fossil fuel emissions (top panel) in the presence (red lines) and absence (blue lines) of the climate impact on the carbon cycle for the RCP4.5 scenario, and the difference between them (bottom panel). Thin lines show annual values and thick lines 10-year smoothed values. This shows the impact of climate change on the compatible fossil fuel CO₂ emissions to achieve the RCP4.5 CO₂ concentration pathway. Models used: CanESM2, GFDL-ESM2M, HadGEM2-ES, IPSL-CM5A-LR and MIROC-ESM.

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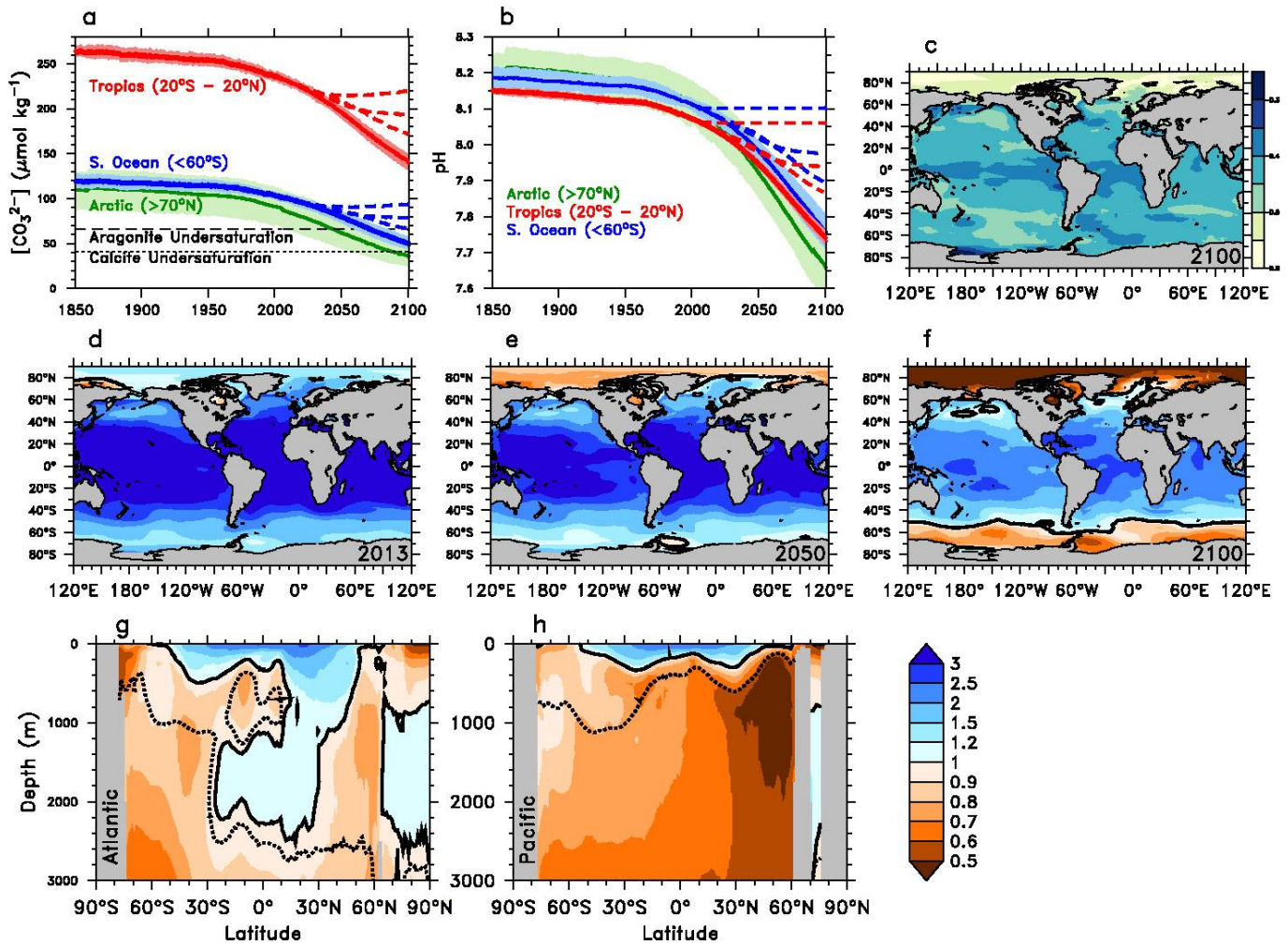
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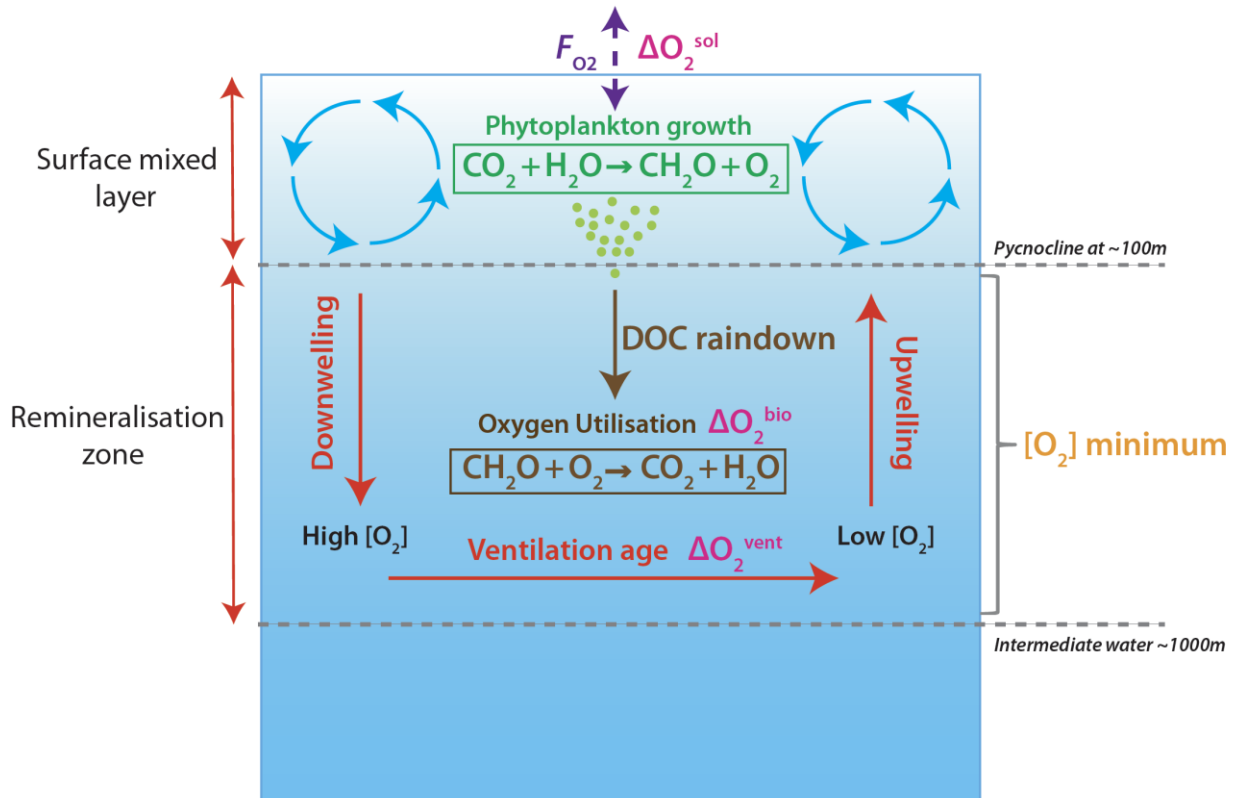


