# Chapter 2

# The carbon cycle

# 2.1 Introduction

 $CO_2$  is increasing in the atmosphere. This can be seen in the record of continuous atmospheric measurements started by C. D. Keeling at Mauna Loa, Hawaii in 1958 (Figure 2.1, solid line). The annual oscillations in  $CO_2$  are due to seasonal variations in uptake and release of carbon by the terrestrial biosphere. The trend is mostly caused by fossil fuel emissions, but is less than would be expected if all fossil fuel  $CO_2$  remained in the atmosphere. The dashed line in Figure 2.1 predicts how atmospheric  $CO_2$  would have increased from 1959 if all fossil fuel  $CO_2$  had remained in the atmosphere, using current best estimates of the fossil fuel source (Marland et al., 1999). Changes in land-use (mainly deforestation) have also caused significant  $CO_2$  input to the atmosphere. The major question in carbon cycle research involves understanding the fate of anthropogenic  $CO_2$ . This requires some knowledge of the natural carbon cycle as well as how human activities have altered it.

On time scales of up to centuries, the main reservoirs involved in the carbon cycle are the atmosphere, the terrestrial biosphere and the oceans. The amount of carbon in each reservoir and the fluxes between them are important quantities, and the best estimates of their values for the period 1980–1989 are shown in Figure 2.2 (IPCC, 1995). The atmosphere currently contains about 750 GtC (1 GtC =  $10^{12}$  kg carbon), the surface ocean about 1020 GtC and the deep ocean about 39,000 GtC. The terrestrial biosphere contains about 2190 GtC, of which about 610 GtC is living vegetation and about 1580 GtC is in the top 1 m of soil (Schimel et al., 1995). There are large, natural fluxes of carbon between the atmosphere and ocean and the atmosphere and biosphere. These gross fluxes arise, for example, due to thermodynamic exchange of molecules across the air-sea interface, or



Figure 2.1: Solid line shows the Mauna Loa  $CO_2$  record (Keeling and Whorf, 1998). Dashed line shows how  $CO_2$  would have increased from 1959 if all fossil fuel  $CO_2$  (Marland et al., 1999) had remained in the atmosphere.

photosynthesis and respiration by plants, and are about 50-100 GtC  $yr^{-1}$  into and out of each reservoir. The gross fluxes for each reservoir are close to balanced, with the difference being the *net flux*. The net uptake of anthropogenic carbon by the ocean and biosphere for 1980–1989 is estimated by IPCC (1995) as 2 GtC  $yr^{-1}$  and 1.4 GtC  $yr^{-1}$ , respectively. There is also believed to be a natural flux of carbon from the biosphere to the oceans via rivers (not shown in Figure 2.2), estimated at 0.3–0.5 GtC  $yr^{-1}$  (Sarmiento and Sundquist, 1992).

Methods that have been used to try to better understand the carbon cycle include analysis of the spatial distribution of  $CO_2$  in the atmosphere, budgeting with the time rate of change of atmospheric  $CO_2$ , calculation of ocean uptake using ocean carbon cycle models (which are often calibrated with <sup>14</sup>C) and the use of atmospheric <sup>13</sup>C or  $O_2$  with  $CO_2$  to partition uptake into oceanic and biospheric components. Generally combinations of these methods are used.

The first half of this chapter provides background information on the carbon cycle, with discussion of the 3 main reservoirs of carbon (the atmosphere, the terrestrial biosphere and the oceans) and a description of some of the methods used to study the carbon cycle. Proportionally more detail is given on the use of  $^{13}$ C, as this is a major focus of the thesis. The second half of the chapter focuses on CO<sub>2</sub> and  $^{13}$ C over the last 1000 years. Records of CO<sub>2</sub> and  $^{13}$ C from ice cores are described in detail. The forcing mechanisms that are



Figure 2.2: The global carbon cycle from IPCC (1995). Estimates of the reservoir sizes in GtC and the magnitudes of the fluxes for 1980–1989 in GtC  $y^{-1}$  are shown.

responsible for variations in  $CO_2$  over the last 1000 years are discussed. This is followed by discussion of the methods generally used to interpret  $CO_2$  on time scales of decades to centuries, and some previous results.

### 2.2 The atmosphere

Figure 2.3 shows the variation of atmospheric  $CO_2$  with time and latitude at the earth's surface. This diagram is often referred to as the 'CO<sub>2</sub> flying carpet', and is constructed by interpolating and smoothing measurements made at between 30 and 100 observing sites around the world (Conway et al., 1994; K. Masarie, NOAA CMDL Carbon Cycle Group, pers. comm., 1999). The flying carpet shows a number of the important features in the variation of atmospheric  $CO_2$ . The seasonal cycle is strongest in the northern hemisphere where there is a higher proportion of land. The seasonal cycle in the southern hemisphere is due to both the southern hemisphere biosphere and transport of  $CO_2$  from the northern hemisphere hemisphere (Pearman and Hyson, 1986; Enting et al., pers. comm.). The annual mean

level of  $CO_2$  in the northern hemisphere is higher than that in the southern hemisphere because the majority of the fossil fuel source is emitted in the northern hemisphere. The difference between the annual mean concentration at high northern and high southern latitudes is about 3–4 ppmv (parts per million by volume) (Conway et al., 1994). The mean growth rate of concentration was about 1.4 ppmv yr<sup>-1</sup> between 1981 and 1992, although the growth rate for individual years varied between about 0.4 and 2.6 ppmv yr<sup>-1</sup> (Conway et al., 1994). Interannual variation in  $CO_2$  concentration and growth rates is an important feature of the carbon cycle.

 $CO_2$  is fairly well mixed in the atmosphere. The interhemispheric exchange time is about 1–1.5 years (Law et al., 1996). Atmospheric transport is very important for short term variations or spatial patterns of  $CO_2$ , but on longer time scales the atmosphere can be considered for most purposes to be well mixed. Prior to direct atmospheric measurements, the best information on  $CO_2$  concentration levels in the atmosphere comes from ice core records. The pre-industrial  $CO_2$  level was about 280 ppmv (Figure 1.1), compared with the current level of around 360 ppmv.



Figure 2.3: 'CO<sub>2</sub> flying carpet' produced by the NOAA CMDL Carbon Cycle Group (Conway et al., 1994; K. Masarie, pers. comm., 1999).

### 2.3 The terrestrial biosphere

Plants absorb  $CO_2$  from the atmosphere through *photosynthesis*, using sunlight to make carbohydrates and  $O_2$  from atmospheric  $CO_2$  and water. The overall reaction is quite complicated and involves a number of steps, but the net effect can be written simply as

$$\mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} + h\nu \to \mathrm{CH}_2\mathrm{O} + \mathrm{O}_2. \tag{2.1}$$

(Schlesinger, 1997, p129). CO<sub>2</sub> diffuses inward, and O<sub>2</sub> and water outward, through openings in the leaves known as stomata. Photosynthesis can be limited by the availability of nutrients, and also by diffusion through stomata, which close to prevent water loss when water is limited. C<sub>3</sub> and C<sub>4</sub> plants conduct photosynthesis by different biochemical pathways. C<sub>3</sub> plants account for much of the plant biomass and are so named because the first product of the photosynthetic reaction is a carbohydrate containing three carbon atoms (Schlesinger, 1997). C<sub>4</sub> plants are largely warm-climate grasses and do not contribute to much of the global biomass because most species are not woody. The distinction between C<sub>3</sub> and C<sub>4</sub> plants is relevant to carbon cycle studies because of isotopic differences. The total amount of carbon fixed annually by photosynthesis is called *gross primary production* (GPP).

Plants respire carbon previously fixed to provide energy to maintain and synthesise their tissue. Respiration occurs all of the time, and dominates over photosynthesis at night and when the plant needs more metabolic energy than it can produce, such as in winter. Integrated over a year, the net amount of carbon fixed from  $CO_2$  by plants, taking into account plant respiration, is called *net primary production* (NPP)

$$NPP = GPP - R_P$$

where  $R_P$  is plant respiration. Typical estimates of global GPP and NPP are about 80-120 GtC yr<sup>-1</sup> and 45-65 GtC yr<sup>-1</sup> respectively. C<sub>4</sub> plants contribute perhaps about 20% of global NPP (Lloyd and Farquhar, 1994).

When plants or their leaves or branches die they usually fall to the ground and are broken down by bacteria and other micro-organisms. This respiration is called *heterotrophic* respiration, meaning that other organisms derive energy from it. (Plant respiration is referred to as *autotrophic* respiration.) In undisturbed, mature ecosystems the annual NPP is approximately equal to the annual total of heterotrophic respiration. This means that (at steady state) the annual growth of a plant in the ecosystem is balanced by the falling litter, so that the total biomass of the ecosystem remains constant. Disturbances such as fire may perturb this balance temporarily. The *net ecosystem production* (NEP) refers to the annual increase in the biomass of an ecosystem

$$NEP = NPP - R_H = GPP - R_P - R_H$$
(2.2)

where  $R_H$  is heterotrophic respiration.

The gross fluxes between the atmosphere and biosphere (GPP and  $R_P + R_H$ ) cause a significant seasonal cycle in CO<sub>2</sub> in the atmosphere, particularly in the northern hemisphere. At steady state these fluxes are approximately balanced over a year. The net uptake of anthropogenic carbon is due to a small imbalance between the fluxes. It has not really been practical to use the difference between the annual global gross fluxes or the change in global biospheric carbon inventory to estimate the global net uptake of CO<sub>2</sub> because the signals are very small, there is significant spatial and temporal variability and the gross fluxes are hard to estimate. There have, however, been recent attempts to work towards this for limited regions (e.g. inventory studies by Kauppi et al. (1992) and estimation of the annual flux imbalance from flux tower measurements in the Amazon by Malhi et al. (1998) and Grace et al. (1996)). Models of carbon cycling in the terrestrial biosphere range from simple, globally-aggregated box models (e.g. Harvey, 1989) to very complex models that take into account the spatial distribution of different vegetation types around the world (e.g. Potter et al., 1993).

Land-use change currently causes significant release of biospheric carbon to the atmosphere, mainly through deforestation (Houghton, 1995a; DeFries et al. 1999). In some cases land-use change can also cause some uptake of carbon due to forest regrowth, such as after abandonment of agriculture.

It is believed that photosynthesis can be stimulated by increased levels of atmospheric  $CO_2$  and/or 'useable' nitrogen, and that this causes a net uptake of  $CO_2$  by the biosphere (Wullschleger et al., 1995). These effects are known as  $CO_2$  and/or nitrogen *fertilisation*. They are confirmed by experiments on small-scale vegetation stands, but estimating the magnitude of the effect on a global scale, or how long it will last, is very difficult.

The terrestrial biosphere responds to variations in climate. In particular, temperature

and precipitation affect both photosynthesis and respiration. The different sensitivities of photosynthesis and respiration to climate variations cause year-to-year changes in the net flux. The effects of temperature and precipitation on small spatial scales are possible to measure, but on the global scale are complicated because both variations in climate and the biospheric response to climate vary spatially. Globally, respiration is more sensitive to temperature than NPP (J. Lloyd, pers. comm). It is believed that cooling due to the eruption of Mt Pinatubo in June 1991 may have caused an increase in terrestrial carbon storage and contributed to the observed reduction in the growth rate of atmospheric  $CO_2$  around 1991-2 (Sarmiento, 1993).

#### 2.4 The oceans

Carbon exists in a number of different forms in the ocean. About 95% is dissolved carbon in the form of bicarbonate  $(HCO_3^-)$  and carbonate  $(CO_3^{--})$  ions and less than 1% is dissolved  $CO_2$  gas. Dissolved  $CO_2$  gas in seawater hydrates to form carbonic acid  $(H_2CO_3)$ which dissociates to form hydrogen ions and bicarbonate ions. The bicarbonate further dissociates into hydrogen ions and carbonate ions (Najjar, 1992). The reaction

$$H_2O + CO_2 + CO_3^{--} \rightleftharpoons 2HCO_3^{-}$$
(2.3)

occurs continually in the ocean. A quantity used frequently to describe the amount of carbon dioxide in water is the total dissolved inorganic carbon, DIC or  $\Sigma CO_2$ , defined as

$$\Sigma CO_2 = [H_2 CO_3] + [HCO_3^-] + [CO_3^{--}]$$
(2.4)

The partial pressure of  $CO_2$  gas in water,  $pCO_2$ , is related to the total DIC by

$$pCO_2 = \frac{1}{\alpha K} \frac{(2\Sigma CO_2 - A)^2}{A - \Sigma CO_2}$$
(2.5)

(Broecker, 1974), where A is the alkalinity,  $\alpha$  is the solubility of CO<sub>2</sub> in sea water and

$$K = \frac{[\text{HCO}_3^-]^2}{[\text{H}_2\text{O}][\text{CO}_2][\text{CO}_3^{--}]}$$
(2.6)

is the equilibrium constant for the reaction given in (2.3). (More precise approximations for these quantities consider borate.) Both  $\alpha$  and K are temperature dependent, and as a result cold water is able to hold more CO<sub>2</sub> than warm water. The difference in partial pressure of  $CO_2$  across the air-sea interface,  $\Delta pCO_2$ , is one of the factors that determines the flux of  $CO_2$  between the atmosphere and the ocean. The gas transfer velocity, which depends on wind speed, is also an important factor (Wanninkhof and McGillis, 1999).

