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Greenhouse Gases and Aerosols

R.T. WATSON, H. RODHE, H. OESCHGER, U. SIEGENTHALER

Contributors:
*M. Andreae; R. Charlson; R. Cicerone; J. Coakley; R. Derwent; J. Elkins;
F. Fehsenfeld; P. Fraser; R. Gammon; H. Grassl; R. Harriss; M. Heimann;
R. Houghton; V. Kirchhoff; G. Kohlmaier; S. Lal; P. Liss; J. Logan; R. Luxmoore;
L. Merlivat; K. Minami; G. Pearman; S. Penkett; D. Raynaud; E. Sanhueza; P. Simon;
W. Su; B. Svensson; A. Thompson; P. Vitousek; A. Watson; M. Whitfield; P. Winkler;
S. Wofsy.*

CONTENTS

EXECUTIVE SUMMARY

The Earth's climate is dependent upon the radiative balance of the atmosphere, which in turn depends upon the input of solar radiation and the atmospheric abundances of radiatively active trace gases (i e , greenhouse gases), clouds and aerosols

Since the industrial revolution the atmospheric concentrations of several greenhouse gases, i e , carbon dioxide (CO_2) methane (CH_4), chlorofluorocarbons (CFCs), nitrous oxide (N_2O), and tropospheric ozone (O_3), have been increasing primarily due to human activities Several of these greenhouse gases have long atmospheric lifetimes, decades to centuries, which means that their atmospheric concentrations respond slowly to changes in emission rates In addition there is evidence that the concentrations of tropospheric aerosols have increased at least regionally

Carbon Dioxide
The atmospheric CO_2 concentration at 353 ppmv in 1990 is now about 25% greater than the pre industrial (1750 1800) value of about 280 ppmv, and higher than at any time in at least the last 160,000 years Carbon dioxide is currently rising at about 1 8 ppmv (0 5%) per year due to anthropogenic emissions Anthropogenic emissions of CO_2 are estimated to be 5 7±0 5 Gt C (in 1987) due to fossil fuel burning, plus 0 6   2 5 Gt C (in 1980) due to deforestation The atmospheric increase during the past decade corresponds to (48±8)% of the total emissions during the same period with the remainder being taken up by the oceans and land Indirect evidence suggests that the land and oceans sequester CO_2 in roughly equal proportions though the mechanisms are not all well understood The time taken for atmospheric CO_2 to adjust to changes in sources or sinks is of order 50 200 years, determined mainly by the slow exchange of carbon between surface waters and deeper layers of the ocean Consequently CO_2 emitted into the atmosphere today will influence the atmospheric concentration of CO_2 for centuries into the future Three models have been used to estimate that even if anthropogenic emissions of CO_2 could be kept constant at present day rates, atmospheric CO_2 would increase to 415 - 480 ppmv by the year 2050, and to 460 - 560 ppmv by the year 2100 In order to stabilize concentrations at present day levels an immediate reduction in global anthropogenic emissions by 60 80 percent would be necessary

Methane
Current atmospheric CH_4 concentration, at 1 72 ppmv is now more than double the pre-industrial (1750 1800) value of about

0 8 ppmv, and is increasing at a rate of about 0 015 ppmv (0 9%) per year The major sink for CH_4, reaction with hydroxyl (OH) radicals in the troposphere, results in a relatively short atmospheric lifetime of about 10 years Human activities such as rice cultivation, domestic ruminant rearing, biomass burning, coal mining, and natural gas venting have increased the input of CH_4 into the atmosphere, which combined with a possible decrease in the concentration of tropospheric OH yields the observed rise in global CH_4 However the quantitative importance of each of the factors contributing to the observed increase is not well known at present In order to stabilize concentrations at present day levels an immediate reduction in global anthropogenic emissions by 15 20 percent would be necessary

Chlorofluorocarbons
The current atmospheric concentrations of the anthropogenically produced halocarbons CCl_3F (CFC 11) CCl_2F_2 (CFC 12) $C_2Cl_3F_3$ (CFC 113) and CCl_4 (carbon tetrachloride) are about 280 pptv 484 pptv 60 pptv and 146 pptv respectively Over the past few decades their concentrations, except for CCl_4 have increased more rapidly (on a percentage basis) than the other greenhouse gases, currently at rates of at least 4% per year The fully halogenated CFCs and CCl_4 are primarily removed by photolysis in the stratosphere, and have atmospheric lifetimes in excess of 50 years Future emissions will, most likely, be eliminated or significantly lower than today's because of current international negotiations to strengthen regulations on chlorofluorocarbons However, the atmospheric concentrations of CFCs 11 12 and 113 will still be significant (30 - 40% of current) for at least the next century because of their long atmospheric lifetimes

Nitrous Oxide
The current atmospheric N_2O concentration, at 310 ppbv, is now about 8% greater than in the pre-industrial era, and is increasing at a rate of about 0 8 ppbv (0 25%) per year The major sink for N_2O, photolysis in the stratosphere, results in a relatively long atmospheric lifetime of about 150 years It is difficult to quantitatively account for the source of the current increase in the atmospheric concentration of N_2O but it is thought to be due to human activities Recent data suggest that the total annual flux of N_2O from combustion and biomass burning is much less than previously believed Agricultural practices may stimulate emissions of N_2O from soils and play a major role In order to stabilize concentrations at present day levels an immediate

reduction of 70 80% of the additional flux of N_2O that has occurred since the pre industrial era would be necessary

Ozone

Ozone is an effective greenhouse gas especially in the middle and upper troposphere and lower stratosphere Its concentration in the troposphere is highly variable because of its short lifetime It is photochemically produced in-situ through a series of complex reactions involving carbon monoxide (CO), CH_4, non-methane hydrocarbons (NMHC), and nitrogen oxide radicals (NO_x), and also transported downward from the stratosphere The limited observational data support positive trends of about 1% per year for O_3 below 8 km in the northern hemisphere (consistent with positive trends in several of the precursor gases, especially NO_x, CH_4 and CO) but probably close to zero trend in the southern hemisphere There is also evidence that O_3 has decreased by a few percent globally in the lower stratosphere (below 25 km) within the last decade Unfortunately, there are no reliable long-term data near the tropopause

Aerosol particles

Aerosol particles have a lifetime of at most a few weeks in the troposphere and occur in highly variable concentrations A large proportion of the particles that influence cloud processes and the radiative balance is derived from gaseous sulphur emissions Due to fossil fuel combustion, these emissions have more than doubled globally, causing a large increase in the concentration of aerosol sulphate especially over and around the industrialized regions of Europe and North America Future concentrations of aerosol sulphate will vary in proportion to changes in anthropogenic emissions Aerosol particles derived from natural (biological) emissions may contribute to climate feedback processes During a few years following major volcanic eruptions the concentrations of natural aerosol particles in the stratosphere can be greatly enhanced

1.1 Introduction

The Earth's climate is dependent upon the radiative balance of the atmosphere, which in turn depends upon the input of solar radiation and the atmospheric abundances of radiatively active trace gases (i e, greenhouse gases), clouds and aerosols Consequently, it is essential to gain an understanding of how each of these climate forcing agents varies naturally, and how some of them might be influenced by human activities

The chemical composition of the Earth's atmosphere is changing, largely due to human activities (Table 1 1) Air trapped in Antarctic and Greenland ice shows that there have been major increases in the concentrations of radiatively active gases such as carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) since the beginning of the industrial revolution In addition industrially-produced chlorofluorocarbons (CFCs) are now present in the atmosphere in significant concentrations, and there is evidence that the concentrations of tropospheric O_3 and aerosols have increased at least regionally

Atmospheric measurements indicate that in many cases the rates of change have increased in recent decades Many of the greenhouse gases have long atmospheric life-times, decades to centuries, which implies that their atmospheric concentrations respond slowly to changes in emission rates

The effectiveness of a greenhouse gas in influencing the Earth's radiative budget is dependent upon its atmospheric concentration and its ability to absorb outgoing long-wave terrestrial radiation Tropospheric water vapour is the single most important greenhouse gas, but its atmospheric concentration is not significantly influenced by direct anthropogenic emissions Of the greenhouse gases that are directly affected by human activities, CO_2 has the largest radiative effect, followed by the CFCs, CH_4, tropospheric O_3, and N_2O Although the present rate of increase in the atmospheric concentration of CO_2 is about a factor of 70,000 times greater than that of CCl_3F (CFC-11) and CCl_2F_2 (CFC-12) combined, and a factor of about 120 times greater than that of CH_4, its contribution to changes in the radiative forcing during the decade of the 1980s was

Table 1.1 Summary of Key Greenhouse Gases Influenced by Human Activities [1]

Parameter	CO_2	CH_4	CFC-11	CFC-12	N_2O
Pre-industrial atmospheric concentration (1750-1800)	280 ppmv[2]	0 8 ppmv	0	0	288 ppbv[2]
Current atmospheric concentration (1990)[3]	353 ppmv	1 72 ppmv	280 pptv[2]	484 pptv	310 ppbv
Current rate of annual atmospheric accumulation	1 8 ppmv (0 5%)	0 015 ppmv (0 9%)	9 5 pptv (4%)	17 pptv (4%)	0 8 ppbv (0 25%)
Atmospheric lifetime[4] (years)	(50 200)	10	65	130	150

1   Ozone has not been included in the table because of lack of precise data
2   ppmv = parts per million by volume,   ppbv = parts per billion by volume,
    pptv = parts per trillion by volume
3   The current (1990) concentrations have been estimated based upon an extrapolation of measurements reported for
    earlier years, assuming that the recent trends remained approximately constant
4   For each gas in the table, except CO_2 the lifetime is defined here as the ratio of the atmospheric content to the total
    rate of removal This time scale also characterizes the rate of adjustment of the atmospheric concentrations if the
    emission rates are changed abruptly CO_2 is a special case since it has no real sinks but is merely circulated between
    various reservoirs (atmosphere ocean biota) The lifetime of CO_2 given in the table is a rough indication of the
    time it would take for the CO_2 concentration to adjust to changes in the emissions (see section 1 2 1 for further
    details)

about 55%, compared to 17% for CFCs (11 and 12), and 15% for CH_4 (see Section 2) Other CFCs and N_2O accounted for about 8%, and 5%, respectively, of the changes in the radiative forcing While the contribution from tropospheric O_3 may be important, it has not been quantified because the observational data is inadequate to determine its trend This pattern arises because of differences in the efficiencies of the gases to absorb terrestrial radiation

Aerosol particles play an important role in the climate system because of their direct interaction (absorption and scattering) with solar and terrestrial radiation, as well as through their influence on cloud processes and thereby, indirectly, on radiative fluxes

There is a clear need to document the historical record of the atmospheric concentrations of greenhouse gases and aerosols, as well as to understand the physical, chemical, geological, biological and social processes responsible for the observed changes A quantitative understanding of the atmospheric concentrations of these gases requires knowledge of the cycling and distribution of carbon, nitrogen and other key nutrients within and between the atmosphere, terrestrial ecosystems, oceans and sediments, and the influence of human actions on these cycles Without knowledge of the processes responsible for the observed past and present changes in the atmospheric concentrations of greenhouse gases and aerosols it will not be possible to predict with confidence future changes in atmospheric composition, nor therefore the resulting changes in the radiative forcing of the atmosphere

1.2 Carbon Dioxide

1.2.1 The Cycle of Carbon in Nature

Carbon in the form of CO_2, carbonates, organic compounds, etc is cycled between various reservoirs, atmosphere, oceans, land biota and marine biota, and, on geological time scales, also sediments and rocks (Figure 1 1, for more detailed reviews see Sundquist, 1985 Bolin, 1981, 1986, Trabalka, 1985, Siegenthaler, 1986) The largest natural exchange fluxes occur between the atmosphere and the terrestrial biota and between the atmosphere and the surface water of the oceans By comparison, the net inputs into the atmosphere from fossil fuel combustion and deforestation are much smaller, but are large enough to modify the natural balance

The turnover time of CO_2 in the atmosphere, measured as the ratio of the content to the fluxes through it, is about 4 years This means that on average it takes only a few years before a CO_2 molecule in the atmosphere is taken up by plants or dissolved in the ocean This short time scale must not be confused with the time it takes for the atmospheric CO_2 level to adjust to a new equilibrium if sources or sinks change This adjustment time, corresponding to the lifetime
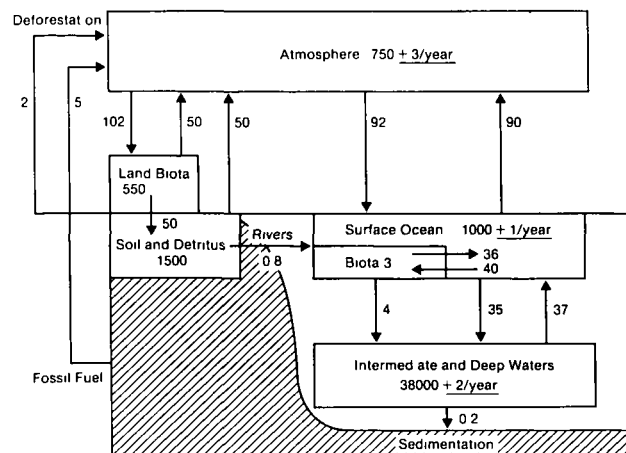
Figure 1.1: Global carbon reservoirs and fluxes The numbers apply for the present-day situation and represent typical literature values Fluxes, e g between atmosphere and surface ocean, are gross annual exchanges Numbers underlined indicate net annual CO_2 accumulation due to human action Units are gigatons of carbon (GtC, 1Gt = 10^9 metric tons = 10^{12}kg) for reservoir sizes and GtC yr^{-1} for fluxes More details and discussions are found in several reviews (Sundquist, 1985, Trabalka, 1985, Bolin, 1986 Siegenthaler, 1986)

in Table 1 1, is of the order of 50 - 200 years, determined mainly by the slow exchange of carbon between surface waters and the deep ocean The adjustment time is important for the discussions on global warming potential, cf Section 2 2 7

Because of its complex cycle, the decay of excess CO_2 in the atmosphere does not follow a simple exponential curve, and therefore a single time scale cannot be given to characterize the whole adjustment process toward a new equilibrium The two curves in Figure 1 2, which represent simulations of a pulse input of CO_2 into the atmosphere using atmosphere-ocean models (a box model and a General Circulation Model (GCM)), clearly show that the initial response (governed mainly by the uptake of CO_2 by ocean surface waters) is much more rapid than the later response (influenced by the slow exchange between surface waters and deeper layers of the oceans) For example, the first reduction by 50 percent occurs within some 50 years, whereas the reduction by another 50 percent (to 25 percent of the initial value) requires approximately another 250 years The concentration will actually never return to its original value, but reach a new equilibrium level, about 15 percent of the total amount of CO_2 emitted will remain in the atmosphere
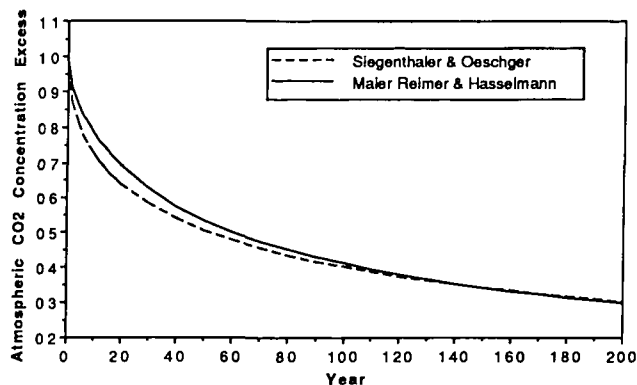
Figure 1.2: Atmospheric CO_2 concentration excess after a pulse input at time 0 (initially doubling the atmospheric CO_2 concentration), as calculated with two ocean-atmosphere models Solid line 3-dimensional ocean-circulation model of Maier-Reimer and Hasselmann (1987), dashed line 1-dimensional box-diffusion model of Siegenthaler and Oeschger (1987) The adjustment towards a new equilibrium does not follow an exponential curve, it is very fast during the first decade, then slows down more and more The concentration excess does not go to zero, after a long time, a new equilibrium partitioning between atmosphere and ocean will be reached, with about 15 percent of the input residing in the atmosphere

Figure 1.3: Atmospheric CO_2 increase in the past 250 years, as indicated by measurements on air trapped in ice from Siple Station, Antarctica (squares, Neftel et al , 1985a, Friedli et al , 1986) and by direct atmospheric measurements at Mauna Loa, Hawaii (triangles, Keeling et al , 1989a)