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4 **Figure 6.28:** Projected ocean acidification from 12 CMIP5 earth system models under the RCP8.5 scenario: time series
 5 of surface (a) carbonate ion concentration and (b) pH shown as the mean (solid line) and range of models (filled), given
 6 as area-weighted averages over the Arctic Ocean (green), the tropical oceans (red), and the Southern Ocean (blue);
 7 maps of the median model's (c) change in surface pH from 1850 to 2100 and its surface Ω_A in (d) 2013, (e) 2050, and
 8 (f) 2100; and zonal mean sections (latitude vs. depth) of Ω_A in 2100 over the (g) Atlantic and (h) Pacific, while the ASH
 9 is shown in 2013 (dotted line) as well as 2100 (solid line). Panels (a) and (b) also include mean model results from three
 10 other scenarios: RCP2.6, RCP4.5, and RCP6.0 (dashed lines). Over most of the ocean, gridded data products of
 11 carbonate system variables (Key et al., 2004) are used to correct each model for its present-day bias by subtracting the
 12 model-data difference at each grid cell following (Orr et al., 2005). Where gridded data products are unavailable (Arctic
 13 Ocean, all marginal seas, and the ocean near Indonesia), results are shown without bias correction. The bias correction
 14 reduces the range of model projections by up to a factor of 4, e.g., in panels (a) and (b) compare the large range of
 15 model projections for the Arctic (without bias correction) to the smaller range in the Southern Ocean (with bias
 16 correction).
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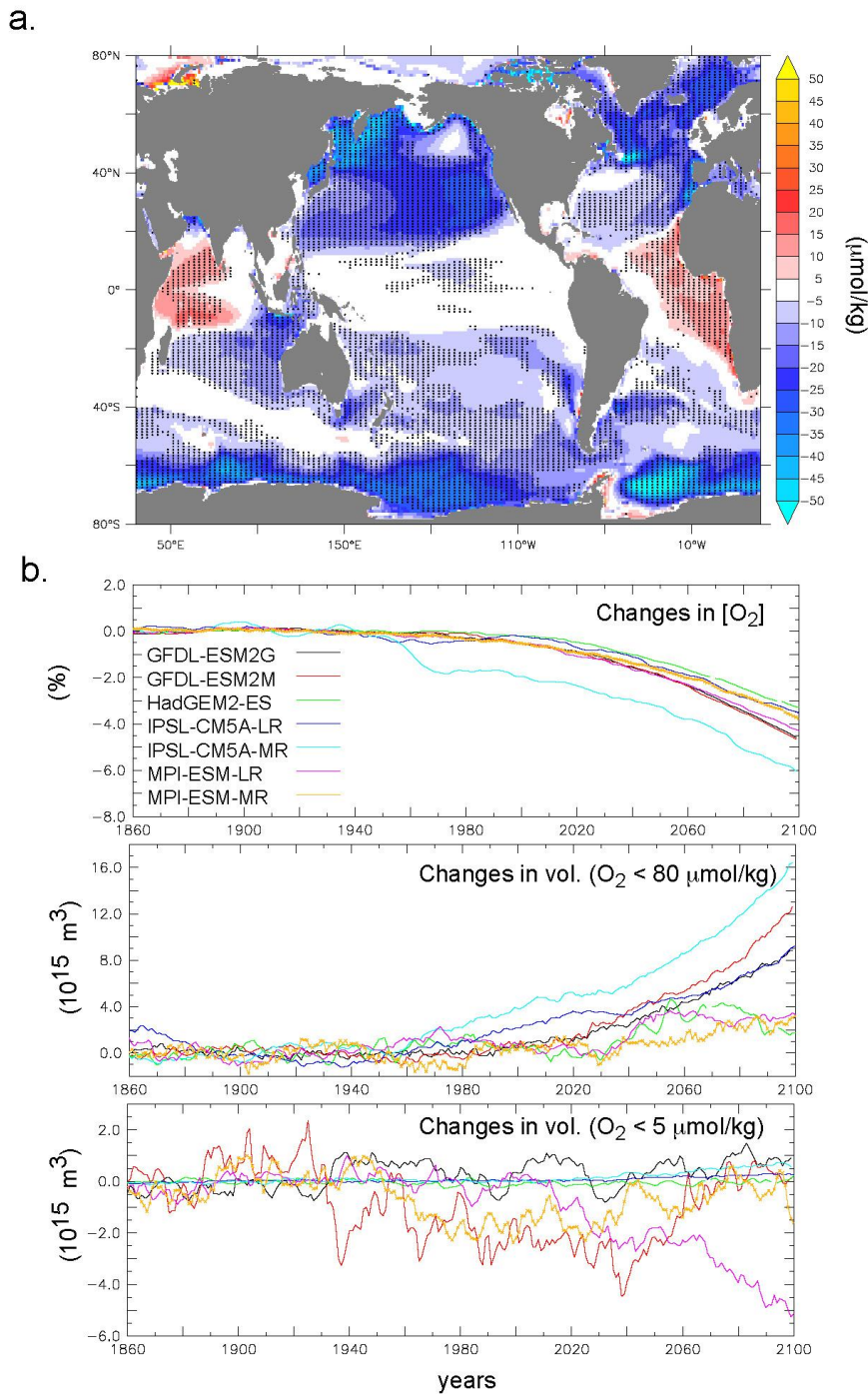
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Box 6.5, Figure 1: The ocean O_2 cycle. The oceanic reservoir of oxygen communicates with the atmosphere via air-sea gas exchange (F_{O_2}). In the ocean interior, a change in dissolved O_2 concentration over time can be driven by changes in: (1) surface ocean O_2 solubility ΔO_2^{sol} , (2) the ventilation age of a water parcel advected into the subsurface (ΔO_2^{vent}) (3) biological utilisation of oxygen in remineralization of Dissolved Organic Carbon (DOC; ΔO_2^{bio}).

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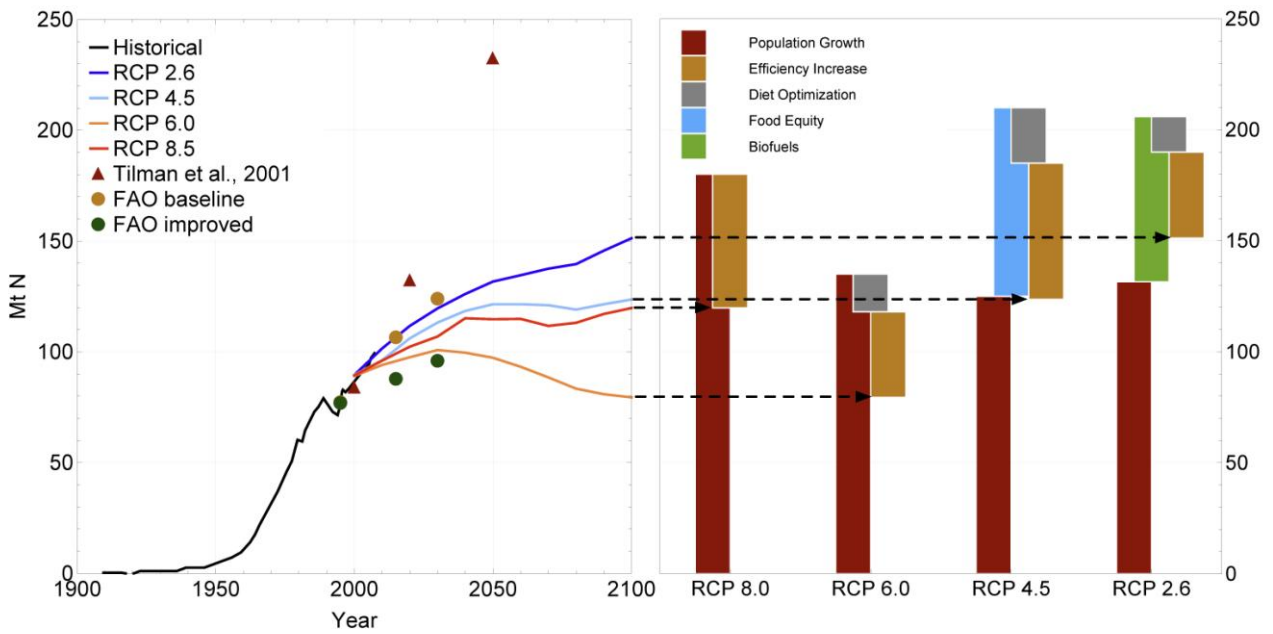
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Figure 6.29: (a) Multi-model mean projected changes in dissolved O₂ (µmol kg⁻¹ in the main thermocline (100–600 m depth average) from 1995–2005 to 2090–2100 under the RCP8.5 scenario. To indicate consistency in the sign of change, regions are stippled where at least 80% of models agree on the sign of the mean change. (b) Modelled evolution from 1850 to 2100 (under RCP8.5 scenario) of the relative change in global mean O₂ concentration, as well as of volume anomalies of hypoxic (O₂ < 80 µmol kg⁻¹) and suboxic (O₂ < 5 µmol kg⁻¹) waters. These diagnostics are detailed in Cocco et al. (subm.) in a previous model intercomparison using the SRES-A2 scenario and have been applied to CMIP5 models under RCP8.5 here. Models used: GFDL-ESM2G, GFDL-ESM2M, HadGEM2-ES, IPSL-CM5A-LR, IPSL-CM5A-MR, MPI-ESM-LR, MPI-ESM-MR.