The chemical equilibrium between  $CO_2$ ,  $HCO_3^-$  and  $CO_3^{--}$  is such that when sea water takes up additional  $CO_2$ , the relative increase of  $pCO_2$  is about 10 times larger than that of  $\Sigma CO_2$  (Siegenthaler and Sarmiento, 1993). This is known as chemical *buffering*, and it partly controls the uptake capacity of the ocean. The *buffer factor*, or Revelle factor (Revelle and Suess, 1957), is defined as

$$\xi = \frac{\Delta p \mathrm{CO}_2 / p \mathrm{CO}_2}{\Delta \Sigma \mathrm{CO}_2 / \Sigma \mathrm{CO}_2} \tag{2.7}$$

where  $\Delta$  is a small change in either  $pCO_2$  or  $\Sigma CO_2$ . The value of the buffer factor,  $\xi$ , depends on temperature and  $\Sigma CO_2$  and to a much lesser extent salinity and alkalinity. It varies from about 9 to 14 for present surface ocean conditions, with an average of about 10 (Najjar, 1992).

Apart from dissolved inorganic carbon, carbon also exists in the ocean as dissolved organic carbon (DOC), particulate organic carbon (POC), particulate inorganic carbon (PIC) and living biomass (phytoplankton and zooplankton and other live forms). The estimated magnitudes of the different forms of carbon in the ocean are 38000, 950, 100, 30 and 3 GtC for DIC, DOC, PIC, POC and live carbon, respectively (Wong, 1997).

Circulation and biology in the ocean are very important for determining the distribution of carbon within the ocean and therefore the exchange between the ocean and the atmosphere. The surface ocean is separated from the intermediate and deep ocean by a layer of water whose density increases rapidly with depth due to changes in temperature and/or salinity. This layer (the *thermocline*) prevents exchange of water and  $CO_2$  between the surface layer, known as the *mixed layer*, and the rest of the ocean. The depth of the mixed layer varies from about 10-20 m in summer for polar and subpolar waters to 200-300 m for mid-latitude waters, with an average depth of about 75 m (Wong, 1997). The mixed layer is well mixed by turbulence, which is driven by atmospheric winds. The winds also drive large scale surface currents. Important features of the surface currents include great anticyclonic gyres thousands of kilometres in diameter in the subtropics.  $CO_2$  in the mixed layer is in active exchange with atmospheric  $CO_2$ , and equilibrates with atmospheric  $CO_2$  within a year.

Apart from the wind-driven currents, there is circulation in the body of the ocean driven by variations in temperature (thermo) and salinity (haline) known as thermohaline circulation. The main aspects of this circulation are often described as the 'ocean's conveyor', after a simplified diagram by Broecker (1987) depicting deep ocean circulation as a conveyor belt. Broecker (1991) described the conveyor and some other features of ocean circulation. The most important feature of the conveyor is the production of deep water in the North Atlantic. Relatively warm, salty North Atlantic surface water is cooled as it moves northward. This increases its density and it sinks to the deep ocean and flows southward. This water mass, known as North Atlantic Deep Water (NADW) has high salinity, low nutrient content and high  ${}^{14}C/{}^{12}C$  ratio, and fills most of the deep Atlantic. Deep water is also formed near Antarctica, where cold temperatures increase the density of surface water that then sinks to form Antarctic Bottom Water (AABW). AABW flows north and mixes with NADW. A rapidly moving deep current (the Antarctic Circumpolar Current) encircles the Antarctic continent southward of 30°S, and mixes NADW, AABW and old, deep waters from the Pacific and Indian Oceans. This mix of water flows into the Indian and Pacific Oceans. Upwelling is widespread throughout the ocean, with a large amount taking place in the Antarctic. Return flow of water to the Atlantic, mainly through the Drake Passage (south of South America) and the Agulhas route (south of Africa) complete the conveyor. Ongoing oceanographic research is refining this simplified view.

Broecker et al. (1985b) suggest that the ocean's conveyor is driven by salt left behind as a result of water vapour transport through the atmosphere. It is believed that addition of fresh water to the northern Atlantic is able to cause a shutdown of the conveyor (Maier-Reimer and Mikolajewicz, 1989), and that in the past during glacial periods, circulation in the Atlantic altered back and forth between conveyor-on and conveyor-off modes on a millennial time scale (Broecker, 1991). Salinity is too low in the Pacific for deep water formation to occur there (Warren, 1983). Pre-industrially, the conveyor circulation may have carried carbon from the northern hemisphere to the southern hemisphere, balancing a return transport of carbon through the atmosphere (Broecker and Peng, 1998). Back extrapolation of the difference in concentration between the South Pole and Mauna Loa by Keeling et al. (1989a) suggested that the South Pole may have been about 0.8 ppmv higher than the northern hemisphere. With the addition of anthropogenic  $CO_2$  (mainly in the northern hemisphere), over time the latitudinal gradient would have decreased to zero around the 1950s, and been in the opposite sense since then. However, with a 3-d ocean biogeochemistry model, Murnane et al. (1999) found that southward transport of carbon in the Atlantic basin was balanced by northward transport in the Pacific and Indian Oceans, giving no significant interhemispheric transport in the ocean on a global scale. If this was the case there would have been no significant pre-industrial atmospheric  $CO_2$ gradient. Recently, Fan et al. (1999) have suggested that the discrepancy between back extrapolation of the Mauna Loa and South Pole difference and ocean transport estimates can be solved with a pre-industrial interhemispheric flux of 0.5-0.7 GtC yr<sup>-1</sup> and biospheric uptake of 0.8-1.2 GtC yr<sup>-1</sup> in the mid-latitude northern hemisphere, balanced by a tropical deforestation source.

Mixing along isopycnal (constant density) surfaces is also important for transport in the ocean, and in particular subduction into the thermocline (Broecker and Peng, 1982; Murray, 1992). The density surfaces that lie in the thermocline at 200–1000 m in the equatorial region rise to the surface, or *outcrop*, at high latitudes. Surface water descends into the main thermocline from the polar outcrops. It leaves the thermocline by a combination of downwelling in the mid-latitudes and upwelling in the equatorial region (Broecker and Peng, 1982). Mixing across isopycnal surfaces occurs at the polar outcrops due to the wind driven surface currents and convection.

Ocean circulation and the  $CO_2$  solubility differences of warm and cold water drive what is known as the *solubility pump* (Volk and Hoffert, 1985). Cold waters in the deep ocean have a higher carbon-holding capacity than warmer surface oceans. When cold, deep water upwells it warms and  $CO_2$  solubility decreases, causing an outgassing flux to the atmosphere such as in the tropics (Murnane et al., 1999). When water moves poleward and cools it can take up additional  $CO_2$ . This occurs in the North Atlantic. As well as influencing spatial distributions of  $CO_2$ , the solubility pump influences the levels of atmospheric  $CO_2$  because it leads to deep ocean concentrations that are much greater than the equilibrium with the atmosphere.

Most biological activity in the ocean occurs near the surface, in the photic zone, where light is available for photosynthesis. This causes depletion of DIC, and incorporation of carbon into organisms as organic tissue and calcium carbonate (CaCO<sub>3</sub>) (the hard parts). When these organisms die, they begin to sink and decompose, and the carbon and other nutrients they contain are reoxidised and mostly returned to the dissolved nutrient pool of the mixed layer. About 10% sink below the photic zone into water too dark to support photosynthesis. The organic materials are remineralised, causing an enrichment of carbon and other nutrients in deep waters relative to the surface ocean. When cold, deep water upwells it brings water rich in carbon and nutrients to the surface. Excess carbon is then stripped out by biological processes at the surface, except in regions where biological uptake is inefficient and carbon escapes to the atmosphere (e.g. in the Southern Ocean, tropics and North Pacific) (Murnane et al., 1999).

The removal of carbon from the surface waters by sinking organic materials is often referred to as the *biological pump*. The biological pump can be subdivided into the organic carbon pump and the carbonate pump (Wong, 1997). The organic carbon pump sequesters  $CO_2$  from the surface mixed layer into organic carbon

$$CO_2 + H_2O + solar energy = CH_2O(organic carbon) + O_2$$
 (2.8)

and by gravity moves it into the deeper part of the ocean below the surface photic zone. The carbonate pump acts in the opposite direction to the organic pump by producing  $CO_2$  and carbonate shells and decreasing alkalinity

$$Ca^{++} + 2HCO_3^- = CaCO_3(hard parts) + H_2O + CO_2$$

$$(2.9)$$

The decrease in alkalinity decreases  $CO_2$  solubility. The net effect of the biological pump on  $pCO_2$  depends on the relative production of carbonate shells and organic carbon. If more organic carbon than carbonate shells is produced then the biological pump lowers the surface water  $pCO_2$ . If carbonate shell formation exceeds organic carbon, as in coccolith blooms in the North Atlantic or foraminifera blooms in the Pacific, ocean  $pCO_2$  can be raised.

The spatial distribution of the air-sea flux of  $CO_2$  is complex, and is mainly determined by the solubility pump, the biological pump, ocean circulation and the gas transfer velocity. Figure 2.4 shows air-sea flux estimates from Takahashi et al. (1999) based on measurements of the air-sea  $pCO_2$  difference. Broadly speaking, the ocean is a source of  $CO_2$  to the atmosphere in regions of upwelling, such as the equatorial waters, where  $pCO_2$  is high due to both the solubility and biological pumps. As south flowing warm subtropical waters cool, their  $pCO_2$  quickly decreases causing a strong sink around 40-55°S. The subtropical gyres are highly alkaline, and therefore sink areas (Wong, 1997). The Atlantic ocean north of 40°N and the Norwegian and Greenland seas are strong  $CO_2$  sink areas, mainly due to cooling of water and photosynthesis. The high latitude North Pacific is a strong  $CO_2$ source because the North Pacific deep waters that have upwelled to the surface have very high  $CO_2$  concentration. In winter this creates a source. In summer the effect is offset by photosynthesis activity causing a sink, although on annual average the region is still a source. (Wong, 1997; Takahashi, 1989)



Figure 2.4: Air-sea flux of  $CO_2$  in g m<sup>-2</sup> y<sup>-1</sup> based on measurements of the air-sea  $pCO_2$  difference (Takahashi et al., 1999). Solid contours indicate a source to the atmosphere, dashed contours uptake by the ocean. (Figure produced by R. Law.)

Exchange between the atmosphere and ocean can vary on interannual time scales and affect atmospheric  $CO_2$ . Associated with the El Niño Southern Oscillation (ENSO) is a change in ocean currents in the central Pacific. In normal years, trade winds drive warm surface waters to the western Pacific, allowing deep waters to upwell along the coast of Peru. In El Niño years, the surface transport breaks down, and the warm waters remain in the eastern Pacific, preventing the upwelling of nutrient- and  $CO_2$ - rich water. This causes a reduction in the normal process of  $CO_2$  release from the cold, upwelling water (Winguth et al., 1994).

Le Quéré et al. (2000) studied interannual variability in ocean exchange with a 3-d

ocean model of circulation and biogeochemistry. They suggested that about half of the interannual variability in the global air-sea flux is in the equatorial Pacific, but that other regions were also important. The North Atlantic made only a small contribution to global variability in the air-sea flux, despite the fact that interannual variability in ocean dynamics in this region is well documented. It is ocean circulation that controls the variability in the tropical Pacific, rather than the biological pump or gas exchange (Le Quéré et al., 2000; Winguth et al., 1994). A number of studies (Winguth et al., 1994; Lee et al., 1998; Le Quéré et al., 2000) have found using 3-d ocean models or  $pCO_2$  measurements that interannual variability in the air-sea flux is much less than the variability in atmospheric  $CO_2$  growth rates. This contradicts estimates of the ocean flux variability from inversion studies by Francey et al. (1995b), Keeling et al. (1995) and Rayner et al. (1999a).