1 2 1 1 The role of the atmosphere

The mean annual concentration of CO_2 is relatively homogeneous throughout the troposphere because the troposphere is mixed on a time scale of about 1 year The pre-industrial atmospheric CO_2 concentration was about 280 ppmv, as reconstructed from ice core analyses (c f Section 1 2 4 1), corresponding to an atmospheric amount of 594 Gigatonnes of carbon (GtC 1 Gt = 10^9t = 10^{15}g, 1 ppmv CO_2 of the global atmosphere equals 2 12 GtC and 7 8 Gt CO_2), today, the level is about 353 ppmv (Figures 1 3 and 1 4) The atmospheric increase has been monitored since 1958 at a growing number of stations (Keeling and Heimann, 1986, Keeling et al , 1989a, Beardsmore and Pearman, 1987, Conway et al , 1988)

Figure 1.4: Monthly average CO_2 concentration in parts per million of dry air, observed continuously at Mauna Loa, Hawaii (Keeling et al 1989a) The seasonal variations are due primarily to the withdrawal and production of CO_2 by the terrestrial biota

1 2 1 2 The role of the ocean

On time scales of decades or more, the CO_2 concentration of the unperturbed atmosphere is mainly controlled by the exchange with the oceans, since this is the largest of the carbon reservoirs There is a continuous exchange of CO_2 in both directions between the atmosphere and oceans The net flux into (or out of) the ocean is driven by the difference between the atmospheric partial pressure of CO_2 and the equilibrium partial pressure of CO_2 (pCO_2) in surface waters

The exchange of carbon between the surface and deeper layers is accomplished mainly through transport by water

motions Ventilation of the thermocline (approximately the uppermost km of the ocean) is particularly important for the downward transport of anthropogenic CO_2 The deep circulation is effective on time scales of 100-1000 years

The natural carbon cycle in the ocean and in particular pCO_2 in surface ocean water are strongly influenced also by biological processes The marine biota serve as a 'biological pump , transporting organic carbon from surface waters to deeper layers as a rain of detritus at a rate of about 4 GtC per year (Eppley and Peterson 1979) which is balanced by an equal upward transport of carbon by deeper water richer in CO_2 than surface water This biological pump has the effect of reducing surface pCO_2

very substantially without the biological pump ("dead ocean) the pre-industrial CO_2 level would have been higher than the observed value of 280 ppmv, at perhaps 450 ppmv (Wenk, 1985, Bacastow and Maier-Reimer, 1990) Alterations in the marine biota due to climatic change could therefore have a substantial effect on CO_2 levels in the future Note, however, that the "biological pump" does not help to sequester anthropogenic CO_2 (see Section 1 2 4 2)

1 2 1 3 The role of terrestrial vegetation and soils
The most important processes in the exchange of carbon are those of photosynthesis, autotrophic respiration (i e , CO_2 production by the plants) and heterotrophic (i e , essentially microbial) respiration converting the organic material back into CO_2 mainly in soils (c f Section 10 for a detailed discussion) Net primary production (NPP) is the net annual uptake of CO_2 by the vegetation, NPP is equal to the gross uptake (gross primary production, GPP) minus autotrophic respiration In an unperturbed world, NPP and decomposition by heterotrophic respiration are approximately balanced on an annual basis, formation of soils and peat corresponds to a (relatively small) excess of NPP

The carbon balance can be changed considerably by the direct impact of human activities (land use changes, particularly deforestation), by climate changes, and by other changes in the environment, e g , atmospheric composition Since the pools and fluxes are large (NPP 50-60 GtC per year, GPP 90 120 GtC per year, Houghton et al 1985b) any perturbations can have a significant effect on the atmospheric concentration of CO_2

1.2.2 Anthropogenic Perturbations
The concentrations of CO_2 in the atmosphere are primarily affected by two anthropogenic processes release of CO_2 from fossil fuel combustion, and changes in land use such as deforestation

1 2 2 1 Historical fossil fuel input
The global input of CO_2 to the atmosphere from fossil fuel combustion, plus minor industrial sources like cement production, has shown an exponential increase since 1860 (about 4% per year), with major interruptions during the two world wars and the economic crisis in the thirties (Figure 1 5) Following the ' oil crisis of 1973, the rate of increase of the CO_2 emissions first decreased to approximately 2% per year, and after 1979 the global emissions remained almost constant at a level of 5 3 GtC per year until 1985, when they started to rise again, reaching 5 7 GtC per year in 1987 (Figure 1 5) The cumulative release of CO_2 from fossil fuel use and cement manufacturing from 1850 to 1987 is estimated at 200 GtC ± 10% (Marland, 1989)

Ninety five percent of the industrial CO_2 emissions are from the Northern Hemisphere, dominated by industrial
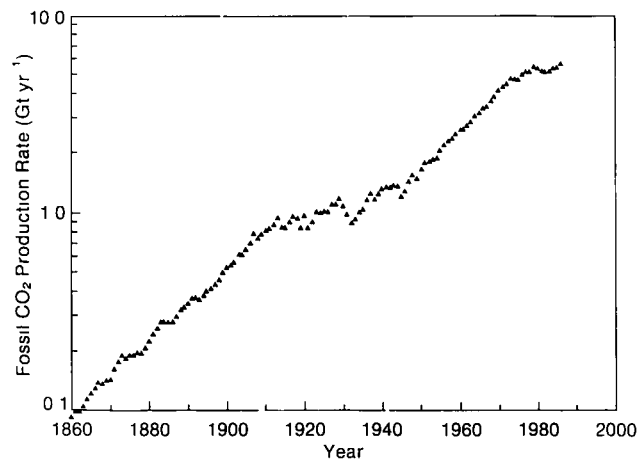
Figure 1.5: Global annual emissions of CO_2 from fossil fuel combustion and cement manufacturing, expressed in GtC yr⁻¹ (Rotty and Marland, 1986, Marland, 1989) The average rate of increase in emissions between 1860 and 1910 and between 1950 and 1970 is about 4% per year

countries, where annual releases reach up to about 5 tC per capita (Rotty and Marland, 1986) In contrast, CO_2 emission rates in most developing countries lie between 0 2 and 0 6 tC per capita per year However, the relative rate of increase of the CO_2 emissions is much larger in the developing countries (~ 6% per year), showing almost no slowing down after 1973 in contrast to Western Europe and North America where the rate of increase decreased from about 3% per year (1945-72) to less than 1% per year (1973-84)

1 2 2 2 Historical land use changes
The vegetation and soils of unmanaged forests hold 20 to 100 times more carbon per unit area than agricultural systems The amount of carbon released to the atmosphere compared to that accumulated on land as a result of land use change depends on the amounts of carbon held in biomass and soils, rates of oxidation of wood products (either rapidly through burning or more slowly through decay), rates of decay of organic matter in soils, and rates of regrowth of forests following harvest or abandonment of agricultural land The heterogeneity of terrestrial ecosystems makes estimation of global inventories and fluxes difficult

The total release of carbon to the atmosphere from changes in land use, primarily deforestation, between 1850 and 1985 has been estimated to be about 115 GtC (Houghton and Skole, 1990), with an error limit of about ±35 GtC The components of the flux to the atmosphere are (1) burning associated with land use change, (2) decay

of biomass on site (roots, stumps, slash, twigs etc.), (3) oxidation of wood products removed from site (paper, lumber, waste etc.), (4) oxidation of soil carbon, minus (5) regrowth of trees and redevelopment of soil organic matter following harvest. Although the greatest releases of carbon in the nineteenth and early twentieth centuries were from lands in the temperate zone (maximum 0.5 GtC per year), the major source of carbon during the past several decades has been from deforestation in the tropics, with a significant increase occurring since 1950. Over the entire 135 yr period, the release from tropical regions is estimated to have been 2-3 times greater than the release from middle and high latitudes. Estimates of the flux in 1980 range from 0.6 to 2.5 GtC (Houghton et al., 1985a, 1987, 1988, Detwiler and Hall, 1988) virtually all of this flux is from the tropics. The few regions for which data exist suggest that the annual flux is higher now than it was in 1980.

1.2.3 Long-Term Atmospheric Carbon Dioxide Variations

The most reliable information on past atmospheric CO_2 concentrations is obtained by the analysis of polar ice cores. The process of air occlusion lasts from about 10 up to 1000 years, depending on local conditions (e.g., precipitation rate), so that an air sample in old ice reflects the atmospheric composition averaged over a corresponding time interval.

Measurements on samples representing the last glacial maximum (18,000 yr before present) from ice cores from Greenland and Antarctica (Neftel et al., 1982, 1988, Delmas et al., 1980) showed CO_2 concentrations of 180-200 ppmv i.e., about 70 percent of the pre-industrial value. Analyses on the ice cores from Vostok, Antarctica, have provided new data on natural variations of CO_2, covering a full glacial-interglacial cycle (Figure 1.6, Barnola et al., 1987). Over the whole period there is a remarkable correlation between polar temperature, as deduced from deuterium data, and the CO_2 profile. The glacial-interglacial shifts of CO_2 concentrations must have been linked to large-scale changes in the circulation of the ocean and in the whole interplay of biological, chemical and physical processes, but the detailed mechanisms are not yet very clear. The CO_2 variations were large enough to potentially contribute, via the greenhouse effect, to a substantial (although not the major) part of the glacial-interglacial climate change (Hansen et al., 1984, Broccoli and Manabe 1987).

Ice core studies on Greenland ice indicate that during the last glaciation CO_2 concentration shifts of the order of 50 ppmv may have occurred within less than 100 years (Stauffer et al., 1984), parallel to abrupt, drastic climatic events (temperature changes of the order of 5°C). These rapid CO_2 changes have not yet been identified in ice cores from Antarctica (possibly due to long occlusion times,
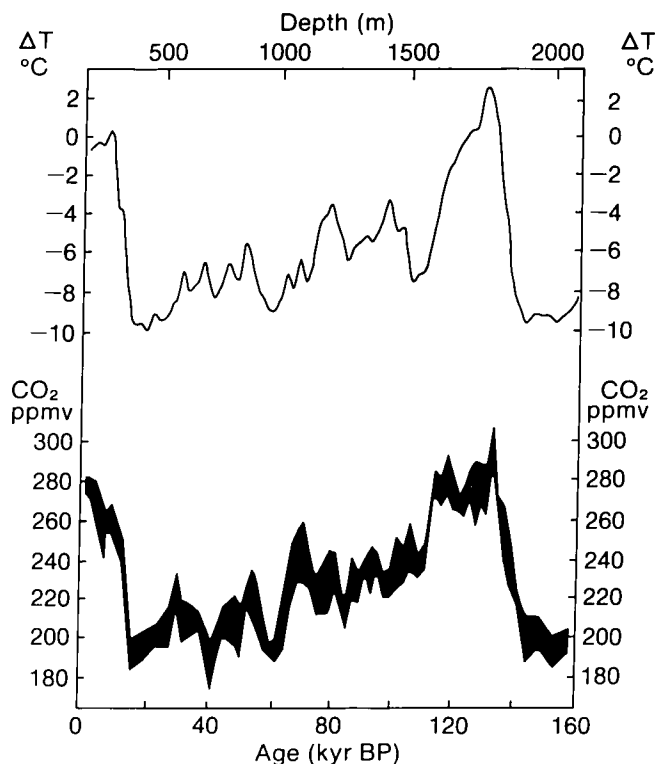
Figure 1.6: CO_2 concentrations (bottom) and estimated temperature changes (top) during the past 160,000 years, as determined on the ice core from Vostok, Antarctica (Barnola et al., 1987). Temperature changes were estimated based on the measured deuterium concentrations

Neftel et al., 1988), therefore, it is not yet clear if they are real or represent artefacts in the ice record.

1.2.4 The Contemporary Record of Carbon Dioxide - Observations and Interpretation

1.2.4.1 The carbon dioxide increase from pre-industrial period

Relatively detailed CO_2 data have been obtained for the last millennium from Antarctic ice cores (Neftel et al., 1985a, Friedli et al., 1986, Siegenthaler et al., 1988, Raynaud and Barnola, 1985, Pearman et al., 1986). They indicate that during the period 1000 to 1800, the atmospheric concentration was between 270 and 290 ppmv. The relative constancy seems surprising in view of the fact that the atmosphere exchanges about 30 percent of its CO_2 with the oceans and biota each year. This indicates that the sensitivity of atmospheric CO_2 levels to minor climatic changes such as the Little Ice Age (lasting from the end of the 16th to the middle of the 19th century), when global mean temperatures probably decreased by about 1°C, is small.

A precise reconstruction of the CO_2 increase during the past two centuries has been obtained from an ice core from Siple Station, Antarctica (Figure 1 3, Neftel et al , 1985a, Friedli et al , 1986) These results indicate that CO_2 started to rise around 1800 and had already increased by about 15 ppmv by 1900 Precise direct atmospheric measurements started in 1958, when the level was about 315 ppmv and the rate of increase 0 6 ppmv per year The present atmospheric CO_2 level has reached 353 ppmv, and the mean growth rate has now reached about 1 8 ppmv per year (Figure 1 4, Keeling et al , 1989a)

1 2 4 2 Uptake by the ocean

The ocean is an important reservoir for taking up anthropogenic CO_2 The relative increase of dissolved inorganic carbon (total CO_2) in ocean water is smaller than in the atmosphere (only 2-3 percent until now see below) Precise measurements of dissolved inorganic carbon can be made with present analytical tools However, an accurate determination of the trend in dissolved inorganic carbon is difficult because of its variability in time and space Hence, repeated transects and time series will be required to assess the total oceanic CO_2 uptake with good precision

The net flux of CO_2 into (or out of) the ocean is given by the product of a gas transfer coefficient and ΔpCO_2 (the CO_2 partial pressure difference between ocean and atmosphere) The gas transfer coefficient increases with increasing wind speed and also depends on water temperature Therefore, the net flux into the ocean can be estimated from a knowledge of the atmospheric CO_2 concentration pCO_2 in surface water (for which the data are still sparse), the global distribution of wind speeds over the ocean as well as the relation between wind speed and gas transfer coefficient (which is known to $\pm 30\%$ only) There have been several estimates of the global net uptake of CO_2 by the oceans using observations (e g Enting and Pearman 1982 1987) The most recent estimate yields 1 6 GtC per year (Tans et al , 1990) the error of this estimate is, according to the authors, not easy to estimate

Estimates of oceanic CO_2 uptake in the past and in the future require models of the global carbon cycle that take into account air-sea gas exchange aqueous carbonate chemistry and the transport from the surface to deep ocean layers The aqueous carbonate chemistry in sea water operates in a mode that if the atmospheric CO_2 concentration increases by e g 10% then the concentration of dissolved inorganic carbon in sea water increases by only about 1% at equilibrium Therefore, the ocean is not such a powerful sink for anthropogenic CO_2 as might seem at first when comparing the relative sizes of the reservoirs (Figure 1 1)

The rate at which anthropogenic CO_2 is transported from the surface to deeper ocean layers is determined by the rate of water exchange in the vertical It is known from measurements of the radioactive isotope ^{14}C that on average it takes hundreds to about one thousand years for water at the surface to penetrate to well below the mixed layer of the major oceans (e g , Broecker and Peng, 1982) Thus, in most oceanic regions only the top several hundred metres of the oceans have at present taken up significant amounts of anthropogenic CO_2 An exception is the North Atlantic Ocean where bomb-produced tritium has been observed even near the bottom of the sea, indicating the active formation of new deep water

The rain of biogenic detrital particles, which is important for the natural carbon cycle, does not significantly contribute to a sequestering of excess CO_2, since the marine biota do not directly respond to the CO_2 increase Their activity is controlled by other factors, such as light, temperature and limiting nutrients (e g , nitrogen, phosphorus, silicon) Thus only the input of fertilizers (phosphate, nitrate) into the ocean through human activities may lead to an additional sedimentation of organic carbon in the ocean, different authors have estimated the size of this additional sink at between 0 04 and 0 3 GtC per year (see Baes et al 1985) It seems thus justified to estimate the fossil fuel CO_2 uptake to date considering the biological flux to be constant as long as climatic changes due to increasing greenhouse gases, or natural causes, do not modify the marine biotic processes Although this appears a reasonable assumption for the past and present situation, it may well not be so in the future