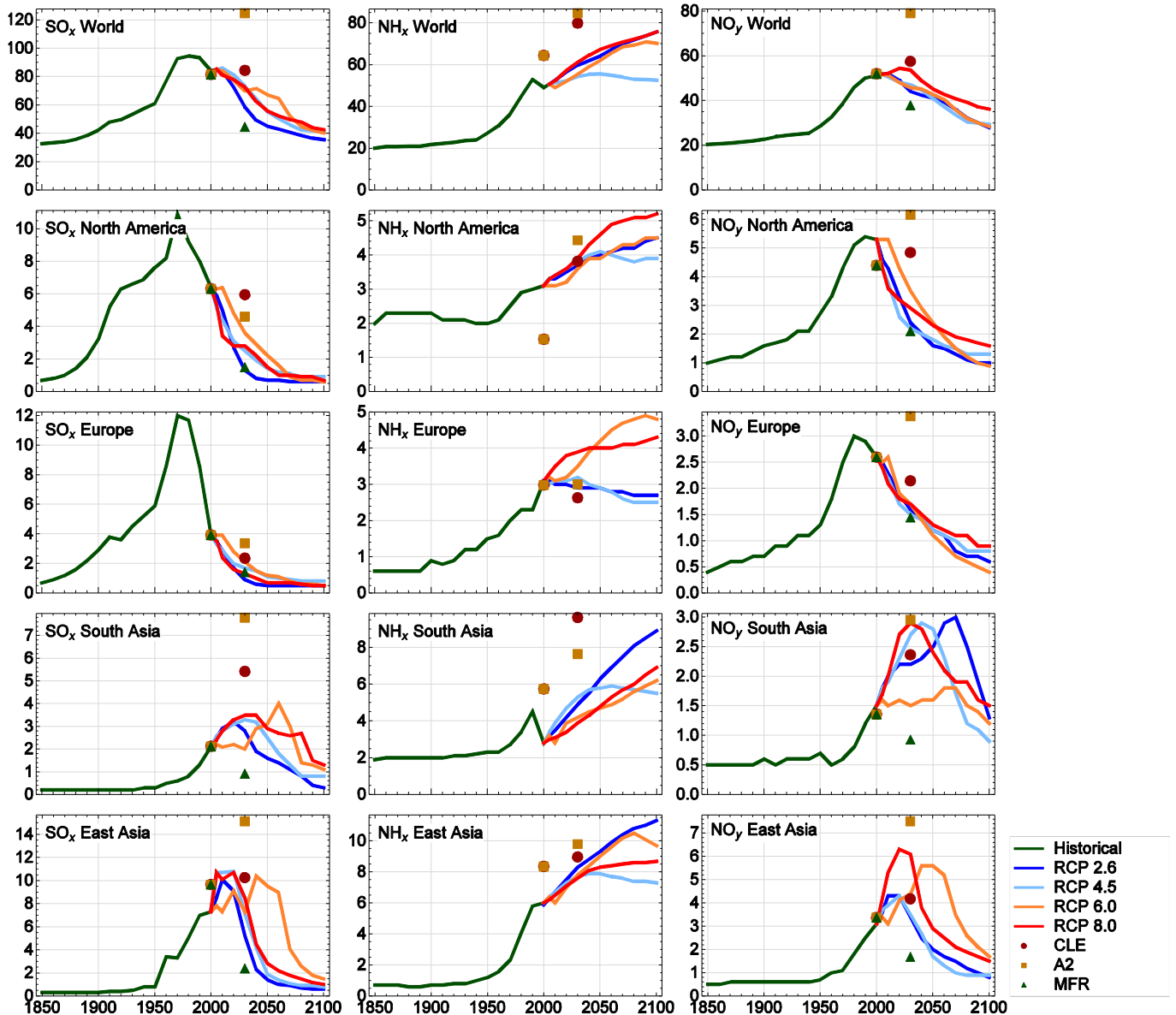
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Figure 6.30: Global fertilizer Nr fixation (TgN yr⁻¹) derived as fertilizer demand, projected till 2100. Lines in the left panel reflect trends based on drivers from the RCP scenarios, dots different independent assessment. The asterisks report the ranges of two different interpretations of the SRES scenarios, with Erisman et al. (2008) using a methodology very similar to the one used for RCPs (Winiwarter et al., subm.).

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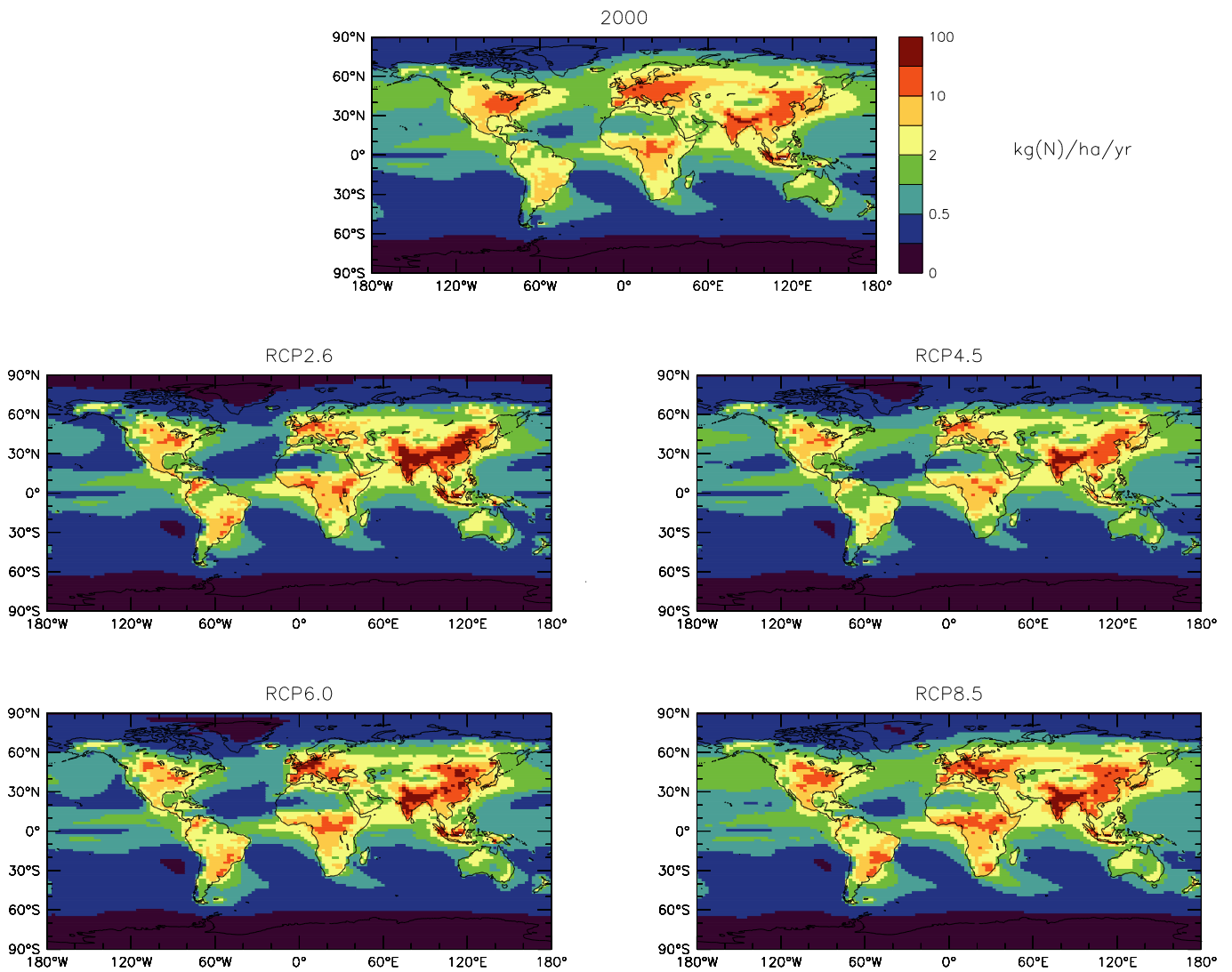
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4 **Figure 6.31:** Deposition of SO_x (left panel, TgS yr⁻¹), NH_x (middle panel, TgN yr⁻¹) and NO_y (right panel, TgN yr⁻¹)
 5 from 1850 to 2000 and projections of deposition to 2100 under the four RCP emission scenarios (Lamarque et al., 2011;
 6 van Vuuren et al., 2011). Also shown are the 2030 scenarios using the SRES B1/A2 energy scenario with assumed
 7 current legislation and maximum technically feasible air pollutant reduction controls (Dentener et al., 2006).