It is important to distinguish between the natural air-sea flux distribution that existed in pre-industrial times and the perturbation associated with uptake of anthropogenic  $CO_2$ . For example, the equatorial Pacific Ocean is a natural source of  $CO_2$  to the atmosphere because of its high  $pCO_2$  values, but it is a relatively strong sink for anthropogenic  $CO_2$ , because the water that upwells has been out of contact with the atmosphere for a long time (Sarmiento et al., 1992). The biological pump contributes little to the spatial distribution of anthropogenic  $CO_2$  uptake, but is important for determining the distribution of natural fluxes (Sarmiento et al., 1995). Deep water formation in the North Atlantic and Southern Ocean is important for uptake of anthropogenic  $CO_2$  because it ventilates the deep ocean. The bottleneck to uptake of anthropogenic  $CO_2$  by the atmosphere is mixing from the surface to the deep ocean, rather than exchange between the atmosphere and surface ocean (Sarmiento et al., 1992). This means that if ocean circulation were to change, for example as a result of the greenhouse warming, it may have a large effect on uptake of carbon. Sarmiento et al. (1998) estimated with a 3-d coupled ocean/atmosphere model that changes in ocean circulation due to greenhouse warming have already begun to slightly decrease  $CO_2$  uptake, and that the effect was likely to worsen in the future.

It is not really possible at present to determine accurately the ocean inventory of anthropogenic  $CO_2$  from ocean measurements (Broecker and Peng, 1998). It requires measurement of a very small signal against significant temporal and spatial variability. A global survey of the DIC content of ocean water was made during the 1970s as part of the

Geochemical Ocean Sections Study, GEOSECS, and another more detailed and accurate survey, the World Ocean Circulation Experiment, WOCE, was made in the 1990s. The earlier study was not of sufficient accuracy for these measurements to be used to estimate the global inventory (Broecker and Peng, 1998), although measurements and estimation methods are constantly improving and moving in that direction. Gruber et al. (1996) developed a method for estimating the ocean inventory from ocean measurements, and applied it to the Atlantic. Sabine et al. (1999) applied a similar method to the Indian Ocean.

Uptake of anthropogenic  $CO_2$  is often calculated by ocean carbon cycle models. These models vary in complexity from the simple 1-d box diffusion model developed by Oeschger et al. (1975) that will be used in subsequent chapters to full 3-d ocean general circulation models incorporating biology and chemistry (e.g. Matear and Hirst, 1999; Le Quéré et al., 2000). The box diffusion model typically has a 75 m mixed layer above a 1-d deep ocean with transport by eddy diffusion calibrated using <sup>14</sup>C. Another ocean model that is often used for decadal to century time scale carbon cycle studies is the outcrop-diffusion model. This model is similar to the box diffusion model, except that it includes ventilation of the deep sea at high latitudes with a direct air-sea exchange for deep waters (Siegenthaler, 1983). The HILDA model (HIgh-Latitude exchange/interior Diffusion-Advection) is another box model that includes the high latitude outcrop (Shaffer and Sarmiento, 1995; Siegenthaler and Joos, 1992). It has 2 surface boxes (high and low latitude), a high latitude deep box and a diffusive interior reservoir and also includes upwelling in the interior reservoir.

### 2.5 <sup>13</sup>C

The stable isotope, <sup>13</sup>C in CO<sub>2</sub>, provides an important way to distinguish between uptake of atmospheric carbon by the terrestrial biosphere and the oceans. About 99 % of CO<sub>2</sub> in the atmosphere is <sup>12</sup>C, about 1 % is <sup>13</sup>C, and a very small amount (about 1 in  $10^{12}$ ) is the radioactive isotope, <sup>14</sup>C. When CO<sub>2</sub> is taken up by the biosphere there is a slight preference for uptake of <sup>12</sup>C over <sup>13</sup>C, leading to a depletion of <sup>13</sup>C relative to <sup>12</sup>C in biospheric carbon. The ocean also preferentially takes up <sup>12</sup>C, but the effect is only about one tenth of that of the biosphere. It is because of these different degrees of discrimination, termed *isotopic fractionation*, associated with exchange with the different reservoirs that  ${}^{13}$ C can be used to partition the net uptake.

Isotopic changes are often expressed in terms of the deviation of the ratio of one isotope to another from a standard ratio. For <sup>13</sup>C, the quantity  $\delta^{13}$ C is defined as

$$\delta^{13} \mathcal{C} = \left(\frac{{}^{13}\mathcal{C}/{}^{12}\mathcal{C}}{r_s} - 1\right) \times 1000$$
(2.10)

in units of ‰ (permil), with the PDB standard ratio,  $r_s = 0.0112378$ . The pre-industrial  $\delta^{13}$ C level in the atmosphere was about -6.5 ‰, and in the biosphere about -25 ‰. (The more negative the  $\delta^{13}$ C value, the more depleted it is in <sup>13</sup>C relative to <sup>12</sup>C.) Because of its biospheric origin, fossil fuel CO<sub>2</sub> has a very similar isotopic ratio to biospheric carbon. The addition of fossil fuel CO<sub>2</sub> to the atmosphere has caused a depletion of atmospheric <sup>13</sup>C over time, so that present levels (late 1990s) are below -8.0 ‰. A useful 'rule of thumb' is that a flux of biospheric CO<sub>2</sub> to the atmosphere that causes a 1 ppm CO<sub>2</sub> increase, decreases the atmospheric  $\delta^{13}$ C by about 0.05 ‰ (Keeling et al., 1989a). Figure 2.5 shows a record of  $\delta^{13}$ C measurements since 1982 from Cape Grim, Tasmania (Francey et al., 1995a; R. J. Francey, pers. comm.). This is one of the longest direct atmospheric records of atmospheric  $\delta^{13}$ C. Another long direct atmospheric record of  $\delta^{13}$ C is that by Keeling et al. (1995). There are significant differences between these two records during the 1980s, which are too large to be biogeochemical. However, in the context of the firn and ice core studies, the two records do not lead to conflicting conclusions.



Figure 2.5:  $\delta^{13}$ C record from Cape Grim, Tasmania (Francey et al., 1995a; R. J. Francey, pers. comm.).

 $\delta^{13}$ C in ocean surface waters varies from about 0.75 to 2.5 %. The spatial distribution of oceanic  $\delta^{13}$ C results from both biological and thermodynamic processes in the ocean that largely cancel each other out, giving relatively small spatial variability (Gruber et al., 1999).  $\delta^{13}$ C of marine organic matter is around -20 to -30 ‰, and as a result biological production raises  $\delta^{13}$ C in surface waters. Subsurface water contains remineralised organic matter with lower  $\delta^{13}$ C, so upwelling lowers the  $\delta^{13}$ C of surface water DIC. Only a small fractionation occurs during the formation of calcium carbonate shells. Kinetic fractionation occurs during transfer across the air-sea interface. The fractionation factor for a one-way flux from atmosphere to ocean differs from unity by about -2 ‰ and from ocean to atmosphere by about -10 ‰, strongly dependent on temperature. At equilibrium these values result in an enrichment in the ocean of about 8 % relative to the atmosphere. The surface ocean  $\delta^{13}$ C is almost never close to isotopic equilibrium with the atmosphere because it takes on the order of 10 years for <sup>13</sup>C to equilibrate between the atmosphere and the ocean mixed layer, yet the residence time of surface water is of the order of a few years or less (Gruber et al., 1999). The time needed to equilibrate <sup>13</sup>C between the atmosphere and the mixed layer is long compared to that for total C because <sup>13</sup>C needs to come to equilibrium with all species of the inorganic carbon system ( $CO_2$ ,  $H_2CO_3$ ,  $HCO_3^-$ ) and  $CO_3^{--}$ ) while chemical buffering speeds up equilibration for total C (Broecker and Peng, 1998; Gruber et al., 1999).

The use of <sup>13</sup>C to determine the partitioning of net CO<sub>2</sub> fluxes is somewhat complicated due to the gross fluxes between the atmosphere and the oceans. The gross flux has been defined in Section 2.3 as photosynthesis and respiration for the biosphere. The gross flux for the ocean is essentially due to molecular diffusion across the air-sea interface, but is limited by the rate of renewal of air and water in the layers above and below the interface. The atmospheric CO<sub>2</sub> budget requires only the small net carbon fluxes, (i.e. the difference between the large one-way gross fluxes), but the  $\delta^{13}$ C budget must include the effects of the gross fluxes between the atmosphere and the ocean and biosphere for the following reason. As the atmospheric  $\delta^{13}$ C level has decreased over the industrial period,  $\delta^{13}$ C of the biosphere and the surface ocean has also decreased, but with a lag relative to the atmosphere. The biosphere and oceans are therefore presently out of isotopic equilibrium with the atmosphere. The effect of the gross fluxes on atmospheric <sup>13</sup>C depends on the amount of *isotopic disequilibrium* between the reservoirs, which is extremely difficult to determine from measurements. It is because of this isotopic disequilibrium that  $\delta^{13}$ C has not been the ideal solution to the partitioning problem that it was initially hoped it would be, however considerable progress is now being made in this area.

Tans et al. (1993) derived equations for the atmospheric mass balances of total CO<sub>2</sub> and its <sup>13</sup>C isotope that are in a form that make the <sup>13</sup>C budget fairly easy to understand. For CO<sub>2</sub>, the change in the atmospheric concentration,  $C_a$ , depends on the fossil fuel source,  $F_f$ , and the net fluxes between the atmosphere and the ocean and the atmosphere and the terrestrial biosphere

$$\frac{d}{dt}C_a = F_f - F_{ab} + F_{ba} - F_{ao} + F_{oa}$$
$$= F_f - F_b - F_o \qquad (2.11)$$

where  $F_{ab}$ ,  $F_{ba}$ ,  $F_{ao}$  and  $F_{oa}$  denote the one-way gross fluxes from the atmosphere to biosphere, biosphere to atmosphere, atmosphere to oceans and oceans to atmosphere, respectively. The net uptake is the difference between the gross fluxes,  $F_o = F_{ao} - F_{oa}$  for the ocean, and  $F_b = F_{ab} - F_{ba}$  for the biosphere.

The budget for  ${}^{13}C$  is given by

$$\frac{d}{dt}(^{13}C_a) = F_f R_f - \alpha_{ab} F_{ab} R_a + F_{ba} R_b - \alpha_{ao} F_{ao} R_a + \alpha_{oa} F_{oa} R_o$$
(2.12)

where  $R_f$ ,  $R_a$ ,  $R_b$  and  $R_o$  denote the ratio of <sup>13</sup>C/ <sup>12</sup>C in fossil fuel, atmospheric, biospheric and surface ocean CO<sub>2</sub>, respectively, and  $\alpha_{ij}$  denotes the fractionation factor for the flux from reservoir *i* to reservoir *j* expressed as a ratio. Since it is generally the isotopic ratio,  $\delta^{13}$ C, rather than <sup>13</sup>C that is measured, Tans et al. (1993) gave an approximation for Equation 2.12 in terms of isotopic ratios. It considers conservation of the quantity  $C \times \delta^{13}C$  which has units of GtC ‰ (Tans, 1980).

$$\frac{d}{dt}(C_a\delta_a) = C_a \frac{d}{dt}\delta_a + \delta_a \frac{d}{dt}C_a$$
(2.13a)
$$\approx F_f(\delta_f - \delta_a) - (F_{ab} - F_{ba})\varepsilon_{ab} + F_{ba}(\delta_a^b - \delta_a) - (F_{ao} - F_{oa})\varepsilon_{ao} + F_{oa}(\delta_a^o - \delta_a)$$
(2.13b)

where  $\varepsilon_{ij} = \alpha_{ij} - 1$  (in permil) is the isotopic shift that occurs for a flux from reservoir *i* to reservoir *j*, and  $\delta_a^b$  and  $\delta_a^o$  are the isotopic ratios that the atmosphere would have if it were in equilibrium with the biosphere and the ocean, respectively. The approximation holds for  $\alpha$ 's near 1 and  $\delta$ 's small compared to unity (1000 permil). The values of the isotopic shifts are  $\varepsilon_{ab} \approx -18$  ‰,  $\varepsilon_{ao} \approx -2$  ‰ and  $\varepsilon_{oa} \approx -11$  ‰.