The carbon cycle models used to date to simulate the atmosphere-ocean system have often been highly simplified, consisting of a few well-mixed or diffusive reservoirs (boxes) (e g , Oeschger et al , 1975, Broecker et al , 1980, Bolin, 1981, Enting and Pearman, 1987, Siegenthaler, 1983) Even though these box models are highly simplified they are a powerful means for identifying the importance of the different processes that determine the flux of CO_2 into the ocean (e g , Broecker and Peng, 1982, Peng and Broecker 1985) The results of these models are considered to be reasonable because, as long as the ocean circulation is not changing, the models need only simulate the transport of excess CO_2 from the atmosphere into the ocean, but not the actual dynamics of the ocean In the simple models, the oceanic transport mechanisms e g , formation of deep water are parameterized The transport parameters (e g , eddy diffusivity) are determined from observations of transient tracers that are analogues to the flux of anthropogenic CO_2 into the ocean If a model reproduces correctly the observed distribution of, e g , bomb produced ^{14}C, then it might be expected to simulate reasonably the flux of CO_2 into the ocean A 1-D box-diffusion model yields an oceanic uptake of 2 4 GtC per year on average for the decade 1980 - 1989, and an outcrop-diffusion model (both described by Siegenthaler, 1983) 3 6 GtC per year The latter model most probably

overpredicts the flux into the ocean, because it includes an infinitely fast exchange between high-latitude surface waters and the deep ocean

However, it is obviously desirable to use 3-dimensional (3-D) general circulation models of the oceans for this purpose At this time, only a few modelling groups have started to do this One 3-D model (Maier-Reimer and Hasselmann, 1987) gives a similar CO_2 uptake as a 1-D box-diffusion model of Siegenthaler (1983) as illustrated by the model response to a pulse input of CO_2 (Figure 1 2) In a recent revised version of this model (Maier-Reimer et al, personal communication) the ocean takes up less CO_2 about 1 2 GtC per year on average for the decade 1980 1989 The GFDL 3-D ocean model (Sarmiento et al, 1990) has an oceanic uptake of 1 9 GtC per year for the same period 3-D ocean models and especially coupled atmosphere-ocean models are the only means to study in a realistic way the feedback effects that climate change may have on atmospheric CO_2 via alteration of the ocean circulation (cf Section 1 2 7 1) However models need to be constrained by more data than are presently available

The oceanic uptake of CO_2 for the decade 1980 1989, as estimated based on carbon models (e g Siegenthaler and Oeschger 1987, Maier Reimer et al personal communication, 1990, Goudriaan, 1989 Sarmiento et al, 1990) is in the range 2 0±0 8 GtC per year

1 2 4 3 Redistribution of anthropogenic carbon dioxide
During the period 1850 to 1986, 195±20 GtC were released by fossil fuel burning and 117±35 GtC by deforestation and changes in land use, adding up to a cumulative input of 312±40 GtC

Atmospheric CO_2 increased from about 288 ppmv to 348 ppmv during this period corresponding to (41±6)% of the cumulative input This percentage is sometimes called the airborne fraction , but that term should not be mis understood all CO_2 anthropogenic and non-anthropogenic is continuously being exchanged between atmosphere ocean and biosphere Conventionally an airborne fraction referring to the fossil fuel input only has often been quoted because only the emissions due to fossil fuel burning are known with good precision However this may be misleading since the atmospheric increase is a response to the total emissions We therefore prefer the definition based on the latter The airborne fraction for the period 1980 - 1989 (see calculation below) corresponds to (48±8)% of the cumulative input

In model simulations of the past CO_2 increase using estimated emissions from fossil fuels and deforestation it has generally been found that the simulated increase is larger than that actually observed An estimate for the decade 1980 1989 is

	GtC/yr
Emissions from fossil fuels into the atmosphere (Figure 1 5)	5 4±0 5
Emissions from deforestation and land use	1 6±1 0
Accumulation in the atmosphere	3 4±0 2
Uptake by the ocean	2 0±0 8
Net imbalance	1 6±1 4

The result from this budget and from other studies is that the estimated emissions exceed the sum of atmospheric increase plus model calculated oceanic uptake by a significant amount The question therefore arises whether an important mechanism has been overlooked All attempts to identify such a missing sink in the ocean have however failed so far A possible exception is that a natural fluctuation in the oceanic carbon system could have caused a decreasing atmospheric baseline concentration in the past few decades, this does not appear likely in view of the relative constancy of the pre-industrial CO_2 concentration There are possible processes on land, which could account for the missing CO_2 (but it has not been possible to verify them) They include the stimulation of vegetative growth by increasing CO_2 levels (the CO_2 fertilization effect) the possible enhanced productivity of vegetation under warmer conditions and the direct effect of fertilization from agricultural fertilizers and from nitrogenous releases into the atmosphere It has been estimated that increased fertilization by nitrogenous releases could account for a sequestering of up to a maximum of 1 GtC per year in terrestrial ecosystems (Melillo private communication 1990) In addition, changed forest management practices may also result in an increase in the amount of carbon stored in northern mid latitude forests The extent to which mid-latitude terrestrial systems can sequester carbon before becoming saturated and ineffective is unknown As mid latitude terrestrial systems become close to saturation and hence ineffective in sequestering carbon this would allow more of the CO_2 to remain in the atmosphere

A technique for establishing the global distribution of surface sources and sinks has been to take global observations of atmospheric CO_2 concentration and isotopic composition and to invert these by means of atmospheric transport models to deduce spatial and temporal patterns of surface fluxes (Pearman et al 1983 Pearman and Hyson 1986, Keeling and Heimann 1986) The observed inter-hemispheric CO_2 concentration difference (currently about 3 ppmv) is smaller than one would expect given that nearly all fossil releases occur in the Northern Hemisphere The results of this approach suggest that there is an unexpectedly large sink in the Northern Hemisphere equivalent to more than half of the fossil fuel CO_2 release (Enting and Mansbridge 1989 Tans et al 1990 Keeling et al 1989b) Furthermore it has been concluded that the oceanic uptake compatible with oceanic and atmospheric CO_2 data and with a 3 dimensional atmospheric transport model is at most 1 GtC

per year (Tans et al., 1990). Thus, a significant terrestrial sink, possibly larger than the oceanic uptake, is suggested by these model analyses.

1.2.4.4 Seasonal variations

Atmospheric CO_2 exhibits a seasonal cycle, dominated by the seasonal uptake and release of atmospheric CO_2 by land plants. Its amplitude is small (1.2 ppmv peak-to-peak) in the Southern Hemisphere and increases northward to a maximum of order 15 ppmv peak-to-peak in the boreal forest zone (55-65° N).

The amplitude of the seasonal cycle has been observed to be increasing (e.g., Pearman and Hyson, 1981: Bacastow et al., 1985; Thompson et al., 1986). For example, at Mauna Loa, Hawaii, the seasonal amplitude has increased by nearly 20% since 1958. The increase has however, not been monotonic, and different evaluation methods yield somewhat different values; still, it is statistically significant. This increasing amplitude could point to a growing productivity (NPP) of the terrestrial ecosystems, and to a sequestering of carbon by a growing biomass, provided the increase in biomass is not fully compensated by respiration. It is important to note that such a change does not necessarily indicate increased productivity or increased storage of carbon (Pearman and Hyson, 1981; Kohlmaier et al., 1989; Houghton, 1987); it could also be due to, e.g., accelerated soil respiration in winter.

1.2.4.5 Interannual variations

Small imbalances in natural exchange fluxes are reflected in interannual CO_2 concentration fluctuations (±1 ppmv over 1-2 years). They are correlated with the El Niño-Southern Oscillation (ENSO) phenomenon (Thompson et al., 1986; Keeling et al., 1989a), which suggests a relation to changes in the equatorial Pacific Ocean, where normally the upwelling causes a high pCO_2 peak and outgassing of CO_2 into the atmosphere. However, a closer inspection shows that this cannot be the dominating mechanism, since during El Niño, the equatorial pCO_2 peak disappears (Feely et al., 1987), while atmospheric CO_2 grows more strongly than normally. Alternatively, processes in the land biosphere, perhaps in response to climatic events connected with ENSO events, may be responsible. This explanation is supported by one set of stable carbon isotope data on atmospheric CO_2 (Keeling et al., 1989a); but not supported by a second set (Goodman and Francey, 1988).

1.2.4.6 Temporal variations of carbon isotopes

The release of CO_2 from biospheric carbon and fossil fuels, both having lower $^{13}C/^{12}C$ ratios than atmospheric CO_2, has led to a decrease of the isotope ratio $^{13}C/^{12}C$ in the atmosphere by about $1^o/oo$. The man-made emissions of ^{14}C-free fossil fuel CO_2 have likewise caused a decrease of the atmospheric ^{14}C concentration (measured on tree-rings)

of the order of 2% from 1800 to 1950. Both isotopic perturbations can be used to constrain the history of the anthropogenic release of CO_2. The observed decrease of ^{13}C, as observed in air trapped in ice cores (Friedli et al., 1986) and ^{14}C, observed in tree rings, agree, within experimental uncertainty, with those expected from model calculations with the same carbon cycle models as used for studying the CO_2 increase (Stuiver and Quay, 1981; Siegenthaler and Oeschger, 1987). The interpretation of ^{13}C trends in tree rings has proven to be difficult because of plant physiological effects on isotope fractionation (Francey and Farquhar, 1982).

1.2.5 Evidence that the Contemporary Carbon Dioxide Increase is Anthropogenic

How do we know that in fact human activity has been responsible for the well documented 25% increase in atmospheric CO_2 since the early 19th century? Couldn't this rise instead be the result of some long-term natural fluctuation in the natural carbon cycle? Simple arguments allow us to dismiss this possibility.

First, the observational CO_2 records from ice cores with good time resolution clearly show that the maximum range of natural variability about the mean of 280 ppmv during the past 1000 years was small (10 ppmv over a 100 year time-scale), that is an order of magnitude less than the observed rise over the last 150 years. A value as high as the current level of 353 ppmv is not observed anywhere in the measured ice core record for the atmospheric history during the past 160,000 years; the maximum value is 300 ppmv during the previous interglacial, 120,000 years ago.

Second, the observed rate of CO_2 increase closely parallels the accumulated emission trends from fossil fuel combustion and from land use changes (c.f. Section 1.2.2). Since the start of atmospheric monitoring in 1958, the annual atmospheric increase has been smaller each year than the fossil CO_2 input. Thus, oceans and biota together must have been a global sink rather than a source during all these years. Further evidence is provided by the fact that the north-to-south CO_2 concentration difference has been observed to increase from 1 ppmv in 1960 to 3 ppmv in 1985, parallel to the growth of the (Northern Hemisphere) fossil fuel combustion sources (Keeling et al., 1989a).

Third, the observed isotopic trends of ^{13}C and ^{14}C agree qualitatively with those expected due to the CO_2 emissions from fossil fuels and the biosphere, and they are quantitatively consistent with results from carbon cycle modelling.

1.2.6 Sensitivity Analyses for Future Carbon Dioxide Concentrations

Future atmospheric CO_2 concentrations depend primarily on emission rates from energy use and deforestation, and on the effectiveness of the ocean and land biota as CO_2

sinks For the sake of illustration, several schematic scenarios are shown in Figures 1 7 and 1 8 Those of Figure 1 7 are based on prescribed total CO_2 emission rates after 1990, for those in Figure 1 8 atmospheric concentrations after 1990 were prescribed and the corresponding emission rates were calculated to fit these concentrations A box-diffusion model of the global cycle was used for these simulations (Enting and Pearman, 1982, 1987), with an oceanic eddy diffusivity of 5350 m^2year^{-1} and an air-sea gas exchange rate corresponding to an exchange coefficient of 0 12 $year^{-1}$ The calculations assume no biospheric-climate feedbacks, and also assume that after 1990 the net biospheric input of CO_2 is zero, i e , the input of CO_2 from tropical deforestation is balanced by uptake of CO_2 by terrestrial ecosystems

In case a (all emissions stopped Figure 1 7), the atmospheric concentration declines, but only slowly (from 351 ppmv in 1990 to 331 ppmv in 2050 and 324 ppmv in 2100), because the penetration of man-made CO_2 to deeper ocean layers takes a long time Even if the emissions were reduced by 2% per year from 1990 on (case b), atmospheric CO_2 would continue to increase for several decades Case c (constant emission rate after 1990) gives CO_2 levels of about 450 ppmv in 2050 and 520 ppmv in 2100 A constant relative growth rate of 2% per year (case d) would yield 575 ppmv in 2050 and 1330 ppmv in 2100 Comparison of cases b, c and d clearly shows that measures to reduce emissions will result in slowing down the rate of atmospheric CO_2 growth

Cases b and c, in comparison to b and c, schematically illustrate the effect of reducing emissions in 2010 instead of in 1990

If an (arbitrary) threshold of 420 ppmv i e , 50% above pre-industrial, is not to be exceeded (case e, Figure 1 8), then CO_2 production rates should slowly decline, reaching about 50% of their present value by 2050 and 30% by 2100 In order to keep the concentration at the present level (case f) emissions would have to be reduced drastically to 30% of present immediately and to less than 20% by 2050

The results of scenario calculations with a 3-D ocean-atmosphere model (Maier-Reimer and Hasselmann, 1987, Maier Reimer et al , personal communication, 1990 - revised model) give higher concentrations than those shown in Figure 1 7 obtained with a box-diffusion model, for instance, about 480 ppmv in the year 2050 and about 560 ppmv in the year 2100 for Scenario C, compared to about 450 ppmv and 520 ppmv On the other hand, calculations with a box model that includes a biospheric CO_2 sink (Goudriaan, 1989) yields somewhat lower concentrations than shown in Figure 1 7, for instance about 415 ppmv in the year 2050 and 460 ppmv in the year 2100 for Scenario C
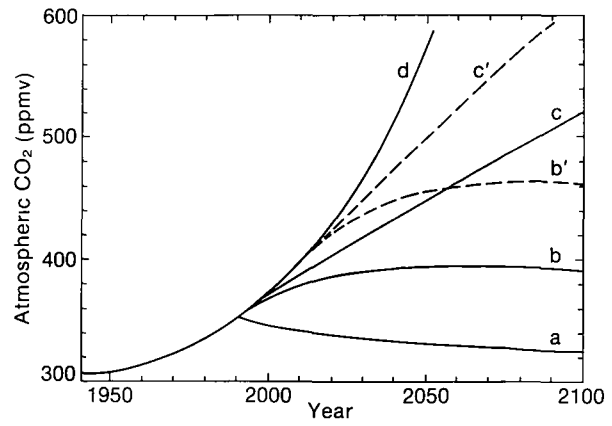
Figure 1.7: Future atmospheric CO_2 concentrations as simulated by means of a box-diffusion carbon cycle model (Enting and Pearman, 1982, 1987) for the following scenarios (a) - (d) anthropogenic CO_2 production rate p prescribed after 1990 as follows (a) p = 0, (b) p decreasing by 2% per year, (c) p = constant, (d) p increasing at 2% per year Scenarios (b) and (c) p grows by 2% per year from 1990-2010, then decreases by 2% per year (b) or is constant (c) Before 1990, the concentrations are those observed (cf Figure 1 3), and the production rate was calculated to fit the observed concentrations
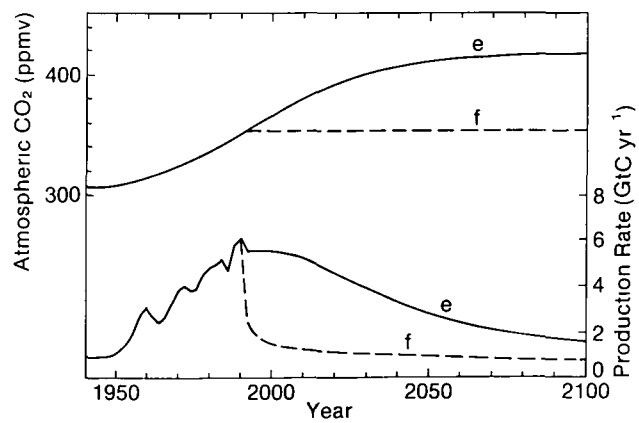
Figure 1.8: Future CO_2 production rates calculated by means of a box-diffusion carbon cycle model (Enting and Pearman, 1982, 1987) so as to yield the prescribed atmospheric CO_2 concentrations after 1990 (e) concentration increasing steadily (logistic function of time) to 420 ppmv (f) concentration constant after 1990

1.2.7 Feedbacks from Climate Change into the Carbon Dioxide Cycle

As increasing greenhouse gas concentrations alter the Earth's climate, changing climate and environmental conditions in their turn act back on the carbon cycle and

atmospheric CO_2 The climate change Earth has exp erienced in the recent past is still within the range of natural short-term variability, and so are probably therefore the feedback effects of anthropogenic climate change However, as the changes in the climate become larger than natural climatic variation the magnitude of the feedback effects should begin to have a significant effect These feedbacks could in general be either positive (amplifying the initial changes) or negative (attenuating them)

1 2 7 1 Oceanic feedback effects
The following are possible feedback effects on the ocean atmosphere carbon system

1 2 7 1 1 Ocean temperature Ocean temperature changes can affect sea water CO_2 chemistry Surface-water pCO_2 will increase with increasing temperature, tending to decrease the net uptake by the oceans The future atmospheric CO_2 increase may be amplified by something like 5 percent due to this effect (Lashof 1989)