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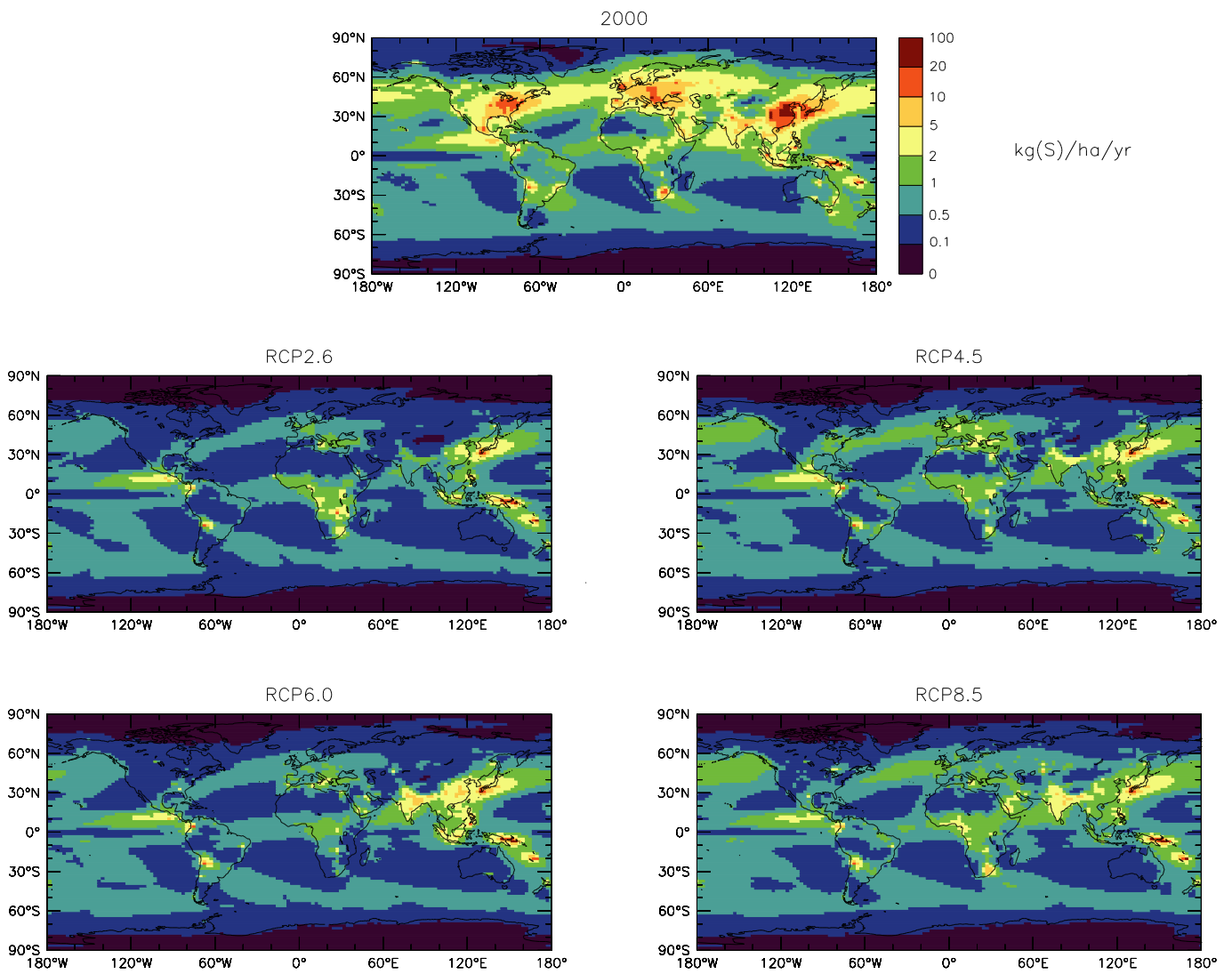
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Figure 6.32: Spatial variability of N deposition in 2000 with projections for 2100, using the 2.6, 4.5, 6.0 and 8.5 RCP scenarios, kg N ha⁻¹ yr⁻¹ adapted from (Lamarque et al., 2011).

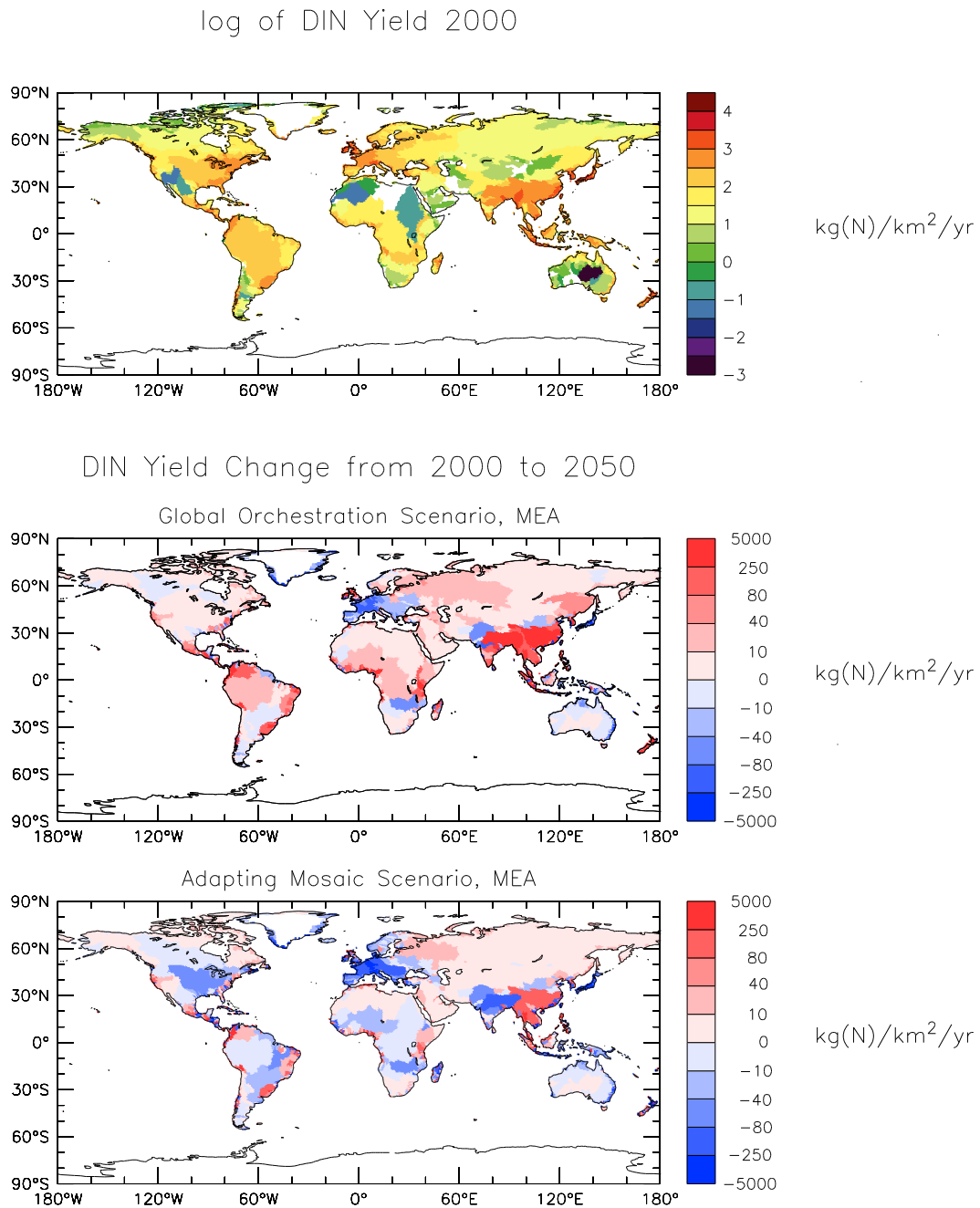
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Figure 6.33: Spatial variability of S deposition in 2000 with projections for 2100, using the 2.6, 4.5, 6.0 and 8.5 RCP scenarios, kg S ha⁻¹ yr⁻¹ (Lamarque et al., 2011).