Equation 2.13b distinguishes the changes in atmospheric  $\delta^{13}$ C due to the net carbon fluxes, (terms  $(F_{ab} - F_{ba})\varepsilon_{ab}$  and  $(F_{ao} - F_{oa})\varepsilon_{ao}$ ), from those caused by gross carbon exchange  $(F_{ba}(\delta_b - \delta_b^e)$  and  $F_{oa}(\delta_a^e - \delta_a)$ ). The gross exchange terms, sometimes called the isotopic disequilibrium fluxes, or *isofluxes*, arise mainly due to the disequilibrium between the atmosphere and the other reservoirs caused by the anthropogenic  $\delta^{13}$ C decrease. These terms are difficult to estimate. For the oceans, the disequilibrium of surface waters differs considerably around the world, and is positive in some regions and negative in others due to thermodynamic and biological processes in the ocean (Gruber et al., 1999). For use in equation 2.13 the disequilibria need to be weighted by the gross fluxes, so that the global disequilibrium flux is the sum of many large terms with different signs. Measuring the global disequilibrium for the biosphere is also not practical. Although the terms are all the same sign, the right pool-weighting of the disequilibria and fluxes is required (Ciais et al., 1995b; Fung et al., 1997). Models provide the best way to estimate the isoflux terms. A detailed review of isoflux estimates will be given in Section 6.1.

One way to represent the joint budgets of CO<sub>2</sub> and  $\delta^{13}$ C is using the 'vector diagram' shown in Figure 2.6 (Enting et al., 1993). The isotopic anomaly (C ×  $\delta^{13}$ C) is shown on the horizontal axis and CO<sub>2</sub> on the vertical axis. Each of the terms in Equation 2.13a and 2.13b is represented by a line, where the slope of the line is the isotopic signature ( $\delta^{13}$ C). If the fossil, isoflux and atmospheric change terms are known, equations 2.11 and 2.13 can be solved for the net biotic ( $F_{ab} - F_{ba}$ ) and net oceanic ( $F_{ao} - F_{oa}$ ) fluxes. This is also depicted on the vector diagram, where the slopes of the two net flux terms (i.e. the  $\delta^{13}$ C values) are known (shown by the dashed lines) and the lengths balance the budgets.

A number of studies have used <sup>13</sup>C flux balances to estimate the contemporary rate of anthropogenic CO<sub>2</sub> uptake by the oceans. Quay et al. (1992) used the estimated change in ocean inventory of <sup>13</sup>C over 20 years from a comparison of ocean measurements in the early 1970s and early 1990s with C and <sup>13</sup>C budget equations for the atmosphere and oceans. They estimated an ocean uptake of 2.1 GtC yr<sup>-1</sup> for 1970–90, but their method requires estimates of the global change in ocean <sup>13</sup>C and the isotopic disequilibrium with



Figure 2.6: 'Vector diagram' for  $CO_2$  and  $\delta^{13}C$  from Enting et al. (1993). The vertical axis shows the carbon budget and the horizontal axis the isotopic anomaly budget.

the biosphere, both of which are quite uncertain. Tans et al. (1993) solved equations 2.11 and 2.13 using an estimate of the ocean isoflux from ocean surface measurements. They estimated a much lower ocean uptake than Quay et al. (1992).

Heimann and Maier-Reimer (1996) developed a third method to estimate ocean uptake of CO<sub>2</sub> with the <sup>13</sup>C budget. They estimated the penetration of CO<sub>2</sub> into the ocean from <sup>13</sup>C/<sup>12</sup>C perturbation changes, assuming the penetration depths for CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> are the same. They called this the 'dynamic constraint', and with it estimated an ocean uptake for 1970–1990 of 3.1 GtC yr<sup>-1</sup>. Heimann and Maier-Reimer (1996) then used a nonlinear estimation procedure to obtain a scenario consistent with their dynamic constraint and the Quay et al. and Tans et al. methods, taking into account all of the uncertainties. This gave a best estimate of ocean uptake for 1970-90 of  $2.1 \pm 0.9$  GtC yr<sup>-1</sup>. The value estimated by Tans et al. (based on measurements) for the ocean isoflux was  $85 \times 0.43 = 36.55$  ‰ GtC yr<sup>-1</sup> whereas the Heimann and Maier-Reimer consistent scenario value was  $94.9 \times$ 0.533 = 50.58 ‰ GtC yr<sup>-1</sup>. The use of different values for the isoflux terms can explain some of the discrepancy in different estimates of net fluxes from <sup>13</sup>C budget studies. An increase in the total (ocean + biosphere) isoflux of  $\delta$ I ‰ GtC yr<sup>-1</sup> translates into an increase in the estimated oceanic net flux (and corresponding decrease in the estimated biospheric net flux) of about  $\delta I/16$  GtC yr<sup>-1</sup> (this comes from equation 2.13b with the given values of  $\varepsilon_{ab}$  and  $\varepsilon_{ao}$ ). For example, the difference between the ocean isofluxes from Tans et al. and the Heimann and Maier-Reimer consistent scenario gives a difference in the ocean uptake of (50.58 - 36.55)/16 = 0.88 GtC yr<sup>-1</sup>. The greatest unknowns in studies involving <sup>13</sup>C are the isofluxes.

Francey et al. (1995b) used the carbon and <sup>13</sup>C budget equations from Tans et al. (1993) to solve for time variations in the net biospheric and oceanic fluxes from 1982–93. They used the  $\delta^{13}$ C record from Cape Grim, taken to represent global variations, with values for the ocean isoflux of -43.8 ‰ GtC yr<sup>-1</sup> (based on Tans et al. measurements) and biosphere isoflux of -25.8 ‰ GtC yr<sup>-1</sup> (from a calculation by Enting et al. (1993) using the Siple ice core  $\delta^{13}$ C record and the Emanuel et al. (1981) 5-box model of the biosphere). They estimated interannual variations in the net fluxes, and found that the CO<sub>2</sub> flattening around 1988–90 probably involved the biosphere, and that there was increased ocean uptake during the ENSO events in 1982, 1986 and 1991–92. The spatial distribution of  $\delta^{13}$ C in the atmosphere can also provide useful information on CO<sub>2</sub> fluxes (Ciais et al., 1995a; 1995b), but the isofluxes may be an even more serious complication than they are for the global budget due to the large heterogeneity.

An isotopic perturbation in the atmosphere dies away faster than a CO<sub>2</sub> perturbation (Siegenthaler and Oeschger, 1987). This is because an isotopic signal in the atmosphere gets diluted in the ocean and biosphere by the large gross fluxes, but it takes a long time for the three reservoirs to equilibrate isotopically. A CO<sub>2</sub> perturbation decreases due to the net fluxes into the ocean and chemical buffering means that equilibration is relatively fast. Joos and Bruno (1998) estimated that the airborne fraction of the fossil  $\delta^{13}$ C signal is about 20 % for the period 1970-1990. This compares with typical estimates for the CO<sub>2</sub> airborne fraction of around 50-60 %. A consequence of this is that  $\delta^{13}$ C responds more than CO<sub>2</sub> to short time scale variations, relative to their long term changes.

### 2.6 <sup>14</sup>C

The radioactive isotope,  ${}^{14}C$ , is often used to calibrate models that predict the uptake of anthropogenic carbon.  ${}^{14}C$  in the atmosphere varies both naturally and as a result of anthropogenic activities. It is produced in the stratosphere by cosmic rays, and the production rate varies with changes in the sun and the Earth's magnetic field. <sup>14</sup>C decays with a half-life of about 5730 years. In the 1950s and 60s, nuclear tests increased the amount of <sup>14</sup>C in the atmosphere to almost double the natural level. After test-ban treaties were set in place, atmospheric levels decreased as <sup>14</sup>C was taken up by the oceans and terrestrial biosphere. <sup>14</sup>C is often expressed as deviations of <sup>14</sup>C/<sup>12</sup>C from a standard ratio, corrected for isotopic fractionation (Stuiver and Polach, 1977)

$$\Delta^{14}C = \delta^{14}C - 2\left(\delta^{13}C + 25\right)\left(1 + \frac{\delta^{14}C}{1000}\right)$$
(2.14)

where

$$\delta^{14} \mathcal{C} = \left(\frac{{}^{14}\mathcal{C}/{}^{12}\mathcal{C}}{r_s} - 1\right) \times 1000 \tag{2.15}$$

Figure 2.7a shows the variation in atmospheric  $\Delta^{14}$ C from tree-ring measurements prior to nuclear testing (Stuiver and Becker, 1993). Figure 2.7b shows the variation after 1950. As fossil fuel CO<sub>2</sub> contains no <sup>14</sup>C, the input of fossil fuel CO<sub>2</sub> to the atmosphere reduces the atmospheric  $\Delta^{14}$ C. This is known as the Suess effect (Suess, 1955). A decrease in atmospheric  $\Delta^{14}$ C of about 20 ‰ between 1900 and 1950 is due partly to the Suess effect and partly to a decrease in the natural cosmic ray production rate (Stuiver and Quay, 1981). After 1950, bomb <sup>14</sup>C overwhelms the Suess effect signal.



Figure 2.7: Atmospheric <sup>14</sup>C records from tree-rings. a) Pre-bomb variations (Stuiver and Becker, 1993). b) Northern hemisphere measurements from Vermunt, Austria (Levin et al., 1985) (triangles) and southern hemisphere measurements from New Zealand, (Manning and Melhuish, 1994) (circles).

Bomb  $^{14}$ C has been used for calibrating a large number of ocean models for uptake of anthropogenic CO<sub>2</sub>, ranging from box diffusion models to 3-d models. However, the time

histories of bomb <sup>14</sup>C and anthropogenic  $CO_2$  in the atmosphere are quite different – the input of bomb <sup>14</sup>C is dominated by a pulse in the early sixties whereas  $CO_2$  emissions have been approximately exponential. Questions have been raised about whether bomb <sup>14</sup>C is a good analogue for anthropogenic  $CO_2$  due to the different forcing functions involved (e.g. Heimann and Maier-Reimer, 1996). There has been some interest recently in the budget of bomb <sup>14</sup>C, with claims that the budget is not balanced. Further details will be given in Chapter 4.

The change in <sup>14</sup>C due to variations in the natural production rate is needed to properly model the observed  $\Delta^{14}$ C decrease in the first half of this century. Beer et al. (1988) showed a good correlation between variations of <sup>14</sup>C and <sup>10</sup>Be, another cosmogenic isotope, on time-scales of about 200 years, giving good evidence that their variations have a common cause (i.e. changes in their production rates due to changes in the cosmic ray flux). A number of studies have used variations in <sup>14</sup>C production rates determined from ice core <sup>10</sup>Be data in a carbon cycle model, and compared modelled and measured  $\Delta^{14}$ C (e.g. Beer et al., 1994; Bard et al., 1997).

## 2.7 Estimating CO<sub>2</sub> fluxes from concentration measurements

There are two main ways concentration data can be used to infer surface fluxes – by interpreting the time rate of change of concentration or the spatial distribution of concentration. A combination of the two is also possible. Use of the time rate of change has already been mentioned. Equation 2.11 can be applied to the global carbon budget to compare observed (global) concentration increases with anthropogenic inputs to deduce uptake of anthropogenic  $CO_2$  by mass balance. Equation 2.13 for the <sup>13</sup>C budget can be used to partition the global non-fossil flux into oceanic and biospheric components. Oxygen provides a second method for partitioning  $CO_2$  uptake, as the carbon and oxygen cycles on earth are linked (Keeling, 1988; Keeling and Shertz, 1992).  $O_2$  is consumed during combustion of fossil fuels and plant respiration, and released during photosynthesis. The relative variations in  $CO_2$  and  $O_2$  for these processes are quite well known. The oxygen budget in the atmosphere on decadal time scales is simpler than that for <sup>13</sup>C and is usually given as

$$\frac{d}{dt}O_2 = S_f F_f + S_b F_b \tag{2.16}$$

where  $S_f$  and  $S_b$  are the O<sub>2</sub>/CO<sub>2</sub> exchange ratios for the fossil fuel and biospheric fluxes (see e.g. Langenfelds et al., 1999) and  $F_f$  and  $F_b$  have already been defined. Most oxygen budget studies to date (e.g. Langenfelds et al., 1999; Rayner et al., 1999a) have used equation 2.16 which includes no long-term contribution due to the ocean. Recent 3-d ocean model calculations by R. Matear (pers. comm., 1999) suggest that there may be a relatively large contribution to the long-term budget due to ocean ventilation. This issue is yet to be resolved.