1 2 7 1 2 Ocean circulation The ocean circulation may change in response to climatic change As a consequence of increasing surface water temperatures the thermocline may become more resistant to vertical mixing and slow down the uptake of anthropogenic CO_2 Modified wind stress may affect the ocean circulation However, the overall change in ocean dynamics and consequently in CO_2 uptake due to a climatic change cannot be estimated from simple considerations, a proper evaluation of such an effect can only be done using dynamical ocean models Studies on Greenland ice cores indicates that during the last glaciation, significant CO_2 concentration shifts may have occurred within less than 100 years (c f Section 1 2 3) probably caused by strong changes of large-scale ocean circulation Therefore, the possibility that, due to climatic changes unexpected abrupt events may take place in the natural carbon system cannot be excluded

1 2 7 1 3 Gas exchange rates A change in the global wind pattern could influence the gas transfer from the atmosphere to the sea surface Carbon cycle models show that the net CO_2 uptake by the global ocean is not sensitive to the gas transfer coefficients (because it is controlled mainly by vertical mixing, not by gas exchange, Oeschger et al 1975 Broecker et al 1980 Sarmiento et al 1990) so this effect would probably be of minor influence

1 2 7 1 4 Modification of oceanic biogeochemical cycling The rain of dead organic particles corresponds to a continuous export flux of carbon (and nutrients) out of the ocean surface which under non-perturbed conditions is balanced by an equal upward transport of dissolved carbon

(and dissolved nutrients) by water motion In polar regions and strong upwelling zones, where productivity is not limited by nitrogen or phosphorus, the balance could become disturbed consequent on variations in ocean dynamics (c f Section 1 2 7 1 2), so as to influence atmospheric CO_2 As a result of climate change, the distribution of marine ecosystems and species composition could change, which could affect pCO_2 in surface waters It is not possible at present to predict the direction and magnitude of such effects

Warming of the oceans might lead to accelerated decomposition of dissolved organic carbon, converting it into CO_2 and thus amplify the atmospheric increase (Brewer, personal communication, 1990)

1 2 7 1 5 UV B radiation A reduction in stratospheric O_3 would increase the intensity of UV-B radiation at the Earth s surface This might have negative effects on the marine biota due to a decrease of marine productivity and thus on the biological carbon pump This could lead to an increase in the concentration of CO_2 in surface waters and consequently in the atmosphere

1 2 7 2 Terrestrial biospheric feedbacks
The following are probable feedback effects on the terrestrial biosphere atmospheric carbon system

1 2 7 2 1 Carbon dioxide fertilization Short-term exp eriments under controlled conditions with crops and other annuals, as well as with a few perennials, show an increase in the rates of photosynthesis and growth in most plants under elevated levels of CO_2 (Strain and Cure, 1985) If elevated levels of CO_2 increase the productivity of natural ecosystems, more carbon may be stored in woody tissue or soil organic matter Such a storage of carbon will withdraw carbon from the atmosphere and serve as a negative feedback on the CO_2 increase Of particular importance is the response of forests (Luxmoore et al , 1986), given that forests conduct about 2/3 of global photosynthesis (50% of this cycles annually through leaves, while 50% is stored in woody tissue) However, it is not clear whether the increases in photosynthesis and growth will persist for more than a few growing seasons, whether they will occur at all in natural ecosystems and to what degree they will result in an increased storage of carbon in terrestrial ecosystems

1 2 7 2 2 Eutrophication and toxification The increased availability of nutrients such as nitrate and phosphate from agricultural fertilizers and from combustion of fossil fuels may stimulate the growth of plants It has been estimated that the effect of eutrophication, both on land and in the oceans, could be as large as 1 GtC per year (Melillo, private communication 1990) However, it should be noted

that the greater availability of nutrients has often been associated with increasing levels of acid precipitation and air pollution, which have been associated with a reduction in the growth of terrestrial biota

1 2 7 2 3 Temperature Under non-tropical conditions, photosynthesis and respiration by plants and by microbes both tend to increase with increasing temperature, but respiration is the more sensitive process, so that a warming of global air temperature is likely to result in an initially increased release of carbon to the atmosphere Estimates indicate that the additional flux might be significant perhaps as large as one or a few GtC per year (Woodwell, 1983, Kohlmaier, 1988, Lashof, 1989, Houghton and Woodwell, 1989) This temperature-enhanced respiration would be a positive feedback on global warming

1 2 7 2 4 Water Changes in soil water may affect carbon fixation and storage Increased moisture can be expected to stimulate plant growth in dry ecosystems and to increase the storage of carbon in tundra peat There is a possibility that stresses brought about by climatic change may be alleviated by increased levels of atmospheric CO_2 At present however, it is not possible to predict reliably either the geographical distribution of changes in soil water or the net effect of these changes on carbon fluxes and storage in different ecosystems Changes in climate are generally believed to be more important than changes in the atmospheric concentration of CO_2 in affecting ecosystem processes (c f Section 10)

1 2 7 2 5 Change in geographical distribution of vegetation types In response to environmental change, the structure and location of vegetation types may change If the rate of change is slow, plant distributions may adjust If, however the rate of change is fast, large areas of forests might not be able to adapt rapidly enough, and hence be negatively affected with a subsequent release of CO_2 to the atmosphere

1 2 7 2 6 UV-B radiation A reduction in stratospheric O_3 would increase the intensity of UV-B radiation at the Earth s surface Increased UV-B may have a detrimental effect on many land biota, including crops (Teramura, 1983), thus affecting the strength of the biospheric sink of CO_2 over land

1.2.8 Conclusions

The atmospheric CO_2 concentration is now about 353ppmv 25% higher than the pre industrial (1750-1800) value and higher than at any time in at least the last 160,000 years This rise, currently amounting to about 1 8 ppmv per year, is beyond any doubt due to human activities Anthropogenic emissions of CO_2 were 5 7±0 5

GtC due to fossil fuel burning in 1987, plus 0 6 to 2 5 GtC due to deforestation (estimate for 1980) During the last decade (1980 - 1989) about 48% of the anthropogenic emissions have stayed in the atmosphere, the remainder has been taken up by the oceans and possibly by land ecosystems Our qualitative knowledge of the global carbon cycle is, in view of the complexity of this cycle, relatively good However, the current quantitative estimates of sources and of sinks of CO_2 do not balance the atmospheric increase is less rapid than expected from carbon cycle models (in which CO_2 fertilization or environmental responses of the biosphere are not included) This, and model analyses of the inter-hemispheric CO_2 gradient, indicate that the Northern Hemisphere terrestrial ecosystems may act as a significant sink of carbon Such a sink has, however, not been directly identified To summarize the total annual input of anthropogenic CO_2 is currently (1980-1989) about 7 0±1 1 GtC assuming a central value for the input of CO_2 from tropical deforestation, the annual uptake by the oceans is estimated (based on the box models, GCMs and Tans et al 1990) to be about 2 0±1 0 GtC, and the annual atmospheric accumulation is about 3 4±0 2 GtC Thus, the annual sequestering by the terrestrial biosphere should be about 1 6±1 5 GtC While several mechanisms have been suggested that could sequester carbon in terrestrial ecosystems, it is difficult to account for the total required sink Therefore, it appears likely that, (i) the uptake of CO_2 by the oceans is underestimated (ii) there are important unidentified processes in terrestrial ecosystems that can sequester CO_2, and/or (iii) the amount of CO_2 released from tropical deforestation is at the low end of current estimates

If the land biota presently act as a sink of carbon due to a fertilization effect, then they might become saturated with respect to this fertilization at some time in the future This means that we cannot assume that the terrestrial sink which may be active currently, will continue to exist unchanged through the next century

In order to avoid a continued rapid growth of CO_2 in the atmosphere severe reductions on emissions will be necessary The time taken for atmospheric CO_2 to adjust to changes in sources or sinks is of the order of 50-200 years, determined mainly by the slow exchange of carbon between surface waters and deeper layers of the ocean Even if all anthropogenic emissions of CO_2 were halted the atmospheric concentration would decline only slowly, and it would not approach its pre-industrial level for many hundreds of years Thus, any reductions in emissions will only become fully effective after a time of the order of a century or more Based on some model estimates which neglect the feedbacks discussed earlier the atmospheric concentration in the year 2050 would be between 530 - 600 ppmv for a constant relative growth of the annual

anthropogenic emissions by 2% per year, and between 415 - 480 ppmv (increasing to 460 - 560 ppmv by the year 2100) for a constant anthropogenic emission rate at the 1990 level In order not to exceed 420 ppmv (50% above pre-industrial), annual anthropogenic emissions would have to be reduced continuously to about 50% of their present value by the year 2050 In order to stabilize concentrations at present day concentrations (353 ppmv), an immediate reduction in global anthropogenic emissions by 60-80 percent would be necessary The size of the estimated reduction depends on the carbon cycle model used

During the millennium preceding the anthropogenic CO_2 growth, the concentration was relatively constant near 280 ppmv, with a variability of less than ± 10 ppmv This indicates that the sensitivity of atmospheric CO_2 levels to minor climatic changes such as the Little Ice Age, where global mean temperatures probably decreased by about 1°C, is within this range However, the anticipated climatic and environmental changes may soon become large enough to act back on the oceanic and terrestrial carbon cycle in a more substantial way A close interaction between climate variations and the carbon cycle is indicated by the glacial-interglacial CO_2 variations The ice-core record shows that CO_2 concentrations during the coldest part of the last glaciation were about 30% lower than during the past 10 000 years The glacial interglacial CO_2 variations were probably due to changes in ocean circulation and marine biological activity, and were correlated to variations in global climate There is some (not fully clear) evidence from ice cores that rapid changes of CO_2, ca 50 ppmv within about a century, occurred during and at the end of the ice age

If global temperatures increase, this could change the natural fluxes of carbon, thus having feedback effects on atmospheric CO_2 Some of the identified feedbacks are potentially large and could significantly influence future CO_2 levels They are difficult to quantify, but it seems likely that there would be a net positive feedback, i e , they will enhance the man-made increase On the longer term, the possibility of unexpected large changes in the mechanisms of the carbon cycle due to a human-induced change in climate cannot be excluded

1.3 Methane

Methane is a chemically and radiatively active trace gas that is produced from a wide variety of anaerobic (i e , oxygen deficient) processes and is primarily removed by reaction with hydroxyl radicals (OH) in the troposphere Oxidation of CH_4 by OH in the stratosphere is a significant source of stratospheric water (H_2O) where it is an important greenhouse gas

Depth (m)
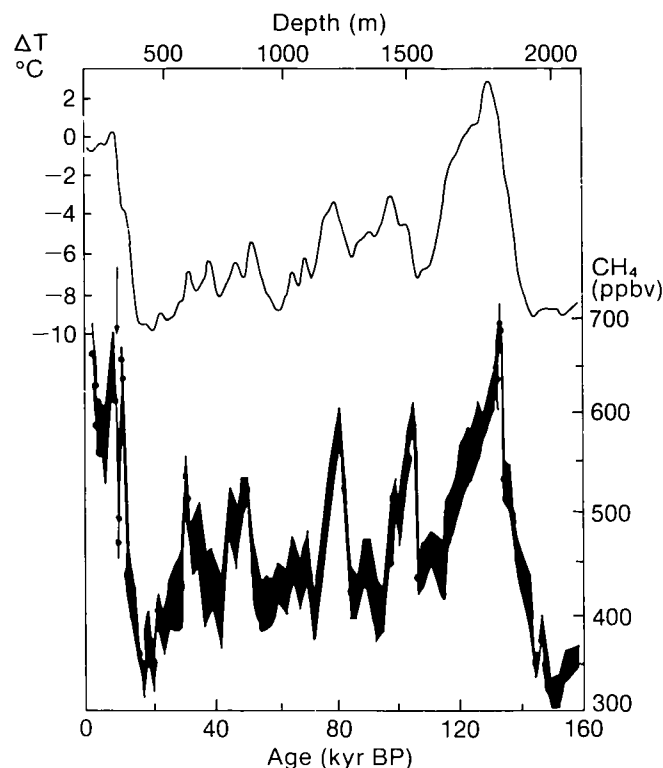
Figure 1.9: Methane concentrations (bottom) and estimated temperature changes (top) during the past 160,000 years as determined on the ice core from Vostok, Antarctica (Chappelaz et al 1990) Temperature changes were estimated based on the measured deuterium concentrations

1 3.1 Atmospheric Distribution of Methane

1 3 1 1 Palaeo-atmospheric record of methane

There are good data on the atmospheric concentration of CH_4 (Figure 1 9) from Antarctic and Greenland ice cores for the period between 10,000 and 160,000 years ago (Raynaud et al 1988, Stauffer et al , 1988, Craig and Chou, 1982, Chappellaz et al , 1990) The minimum concentration during the last glacial periods (about 20,000 and 150,000 years ago) was around 0 35 ppmv, and rose rapidly, in phase with the observed temperature increases, to about 0 65 ppmv during the glacial-interglacial transitions (about 15,000 and 130,000 years ago) The atmospheric concentrations of CH_4 decreased rapidly, prior to, and during the last deglaciation period about 10,000 11,000 years ago (the Younger Dryas period when there were abrupt temperature decreases in Greenland and northern Europe), and increased rapidly thereafter

Because of the brittle nature of the ice cores, data on the atmospheric concentrations of CH_4 are reliable only during the last 2,000 years of the Holocene period (last 10 000 years)

1 3 1 2 Contemporary record of methane

Ice core data (Figure 1 10) indicate that the atmospheric concentrations of CH_4 averaged around 0 8 ppmv between two hundred and two thousand years ago, increasing to 0 9 ppmv one hundred years ago (Craig and Chou, 1982, Rasmussen and Khalil, 1984, Stauffer et al , 1985, Pearman and Fraser, 1988, Pearman et al , 1986, Etheridge et al , 1988) Since then, the atmospheric concentration of CH_4 has increased smoothly to present levels, highly correlated with global human population Analysis of infrared solar spectra has shown that the atmospheric concentration of CH_4 has increased by about 30% over the last 40 years (Rinsland et al , 1985, Zander et al , 1990)

Atmospheric concentrations of CH_4 have been measured directly since 1978 when the globally averaged value was 1 51 ppmv (e g , Rasmussen and Khalil, 1981, Blake and Rowland, 1988) Currently the value is 1 72 ppmv, corresponding to an atmospheric reservoir of about 4900 Tg (1 Tg = 10^{12} g) and it is increasing at a rate of 14 to 17 ppbv per year (40 to 48 Tg per year), i e , 0 8 to 1 0% per year (Blake and Rowland 1988, Steele et al , 1987) The atmospheric concentration of CH_4 in the Northern Hemisphere is 1 76 ppmv compared to 1 68 ppmv in the Southern Hemisphere (Figure 1 11) The magnitude of the seasonal variability varies with latitude (Steele et al 1987, Fraser et al 1984), being controlled by the temporal variability in source strengths and atmospheric concentration of OH radicals

1 3 1 3 Isotopic composition of methane

Methane is produced from different sources with distinctive proportions of carbon ^{12}C ^{13}C and ^{14}C, and hydrogen isotopes H, D (^2H) and T (^3H) Similarly the rates of processes that destroy CH_4 depend upon its isotopic composition Consequently the CH_4 budget can be constrained by knowledge of the isotopic composition of atmospheric CH_4, the extent of isotopic fractionation during removal, and the isotopic signatures of CH_4 from different sources Recent work to elucidate the sources of CH_4 has proceeded through an analysis of carbon isotopic signatures (Cicerone and Oremland 1988 Wahlen et al 1989, Lowe et al , 1988 and references therein) One example of this is an analysis of ^{14}C data which suggests that about 100 Tg CH_4 per year may arise from fossil sources (Cicerone and Oremland 1988, Wahlen et al 1989) Such a distinction is possible because CH_4 from fossil sources is ^{14}C-free while that from other sources has essentially the ^{14}C concentration of modern carbon