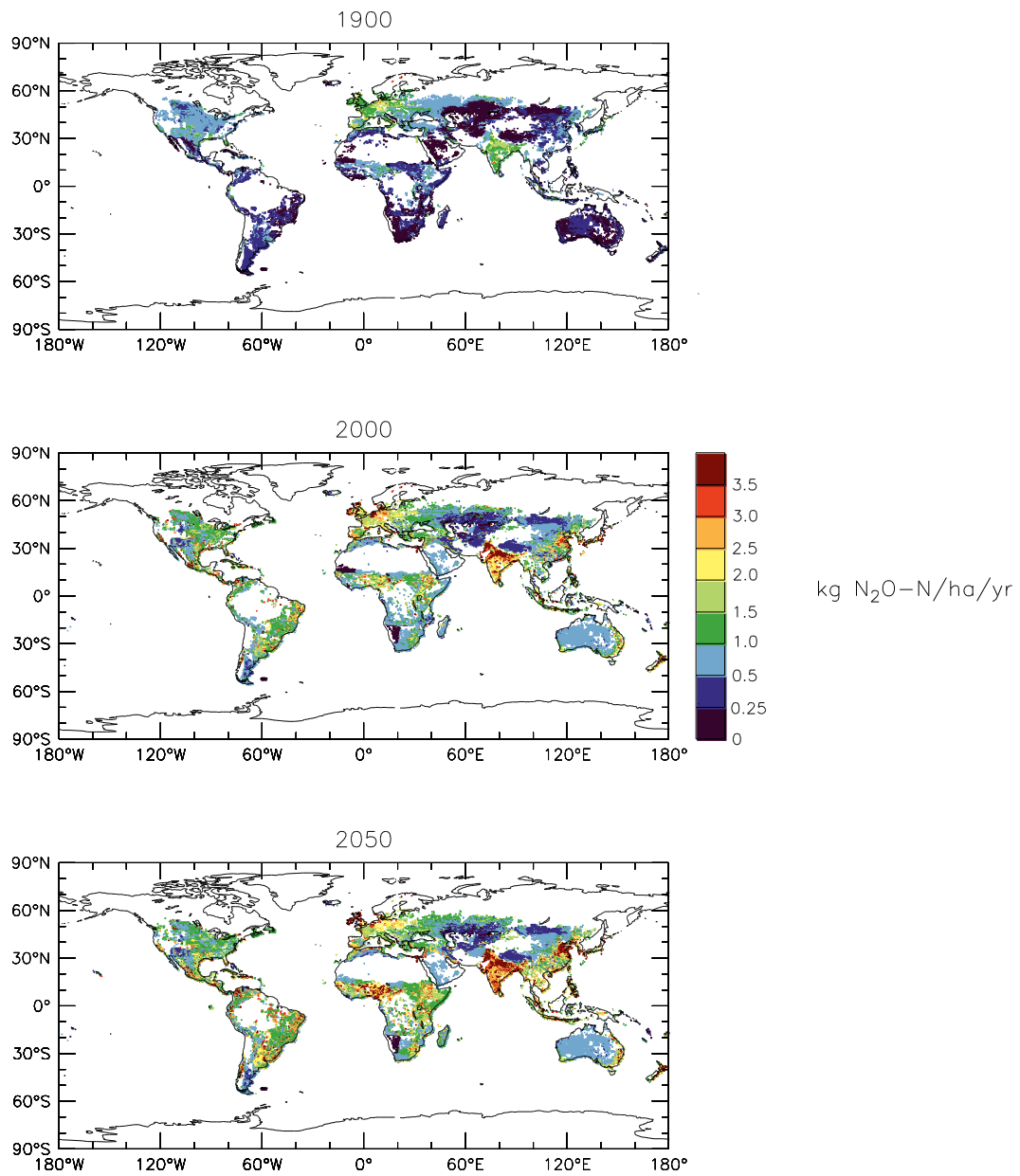
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Figure 6.34: (a) Dissolved inorganic nitrogen river discharge to coastal zone (mouth of rivers) in 2000, based up on Global NEWS 2 model, (b) change in DIN discharge from 2000 to 2050, based upon Global Orchestration and the Adapting Mosaic scenarios, Millennium Ecosystem Assessment (Mayorga et al., 2010; Seitzinger et al., 2010). Units are kg N per km² watershed per year, as an average for each watershed.

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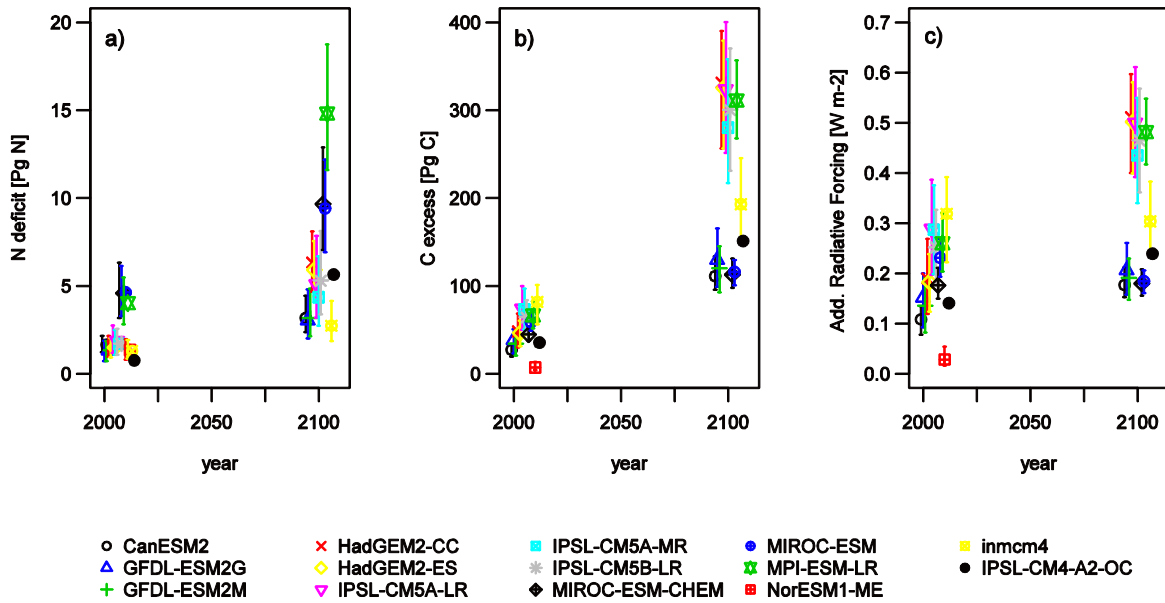
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Figure 6.35: N₂O emissions in 1900, 2000 and projected to 2050 (Bouwman et al., 2011a).

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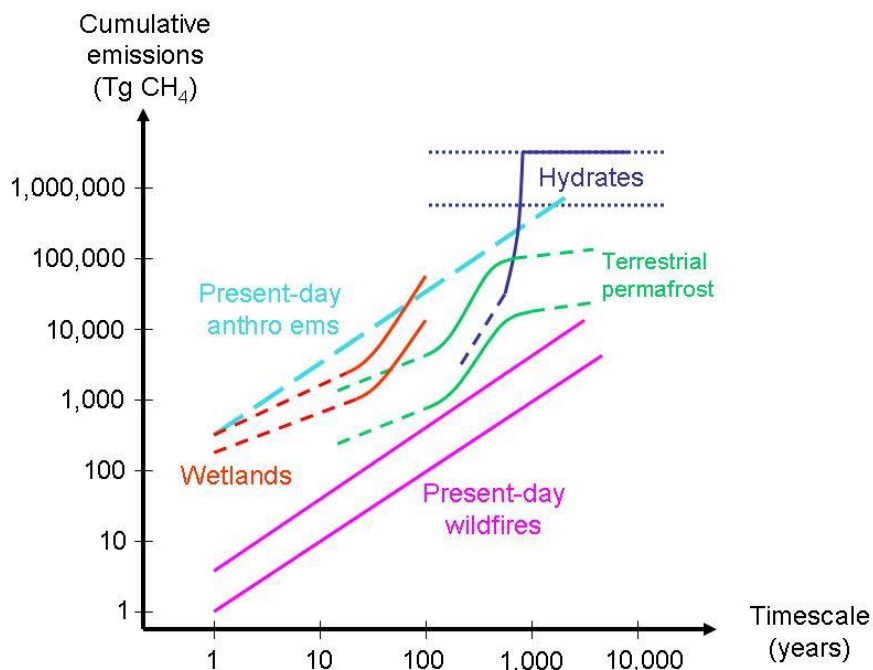
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Figure 6.36: (a) Implied global terrestrial nitrogen deficit of the RCP8.5 carbon sequestration projections; (b) implied overestimation of terrestrial C sequestration due to neglecting N limitations; (c) Additional radiative forcing resulting from the nitrogen limitation of terrestrial C sequestration. The N deficit was calculated as follows: The simulated increase in terrestrial C stocks were converted into N requirements as described by Wang and Houlton (2009). The yearly evolution of the nitrogen requirements were compared on a model grid-cell bases against the newly available nitrogen due to changes in biological nitrogen fixation and atmospheric deposition. The error bars represent the range of results obtained using alternative assumption about terrestrial C:N stoichiometry, N retention from N deposition and changes in fixation. Values are presented for the year 2005 and 2100 and displaced in time for clearer visibility. Radiative forcing was calculated using the formulation of Ramaswamy et al. (2001), assuming an air-borne fraction of 0.6, and are evaluated as change in atmospheric CO₂ burden against the RCP8.5 scenario abundances in 2005 (377 ppm) and 2100 (935 ppm). The panels also show simulations of the IPSL-CM4-A2-OC model (Zaehle et al., 2010a), driven with the SRES-A2 scenario projections of the IPSL-CM4 model for which both a C-cycle only and dynamically coupled C-N cycle simulation are available, and for which the N deficit of the C-cycle model can therefore be determined explicitly.