The spatial distribution of  $CO_2$  in the atmosphere can be used to infer surface fluxes which can then be interpreted in terms of processes. This type of calculation must include the effect of transport in the atmosphere. Some studies have used 2-d models (latitude, height) with the latitudinal gradient of  $CO_2$  at the Earth's surface and mass balance to invert for the net surface source as a function of latitude (e.g. Enting and Mansbridge, 1989; Tans et al., 1989). Ciais et al. (1995a; 1995b) included the latitudinal gradient in  $\delta^{13}C$  to partition uptake between the ocean and biosphere. They deduced a large terrestrial biospheric sink between 35°N and 65°N in 1992 and 1993.

Extension of the spatial mass balance inversion to use with 3-d transport models is difficult because the latitude-longitude surface CO<sub>2</sub> distribution is not really adequately constrained by observational data. A few studies have tried to deal with this by assuming zonally uniform concentrations or by interpolating (e.g. Law et al., 1992; Law, 1999) but most 3-d inversions have used what is known as the synthesis approach (e.g. Keeling et al, 1989b; Tans et al., 1990; Enting et al., 1995). This involves choosing a set of source distributions, usually associated with different processes or regions, and finding the linear combination that when run in the transport model best fits the concentration measurements. This type of calculation can include  $\delta^{13}$ C or O<sub>2</sub> data for distinguishing oceanic from biotic fluxes.

These calculations generally use the time rate of change to constrain the total source and the spatial gradients to distribute it around the world. The direct records currently available for use in spatial inversions cover only a relatively short time period. Most studies have considered observations averaged over a number of years, with the assumption of annually periodic fluxes (e.g. Tans et al., 1990; Enting et al., 1993; Enting et al., 1995). A recent synthesis inversion by Rayner et al. (1999a) estimated time varying sources between 1980 and 1995. These calculations suggest that there is considerable interannual variability in the sources, and the important question of how much of this variability is natural, (e.g., due to climate) can be addressed by looking back in time with ice core records.

Estimation of sources from concentration measurements is an inverse problem, and therefore suffers from the following difficulties. Fluxes are calculated from rates of change of concentration. This involves numerical differentiation of observational data, which is an ill-conditioned problem. The ill-conditioning means that estimates of sources are subject to amplification of errors in observations. Spatial inversions are also ill-conditioned because atmospheric mixing smears out the spatial concentration distribution, causing loss of information.

Carbon cycle studies need to distinguish between carbon storage and fluxes. One reason for the difference is that carbon entering the oceans via rivers is not seen by methods that calculate or measure fluxes, but contributes to the ocean inventory of carbon. The distinction is important for comparisons between methods that calculate different quantities (Tans et al., 1995).

# **2.8** CO<sub>2</sub> and $\delta^{13}$ C ice core records

Continuous measurements of  $CO_2$  began in 1958, and  $\delta^{13}C$  much later than that. Presently the best way to reconstruct  $CO_2$  and  $\delta^{13}C$  levels prior to direct measurements is by analysing air trapped in bubbles in polar ice, i.e. ice core records. Attempts to measure  $CO_2$  from ice cores date back to at least the early 1960s (e.g. Scholander et al., 1961) but it was not until the late 1970s and early 1980s that the experimental techniques were thought to be successful and atmospheric levels could be reliably estimated. The measurements at this time were used to estimate that the pre-industrial  $CO_2$  concentration had been around 260 ppmv (Barnola et al., 1983) and that during the coldest part of the Ice Age, atmospheric  $CO_2$  concentration was about 160 ppmv (Delmas et al., 1980).

As understanding of the dating improved, sequences of  $CO_2$  measurements were used to look at the variation of  $CO_2$  over time. Air from the very low accumulation rate site, Vostok, in Antarctica, gave information about variations in  $CO_2$  and  $CH_4$  between glacial and interglacial periods (Barnola et al., 1987). The first ice core records of  $CO_2$  over recent centuries were constructed in the mid 1980s from measurements at a few different sites (Figure 2.8a). Measurements from Siple Station, West Antarctica (Neftel et al., 1985) covering roughly 1750–1970 gave estimates of the time dependence of the anthropogenic  $CO_2$  increase with good time resolution and little scatter.  $CO_2$  from D57, East Antarctica (Raynaud and Barnola, 1985) covering the centuries preceding the anthropogenic perturbation, showed lower pre-industrial levels than other records and significant fluctuations in pre-industrial  $CO_2$ . The South Pole record (Siegenthaler et al., 1988) covers roughly 900–1800 AD and suggests a rise in concentration during the 13<sup>th</sup> century. Pearman et al. (1986) and Etheridge et al. (1988) reported measurements from BHD on Law Dome in Antarctica, covering 1520–1966.

The first ice core  $\delta^{13}$  CO<sub>2</sub> measurements were by Friedli et al. (1984) on ice from South Pole, and estimated a mean level of about -6.7 ‰ for 430–770 AD.  $\delta^{13}$ C was measured for the samples from Siple Station (Friedli et al. 1986) and South Pole (Siegenthaler et al., 1988) and these are shown in Figure 2.8b. Siegenthaler et al. (1988) gave their South Pole results with and without their standard-air correction, and didn't know which set was likely to be more correct. The Siple  $\delta^{13}$ C values are more scattered than the CO<sub>2</sub> measurements for that core, as the  $\delta^{13}$ C changes are proportionally much smaller and require much greater measurement precision than CO<sub>2</sub>.

In the 1990s, Barnola et al. (1995) published a new CO<sub>2</sub> record from D57 and one from D47 (East Antarctica) (Figure 2.8c). The D57 measurements suggest an increase of about 10 ppmv in CO<sub>2</sub> in the 13<sup>th</sup> century, as had been seen in the South Pole record (Siegenthaler et al., 1988), followed by a slow decrease to the 18<sup>th</sup> century. Results of CO<sub>2</sub> and  $\delta^{13}$ C from H15 (East Antarctica) were presented by Nakazawa et al. (1993) and Kawamura et al. (1997). Their record covers the industrial period (Figure 2.8c and d).

A new, high precision, high time-resolution ice core record of  $CO_2$  from Law Dome, East Antarctica (Figure 2.8e) was published by Etheridge et al. (1996). The record consists of ice core measurements from 3 cores on Law Dome (DE08, DE08-2 and DSS) and firn measurements from DE08-2. It covers the period 1006–1993, and a particular advantage of the record is that it overlaps with the modern record. The snow accumulation rates at DE08 and DE08-2 are very high (1100 kg m<sup>-2</sup> yr<sup>-1</sup>, compared with 650 kg m<sup>-2</sup> yr<sup>-1</sup> for BHD which has the next highest rate of the sites mentioned above). The high accumulation rate means that the temporal smoothing due to the firn processes is low (see Chapter 3).



Figure 2.8: Various CO<sub>2</sub> and  $\delta^{13}$ C records from Antarctic ice cores. a) CO<sub>2</sub> records published in the 1980s: Siple (Neftel et al., 1985; Friedli et al., 1986), D57 (Raynaud and Barnola, 1985), South Pole (Siegenthaler et al., 1988), BHD (Pearman et al., 1986; Etheridge et al., 1988). The direct record from Mauna Loa is also shown (Keeling and Whorf, 1998). b)  $\delta^{13}$ C records published in the 1980s: Siple (Friedli et al., 1986), South Pole (Siegenthaler et al., 1988), where (A) are standard-air corrected and (B) are not standard-air corrected. The Cape Grim direct record is also shown (Francey et al., 1995a). c) CO<sub>2</sub> ice core records from D57 and D47 (Barnola et al., 1995) and H15 (Nakazawa et al., 1993). d)  $\delta^{13}$ C record from H15 (Nakazawa et al., 1993). e) Law Dome CO<sub>2</sub> ice core record (Etheridge et al., 1996). f) Law Dome  $\delta^{13}$ C ice core record (Francey et al. 1999a).



Figure 2.9: Law Dome ice core CO<sub>2</sub> record from Etheridge et al. (1996) and  $\delta^{13}$ C record from Francey et al. (1999a) over the industrial period. Siple measurements (Friedli et al., 1986) are also shown in b).

DE08 may be about at the upper limit of age resolution for ice core records (Etheridge et al., 1996).

The Law Dome CO<sub>2</sub> record shows, with high precision, the significant variability in the pre-industrial and the increase during the industrial period. The measurements suggest that the level of CO<sub>2</sub> dropped by about 6 ppmv around 1550, and stayed low until about 1800. This period is around the time of reported low temperatures in Europe often referred to as the 'Little Ice Age' (e.g. Grove, 1988). The Law Dome record does not show the increase in the 13<sup>th</sup> century that was suggested by the South Pole record and the Barnola et al. (1995) D57 record. The rapid drop before 1600 in the Law Dome record is also not seen in the D47 and D57 records, but Etheridge et al. (1996) suggested that the different time resolutions of the cores may explain the difference. Figure 2.9a shows the Law Dome CO<sub>2</sub> record after 1800. A prominent feature is the flattening in CO<sub>2</sub> around 1940. There is also an increased growth rate for a short period around 1880, followed by a decrease in the growth rate in the 1890s. Etheridge et al. (1996) gave an uncertainty of 1.2 ppmv for the Law Dome CO<sub>2</sub> measurements.

A preliminary record of  $\delta^{13}$ C from Law Dome was presented by Leuenberger et al. (1993). After more comprehensive analysis, Francey et al. (1999a) published the fully corrected Law Dome  $\delta^{13}$ C record shown in Figures 2.8f and 2.9b. The record is less scattered than the earlier  $\delta^{13}$ C records. It allows quite precise estimation of the magnitude of the anthropogenic decrease, and shows multi-decadal variations in  $\delta^{13}$ C. The  $\delta^{13}$ C record includes a number of corrections associated with extraction and measurement of  $\delta^{13}$ C as detailed in Francey et al. (1999a), as well as corrections for fractionation due to gravitational settling and diffusion in the firn that will be developed in Chapter 3. The earlier  $\delta^{13}$ C records in general do not include the gravitation and diffusion corrections, although the corrections are small compared to the scatter in those records, and only become important with the higher measurement precision. Francey et al. (1999a) gave uncertainties of 0.025 ‰ for most of the  $\delta^{13}$ C measurements, but slightly higher for some samples with suspected systematic bias.

Between 1550 and 1800, when  $CO_2$  was low,  $\delta^{13}C$  was the highest it has been since 1000. Friedli et al. (1986) described a 'step-like shift before 1900 and a plateau between 1920 and 1950' in their Siple  $\delta^{13}C$  record. The Siple and Law Dome records (Figure 2.9b) generally agree, although the scatter makes it difficult to compare multi-decadal variability in the two records. Francey et al. (1999a) described the 'step-like' behaviour in the decrease of  $\delta^{13}C$  through the industrial period in the Law Dome record. They pointed out that the multi-decadal features in  $\delta^{13}C$  are larger than those in  $CO_2$ , relative to the overall industrial signatures.

The records shown in Figure 2.8 are all from Antarctic ice cores. There have been records constructed with measurements from northern hemisphere ice cores (e.g. Wahlen et al., 1991; Staffelbach et al., 1991) however measured CO<sub>2</sub> levels are significantly higher than those from southern hemisphere cores (Barnola et al., 1995; Francey et al., 1997). The differences are up to 20 ppmv, and too high to represent real inter-hemispheric differences. The elevated CO<sub>2</sub> in Greenland ice core measurements is believed to be due to impurities in the ice (Delmas, 1993; Anklin et al., 1995). R. J. Francey and coworkers are working on a comparison of CO<sub>2</sub> and  $\delta^{13}$ C from Antarctic and Greenland cores, and plan to use the  $\delta^{13}$ C signature to estimate the cause of the contamination in the Greenland ice (R. J. Francey, pers. comm., 1999).

In addition to ice core records, it is also possible to use measurements of air extracted from firm to reconstruct  $CO_2$  and  $\delta^{13}C$  prior to direct measurements. This is an important way to confirm the records of trapped air and check understanding of the trapping process and air extraction techniques. Firm measurements of air dating back to early this century have been made at a couple of different sites, but as they require significant interpretation and correction with a model of firn processes, discussion of these records is postponed until Chapter 3.