1.3.2 Sinks of Methane

The major sink for atmospheric CH_4 is reaction with OH in the troposphere the OH concentration being controlled by a complex set of reactions involving CH_4 CO NMHC NO_x and tropospheric O_3 (discussed in Section 1 7 S/e
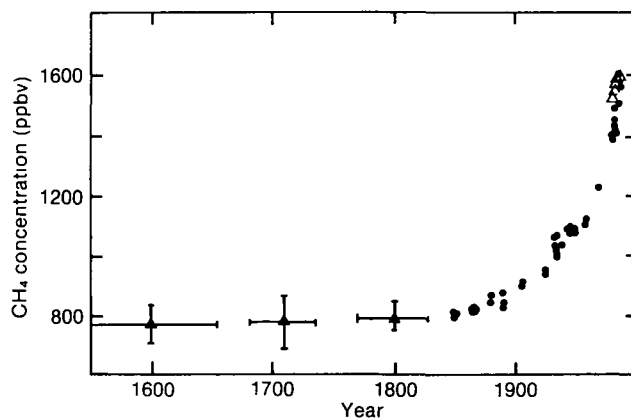
Figure 1.10: Atmospheric methane variations in the past few centuries measured from air in dated ice cores (Etheridge et al 1988 Pearman and Fraser 1990)
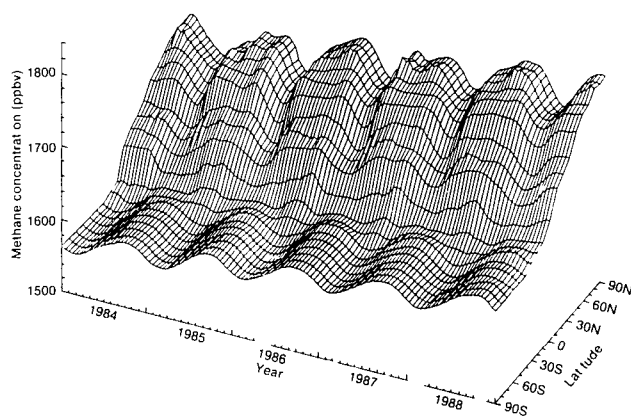
Figure 1.11: The global distribution, seasonality and trend of methane from the GMCC network (Steele et al , 1987 and unpublished data)

1977, Crutzen 1987) Based on the reaction rate coefficient between CH_4 and OH, and the estimated tropospheric distribution of OH an atmospheric lifetime for CH_4 of between 8 and 11 8 years has been estimated (Prinn et al 1987) This estimate is supported by the fact that models of global OH are tested by analyses of the budgets for CH_3CCl_3 (Logan et al 1981, Fraser et al 1986a Prinn et al 1987) and ^{14}CO (Appendix to WMO 1989b) The reaction between CH_4 and OH currently represents a sink of 400 to 600 Tg of CH_4 per year The efficiency of this sink may however have decreased during the last century because the atmospheric concentration of OH in the troposphere may have decreased hence the lifetime of CH_4 would have increased in response to increasing concentrations of CO NMHC and CH_4 (S/e 1977)

Table 1 2   Estimated Sources and Sinks of Methane

	Annual Release (Tg CH4)	Range (Tg CH4)
Source		
Natural Wetlands (bogs, swamps, tundra, etc)	115	100 - 200
Rice Paddies	110	25 - 170
Enteric Fermentation (animals)	80	65 - 100
Gas Drilling, venting, transmission	45	25 - 50
Biomass Burning	40	20 - 80
Termites	40	10 - 100
Landfills	40	20 - 70
Coal Mining	35	19 - 50
Oceans	10	5 - 20
Freshwaters	5	1 - 25
CH4 Hydrate Destabilization	5	0 - 100
Sink		
Removal by soils	30	15 - 45
Reaction with OH in the atmosphere	500	400 - 600
Atmospheric Increase	44	40 - 48

Soils may represent a removal mechanism for CH_4 The magnitude of this sink has been estimated (this assessment) to be 30 ± 15 Tg CH_4 per year from the work of Harriss et al 1982 and Seiler and Conrad, 1987

1.3.3 Sources of Methane

Methane is produced from a wide variety of anaerobic sources (Cicerone and Oremland, 1988) Two main pathways for CH_4 production have been identified (i) reduction of CO_2 with hydrogen, fatty acids or alcohols as hydrogen donors, or (ii) transmethylation of acetic acid or methyl alcohol by CH_4-producing bacteria Table 1 2 summarizes identified sources of CH_4 with ranges of likely annual emissions The total annual CH_4 source must equal the atmospheric sink of about 500 (400 to 600) Tg CH_4 per year the possible soil sink of about 30 (15 to 45) Tg CH_4 per year, and the annual growth of 40 to 48 Tg CH_4 in the atmosphere The sum of the present best estimates of the sizes of the individual sources identified in Table 1 2 equal 525 Tg CH_4 per year It should be noted that the newest data for rice paddies, biomass burning, and coal mining sources suggest that the values may be even less than those of Table 1 2, possibly indicating a missing source of CH_4, or an overestimate of the sink for CH_4

1 3 3 1 Natural wetlands

Significant progress has been made in quantifying the magnitude of the source of CH_4 from natural wetlands (Svensson and Rosswall, 1984, Sebacher et al , 1986, Whalen and Reeburgh, 1988, Moore and Knowles, 1987, Mathews and Fung, 1987, Harriss et al , 1985, Crill et al , 1988, Andronova, 1990, Harriss and Sebacher, 1981, Burke et al , 1988, Harriss et al , 1988, Aselmann and Crutzen, 1989) Recent data support earlier estimates of a global flux of 110 - 115 Tg CH_4 per year, but reverses the relative importance of tropical and high latitude systems (Bartlett et al , 1990) The data base, which is still quite limited (no data from Asia), suggests 55 Tg CH_4 per year (previously 32 Tg CH_4 per year) from tropical wetlands, and 39 Tg CH_4 per year (previously 63 Tg CH_4 per year) from high latitude wetlands Since CH_4 is produced through biological processes under anaerobic conditions, any factors affecting the physical, chemical or biological characteristics of soils could affect CH_4 emission rates

1 3 3 2 Rice paddies

Rice paddies are an important source of CH_4 with estimates of the globally averaged flux ranging from 25 - 170 Tg CH_4 per year (Neue and Scharpenseel, 1984, Yagi and Minami, 1990, Holzapfel-Pschorn and Seiler, 1986, Cicerone and Shetter, 1981, Cicerone et al , 1983) The flux of CH_4 from rice paddies is critically dependent upon

several factors including (i) agricultural practices (e g , fertilization, water management, density of rice plants, double cropping systems, application of manure or rice straw), (ii) soil / paddy characteristics (soil type, acidity, redox potential, temperature, nutrient availability, substrate, profile of anaerobic environment), and (iii) time of season One difficulty in obtaining accurate estimates is that almost 90% of the world's harvested area of rice paddies is in Asia, and of this about 60% are in China and India from which no detailed data are available The annual production of rice since 1940 has approximately doubled as a result of double cropping practices and an increased area of cultivation It is likely that CH4 emissions have increased proportionally as well

1 3 3 3 Biomass burning
Biomass burning in tropical and sub tropical regions is thought to be a significant source of atmospheric CH_4, with estimates of global emission rates ranging from 20 to 80 Tg CH_4 per year (Andreae et al , 1988, Bingemer and Crutzen, 1987, Crutzen et al , 1979, Crutzen et al , 1985, Crutzen 1989, Greenberg et al , 1984 Stevens et al 1990 Quay et al , 1990) Improved estimates require an enhanced understanding of (i) CH_4 emission factors, (ii) the amount, by type, of vegetation burnt each year on an area basis and (iii) type of burning (smouldering vs flaming) Current estimates indicate that over the last century the rate of forest clearing by burning has increased (c f Section 1 2 2 2)

1 3 3 4 Enteric fermentation (animals)
Methane emissions from enteric fermentation in ruminant animals including all cattle, sheep and wild animals is estimated to provide an atmospheric source of 65 - 100 Tg CH_4 per year (Crutzen et al , 1986 Lerner et al 1988) Methane emissions depend upon animal populations as well as the amount and type of food It is difficult to estimate the change in this source over the last century accurately because the significant increase in the number of cattle and sheep has been partially offset by decreases in the populations of elephants and North American bison One estimate suggests that the magnitude of this source has increased from 21 Tg CH_4 per year in 1890 to 78 Tg CH_4 per year in 1983 (Crutzen et al , 1986)

1 3 3 5 Termites
There is a large range in the magnitude of the estimated fluxes of CH_4 from termites, 10 - 100 Tg CH_4 per year (Cicerone and Oremland, 1988, Zimmerman et al , 1982, Rasmussen and Khalil, 1983, Seiler et al 1984 Fraser et al 1986b) The values are based on the results of laboratory experiments applied to estimates of global termite populations and the amount of biomass consumed by termites both of which are uncertain, and field

experiments It is important to determine whether the global termite population is currently increasing, and whether it is likely to respond to changes in climate

1 3 3 6 Landfills
The anaerobic decay of organic wastes in landfills may be a significant anthropogenic source of atmospheric CH_4, 20 - 70 Tg CH_4 per year However, several factors need to be studied in order to quantify the magnitude of this source more precisely, including amounts, trends, and types of waste materials, and landfill practices (Bingemer and Crutzen, 1987)

1 3 3 7 Oceans and freshwaters
Oceans and freshwaters are thought to be a minor source of atmospheric CH_4 The estimated flux of CH_4 from the oceans is based on a limited data set taken in the late 1960 s / early 1970 s when the atmospheric concentration of CH_4 was about 20% lower They showed that the open oceans were only slightly supersaturated in CH_4 with respect to its partial pressure in the atmosphere There are inadequate recent data from either the open oceans or coastal waters to reduce the uncertainty in these estimates (Cicerone and Oremland, 1988)

1 3 3 8 Coal mining
Methane is released to the atmosphere from coal mine ventilation, and degassing from coal during transport to an end-use site A recent unpublished study estimated the flux of CH_4 from coal mining, on a country basis, for the top twenty coal producing countries, and deduced a global minimum emission of 19 Tg CH_4 per year Global CH_4 fluxes from coal mining have been estimated to range from 10 - 50 Tg CH_4 per year (Cicerone and Oremland 1988, ICF, 1990, and recent unpublished studies by others)

1 3 3 9 Gas drilling venting and transmission
Methane is the major component of natural gas hence leakage from pipelines and venting from oil and gas wells could represent a significant source of atmospheric CH_4 (Cicerone and Oremland, 1988) The global flux from these sources is estimated based on limited data of questionable reliability, to range from 25 - 50 Tg CH_4 per year

1.3.4 Feedbacks from Climate Change into the Methane Cycle
Future atmospheric concentrations of CH_4 will depend on changes in the strengths of either the sources or sinks which are dependent upon social, economic, and political and also environmental factors and in particular changes in climate Methane emissions from wetlands are particularly sensitive to temperature and soil moisture and hence future climatic changes could significantly change the fluxes of CH_4 from both natural wetlands and rice paddies

Tropospheric OH, which provides the atmospheric sink for CH_4, is dependent upon a number of factors, including the intensity of UV-B radiation, and the ambient concentrations of H_2O, CO, CH_4, reactive nitrogen oxides, and tropospheric O_3 (See Section 1.7) (Crutzen, 1987; Isaksen and Hov, 1987; Thompson and Cicerone, 1986).

1.3.4.1 Tropical methane sources

The major sources of CH_4 in tropical regions (natural wetlands and rice paddies) are quite sensitive to variations in soil moisture. Consequently, changes in soil moisture, which would result from changes in temperature and precipitation, could significantly alter the magnitude of these large sources of atmospheric CH_4. Increased soil moisture would result in larger fluxes, whereas a decrease in soil moisture would result in smaller fluxes.

1.3.4.2 High latitude methane sources

Methane fluxes from the relatively flat tundra regions would be sensitive to changes of only a few centimetres in the level of the water table, with flooded soils producing a factor of 100 more CH_4 than dry soils. Similarly, emissions of CH_4 are significantly larger at warmer temperatures, due to accelerated microbiological decomposition of organic material in the near-surface soils (Whalen and Reeburgh, 1988; Crill et al., 1988). Consequently, an increase in soil moisture and temperatures in high latitude wetlands would result in enhanced CH_4 emissions, whereas warmer dryer

soils might have decreased CH_4 emissions.

Higher temperatures could also increase the fluxes of CH_4 at high northern latitudes from; (i) CH_4 trapped in permafrost, (ii) decomposable organic matter frozen in the permafrost, and (iii) decomposition of CH_4 hydrates (Cicerone and Oremland, 1988; Kvenvolden, 1988; Nisbet, 1989). Quantifying the magnitudes of these positive feedbacks is difficult. Time-scales for thawing the permafrost, located between a few centimetres to metres below the surface, could be decades to centuries, while the time for warming the CH_4 hydrates could be even longer, although one study (Kvenvolden, 1988) estimated that the flux of CH_4 from hydrate decomposition could reach 100 Tg CH_4 per year within a century.

1.3.5 Conclusions

Current atmospheric CH_4 concentrations, at 1.72 ppmv, are now more than double the pre-industrial value (1750-1800) of about 0.8 ppmv, and are increasing at a rate of 0.9% per year. The ice core record shows that CH_4 concentrations were about 0.35 ppmv during glacial periods, and increased in phase with temperature during glacial-interglacial transitions. The current atmospheric concentration of CH_4 is greater than at any time during the last 160,000 years.

Reaction with OH in the troposphere, the major sink for CH_4, results in a relatively short atmospheric lifetime of 10 ± 2 years. The short lifetime of CH_4 implies that atmospheric concentrations will respond quite rapidly, in

Table 1.3 Halocarbon Concentrations and Trends (1990) †

Halocarbon		Mixing Ratio pptv	Annual Rate of Increase		Lifetime Years
			pptv	%	
CCl_3F	(CFC-11)	280	9.5	4	65
CCl_2F_2	(CFC-12)	484	16.5	4	130
$CClF_3$	(CFC-13)	5			400
$C_2Cl_3F_3$	(CFC-113)	60	4-5	10	90
$C_2Cl_2F_4$	(CFC-114)	15			200
C_2ClF_5	(CFC-115)	5			400
CCl_4		146	2.0	1.5	50
$CHClF_2$	(HCFC-22)	122	7	7	15
CH_3Cl		600			1.5
CH_3CCl_3		158	6.0	4	7
$CBrClF_2$	(halon 1211)	1.7	0.2	12	25
$CBrF_3$	(halon 1301)	2.0	0.3	15	110
CH_3Br		10-15			1.5

† There are a few minor differences between the lifetimes reported in this table and the equivalent table in WMO 1989b. These differences are well within the uncertainty limits. The 1990 mixing ratios have been estimated based upon an extrapolation of measurements reported in 1987 or 1988, assuming that the recent trends remained approximately constant.
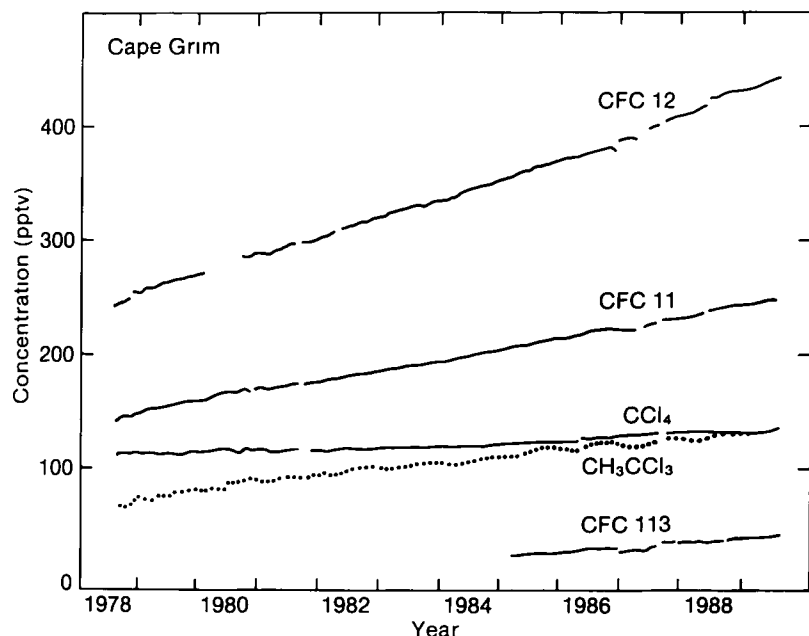
Figure 1.12: Halocarbon concentrations measured at Cape Grim, Tasmania during the period 1978-1989 (Fraser and Derek, 1989, and unpublished data)

comparison to the longer lived gases such as CO_2, N_2O, and CFCs, to changes in emissions In order to stabilize concentrations at present day levels, an immediate reduction in global man-made emissions by 15-20 percent would be necessary (this and other scientific sensitivity analyses are discussed in the Annex) Global concentrations of OH are dependent upon the intensity of UV-B radiation, and the concentrations of gases such as H_2O, CO, CH_4, NO_x, NMHC, and O_3 and may have declined during the twentieth century due to changes in the atmospheric concentrations of these gases

The individual sources of atmospheric CH_4 have been qualitatively identified, but there are significant uncertainties in the magnitude of their strengths Human activities such as rice cultivation, rearing of domestic ruminants, biomass burning, coal mining, and natural gas venting have increased the input of CH_4 into the atmosphere, and these combined with an apparent decrease in the concentration of tropospheric OH, yields the observed rise in global CH_4 However, the quantitative importance of each of the factors contributing to the observed increase is not well known at present