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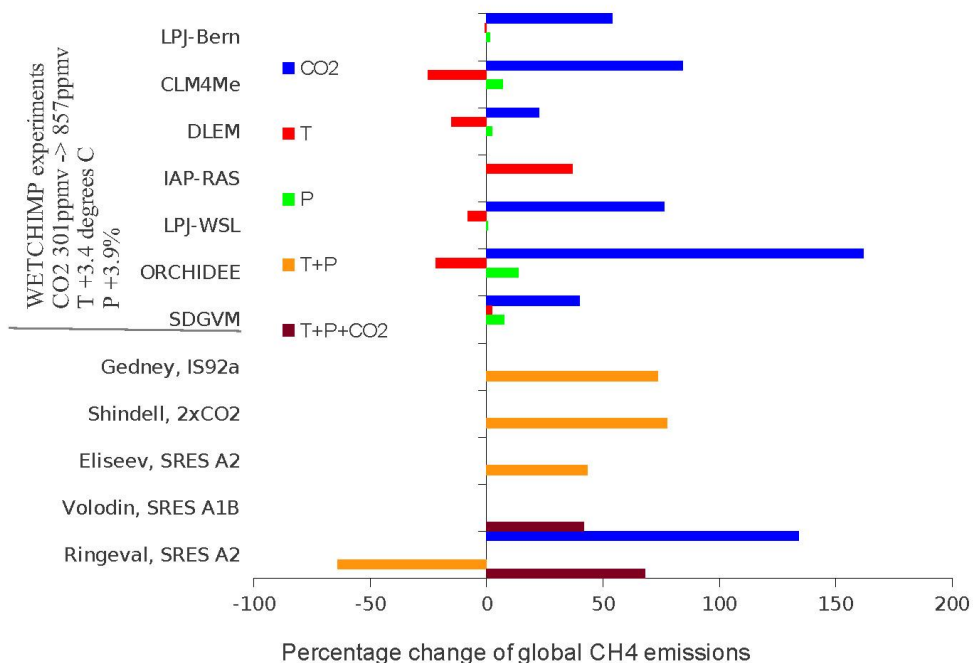
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Figure 6.37: Summary of the sizes and time scales associated with future CH₄ emissions (adapted from O’Connor et al., 2010). Uncertainty in these future changes is large, and so this figure demonstrates the relative magnitude of possible future changes. Anthropogenic emissions continuing at a present day level of 300 Tg(CH₄) yr⁻¹ (consistent with Table 6.7) are shown for reference. Wetland emissions are taken as 140–280 Tg(CH₄) yr⁻¹ present day values (Table 6.7) and increasing by between 0–100% (Section 6.4.7.1; Figure 6.38). Permafrost emissions may become important during the 21st century. Large CH₄ hydrate release to the atmosphere is not expected during the 21st century. No quantitative estimates of future changes in CH₄ emissions from wildfires exist, so plotted here are continued present day emissions of 1–4 Tg(CH₄) yr⁻¹ (Table 6.7).

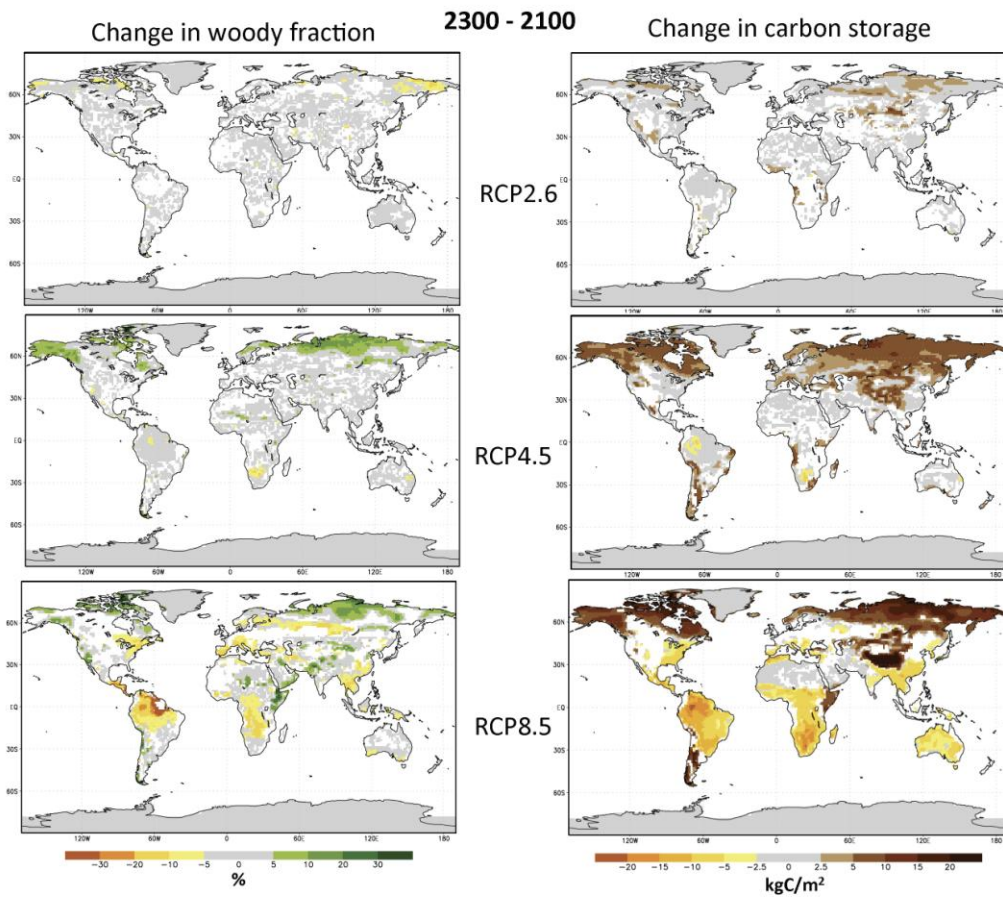
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Figure 6.38: Relative changes of global CH₄ emissions from either pre-industrial or present day conditions and environmental changes that reflect potential conditions in 2100. The first seven models took part in the WETCHIMP intercomparison project and were run under a common protocol (Melton et al., *subm.*). Other studies used different future conditions as listed in the figure: Eliseev et al. (2008), Gedney et al. (2004), Ringeval et al. (2011), Shindell et al. (2004), Volodin (2008).

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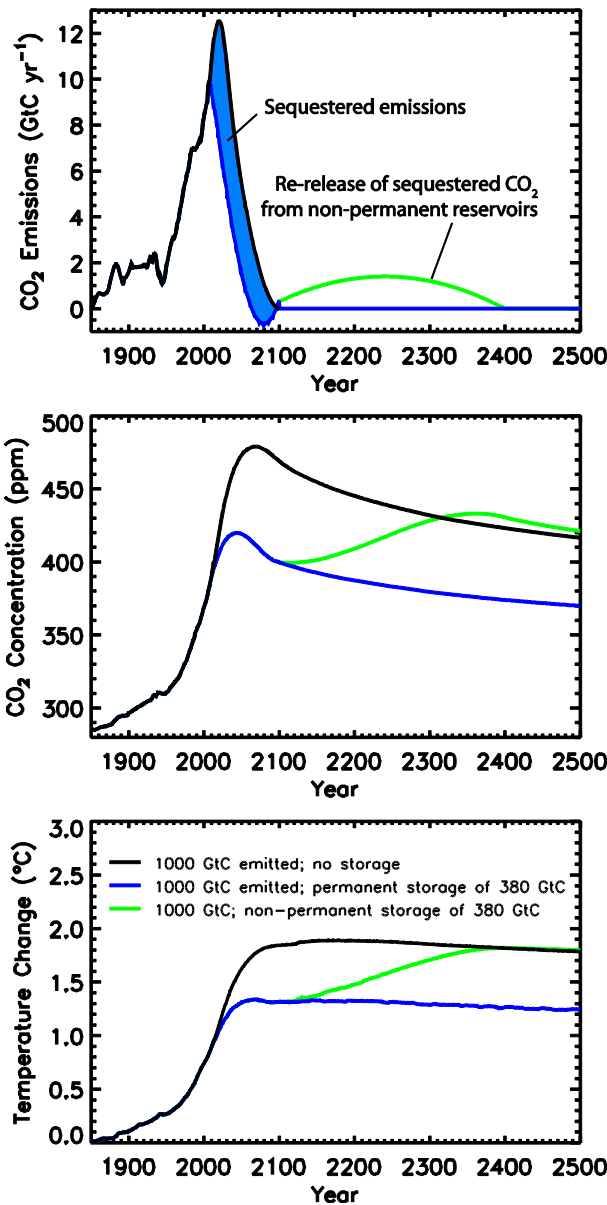
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3 **Figure 6.39:** Maps of changes in woody cover fraction, %, (left) and terrestrial carbon storage, kg C m^{-2} , (right) for
 4 three RCP extension scenarios 2.6 (top), 4.5 (middle), and 8.5 (bottom) between years 2100 and 2300 averaged for two
 5 models, HadGEM2-ES and MPI-ESM, which simulate vegetation dynamics. Model results were interpolated on $1^\circ \times 1^\circ$
 6 grid; white colour indicate areas where models disagree in sign of changes. Note the RCP6.0 extension was not a
 7 CMIP5 required simulation. Anthropogenic land use in these extension scenarios is kept constant at 2100 levels, so
 8 these results show the response of natural ecosystems to the climate change.