There are a number of advantages of using Antarctic ice cores to reconstruct atmospheric levels of CO<sub>2</sub> and  $\delta^{13}$ C. Antarctica is far from most CO<sub>2</sub> source regions. As CO<sub>2</sub> is well mixed in the atmosphere, with inter-hemispheric transport times of the order of 1 year, the changes in ice core records reflect global changes. There can be a small difference between high southern latitudes and the actual global average surface concentration, due to the spatial distribution of sources, but this is generally of similar magnitude to the current uncertainty on the ice core measurements. The effect of this difference will be quantified in Chapter 4. The processes involved in trapping air into bubbles cause smoothing of the record in time. This can be a disadvantage (causing loss of information) as well as an advantage (smoothing out variations on shorter than decadal time scales, leaving averages of about 10 years or more). Ice cores don't have the problems associated with biological processes that complicate the use of material such as tree-rings, corals and sponges in the reconstruction of past CO<sub>2</sub> and  $\delta^{13}$ C changes.

While ice core records almost certainly provide the best way to reconstruct past CO<sub>2</sub> and  $\delta^{13}$ C, other methods can be useful and complementary. Francey et al. (1999a) described many of the methods that have been used to try to reconstruct  $\delta^{13}$ C on the century time scale. There have been a number of attempts to use  $\delta^{13}$ C from tree rings (e.g. Freyer and Belacy, 1983; Stuiver, 1986; Freyer, 1986). Tree rings offer annual time resolution and excellent dating, however these records show large variability in  $\delta^{13}$ C due to the effects of plant physiology. Photosynthetic fractionation varies with a number of factors (such as temperature, water stress) and this is recorded in the  $\delta^{13}$ C (Farquhar et al., 1982; Francey and Farquhar, 1982). Other attempts have used C<sub>4</sub> plants such as historic sugar samples, maize cobs and kernels, mosses and peat, but obtain quite low precision (see Francey et al., 1999a).

Slow growing sponges in the tropics have been used apparently quite successfully to reconstruct  $\delta^{13}$ C in surface ocean waters. Druffel and Benavides (1986) measured  $\delta^{13}$ C in the skeleton of living sclerosponge which accrete aragonite in isotopic equilibrium with the surrounding DIC system, avoiding the kinetic effects associated with photosynthesis.

The sponge record suggests a  $\delta^{13}$ C decrease of 0.5±0.15 ‰ between 1800 and 1972 in the ocean surface waters near Jamaica. Böhm et al. (1996) produced a high precision record of surface water  $\delta^{13}$ C using demosponges in the Caribbean and Coral Sea. The slow growth rate of the sponges means that they record  $\delta^{13}$ C<sub>DIC</sub> on time scales of decades to centuries. The samples are dated by measuring <sup>14</sup>C in a few samples and assuming a constant growth rate. The Caribbean record gives a decrease of  $0.9\pm0.2$  ‰ from the early 19<sup>th</sup> century to 1990 and the Coral Sea record  $0.7\pm0.3$  ‰. The decrease in the surface ocean is less than the atmospheric decrease (of about 1.4 ‰) because isotopic equilibrium between the surface ocean and the atmosphere is incomplete. The measured decrease agrees quite well with that expected for an equilibration time of the order of 10 years (Böhm et al., 1996). Enhanced subsurface water mixing in the Coral Sea is suggested to explain the smaller decrease there than in the Caribbean. New demosponge measurements have recently been made (Böhm et al., 2000).

It is useful to put the changes in  $CO_2$  over the last 1000 years into perspective in terms of changes over much longer time scales. Figure 2.10 shows the variation of  $CO_2$ ,  $CH_4$  and temperature extending back more than 400,000 years from the Vostok ice core (Petit et al., 1999). The Vostok record, covering four glacial-interglacial cycles, shows a strong correlation between temperature and the atmospheric concentrations of  $CO_2$ and  $CH_4$ .  $CO_2$  has oscillated between high values of 280–300 ppmv in warm periods and low values of around 180–200 ppmv during glacial intervals.  $\delta^{13}$ C during the last ice age was more negative than pre-industrial values (Leuenberger et al., 1992). Much of the variation in climate has periodicities corresponding to precession, obliquity and eccentricity of the Earth's orbit (Milankovitch cycles). The link between CO<sub>2</sub> and climate on these time scales is not well understood, although it is likely that the oceans played an important role for  $CO_2$ , perhaps through changes in the biological pump strength and in ocean alkalinity (Leuenberger et al., 1992). It is possible that  $CO_2$  and  $CH_4$  may have contributed significantly to the glacial-interglacial climate changes by amplifying the effects of the orbital forcing (Petit et al., 1999). The recent increase in  $CO_2$  during the industrial period to today's 360 ppmv has been very rapid, and to levels that are unprecedented during the past 420 kyr.



Figure 2.10: Vostok  $CO_2$ , temperature and methane records over four glacial-interglacial cycles from Petit et al. (1999).

### 2.9 Forcing mechanisms

In this section, many of the forcing mechanisms that may be responsible for variations in  $CO_2$  over the last 1000 years are discussed. These include both natural and anthropogenic forcings.

### 2.9.1 Anthropogenic inputs

The greatest influence man has had on the carbon cycle is through the burning of fossil fuels. Figure 2.11a shows recent estimates of the source due to fossil fuel burning and cement production by Marland et al. (1999). The estimates are based on United Nations fuel production data and a number of assumptions and approximations to convert fuel production to  $CO_2$  emissions (Keeling, 1973; Marland and Rotty, 1984).  $CO_2$  emissions due to cement production are around 1–2 % of that due to fossil fuel burning. Uncertainties in the global annual emissions were estimated at 6–10 % by Marland and Rotty (1984).

Figure 2.11b shows estimates of the  $\delta^{13}$ C of the fossil fuel source (Andres et al., 2000), which varies with time because of the changing mix of coal, petroleum and natural gas being consumed, and the changing mix of petroleum from different areas with characteristic isotopic signatures.



Figure 2.11: a) Estimated flux of CO<sub>2</sub> to the atmosphere due to fossil fuel burning and cement production (Marland et al., 1999) and land-use change (Houghton, 1995a). b) Estimated  $\delta^{13}$ C of the fossil fuel source (Andres et al., 2000).

There are other ways in which man has had an impact on atmospheric  $CO_2$ . Houghton et al. (1983) estimated the net flux of  $CO_2$  to the atmosphere between 1860 and 1980 due to changes in the use of land worldwide. Their net flux estimates considered harvest of forests, clearing of natural ecosystems for agriculture and afforestation. They modelled changes in vegetation, soil and products from the forest with a 'bookkeeping' model that accounted for the changes over time that follow a disturbance, with different components regrowing or decaying at various rates. Houghton (1995a) updated the land-use change estimates for 1850–1990, and these are shown in Figure 2.11a (dashed line). More recent estimates (Houghton, 1999) have just been published, and these are slightly higher after about 1950 than those shown. A large component of land-use change today is due to tropical biomass burning. The global net carbon flux due to land-use change has been predominantly due to tropical regions since about 1940, and was mainly due to temperate and boreal regions prior to that (Houghton, 1995b). Clearing of forests in Europe dates back many centuries (Darby, 1956), although information on this is pretty limited.

DeFries et al. (1999) estimated the total emission of carbon due to human-induced

land-use change from a comparison of maps of existing and natural vegetation with the CASA biosphere model. The estimated total biospheric carbon losses of 182 and 199 GtC up to 1987 for two different simulations. They compared this to the Houghton (1999) total flux of 124 GtC between 1850 and 1990, and suggested that the difference (one third of the DeFries et al. total) is due to emissions before 1850.

There are a number of studies that have looked at different components of the gross release of biospheric  $CO_2$  to the atmosphere due to anthropogenic activities. Kammen and Marino (1993) produced a timeseries for the period 800-1990 AD of global  $CO_2$  emissions from biomass combustion due to domestic consumption (cooking and heating), mercantile activities (e.g. firing ceramics and metallurgy), construction and wetland and dryland agricultural land management. The emission estimates (Figure 2.12a) are based on per capita wood use for the different activities and world population data. These are gross fluxes as they don't take into account regrowth in response to harvest, and are therefore difficult to compare directly with the Houghton net flux estimates.

Woodcock and Wells (1994) discuss broadcast burning, the practice of lighting fires that are allowed to spread freely. Native peoples in North, Central and South America (as well as in other countries) set fires for a variety of reasons, including driving game, clearing land, encouraging fodder and as a tactical weapon in battle. European settlement in the New World brought about a decline in these burning practices. Although the estimated annually burned biomass for the high frequency burning state is similar to estimates of present day burning, the earlier biomass burning was more widely distributed latitudinally than today. The change in the burning practices over the last 400-500 years, shifting to a higher biomass/lower fire-frequency state may have contributed to an increased mid- to high-latitude carbon sink (Woodcock and Wells 1994).

The 'Pioneer Agriculture Revolution' (PIAGREV), a period of increased biomass burning around 1850-1900, was discussed by Holdsworth et al. (1996). The event was first noted by Wilson (1978) who saw a sharp decrease in tree ring  $\delta^{13}$ C between 1860 and 1890, and blamed the rapid development of agriculture in North America, New Zealand, Australia, South Africa and Eastern Europe (the 'pioneer revolution'). Although Holdsworth et al. questioned Wilson's data and methods, they found evidence for the PIAGREV in ammonium, particulate concentrations and black carbon in Greenland ice cores, as well as in



Figure 2.12: a) Estimates of non-fossil, anthropogenic carbon emissions from Kammen and Marino (1993). b)  $CO_2$  flux due to the PIAGREV estimated by Holdsworth et al. (1996). The Houghton (1995a) land-use change and Marland et al. (1999) fossil fuel fluxes are shown for comparison. c) Houghton et al. (1999) land-use change estimates for the United States (solid line) and the Houghton (1995a) global estimates.

other tree ring  $\delta^{13}$  C. CO<sub>2</sub> levels in Greenland ice cores for this period are elevated compared to Antarctic values, and this is taken by Holdsworth et al. (1996) as further evidence of the PIAGREV, which it is believed was predominantly in the northern hemisphere. The PIAGREV apparently consisted of 2 main episodes, 1850-1860 and 1890-1900, with the second episode being the larger one. Railways were being established in the last decades of the 19<sup>th</sup> century, opening up land previously not accessible for clearing. Holdsworth et al. constructed an input function (Figure 2.12b, solid line) by successive trial such that when run in a 2-d carbon cycle model gave an increase in the northern hemisphere CO<sub>2</sub> concentration of about 5-10 ppmv above the Antarctic level between 1850-1920, and using additional sinks, agreement with Antarctic levels in the southern high latitudes. The Holdsworth et al. estimates are essentially a deconvolution (see section 2.10), but they assume that the Greenland ice core  $CO_2$  levels accurately reflect northern hemisphere atmospheric levels, which may not be the case. Processes affecting  $CO_2$  in Greenland ice are not yet well enough understood (see Section 2.8). Nonetheless, the PIAVREV may still have been a significant event. Increased releases are not seen in the Houghton global estimates around this time. Houghton et al. (1999) recently revised the net flux estimate due to land-use change for the United States between 1700–1990. Their estimates show a broad peak between 1850 and 1900, with a sharp increase through the 1850s, another sharp increase to a maximum in the 1870s then slightly lower, stable values in 1880–1900 (Figure 2.12c). The decadal scale peaks are mainly due to burning of vegetation for croplands. The previous estimates for the U.S. used in the global totals published to date were much smoother and without peaks (Houghton, 1999, Figure 5). It is not clear whether agricultural expansion in other parts of the world would have peaked at different times or synchronously with the U.S. Careful analysis for the rest of the world similar to that done for the U.S., provided the necessary data exist, may be able to answer this question.

#### 2.9.2 Climate

Climate is a major natural forcing mechanism for the carbon cycle and some of the ways it can influence fluxes of  $CO_2$  have already been discussed in Sections 2.3 and 2.4. This section will focus mainly on describing variations in climate over the last 1000 years as well as some of their possible causes. Climate variations on time scales of about 10 years and longer are most relevant to the understanding of  $CO_2$  ice core records.