Several potential feedbacks exist between climate change and CH_4 emissions, in both tropical and high latitude wetland sources In particular, an increase in high latitude temperatures could result in a significant release of CH_4 from the melting of permafrost and decomposition of CH_4 hydrates

1.4 Halocarbons

Halocarbons containing chlorine and bromine have been shown to deplete O_3 in the stratosphere In addition, it has been recognized that they are important greenhouse gases Their sources, sinks, atmospheric distributions, and role in perturbing stratospheric O_3 and the Earth's radiative balance have been reviewed in detail (WMO 1985, 1989a, 1989b) Many governments, recognizing the harmful effects of halocarbons on the environment, signed the Montreal Protocol on Substances that Deplete the Ozone Layer' (UNEP 1987) in 1987 to limit the production and consumption of a number of fully halogenated CFCs and halons The control measures of the Montreal Protocol freeze the production and consumption of CFCs 11, 12, 113, 114, and 115 in developed countries at their 1986 levels from the year 1990, a reduction to 80% of their 1986 levels from the year 1993, with a further reduction to 50% of their 1986 levels from the year 1998 Developing countries, with a per capita use of CFCs of less than 0 3 kg per capita, are allowed to increase their per capita use up to this limit and can delay compliance with the control measures by 10 years All major producing and consuming developed countries, and many developing countries, have signed and ratified the Montreal Protocol

1.4.1 Atmospheric Distribution of Halocarbons

The mean atmospheric concentrations of the most abundant radiatively active halocarbons are shown in Table 1 3 The atmospheric concentrations of the halocarbons are currently increasing more rapidly on a global scale (on a percentage

basis) than the other greenhouse gases (Figure 1 12) The concentrations of the fully halogenated chloro fluorocarbons (CFCs), slightly greater in the northern hemisphere than in the southern hemisphere, are consistent with the geographical distribution of releases (>90% from the industrialized nations), a 45°N - 45°S mixing time of about 1 year, and their very long atmospheric lifetimes

1.4.2 Sinks for Halocarbons

There is no significant tropospheric removal mechanism for the fully halogenated halocarbons such as CCl_3F (CFC-11), CCl_2F_2 (CFC 12), $C_2Cl_3F_3$ (CFC 113), $C_2Cl_2F_4$ (CFC-114), C_2ClF_5 (CFC-115), carbon tetrachloride (CCl_4), and halon 1301 ($CBrF_3$) They have long atmospheric lifetimes decades to centuries, and are primarily removed by photodissociation in the mid - upper stratosphere There is currently a significant imbalance between the sources and sinks giving rise to a rapid growth in atmospheric concentrations To stabilize the atmospheric concentrations of CFCs 11, 12 and 113 at current levels would require reductions in emissions of approximately 70-75%, 75-85%, and 85-95%, respectively (see Annex)

Non fully halogenated halocarbons containing a hydrogen atom such as methyl chloride (CH_3Cl), methylchloroform (CH_3CCl_3), $CHClF_2$ (HCFC-22), and a number of other HCFCs and HFCs being considered as substitutes for the current CFCs (c f Section 1 4 4) are primarily removed in the troposphere by reaction with OH These hydrogen containing species have atmospheric lifetimes ranging from about one to forty years, much shorter on average than the fully halogenated CFCs To stabilize the atmospheric concentrations of HCFC-22 at current levels would require reductions in emissions of approximately 40-50%

1.4.3 Sources of Halocarbons

Most halocarbons, with the notable exception of CH_3Cl, are exclusively of industrial origin Halocarbons are used as aerosol propellants (CFCs 11, 12, and 114), refrigerants (CFCs 12 and 114, and HCFC-22) foam blowing agents (CFCs 11 and 12) solvents (CFC-113 CH_3CCl_3, and CCl_4), and fire retardants (halons 1211 and 1301) Current emission fluxes are approximately CFC 11 350Gg/y CFC 12 450 Gg/y CFC-113 150 Gg/y HCFC-22 140 Gg/y, others are significantly smaller The atmospheric concentration of methyl chloride is about 0 6 ppbv, and is primarily released from the oceans and during biomass burning There is no evidence that the atmospheric concentration of CH_3Cl is increasing Methyl bromide (CH_3Br) is produced by oceanic algae and there is evidence that its atmospheric concentration has been increasing in recent times due to a significant anthropogenic source (Penkett et al 1985 Wofsy et al 1975)

1.4.4 Future Atmospheric Concentration of Halocarbons

Future emissions of CFCs 11, 12, 113, 114, and 115 will be governed by the Montreal Protocol on "Substances that Deplete the Ozone Layer as discussed in Section 1 4 In addition, international negotiations are currently in progress that will likely (i) result in a complete global phase-out of production of these chemicals by the year 2000, and (ii) enact limitations on the emissions (via production and consumption controls) of CCl_4, and CH_3CCl_3 However, even with a complete cessation of production of CFCs 11, 12 and 113 in the year 2000 their atmospheric concentrations will still be significant for at least the next century because of their long atmospheric lifetimes It should be noted that emissions of these gases into the atmosphere will continue for a period of time after production has ceased because of their uses as refrigerants, foam blowing agents fire retardants, etc

A number of hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) are being considered as potential replacements for the long-lived CFCs (11, 12, 113, 114, and 115) that are regulated under the terms of the Montreal Protocol The HFCs and HCFCs primarily being considered include HCFC 22, HCFC-123 ($CHCl_2CF_3$), HCFC 124 ($CHClFCF_3$), HFC 125 (CHF_2CF_3), HFC-134a (CH_2FCF_3), HCFC-141b (CH_3CCl_2F), HCFC-142b (CH_3CClF_2), HFC 143a (CH_3CF_3), and HFC-152a (CH_3CHF_2) The calculated atmospheric lifetimes of these chemicals are controlled primarily by reaction with tropospheric OH and range between about 1 and 40 years It has been estimated (UNEP 1989) that a mix of HFCs and HCFCs will replace the CFCs currently in use at a rate of about 0 4 kg of substitute for every kg of CFCs currently produced, with an annual growth rate of about 3% Because of their shorter lifetimes, and expected rates of substitution and emissions growth rates, the atmospheric concentrations of HFCs and HCFCs will be much lower for the next several decades than if CFCs had continued to be used, even at current rates However, continued use, accompanied by growth in the emission rates of HFCs and HCFCs for more than several decades would result in atmospheric concentrations that would be radiatively important

1.4.5 Conclusions

The atmospheric concentrations of the industrially-produced halocarbons, primarily CCl_3F, CCl_2F_2, $C_2Cl_3F_3$, and CCl_4 are about 280 pptv, 484 pptv, 60 pptv, and 146 pptv, respectively Over the past few decades their concentrations (except CCl_4) have increased more rapidly (on a percentage basis) than the other greenhouse gases, currently at rates of at least 4% per year The fully halogenated CFCs and CCl_4 are primarily removed by photolysis in the stratosphere and have atmospheric lifetimes in excess of 50 years

Most halocarbons, with the notable exception of methyl chloride, are exclusively anthropogenic and their sources (solvents, refrigerants, foam blowing agents, and aerosol propellants) are well understood.

To stabilize, and then reduce, the current atmospheric concentrations of the fully halogenated CFCs (e.g , 11, 12 and 113) would require approximate reductions in emissions of 70-75%, 75-85%, and 85-95%, respectively. Future emissions of CFCs and CCl_4 will, most likely, be eliminated or be significantly lower than today's because the stringency, scope, and timing of international regulations on chlorine and bromine containing chemicals, (i.e., the Montreal Protocol on Substances that Deplete the Ozone Layer) are currently being renegotiated. However, the atmospheric concentrations of CFCs 11, 12 and 113 will still be significant (30 - 40% of current) for at least the next century because of their long atmospheric lifetimes.

1.5 Nitrous Oxide

Nitrous oxide is a chemically and radiatively active trace gas that is produced from a wide variety of biological sources in soils and water and is primarily removed in the stratosphere by photolysis and reaction with electronically excited oxygen atoms.

1.5.1 Atmospheric Distribution of Nitrous Oxide

The mean atmospheric concentration of N_2O in 1990 is about 310 ppbv, corresponding to a reservoir of about 1500 TgN, and increasing at a rate of 0 2 - 0.3% per year (Figure 1 13, Weiss, 1981; Prinn et al , 1990; Robinson et al., 1988; Elkins and Rossen, 1989, Rasmussen and Khalil, 1986). This observed rate of increase represents an atmospheric growth rate of about 3 to 4.5 TgN per year. The atmospheric concentration of N_2O is higher in the Northern Hemisphere than in the Southern Hemisphere by about 1 ppbv Ice core measurements show that the pre-industrial value of N_2O was relatively stable at about 285 ppbv for most of the past 2000 years, and started to increase around the year 1700 (Figure 1 14, Pearman et al , 1986, Khalil and Rasmussen, 1988b, Etheridge et al , 1988; Zardini et al , 1989) Figure 1.14 shows that the atmospheric concentrations of N_2O may have decreased by a few ppbv during the period of the "Little Ice Age"

1.5.2 Sinks for Nitrous Oxide

The major atmospheric loss process for N_2O is photochemical decomposition in the stratosphere, and is calculated to be 10± 3 Tg N per year (Table 1 4) Nitrous oxide has an atmospheric lifetime of about 150 years The observed rate of growth represents a 30% imbalance between the sources and sinks (Hao et al , 1987) Tropospheric sinks such as surface loss in aquatic and soil
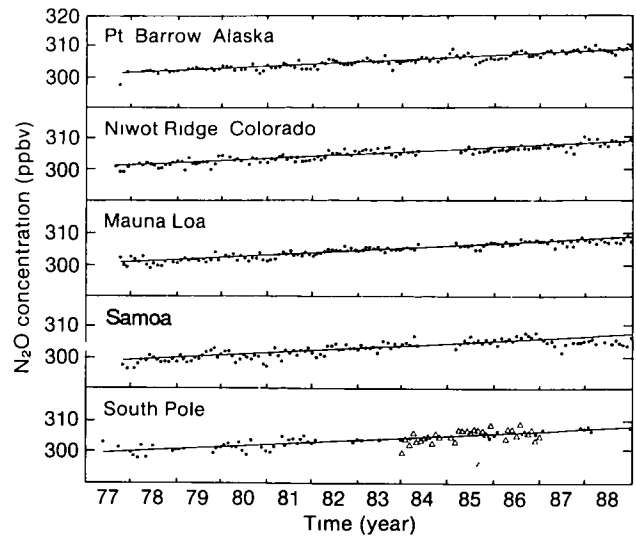
Figure 1.13: Atmospheric measurements of nitrous oxide from the NOAA/GMCC network (Elkins and Rossen, 1989)
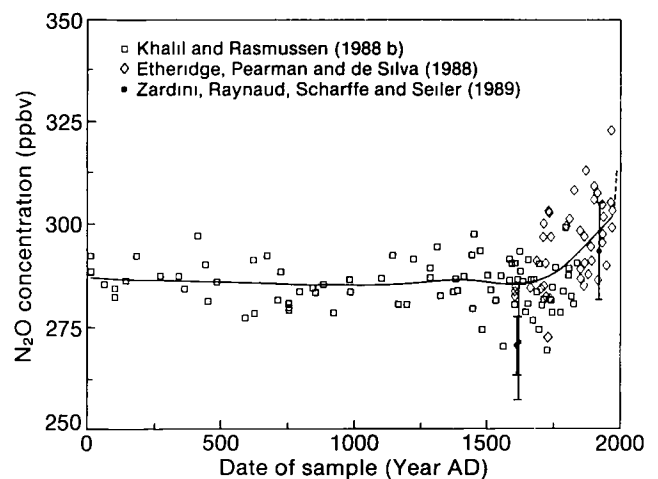
Figure 1.14: Nitrous oxide measurements from ice-core samples

systems are considered to be small (Elkins et al., 1978, Blackmer and Bremner, 1976).

1.5.3 Sources of Nitrous Oxide

1 5 3 1 Oceans

The oceans are a significant, but not dominant source of N_2O (McElroy and Wofsy, 1986) Based on measurements of the concentration gradients between the atmosphere and surface waters (Butler et al., 1990, and NOAA GMCC unpublished data), and on estimates of the gas exchange coefficient, the current estimate of the magnitude of the

Table 1 4 Estimated Sources and Sinks of Nitrous Oxide

	Range (TgN per year)
Source	
Oceans	1 4 - 2 6
Soils (tropical forests)	2 2 - 3 7
(temperate forests)	0 7 - 1 5
Combustion	0 1 - 0 3
Biomass burning	0 02 - 0 2
Fertilizer (including ground-water)	0 01 - 2 2
TOTAL	4 4 10 5
Sink	
Removal by soils	?
Photolysis in the stratosphere	7 - 13
Atmospheric Increase	3 4 5

ocean source ranges from 1 4 - 2 6 Tg N per year, significantly lower than earlier estimates (Elkins et al , 1978, Cohen and Gordon, 1979, Cline et al , 1987) An accurate determination of the global annual ocean flux is difficult because of uncertainties associated with quantifying the gas exchange coefficient and because the partial pressure of N_2O in the surface waters is highly variable, both spatially and temporally The partial pressure of N_2O in surface waters varies considerably, ranging from being supersaturated by up to 40% in upwelling regions to being undersaturated by a few percent in areas around Antarctica and within gyres Data suggest that during El Niño events when upwelling in the Pacific ocean is suppressed the ocean fluxes of N_2O are significantly lower (Cline et al 1987, Butler et al , 1990) It is still unclear whether N_2O is primarily produced from nitrification in near surface waters, or denitrification in oxygen deficient deep waters Based on vertical profile measurements of oceanic N_2O (NOAA GMCC, unpublished) the oceanic reservoir has been estimated to be between 900 and 1100 Tg N comparable to the atmosphere Consequently, changes in the exchange fluxes of N_2O between the ocean and the atmosphere could have a significant impact on its atmospheric concentration

1 5 3 2 Soils

Denitrification in aerobic soils is thought to be a dominant source of atmospheric N_2O (Keller et al , 1986, Matson and Vitousek, 1987, Matson and Vitousek 1989, Slemr et al 1984) Nitrification under anaerobic conditions could,

however, produce higher yields of N_2O per unit of transformed nitrogen Quantification of global N_2O emissions from soils is difficult because of the heterogeneity of terrestrial ecosystems and the variability in environmental conditions that control the fluxes of N_2O

Estimates of global fluxes of N_2O from tropical forests range from 2 2 - 3 7 Tg N per year The impact of deforestation on the emissions of N_2O from tropical soils is unclear, with some studies suggesting that the emissions of N_2O from deforested land are enhanced by as much as a factor of three (Luizao et al , 1990), whereas other studies concluded that N_2O fluxes decreased if vegetation did not return (Robertson and Tiedje, 1988)

Quantifying the roles of temperate forest soils and grasslands in the N_2O budget is difficult because of the paucity of data, and conflicting results Estimates of N_2O fluxes from temperate forest soils range from 0 7 - 1 5 Tg N per year in one study (Schmidt et al , 1988), to almost none in another study (Bowden et al , 1990) One study also reported that deforestation in temperate forests would lead to enhanced emissions of N_2O (Bowden and Bormann, 1986) Reliable global N_2O fluxes from grasslands are impossible to derive from the fragmented data available One study (Ryden, 1981) concluded that English grassland soils, with no fertilization, are a sink for N_2O, whereas limited studies of tropical grasslands and pastures suggest that they may be a moderate to significant source of N_2O (Luizao et al , 1990, Robertson and Tiedje, 1988)

1 5 3 3 Combustion

Until recently, the combustion of fossil fuels was thought to be an important source of atmospheric N_2O (Pierotti and Rasmussen, 1976, Weiss and Craig, 1976, Hao et al , 1987) However, a recent study has shown that the earlier results are incorrect because N_2O was being artificially produced in the flasks being used to collect N_2O from combustion sources (Muzio and Kramlich, 1988) The latest estimate of the global flux of N_2O from combustion sources is between 0 1 and 0 3 Tg N per year, compared to earlier values which were as high as 3 2 Tg N per year

1 5 3 4 Biomass burning

Biomass burning is now thought to be a minor source of atmospheric N_2O with a global flux of less than 0 2 Tg N per year (Muzio and Kramlich, 1988, Crutzen 1989, Elkins et al , 1990, Winstead et al , 1990, Griffith et al , 1990) This value is 1-2 orders of magnitude less than previous estimates (Crutzen et al , 1979, 1985) which were influenced by artifacts involving N_2O analysis (Crutzen et al , 1985) and N_2O production in sampling flasks (Muzio and Kramlich, 1988)