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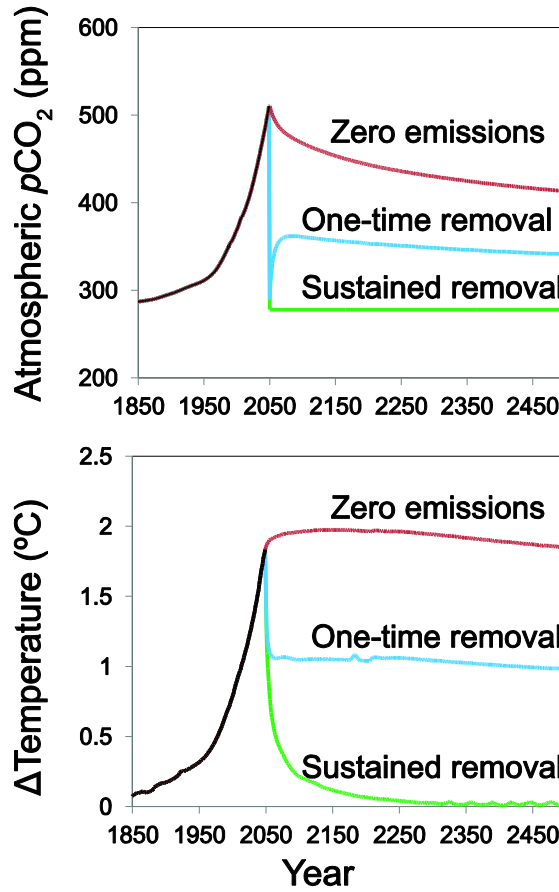
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Figure 6.40: Idealized model simulations (Matthews, 2010) to illustrate the effects of CDR methods associated respectively with either permanent or non-permanent carbon sequestration after CO₂ is removed from the atmosphere. There is an emission of 1000 PgC in the reference case (black line) between 1800 and 2100. Permanent sequestration of the additional emitted CO₂ of 380 PgC, assuming no leakage of sequestered carbon, has the potential to reduce the radiative forcing of CO₂ and to mitigate climate change (blue line, compared to black line). By contrast, the green line shows an idealized case of a non permanent sequestration CDR method where, after CO₂ removal from the atmosphere, carbon will be sequestered in a non-permanent reservoir, in such a manner that all of the sequestered carbon will get returned as CO₂ back to the atmosphere over three centuries. In this non-permanent sequestration case, climate change would only be only delayed whereas the eventual magnitude of climate change will be equivalent to the no-sequestration case (green line, compared to black). Figure adapted from Figure 5 of Matthews (2010).

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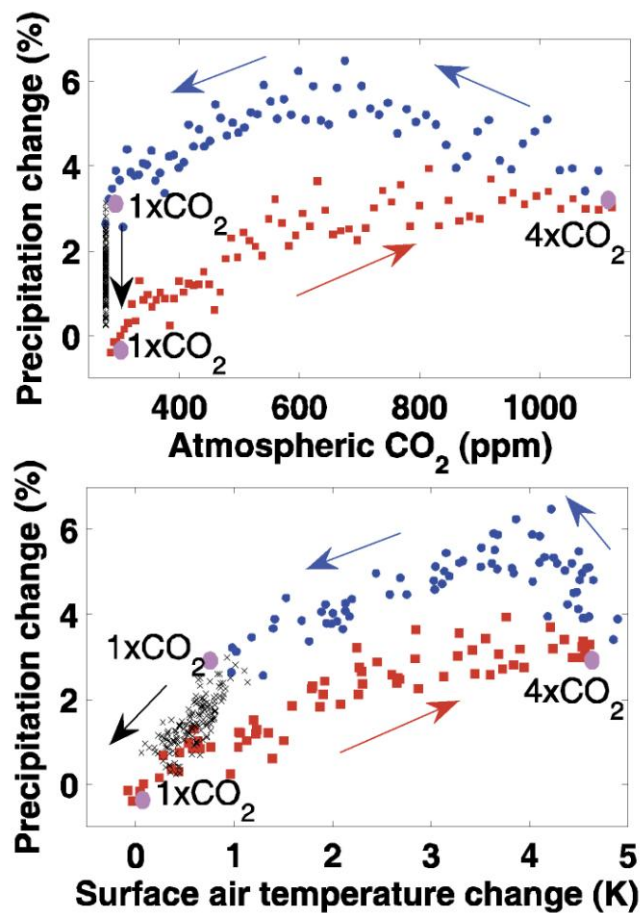
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Figure 6.41: Idealized simulations with a simple global carbon cycle model (Cao and Caldeira, 2010b) to illustrate the ‘rebound effect’. Effects of an instantaneous cessation of CO₂ emissions (amber line), one-time removal of excess atmospheric CO₂ (blue line) and removal of excess atmospheric CO₂ followed by continued removal of CO₂ that degasses from the atmosphere and ocean (green line). To a first approximation, a cessation of emissions prevents further warming but does not lead to significant cooling on the century time scale. A one-time removal of excess atmospheric CO₂ eliminates approximately half of the warming experienced at the time of the removal. To cool the planet back to pre-industrial levels would require the removal of all previously emitted CO₂, i.e., an amount equivalent to approximately twice the amount of excess CO₂ in the atmosphere above pre-industrial level. Simulations were started in 1800 but results are shown from 1850. Figure adapted from Cao and Caldeira (2010b).

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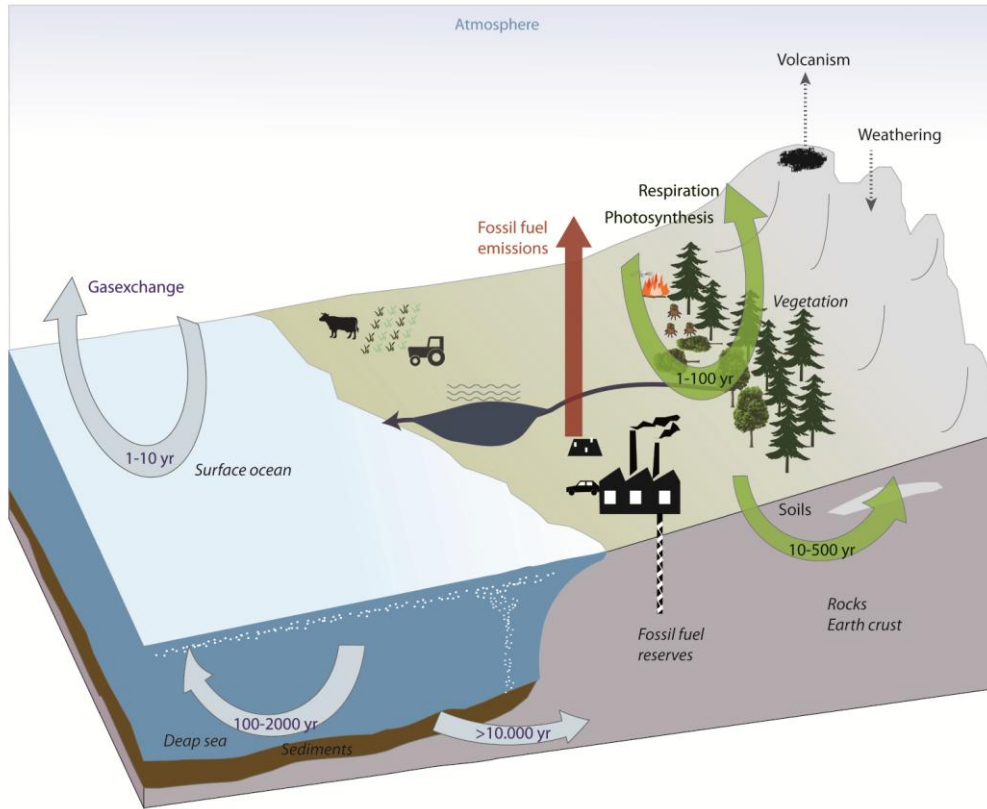
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4 **Figure 6.42:** HadCM3L results from an idealized simulation (Cao et al., 2011) with 2% annual change in atmospheric
 5 CO₂: (a) global and annual mean changes in precipitation as a function of atmospheric CO₂; (b) global and annual mean
 6 changes in precipitation as a function of global and annual mean changes in surface temperature. Red dots represent the
 7 first 70-year simulation phase with 2% annual CO₂ increase (ramp_up) and time moves forward from the lower left to
 8 the upper right. Blue dots represent the subsequent 70-year period with 2% annual CO₂ decrease (ramp_down) and time
 9 moves forward from the upper right to the lower left. Black dots represent the following 150-years with the constant
 10 control CO₂ concentration and time moves forward from the upper right to the lower left. The simulation states when
 11 atmospheric CO₂ reaches 1 × CO₂ and 4 × CO₂ concentrations are marked with pink circles. Due to the ocean thermal
 12 inertia one atmospheric CO₂ state corresponds to two different states of temperature and precipitation, and due to the
 13 precipitation sensitivity to atmospheric CO₂ content changes (Bala et al., 2009), one temperature state corresponds to
 14 two different precipitation states. Figure adopted from Cao et al. (2011).