Reliable instrumental temperature records begin in the late  $17^{\text{th}}$  and early  $18^{\text{th}}$  centuries for Western Europe and later for other parts of the world (Jones and Bradley, 1992a). Climate information prior to this is fairly limited, and comes primarily from historical records (such as accounts of extreme events) and from proxy records (mainly tree rings, ice cores, corals and records of the retreat and advance of glaciers). Proxy records often reflect climate for a particular season. Care is needed when different temperature records are compared as climatic variations at a site may not be the same for all seasons (Jones and Bradley, 1992b; Borisenkov, 1992). In addition, when relating CO<sub>2</sub> variations to climate variations, some seasons and regions will have more impact on global CO<sub>2</sub> than others.

Discussion of climate over the last 1000 years very often involves mention of the 'Medieval Warm Period' (MWP) and the 'Little Ice Age' (LIA). The MWP is described as an interval of apparently elevated temperatures between about 900–1300 AD, which was followed by the LIA, a centuries-long period of cool, dry conditions (Lamb, 1982; Grove, 1988; Hughes and Diaz, 1994; Pfister et al., 1998). Description of climate in terms of these century-scale features was originally based mainly on climate histories from England and surrounding areas. The MWP was characterised by the withdrawal of glaciers, few poor harvests and the colonisation of Greenland by the Vikings. Reduced sea ice and friendly seas made communication between Europe, Greenland and Iceland possible. In the LIA there were reports of glaciers over-running farms in Iceland, damaging frosts and sea ice surrounding Iceland and cutting off Greenland. Lower summer temperatures meant a shorter growing season and failures of crops, at times causing famine and loss of life (Lamb, 1982). Lamb (1982) estimated the 50-year-averaged temperature and rainfall in central England since 900 AD (Figures 2.13a and 2.13b). These estimates, which are based on historical records, show the warmth of the high Middle Ages and the cool, dry conditions of the LIA which culminated around the 17<sup>th</sup> century. The magnitude of the average temperature variations on this time scale is around 1°C.

There has been some debate as to whether the terms MWP and LIA are in fact misleading. Hughes and Diaz (1994) and Jones and Bradley (1992b) objected to this simple description of climate variation, because it suggests that these were prolonged, globally synchronous events, when in fact these periods had both warm and cold climatic anomalies, and the extremes in one region were often not coincident with those in other regions. However, as Mann et al. (1999) pointed out, Lamb (1982) had not suggested that the MWP or LIA were global or sustained events, and had in fact talked in detail about the complex variability in different regions on annual and decadal time scales as well as the longer, century time scale.

There are many individual temperature records covering the period of the MWP and the LIA, particularly from tree-rings. These records show significant variability on interannual and decadal time scales. On the longer time scale, some records show evidence of reduced temperatures during the LIA (e.g. in South America (Boninsegna, 1992 and Villalba 1994), northeastern US (Baron, 1992), Siberia (Briffa et al., 1995), the Arctic (Tarussov,



Figure 2.13: a) 50-year averages of temperature in Central England from Lamb (1982). b) 50-year averages of precipitation. c) Combined northern hemisphere temperatures from Bradley and Jones (1993). Combined temperatures for d) North America, e) Europe and f) China.

1992) and the Eastern Pacific (Dunbar et al., (1994)) while some records show no evidence (e.g. in India (Yadav et al., 1999), Camp Century, Greenland and Siple, Antarctica (Thompson, 1992) and Spain and Morocco (Serre-Bachet et al., 1992)). Bradley and Jones (1993) combined many of the northern hemisphere summer temperature records dating back to 1400, and found that the combined record did in fact show colder conditions between about 1570-1730 and in the 19<sup>th</sup> century (Figure 2.13c). Figures 2.13d–2.13f show combined temperature records for North America, Europe and China. In the southern hemisphere there are a limited number of fine resolution records, and the large area of ocean makes it difficult to reconstruct the average behaviour of the hemisphere.

While the MWP and LIA may not have been persistent, homogeneous events, there is evidence that conditions were warmer during the MWP and cooler during the LIA, at least in some seasons and in some regions (Hughes and Diaz, 1994; Bradley and Jones, 1993). Apart from lower temperature and precipitation, the LIA is characterised by increased variability in temperature and precipitation, both from one year to the next and from one group of 6-8 years to the next (Lamb, 1982; Pfister, 1992). Kreutz et al. (1997) found indications that atmospheric circulation intensity in the South Pacific and North Atlantic increased abruptly and synchronously around 1400 at the beginning of the LIA. This may be related to the relatively large climate variability in the LIA. Although the LIA temperature perturbation ceased around 1800, the increased circulation has persisted through the 20<sup>th</sup> century.

Figure 2.14 shows the variation in surface air temperature over the last 150 years from a combination of land and marine measurements (Jones et al., 1999). A major feature of this record is the warming in the 20<sup>th</sup> century, which may be natural variability but could also be due to the enhanced greenhouse effect, or both. The temperature record shows significant annual and decadal variability.



Figure 2.14: Hemispheric and global average surface air temperature records for the whole year relative to 1961–1990 from Jones et al. (1999).

An understanding of the causes of climate variations may help in the reconstruction of climate in the past, as well as helping to determine the possible impact of these variations on CO<sub>2</sub>. Likely causes of climate variation on time scales of years to centuries include changes in solar forcing, volcanic eruptions, greenhouse gas forcing and ocean circulation. Discussion of these processes follows. (In the 16<sup>th</sup> century it was believed by some that witches were directly responsible for the climate anomalies of the LIA (Behringer, 1999). This, however, will not be discussed).

There have been many studies describing the similarities between surface temperature and solar variability records (e.g. Eddy, 1976; Lean et al., 1995; Reid, 1991; Friis-Christensen and Lassen, 1991). In particular, the Maunder Minimum (1645-1715), when practically no sunspots were seen, coincided with the coldest excursion of the LIA and the Grand Maximum (1100-1250) coincided with the warmest part of the MWP (Eddy, 1976). The Spörer Minimum (1450-1550) and the Dalton Minimum (1790-1830) also coincided with cold episodes of the LIA (Eddy, 1976; Reid, 1997). (High solar activity corresponds to large sunspot numbers, high total and UV radiative outputs from the sun and low cosmic ray production of <sup>14</sup>C and <sup>10</sup>Be in the atmosphere (Eddy, 1976; Lean and Rind, 1998).) The response of the climate system to these solar variations is not well understood (Lean and Rind, 1998; Marcus et al., 1999). In addition, climate sensitivity may be different for decadal and century scale perturbations (Lean and Rind, 1998), since positive feedbacks, for example involving ocean circulation (Stuiver and Braziunas, 1993), may be important for the longer time scale. A number of studies have tried to empirically determine the relationship between climate and solar forcing and use this to test whether the measured increase in solar forcing since 1900 may have contributed to the observed warming in the 20<sup>th</sup> century (e.g., Lean and Rind, 1999; Reid, 1997). Results vary quite considerably, depending on the data sets and model assumptions used. Most studies have concluded that solar forcing accounts for less than half of the observed warming (e.g. Lean and Rind, 1999; Reid, 1997). In general, higher correlations are seen between solar forcing and temperature variations before 1800 than after (Lean and Rind, 1998; 1999).

Large volcanic eruptions can have a short-lived but significant and widespread influence on climate. An abundance of sulphur aerosols in the stratosphere caused by a volcanic eruption reflects solar radiation back to space, cooling the troposphere and the surface, and absorbs radiation, warming the stratosphere. After 1-3 years the aerosols fall into the troposphere and are deposited at the surface (Free and Robock, 1999). The response of climate to a volcanic eruption depends on the strength of the eruption, the geographic location of the volcano and the prevailing atmospheric circulation (Andronova et al., 1999). The response can vary greatly for different eruptions, and is sometimes in the same year as the eruption, sometimes the next year. The phase of the quasi-biennial oscillation can influence how quickly the products of tropical eruptions are dispersed to higher latitudes (Pyle, 1998). The response in mid-latitudes to mid-latitude eruptions is more immediate. Some volcanoes affect both hemispheres, others only one (Andronova et al., 1999).

Proxy climate records show a sharp temperature decrease in the years following a number of the larger volcanic eruptions (Briffa et al., 1998; White et al., 1997; D'Arrigo and Jacoby, 1999). Some notable examples of climatically significant volcanic events over the last 1000 years are the following: The eruption of Huaynaputina in Peru in February 1600 proceeded what temperature records show to have been the coldest summer of the past 600 years in 1601 (de Silva and Zielinski, 1998; Briffa et al., 1998; Jones et al., 1995). The well-known 'year without a summer' in 1816 and subsequent cold summers of 1817-1819 followed the April 1815 eruption of Tambora, Indonesia (Briffa et al., 1998; D'Arrigo and Jacoby, 1999). The eruption of Laki (Lakagígar) in Iceland in 1783 apparently caused the 'Great Dry Fog' of 1783 that spread across Europe, and the famine in Iceland that was known as the 'famine of the mist' (Stothers, 1996; Demarée et al., 1998). 1783 was also known as the 'year without a summer' in Japan (D'Arrigo and Jacoby, 1999). The recent major eruption of Mt. Pinatubo in the Philippines in June, 1991 has been widely studied due to the wealth of data collected, particularly by satellites. This eruption is believed to have caused a significant perturbation to climate (Dutton and Christy, 1992) and the carbon cycle (Sarmiento, 1993).

There have been a number of different indices developed to quantify the effects of volcanic eruptions, such as the dust veil index (DVI), the volcanic explosivity index (VEI) and the ice core volcanic index (IVI) (Briffa et al., 1998). These reflect different aspects of volcanic eruptions, but none are ideal for characterising the climate response (Bradley and Jones, 1995). Although the effect of one volcano on climate is predominantly on the interannual time scale, a change in the frequency of major eruptions is believed to

also affect climate on decadal or century time scales. A decrease in the number of major eruptions in the 19<sup>th</sup> and 20<sup>th</sup> centuries may have contributed to the observed warming over this period (Andronova et al., 1999; Free and Robock, 1999).

Greenhouse gases are believed by some to have been responsible for at least part of the observed increase in temperature in the  $20^{\text{th}}$  century. However, variations in greenhouse gases in the 800 years preceding the industrial period are too small to have been a significant driver of climate. In particular, it is very unlikely that the reduced temperatures in the LIA were primarily due to the lower CO<sub>2</sub> levels, although CO<sub>2</sub> may have caused a positive feedback to slightly increase the cooling (Etheridge et al., 1996; Etheridge, 1999).

Broecker et al. (1999) suggested that the reduced temperatures in the LIA may have been due to greater deep water formation in the Southern Ocean at that time. It has also been suggested that the LIA is only the last in a series of climate oscillations (Kerr, 1999). Showers and Bond (1999) found evidence of similar cold periods every millennium or two for at least the last 140,000 years in deep sea sediment records. Probably the most likely drivers of these climate variations are solar variability or an oscillation in ocean circulation. Evidence for a roughly 1500-year cycle in the speed of ocean bottom water currents, which are slower during cold phases, has also been found (Kerr, 1999).

Apart from externally forced natural variation, there is also significant internal variability in the climate system. Many climate models exhibit variability with similar characteristics to that observed when run without any variation in forcings (Free and Robock, 1999). This variability is due to chaotic dynamics in non-linear interactions between different processes. Hunt (1998) ran a global climate model for 500 years and compared the calculated temperature variability with that observed. The model generated decadal scale variations of similar magnitude to observations, but no multi-century trends. In the model, averages over land and ocean and northern and southern hemispheres exhibit similar long term variability in surface temperature, but temperature variability at individual gridpoints was not so coherent. This is similar to observed. The more intense climate anomalies were seen in the northern hemisphere, probably due to the higher proportion of land in the northern hemisphere and the lower heat capacity of land compared to ocean. The model calculations suggest that internal variability may be responsible for a large proportion of the observed natural climate variability. The scarcity of climate data prior to instrumental records makes it difficult to characterise temperature variability over large spatial scales. Mann et al. (1998) tried to address this. They decomposed the  $20^{\text{th}}$  century instrumental temperature record into its dominant patterns of variability and used the relationship of temperature at an individual site to these dominant patterns with proxy temperature records over the last 600 years to reconstruct temperature patterns back to 1400. Long term trends in the reconstructed annual mean northern hemisphere temperature are quite similar to the decadal northern hemisphere summer temperature anomalies of Bradley and Jones (1993). The reconstructed temperatures were then compared with external forcings (CO<sub>2</sub>, solar and volcanic variations). They found, as did Free and Robock (1999), that a combination of solar and volcanic forcings explained much of the LIA climate change.