1 5 3 5 Fertilizer / Ground-Water

Nitrous oxide production from the use of nitrate and ammonium fertilizers is difficult to quantify because the N_2O fluxes are dependent upon numerous factors including type of fertilizer, soil type, soil temperature, weather, and farming practices (e g , ploughing, sowing, irrigating) Conversion of fertilizer N to N_2O ranges from 0 01 - 2 0% (Conrad et al , 1983, Bremner et al , 1981) This range, coupled with a global fertilizer production of 55 Tg N per year in 1980, results in a total N_2O emission of between 0 01 - 1 1 Tg N per year (Conrad et al , 1983) Leaching of nitrogen fertilizers from soils into groundwater may result in additional fluxes of N_2O up to 1 1 Tg N per year (Conrad et al , 1983, Ronen et al , 1988) Consequently, a range of 0 01 - 2 2 Tg N per year can be derived for the flux of N_2O from fertilizer use

1.5.4 Conclusions

Nitrous oxide is a greenhouse gas whose atmospheric concentration, at 310 ppbv, is now about 8% greater than in the pre-industrial era, and is increasing at a rate of about 0 2 - 0 3% per year, corresponding to about 3 - 4 5 Tg N per year This represents an excess of 30% of current global emissions over current sinks The major sink for N_2O is photolysis in the stratosphere, resulting in a relatively long atmospheric lifetime of about 150 years The magnitude of the sink for N_2O is relatively well known (± 30%) In order to stabilize concentrations at present day levels, an immediate reduction of 70   80% of the additional flux of N_2O that has occurred since the pre-industrial era would be necessary

Quantification of the various natural and anthropogenic sources is uncertain Since the latest studies indicate that the total combined flux of N_2O from combustion and biomass burning is between 0 1 to 0 5 Tg N per year in contrast to earlier estimates of about 5 Tg N per year, and production of N_2O from fertilizer (including groundwater) is believed to be less than or equal to 2 2 Tg N per year, it is difficult to account for the annual increase based on known sources Stimulation of biological production due to agricultural development may account for the missing anthropogenic emissions Estimates of the removal rate of N_2O by photodissociation in the stratosphere range from 7 - 13 Tg N per year Therefore, the total source needed to account for the observed annual atmospheric growth is 10 - 17 5 Tg N per year against a flux of N_2O from known sources of 4 4 - 10 5 Tg N per year These data suggest that there are missing sources of N_2O, or the strengths of some of the identified sources have been underestimated Despite these uncertainties, it is believed that the observed increase in N_2O concentrations is caused by human activities

1.6 Stratospheric Ozone

Stratospheric O_3 is an important constituent of the Earth s atmosphere It protects the Earth's surface from harmful solar ultraviolet radiation and it plays an important role in controlling the temperature structure of the stratosphere by absorbing both incoming solar ultraviolet radiation and outgoing terrestrial (longwave) radiation Part of the absorbed outgoing longwave radiation is then re-radiated back to the surface-troposphere system Reductions in stratospheric O_3 can modify the surface temperature via two competing processes   more solar radiation is transmitted to the surface-troposphere system, thereby contributing to a surface warming, on the other hand, the cooler stratosphere (due to decreased solar and long-wave absorption) emits less to the troposphere which would tend to cool the surface The solar warming (a function of total column amount of O_3) and longwave cooling (a function of the vertical distribution of O_3) are similar in magnitude Therefore, the magnitude as well as the sign of the change in surface temperature depends critically on the magnitude of the O_3 change, which in turn is depends strongly on altitude, latitude and season

The concentration and distribution of stratospheric O_3 is controlled by dynamical, radiative and photochemical processes Stratospheric O_3 is photochemically controlled by chemically active species in the (i) oxygen, (ii) hydrogen, (iii) nitrogen, (iv) chlorine, and (v) bromine families The precursors for the photochemically active species are (i) O_2, (ii) H_2O and CH_4, (iii) N_2O, (iv) CFCs, CCl_4, CH_3CCl_3, CH_3Cl, and (v) halons and CH_3Br, respectively

1.6.1 Stratospheric Ozone Trends

1 6 1 1 Total column ozone trends

The Antarctic ozone hole, which formed during the mid to late 1970s, recurs every springtime To determine O_3 trends more widely, data from the ground-based Dobson network have been re-evaluated, station by station, and used to determine changes in total column O_3 over the past two decades Unfortunately, the network and data are adequate for only a limited geographical region, i e , 30 - 64°N They are inadequate to determine total column O_3 changes in the Arctic, tropics, subtropics, or southern hemisphere apart from Antarctica Satellite data can provide the desired global coverage, but the current record is too short (about one solar cycle, 1978 to present) to differentiate between the effects of natural and human influenced processes on O_3 The re evaluated data was analysed for the effects of known natural geophysical processes (seasonal variation, the approximately 26-month quasi-biennial-oscillation, and the 11-year solar cycle) and possible human perturbations After allowing for natural variability, the analyses, using a variety of statistical models and assumptions, showed measurable zonal mean

O3 decreases in the range 3.4% to 5.1% between 30 and 64°N latitude for the winter months (December - March) between 1969 and 1988, with the larger decreases at the higher latitudes (WMO, 1989a,b). No statistically significant zonal trends were found for the summer period (May - August). Lastly, within longitudinal sectors, regional differences in the O3 trends were indicated, with the largest values over North America and Europe and the smallest over Japan.

1.6.1.2 Changes in the vertical distribution of ozone

Substantial uncertainties remain in defining changes in the vertical distribution of O3. Analysis of SAGE I and II satellite data, averaged over 20 to 50°N and S latitudes, indicates that near 40 km O3 decreased by (3±2)% between February 1979 - November 1981 and October 1984 - December 1988 (WMO, 1989b). Because the SAGE record is so short (less than one solar cycle), no attempt has been made to distinguish between solar-induced and human-influenced contributions to these changes. A thorough analysis of data from 10 ground-based Umkehr stations in the Northern Hemisphere for the period 1977 to 1987 indicates a statistically significant decrease in O3 between 30 and 43 km. The decrease near 40 km of (4.8±3.1)%, after allowing for seasonal and solar-cycle effects and correcting the data for aerosol interferences, is broadly consistent with theoretical predictions. Based on satellite, ground-based, and ozonesonde data, there are indications of a continuing stratospheric O3 decrease since the late 1970s of a few percent at 25 km and below. Photochemical models (which do not take into account heterogeneous processes) do not predict these changes, but the measurements are qualitatively consistent with those required for compatibility with the total column measurements.

1.6.2 Future Changes

Future changes in stratospheric O3 are critically dependent upon future emissions of CFCs, other halocarbons, CH4, N2O, and CO2. Assuming that the current regulatory measures agreed under the Montreal Protocol are not strengthened, then the chlorine loading of the atmosphere is predicted to reach about 9 ppbv by the year 2060, about three times today's level, and a bromine loading of about 30 pptv, about twice today's level. Models predict column O3 reductions of 0 to 4% in the tropics, and from 4 to 12% at high latitudes in late winter. These predictions do not include the effects of heterogeneous processes, which play a critical role in the formation of the Antarctic ozone hole. Consequently, models that include the effects of heterogeneous processes would predict larger O3 depletions, at least in polar regions. Ozone is predicted to decrease by 25 - 50% at 40 km and result in stratospheric temperature decreases of 10 to 20 K. If, as expected, the

Montreal Protocol is modified to eliminate the emissions of CFCs 11, 12, 113, 114, 115, halons 1211 and 1301, and restrict the emissions of CCl_4 and CH_3CCl_3, by the year 2000, then the chlorine loading of the atmosphere by the year 2060 will probably lie between 2.5 and 4 ppbv (depending upon the emissions of CCl_4 and CH_3CCl_3, and HCFCs). Models that do not include heterogeneous processes predict that global O3 levels would be similar to today. However, if the atmospheric chlorine loading approaches 4 ppbv the implications for polar O3, and its subsequent impacts on O3 at mid-latitudes, are unknown.

1.7 Tropospheric Ozone and Related Trace Gases (Carbon Monoxide, Non-Methane Hydrocarbons, and Reactive Nitrogen Oxides)

1.7.1 Tropospheric Ozone

Tropospheric O3 is a greenhouse gas, of particular importance in the upper troposphere in the tropics and sub-tropics.Its distribution is controlled by a complex interplay between chemical, radiative, and dynamical processes. Ozone is: (i) transported down into the troposphere from the stratosphere; (ii) destroyed by vegetative surfaces; (iii) produced by the photo-oxidation of CO, CH_4, and NMHC in the presence of reactive nitrogen oxides (NO_x), and (iv) destroyed by uv-photolysis and by reaction with hydrogen oxide radicals (HO_2) (Danielsen, 1968; Mahlman and Moxim, 1978; Galbally and Roy, 1980; Crutzen, 1974; Isaksen et al., 1978). Chemical processes in clouds could have a strong influence on O3 production and destruction rates (Lelieveld and Crutzen, 1990).

Consequently, while CO, NMHC, and NO_x are not important greenhouse gases in themselves, they are important precursors of tropospheric O3 and they are therefore treated in some detail in this sub-section.

1.7.1.1 Atmospheric distribution

Ozone in the troposphere has a lifetime of at most several weeks, hence its concentration varies with latitude, longitude, altitude and season (Chatfield and Harrison, 1977; Logan, 1985). Near the surface, monthly mean concentrations (30 - 50 ppbv) are highest in spring and summer at northern mid-latitudes (Figure 1.15). In the middle troposphere at northern mid-latitudes values are highest also in spring and summer, 60 - 65 ppbv. The summer maximum results from photo-oxidation of O3 precursors from fossil fuel combustion and industrial activity (Isaksen et al., 1978; Fishman et al., 1985; Logan 1985). Ozone values are highest in winter and spring at other latitudes, in part because the stratospheric source is largest then (Levy et al., 1985). There is 35% more O3 at 40°N than at 40°S, in the middle troposphere (Logan, 1985).
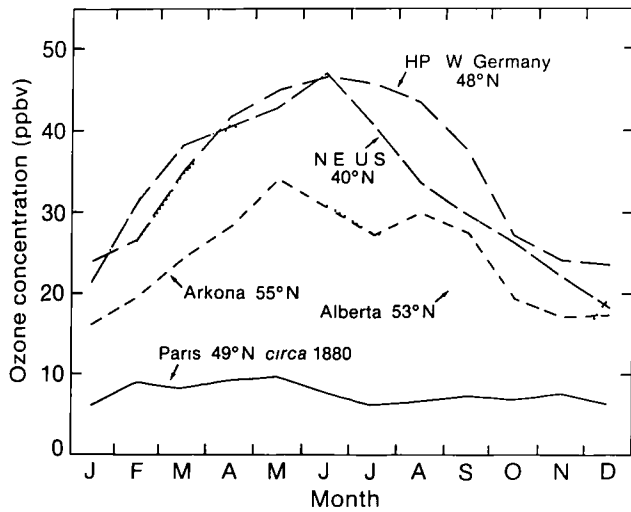
Figure 1.15: The seasonal variation of surface ozone The solid line shows data from Montsouris, France, for 1876 86 (Volz and Kley, 1988) All other data are from the 1970s and 1980s dashed line, Arkona, GDR (Feister and Warmbt, 1987), dotted line Ellershe, Alberta, Canada (Angle and Sandhu, 1986) dot-dash line, average of eight rural sites in the northeastern U S the SURE sites (Logan, 1988) long dashed line Hohenpeissenberg FRG (Logan 1985) All the recent data are shown as monthly means of daily average values

Concentrations of O_3 tend to be smaller in the tropics than in mid-latitudes, except in the dry season when emissions of O_3 precursors from biomass burning provide a photochemical source (Delany et al , 1985, Crutzen et al , 1985, Logan and Kirchhoff 1986 Fishman et al 1990) Ozone values during the southern spring over South America can reach almost as high values as found over the industrialized mid-latitudes in summer Large regions of the tropical troposphere appear to be influenced by sources of O_3 from biomass burning (Fishman et al 1990) Remote marine air and continental air during the wet season may provide a photochemical sink for O_3 in the tropics mean surface concentrations as low as 4 12 ppbv have been measured (Liu et al 1980 Oltsmans and Komhyr 1986, Kirchhoff 1990)

1 7 1 2 Trends

Most long-term measurements of O_3 have been made at northern mid-latitudes from surface sites and from balloons Only sporadic data are available before the 1970s A comparison of data obtained in Paris from 1876-1910 (Volz and Kley 1988) with rural data from the present day from Europe and North America (Logan 1985 1989) suggests that surface O_3 has increased by a factor of 2 3 on average the increase is largest in summer the factor then being 4 6 (Figure 1 15) Ozone values in Europe in

the 1970s appear to be about twice those found between 1930 and 1950 (Crutzen, 1988) Data from Europe suggest an increase of 1 - 2% per year from the mid-1950s to the early 1980s, with increases in winter and summer (Feister and Warmbt, 1987, Bojkov, 1988) Since the mid-1970s O_3 has increased by 0 8% per year at remote sites in Alaska and Hawaii, shown no annual trend at Samoa, but has decreased by 0 5% per year at the South Pole (Oltmans et al , 1988) Decreases of 1 8% per year are found at both Samoa and South Pole in summer Trend data are lacking for tropical continental sites

Ozonesonde data for northern mid-latitudes between 1965 and 1986 suggest that O_3 has increased by about 1% per year below 8 km, primarily over North Europe and Japan (Angell and Korshover, 1983, Logan 1985, Tiao et al , 1986, WMO, 1989a,b), but there are no clear trends in the upper troposphere By contrast O_3 has decreased in the lower stratosphere (below 25 km), the crossover in the trend being near the tropopause There is no trend in O_3 at the single sonde station at southern mid-latitudes, and long term sonde data are lacking in the tropics

1 7 1 3 Relationships between ozone and its precursors
The concentration of tropospheric O_3 is dependent in a very non-linear manner on the atmospheric concentrations of its precursor gases, i e , CO, CH_4, NMHC, and, in particular NO_x (NO_x = NO + NO_2) Nitrogen oxide concentrations and trends control changes in the concentration of O_3 (Dignon and Hameed 1985) At low NO_x concentrations (where NO_x is less than 5 - 30 pptv this threshold depends on the concentrations of O_3 and hydrocarbons) increases in CO CH_4 and NMHC lead to a decrease in O_3 whereas at high NO_x concentrations increases in CO CH_4 and NMHC lead to significant enhancements in O_3 Therefore no simple relationship exists between increases in the precursor gases and changes in tropospheric O_3 Several model calculations have been performed to investigate the sensitivity of O_3 changes to changes in the precursor gases both individually and collectively All models that have attempted to simulate changes in O_3 during the past century have calculated increases in Northern Hemisphere O_3 by up to a factor of two broadly consistent with observations, depending upon the assumptions made regarding the initial concentration distribution and changes in precursor gas concentrations particularly NO_x

Understanding the feedbacks among O_3 and its precursor gases is essential to understand tropospheric OH which controls the atmospheric lifetimes of CH_4 and the NMHCs The global concentration of OH which determines the oxidizing capacity of the troposphere can be either enhanced because of elevated levels of tropospheric O_3 NO_x or water vapour (associated with a global warming) or suppressed because of increases in

CH4, CO, and NMHC (Crutzen, 1987, Thompson et al , 1989) Prediction of regional and global trends in OH concentrations requires an understanding of regional emissions of CH4, CO, NMHC and NOx, as well as transport of O3 between its source regions and the remote troposphere One key point is that a continued increase in levels of CO would reduce the global concentration of OH because NOx is too short-lived to counteract that effect over much of the globe This would increase the atmospheric lifetime of CH4

1.7.2 Carbon Monoxide

1 7 2 1 Atmospheric distribution of carbon monoxide

The atmospheric concentration of CO exhibits significant spatial and temporal variability because of its short atmospheric lifetime (2 - 3 months) The short atmospheric lifetime, coupled with an inadequate monitoring network, means that the global spatial variability and long-term trends in CO are not well documented The limited observational data base (Heidt et al , 1980, Dianov-Klokov and Yurganov, 1981, Seiler and Fishman, 1981, Seiler et al , 1984, Khalil and Rasmussen, 1984, 1988a, Fraser et al , 1986a, c, Newell et al , 1989, Zander et al , 1989, Kirchhoff and Marinho, 1989, Kirchhoff et al , 1989) has demonstrated that the concentration of CO, (i) is about a factor of two greater in the Northern than in the Southern Hemisphere where the annual average is about 50 - 60 ppbv, (ii) increases with latitude in the Northern Hemisphere, (iii) exhibits strong seasonal variations in both hemispheres at mid to high latitudes, and (iv) decreases with altitude CO appears to be increasing at about 1% per year in the Northern Hemisphere, but the evidence for increases in the Southern Hemisphere is ambiguous