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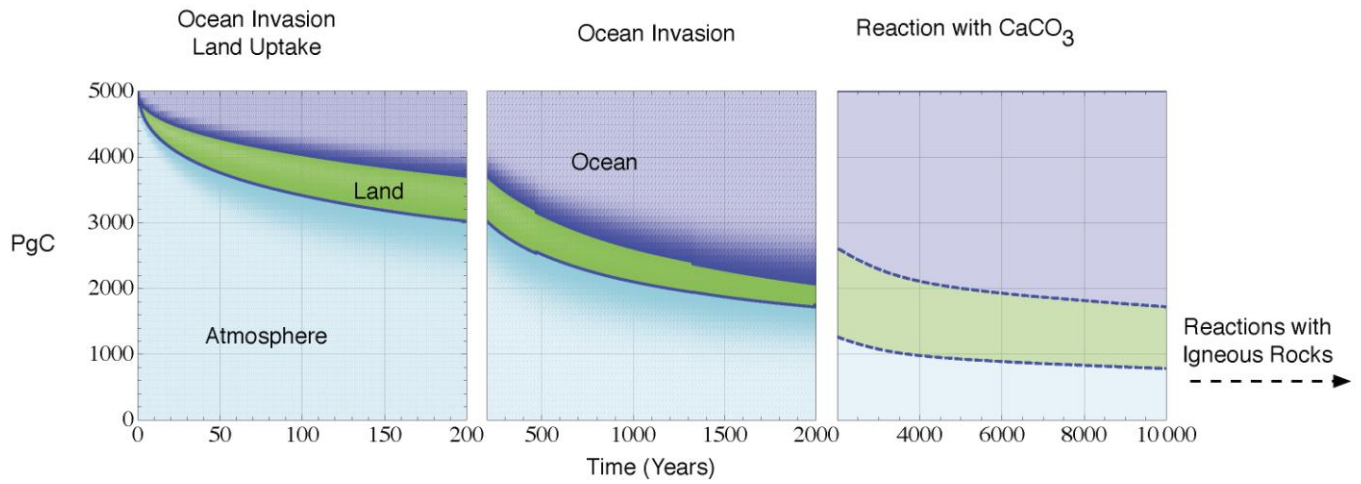
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FAQ 6.1, Figure 1: Simplified schematic of the global carbon cycle showing the typical turnover time scales for carbon transfers through the major reservoirs.

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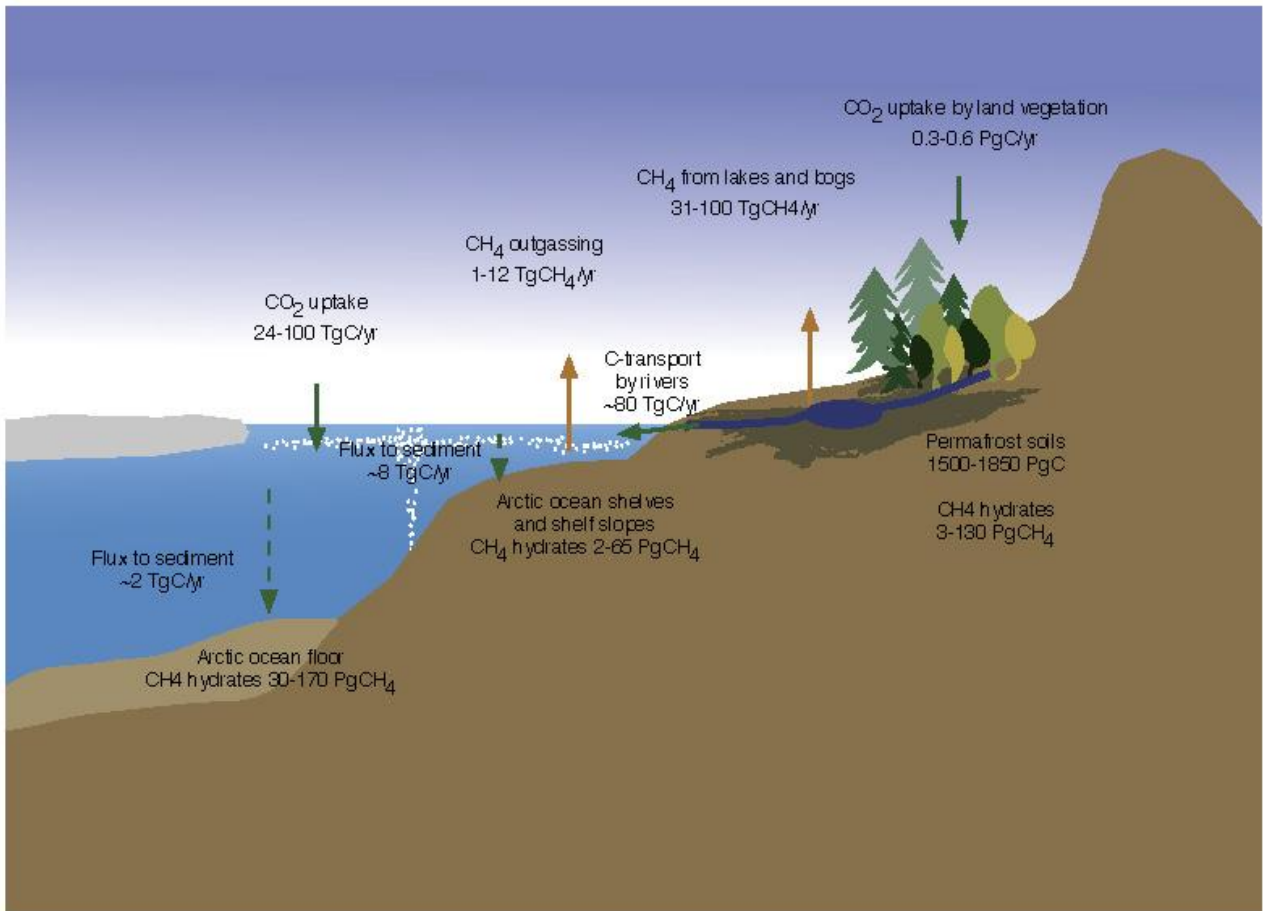
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FAQ 6.1, Figure 2: Decay of a CO₂ excess amount of 5000 PgC emitted at time zero into the atmosphere, and its subsequent redistribution into land and ocean as a function of time, computed by coupled carbon–cycle climate models. The size of the colour bands indicate the carbon uptake by the respective reservoir. The first two panels show the multi-model mean from a model intercomparison project (Joos et al., submitted). The last panel shows the longer term redistribution including ocean dissolution of carbonaceous sediments as computed by the CLIMBER-2 model (after Archer et al, 2009b).

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FAQ 6.2, Figure 1: A simplified graph of current major carbon pools and flows in the Arctic domain, including permafrost on land, continental shelves and ocean (adapted from McGuire et al. (2009) and Tarnocai et al. (2009)). TgC = 10^{12} gC, and PgC = 10^{15} gC.