### 2.9.3 Other natural forcings

Most of the natural forcings that influence  $CO_2$  do so via climate, as discussed in the previous section, although some can also have a direct influence on  $CO_2$ . For example, ocean circulation can affect  $CO_2$  directly by perhaps changing the inter-hemispheric gradient or mean atmospheric level as well as affecting climate. Another possible natural forcing on the carbon cycle is fires that are started by natural causes (lightening). 80 % of the total area burned in the boreal is by natural fires (Savarino and Legrand, 1998). The occurrence and extent of natural fires responds to climatic conditions, such as length and intensity of dry season. In addition, cold climate causes stable air masses and reduced occurrence of lightening. Savarino and Legrand (1998) identified 3 active burning periods since 1193 AD – 1200-1350, 1830-1930 and to a lesser extent 1500-1600. Depending on the amount of biomass burned, this may have caused some variability in pre-industrial  $CO_2$  levels.

Although ENSO is essentially a climate oscillation, it is believed to have a distinctive affect on the carbon cycle through both biospheric and oceanic processes, so it will be discussed in this section rather than in the previous section on climate. The relationship between ENSO and atmospheric  $CO_2$  growth rates has been studied by a number of authors (e.g., Bacastow, 1976; Thompson et al., 1986; Elliot et al., 1991; Rayner et al., 1999b). There are a number of ways in which ENSO can affect  $CO_2$  in the atmosphere, the main ones are the reduction in the tropical ocean source as described in Section 2.4, and reduced photosynthesis, increased respiration and increased biomass burning due to reduced rainfall and increased temperature over land (Elliot et al., 1991; Rayner et al., 1999b). The overall effect of ENSO on  $CO_2$  is quite complex. Rayner et al. (1999b) compared tropical  $CO_2$  fluxes from 3 spatial inversions with the SOI index. They found that the initial response of  $CO_2$  fluxes to ENSO is a reduced source from the ocean, which is later offset by increased  $CO_2$  release from the land. The different behaviour of the  $CO_2$ fluxes at different stages of an event implies that the overall effect probably depends on its duration. For  $CO_2$  changes recorded in ice cores, the extended sequences of El Niño and La Niña, such as those identified by Allan and D'Arrigo (1999), are probably most relevant, and the effect of these extended events may be quite different to that from shorter events. It is also possible that a change in the frequency of El Niño events may impact longer term averages of temperature or precipitation, as well as  $CO_2$  levels.

## 2.10 Methods for inversion of ice core records

There are a number of different modelling approaches that can be used to interpret variations in the CO<sub>2</sub> and  $\delta^{13}$ C ice core records in terms of CO<sub>2</sub> sources. Typically these involve either a *forward calculation*, where concentrations are calculated for a given source history, or a *deconvolution*, which is a type of *inverse calculation*, where the source history is deduced to match specified concentrations. The forward calculation is a convolution of a set of sources and how the atmosphere responds to them. It can use forcings such as those described in the previous section, either directly (e.g. the fossil fuel source) or with additional modelling (e.g. fluxes from a biospheric model). Calculated concentrations can be compared with the ice core record, but as information on sources is fairly limited, some of the observed CO<sub>2</sub> and  $\delta^{13}$ C variability is left unexplained by this technique.

The deconvolution is widely used because concentrations are generally better known than sources. Two quite specific calculations that are commonly applied to CO<sub>2</sub> (and  $\delta^{13}$ C) ice core records are known as the *single deconvolution* and *double deconvolution*. In a single deconvolution, the source due to fossil fuel burning is specified, uptake by the ocean calculated and mass balance (i.e. equation 2.11 in section 2.5) used to determine an additional flux that is attributed to biospheric uptake or release (e.g. Siegenthaler and Oeschger, 1987; Siegenthaler and Joos, 1992; Bruno and Joos, 1997).  $\delta^{13}$ C can be calculated and compared with observations as a check on the calculation. The single deconvolution relies on an ocean model to determine oceanic  $CO_2$  uptake. In general, simple ocean carbon cycle models mainly describe the 'passive' response of the ocean to changing atmospheric levels, and are not able to capture some of the variation in ocean uptake, for example on ENSO time-scales. More complex, mechanistic models are required to model the 'active' response induced by climate variations.

The mass balance equation (equation 2.11) requires knowledge of the derivative of  $CO_2$  concentration with time,  $dC_a/dt$ , at every timestep. Estimation of this quantity from ice core records is usually done by fitting a smoothing spline to the measurements. An important issue for the single deconvolution calculation is that the degree of smoothing used for the spline has a large impact on the  $CO_2$  derivative and therefore on the calculated fluxes. Therefore, although the  $CO_2$  concentration is quite well known from ice core records, its derivative is subject to some uncertainty.

In a double deconvolution, the fossil-fuel source is again specified, and the stable isotope, <sup>13</sup>C, is used with CO<sub>2</sub> to partition the remaining source/sink into oceanic and terrestrial components. Keeling et al. (1989a) introduced the terms *single* and *double* deconvolution. They performed a double deconvolution using direct measurements of  $\delta^{13}$ C after 1978. Their double deconvolution method consisted of using mass balance to estimate  $F_{\rm rem}$  with

$$F_{\rm rem} = \frac{d}{dt}C_a - F_f + F_o \tag{2.17}$$

where  $F_o$  is calculated by an ocean model and  $F_{\rm rem}$  is the 'remaining' net CO<sub>2</sub> flux (i.e. that not already accounted for).  $F_{\rm rem}$  is partitioned between oceanic and biospheric exchange using an iterative search by Newton's method at the end of each timestep to find the partitioning that gives agreement between modelled  $\delta^{13}$ C and a spline fit to observations.

Subsequent double deconvolutions have used the C and <sup>13</sup>C budget equations developed by Tans et al. (1993) and described in section 2.5 (equations 2.11 and 2.13). Francey et al. (1995b) solved these equations using annual averages of CO<sub>2</sub> and  $\delta^{13}$ C from direct measurements between 1982 and 1993. They used constant values for the isoflux terms. Joos and Bruno (1998) describe the application of the double deconvolution technique to ice core CO<sub>2</sub> and  $\delta^{13}$ C, and demonstrate the method with Law Dome CO<sub>2</sub> and Siple and Dye 3  $\delta^{13}$ C. (The Dye 3 record (Leuenberger, 1992) is a northern hemisphere record, and therefore was not discussed in the previous section.) They used spline fits to the ice core measurements, and models of the oceans and biosphere to estimate the temporal evolution of the isofluxes required for the  ${}^{13}$ C budget. This type of calculation will be referred to as a mass balance double deconvolution.

Both the forward and inverse techniques are useful for studies of the ice core records, but sometimes the distinction between forward and inverse can become a bit blurred. There is a sense in which a forward model can be used for an inverse calculation, with source estimates run in a forward model, but iteratively adjusted (either by trial-and-error or with a formal inversion technique) to give better agreement of modelled and observed concentrations (Enting and Pearman, 1993). Perhaps a good distinction is that sources used by the forward calculation are generally based on independent information (e.g. climate data, emissions estimates), while the deconvolution calculates the source history from changes in concentration, and the deduced sources can later be interpreted in terms of processes.

### 2.11 Previous inversions of ice core records

The single deconvolution technique has been applied by a number of authors to the Siple ice core  $CO_2$  record (Siegenthaler and Oeschger, 1987; Siegenthaler and Joos, 1992; Keeling et al., 1989a; Sarmiento et al., 1992) and similar results were obtained for the estimated biospheric flux by these studies, using a range of models of ocean uptake. The calculated non-fossil flux was a source to the atmosphere and either fairly constant or gradually increasing through the 19<sup>th</sup> century and first part of the 20<sup>th</sup> century. The flux then decreased to become a sink before increasing rapidly during the 1980s (Figure 2.15).

Craig et al. (1997) and Bruno and Joos (1997) performed single deconvolutions on both the Siple and Law Dome  $CO_2$  records, and estimated the uncertainties in the deduced fluxes. They both found an abrupt shift in the non-fossil flux around the 1930s from a source to a sink using the Law Dome record. A similar shift is seen with the Siple record if the same smoothing is used for the  $CO_2$  spline as was used for Law Dome. The earlier single deconvolutions for Siple mentioned above used splines that were smoother because of the larger uncertainties in the Siple measurements (3 ppmv compared with 1.2 ppmv for Law Dome), so the shift to a sink was more gradual. The deduced non-fossil flux was compared in both studies with estimates of the source due to land-use change (Houghton,



Figure 2.15: Results from the single deconvolution study by Siegenthaler and Joos (1992). Solid line shows emissions due to fossil  $CO_2$  production, the dashed line is ocean uptake calculated with the HILDA model and the dotted line is the net contribution from the terrestrial biota (emissions - uptake) deduced using a fit to Siple  $CO_2$  data.

1993) and found to be consistent (within the uncertainties) up to about the 1950s. After that time an increasing sink is required to match observed  $CO_2$ . This is often referred to as the 'missing sink', and may be due to  $CO_2$  or nitrogen fertilisation, climate variability or errors in the calculated ocean uptake or land-use change estimates.

Enting and Mansbridge (1987a) and Enting (1992) used linear programming to test whether estimates of the fossil fuel and land use change sources are compatible with the Siple CO<sub>2</sub> ice core record and CO<sub>2</sub> uptake that is driven by the atmospheric CO<sub>2</sub> increase (e.g. ocean uptake and fertilisation). An incompatibility was found, that was attributed to there being a perturbation associated with recovery from the Little Ice Age at the beginning of the Siple record. The Law Dome record suggests that this is in fact likely.

Friedlingstein et al. (1995) calculated variation of the fertilisation sink with time using  $5^{\circ} \times 5^{\circ}$  biosphere model and compared this with the missing sink from a single deconvolution (non-fossil - land-use change) of the Siple CO<sub>2</sub> record. The time evolution of the two are quite different, suggesting that either there are under-estimated errors in the sources and sinks already considered, or that other mechanisms (e.g. nitrogen fertilisation and climate) contribute to the missing sink (or both). They concluded that CO<sub>2</sub> fertilisation may be responsible for up to 75% of the 1850-1990 integrated sink.

Dai and Fung (1993) looked at the effect of climate variability on the carbon budget, using gridded global temperature and precipitation data sets for the period 1940–1988 in a model of the biosphere. They found that the different sensitivities of NPP and respiration to climate perturbations had caused an accumulation of carbon in the biosphere between 1950 and 1984. Their estimated uptake for the period due to climate variations was  $20\pm5$  GtC.

Joos and Bruno (1998) performed a double deconvolution on the Law Dome CO<sub>2</sub> and Siple and Dye 3  $\delta^{13}$ C ice core records. The results show the biospheric flux change from a source to a sink during the first half of this century, as seen in the single deconvolution. The cumulative ocean uptake is much larger for the single deconvolution calculation than for the double, and there are large fluctuations in the deduced ocean flux, including an ocean source to the atmosphere between 1850 and 1878. The results of this calculation were treated with caution by the authors because of the large uncertainties on the  $\delta^{13}$ C data, and the fact that these records have no  $\delta^{13}$ C data between 1956 and 1982.

A very recent paper by Joos et al. (1999) applied the double deconvolution method described in Joos and Bruno (1998) to the Law Dome CO<sub>2</sub> and  $\delta^{13}$ C records used here. Discussion of their results is postponed until Chapter 5.

### 2.12 Concluding remarks

This chapter has given the background information on the carbon cycle necessary for interpretation of the new Law Dome CO<sub>2</sub> and  $\delta^{13}$ C ice core record. In particular, this discussion has included description of carbon cycling in the atmosphere, terrestrial biosphere and ocean; the use of carbon isotopes to help infer fluxes; anthropogenic and natural forcings on atmospheric carbon and methods for inverting concentration measurements to estimate fluxes. Methods for interpreting CO<sub>2</sub> and  $\delta^{13}$ C on the time scale of years to centuries and previous results were discussed in some detail.

The main effort in carbon cycle research involves understanding how net  $CO_2$  uptake is partitioned, what processes are responsible, and whether they are likely to continue in the future. A major part of this is understanding natural variability in  $CO_2$ . Analysis of the Law Dome ice core record will give useful insight into both the anthropogenic change and natural variability.