1 7 2 2 Sources and sinks of carbon monoxide

The total annual source of CO is about 2400 Tg CO, being about equally divided between direct anthropogenic (incomplete combustion of fossil fuels and biomass) and atmospheric (oxidation of natural and anthropogenic CH4 and NMHC) sources (Logan et al 1981, Cicerone, 1988) Atmospheric concentrations of CO may have increased in the Northern Hemisphere because of the fossil fuel source, and because of changes in the rate of oxidation of CH4, whose atmospheric concentration has increased since pre-industrial times Fossil fuel sources of CO are at present decreasing in North America (EPA, 1989) and possibly in Europe, but may be increasing elsewhere

The major removal process for atmospheric CO is reaction with OH (Logan et al 1981) The observed seasonal variability in the Southern Hemisphere distant from seasonally varying sources can be explained by the seasonal variability in the concentration of tropospheric OH Soils may provide a minor sink for CO (Conrad and Seiler, 1985)

1.7.3 Reactive Nitrogen Oxides

The key constituents of tropospheric NOy, defined as the sum of all nitrogen oxide species except for N2O, are NOx, nitric acid (HNO3), peroxyacetylnitrate (PAN CH3CO3NO2), and organic nitrates Most primary sources of nitrogen oxides release NOx (mainly NO), the other species are produced by photochemical reactions in the atmosphere While the atmospheric lifetime of NOx is short (about 1 day), the atmospheric lifetime of NOy can range up to several weeks Thus NOy can transport nitrogen compounds away from source regions to more remote locations, where photolysis of HNO3 and PAN, and thermal decomposition of PAN, can regenerate NOx

1 7 3 1 Atmospheric distribution of nitrogen oxides

The atmospheric concentrations of NOx exhibit significant spatial and temporal variability, reflecting the complex distribution of sources and the short atmospheric lifetime The near surface and free tropospheric concentrations of NOx each vary by several orders of magnitude, highly influenced by the proximity of source regions Near surface concentrations of NOx range from as low as 0 001 ppbv in remote maritime air to as high as 10 ppbv in Europe and Eastern North America (excluding urban areas), while free tropospheric concentrations range from 0 02 ppbv in remote regions to more than 5 ppbv over populated areas (Fehsenfeld et al , 1988)

The spatial inhomogeneity, coupled with a sparsity of measurements, means that the spatial and temporal distribution and long-term trends in NOx and NOy are not adequately documented, although reconstructed emissions inventories of NOx suggest large increases throughout this century (Dignon and Hameed, 1989) Data from a Greenland ice core have shown that the concentration of nitrate ions (dissolved nitrate from HNO3) remained constant from 10,000 years ago to about 1950, then doubled by the late 1970 s, consistent with the increase in industrial emissions (Neftel et al 1985b) Data from glacier ice in Switzerland indicates that nitrate ions increased by a factor of 4 5 between 1900 and the 1970's in Western Europe (Wagenbach et al 1988)

1 7 3 2 Sources and sinks of nitrogen oxides

The sources of atmospheric NOx are about equally divided between anthropogenic (combustion of fossil fuels 21 Tg N per year, and biomass burning 2 - 5 Tg N per year), and natural (microbial processes in soils 20 Tg N per year, lightning 2 - 8 Tg N per year, and transport from the stratosphere 1 Tg N per year) (Galbally, 1989) Emissions of NOx (6 3 Tg N per year) from the combustion of fossil fuels have not increased in North America since 1970 (EPA, 1989) Soil emissions of NO are stimulated by agricultural activity (e g , addition of fertilizer, manure,

etc), hence, agricultural soil emissions may provide significant sources of NO_x in many areas

The dominant removal processes for NO_x are (i) conversion to HNO_3, PAN, and organic nitrates by photochemical mechanisms, (ii) reactions involving NO_3 radicals, and possibly (iii) deposition of NO_2 on vegetation The resulting NO_y species are then removed from the atmosphere by wet and dry deposition, or by conversion back to NO_x

1.7.4 Non-Methane Hydrocarbons

1 7 4 1 Atmospheric distribution of non-methane hydrocarbons

The NMHC can be classified by atmospheric lifetime (i) relatively long-lived (lifetimes > week) where the highest concentrations (up to 3 ppbv for ethane) are observed at middle to high northern latitudes, (ii) more reactive (lifetimes between half a day and one week) such as C_2 - C_5 alkenes whose concentrations exhibit significant temporal and latitudinal variability from <0 1ppbv in remote areas to a few ppbv close to source regions, and (iii) extremely short lived (lifetimes of hours) such as terpenes or isoprene whose local concentrations may reach about 10 ppbv very close to their sources Trends in the atmospheric concentrations of NMHC have not been established due to a lack of measurements

1 7 4 2 Sources and sinks for non methane hydrocarbons

The oceans are a major source of NMHC, mainly alkenes Estimates of the source strength of ethene and propene range from 26 Tg C per year (Bonsang et al , 1988) to as high as 100 Tg C per year (Penkett, 1982) Emissions of NMHC from terrestrial vegetation are dependent upon environmental factors as well as the type of vegetation Isoprene is primarily emitted from deciduous plants, whereas conifer trees are primarily a source of terpenes Isoprene and terpene emission rates are very large, about 500 Tg per year for each (Rasmussen and Khalil, 1988) The source strength of NMHC from anthropogenic activities such as biomass burning, solvents and fossil fuel combustion has been estimated to be about 100 Tg per year

The dominant loss mechanism for most NMHC is rapid (much faster than CH_4) reaction with OH The products of these reactions are capable of forming O_3 in the presence of NO_x

1.7.5 Feedbacks Between Climate and the Methane/Non-Methane Hydrocarbon/ Carbon Monoxide/Oxides of Nitrogen/ Tropospheric Ozone System

There are numerous potentially important feedbacks between climate change and tropospheric O_3 and OH Changes in cloud cover, precipitation and circulation patterns, as well as changes in the biospheric source

strengths of CH_4, CO, NMHC and NO_x, will induce changes in homogeneous and heterogeneous reactions controlling O_3 and OH In addition, changes in stratospheric O_3 may induce changes in tropospheric processes, through changes in ultraviolet radiation Stratospheric O_3 depletion is likely to increase tropospheric O_3 when the levels of CO, NO_x, and NMHC are high, but reduce it in regions of very low NO_x The importance of these feedback processes remains to be determined

1.7.6 Conclusions

Tropospheric O_3 is a greenhouse gas that is produced photochemically through a series of complex reactions involving CO, CH_4, NMHC and NO_x Hence, the distribution and trends of tropospheric O_3 depend upon the distribution and trends of these gases whose atmospheric concentrations are changing

The short atmospheric lifetimes of O_3 (several weeks), and many of its precursor gases, coupled with inadequate observational networks, leave their distributions and trends inadequately documented Most data support positive trends of about 1% per year for O_3 below 8 km altitude in the Northern Hemisphere (consistent with positive trends in several of the precursor gases, especially NO_x, CH_4, and CO), and a similar trend for CO in the Northern Hemisphere, but not in the Southern Hemisphere While there is no systematic series of data that allow quantitative estimates of trends in NMHC and NO_x to be made, their atmospheric concentrations are likely to have increased during the past few decades because of increased anthropogenic sources The ice core records of nitrate levels provide indirect evidence for a Northern Hemisphere increase in atmospheric NO_x

1.8 Aerosol Particles

1.8.1 Concentrations and Trends of Aerosol Particles in the Troposphere

Aerosol particles play an important role in the climate system because of their direct interaction (absorption and scattering) with solar and terrestrial radiation, as well as through their influence on cloud processes and thereby, indirectly, on radiative fluxes These processes are discussed in more detail in Sections 2 3 2 and 2 3 3 Two separate issues should be identified The first is the effect of increasing or decreasing anthropogenic emissions of aerosol particles and their precursors in regions impacted by these emissions The second is the role of feedback processes linking climate change and natural (biological) production of particles in unpolluted regions, especially over the oceans (cf Section 10 8 3)

Total suspended particulate matter in air varies from less than 1 $\mu g\ m^{-3}$ over polar ice caps or in the free mid-ocean

troposphere to 1 mg m^{-3} in desert dust outbreaks or in dense plumes from for example, forest fires In a typical sample of continental air, mineral dust, sulphuric acid, ammonium sulphate as well as organic material and elemental carbon (soot) may be found both as pure or mixed particles Most of the soluble particles become solution droplets at relative humidities above 80%, thus the radiative properties of aerosol particles even vary with relative humidity at constant dry aerosol mass

A large part of the aerosol mass in submicron size particles is derived from gas-to-particle conversion through photochemical processes involving gaseous sulphur and hydrocarbon compounds Such conversion may take place through photochemical processes involving the oxidation of sulphur dioxide (SO_2) and other sulphur gases to sulphuric acid (H_2SO_4) by reaction with OH The H_2SO_4 so formed, having a low equilibrium vapour pressure, immediately condenses onto existing aerosol particles or forms new ones Transformation to sulphuric acid and sulphate also takes place in cloud droplets, the majority of which eventually evaporate leaving the sulphate in the aerosol phase Trends in the emission of these gaseous precursors especially the sulphur gases, are therefore of great importance for the regional aerosol burden and thereby potentially for climate

Large quantities of aerosol particles are also emitted from the burning of savannas and forests in tropical regions The directly emitted particles consist largely of carbonaceous materials including black carbon (soot) (Andreae et al 1988) In addition particles are formed from precursor gases like SO_2 and hydrocarbons emitted by fires

The average tropospheric lifetime of aerosol particles and of their precursor gases is of the order of only days or weeks This is much shorter than the lifetime of most greenhouse gases It implies that the atmospheric loading at any one time reflects the emissions that have taken place during the past few weeks only No long-term accumulation in the troposphere is thus possible and any reduction in anthropogenic emissions will immediately result in a corresponding reduction in tropospheric concentrations The short lifetime also implies large spatial and temporal variability in the concentrations of aerosol particles

It has been established from analyses of Greenland ice cores that the amounts of sulphate, nitrate and trace metals derived mainly from atmospheric aerosols have been increasing since industrialisation began (Neftel et al 1985b Mayewsky et al , 1986) However, there are almost no long-term, continuous direct observations of aerosol parameters in the atmosphere outside urban and industrial areas (Charlson 1988) Indirect evidence from visibility observations indicates that the concentration of submicron

aerosols over much of the eastern part of the U S has increased during the period 1948-1978 (Husar et al , 1981)

Another example of a trend analysis of atmospheric aerosols is due to Winkler and Kaminski (1988), who concluded that submicrometer aerosol mass outside Hamburg has increased by a factor of nearly two between 1976 and 1988 due to long range transport from industrialized centres in the region

The hypothesis by Charlson et al (1987) of a connection between climate and phytoplankton activity in ocean surface waters is based on the role played by soluble aerosol particles in determining the microphysical properties of clouds The proposed climate-phytoplankton feedback rests on the facts that cloud condensation nucleus (CCN) concentrations in air are low over oceans far from land, that the CCN available in clean maritime air are composed almost totally of sulphate particles, and that this sulphur originates almost entirely from emissions of reduced sulphur gases (principally dimethylsulphide (DMS)) from the ocean surface There is a significant non-linearity in the effect on cloud microphysics of given changes in CCN concentration, depending on the starting CCN concentration characteristics of clean oceanic air

There is abundant evidence in the literature to confirm the role played by CCN concentration in determining cloud droplet size distribution However, at this stage neither the sign nor magnitude of the proposed climate feedback can be quantitatively estimated, though preliminary calculations based on plausible scenarios indicate that this hypothesis merits careful consideration Preliminary attempts to test this hypothesis using existing historical data of various types have been inadequate and have yielded only equivocal conclusions

1.8.2 The Atmospheric Sulphur Budget

Current estimates of the global sulphur cycle show that anthropogenic emissions of SO_2 are likely to be at least as large as natural emissions of volatile sulphur species, cf Table 1 5 (based essentially on Andreae, 1989) Within the industrialized regions of Europe and North America, anthropogenic emissions dominate over natural emissions by about a factor of ten or even more (Galloway et al , 1984, Rodhe, 1976) The anthropogenic SO_2 emissions have increased from less than 3 TgS per year globally in 1860, 15 in 1900, 40 in 1940 and about 80 in 1980 (Ryaboshapko 1983) It is evident from these numbers that the sulphur fluxes through the atmosphere have increased very substantially during the last century, especially in the Northern Hemisphere During the past decade the anthropogenic sulphur emissions in North America and parts of Europe have started to decline

Small amounts of carbonyl sulphide (COS) are also emitted into the atmosphere They do not significantly affect the sulphur balance of the troposphere but they are

Table 1 5 Estimates of Global Emission to the Atmosphere of Gaseous Sulphur Compounds †

Source	Annual Flux (TgS)
Anthropogenic (mainly SO_2 from fossil fuel combustion)	80
Biomass burning (SO_2)	7
Oceans (DMS)	40
Soils and plants (H_2S, DMS)	10
Volcanoes (H_2S, SO_2)	10
TOTAL	147

† The uncertainty ranges are estimated to be about 30% for the anthropogenic flux and a factor of two for the natural fluxes

important in maintaining an aerosol layer in the stratosphere

Because of the limited atmospheric lifetime of most sulphur compounds, the augmentation of the sulphur concentrations brought about by industrialization is not evenly distributed around the globe This is illustrated by Figure 1 16, which shows an estimate of how much more aerosol sulphate there is at present in the lower atmosphere (900 hPa level) than in the pre-industrial situation (Langner and Rodhe 1990) Over the most polluted regions of Europe and North America the sulphate levels have gone up by more than a factor of 10 Smaller increases have occurred over large parts of the oceans
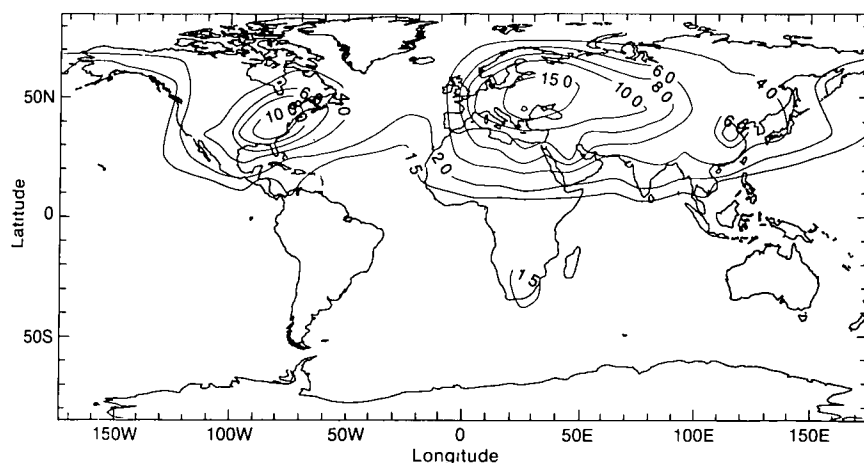
1.8.3 Aerosol Particles in the Stratosphere

The vertical profile of aerosol particle concentration normally exhibits a marked decline up through the troposphere followed by a secondary maximum in the lower stratosphere at around 20 km The stratospheric aerosol layer is maintained by an upward flux of gaseous precursors, mainly carbonyl sulphide (COS) Concentrations may be greatly enhanced over large areas for a few years following large volcanic eruptions, such as El Chichon in 1982 No significant trends have been detected in the global background aerosol layer in the stratosphere during periods of low volcanic activity (WMO, 1989a) The potential impact on climate of stratospheric aerosols is discussed in Section 2 3 2

1.8.4 Conclusions

Aerosol particles have a lifetime of at most a few weeks in the troposphere and occur in highly variable concentrations A large proportion of the particles which influence cloud processes and for radiative balance are derived from gaseous sulphur emissions These emissions have more than doubled globally, causing a large increase in the concentration of aerosol sulphate especially over and around the industrialized regions in Europe and North America If anthropogenic sulphur emissions are indeed a major contributor to cloud condensation nuclei concentrations on a global scale, then any climate prediction must take account of future trends in regional and global anthropogenic sulphur emission, which may be quite different from those of the greenhouse gases

Aerosol particles derived from natural (biological) emissions may contribute in important ways to climate feedback processes During a few years following major volcanic eruptions the concentration of aerosol particles can be greatly enhanced

Figure 1.16: Simulated concentration of sulphate at 900 hPa Ratio of concentrations based on total emissions (natural plus anthropogenic) divided by concentrations based on natural emissions in July (Langner and Rodhe, 1990)

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