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Greenhouse Gases: Sources and Sinks

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EXECUTIVE SUMMARY

There have been no major changes in our understanding of greenhouse gases since the 1990 Scientific Assessment for the Intergovernmental Panel on Climate Change (IPCC, 1990). While most of the key uncertainties identified in IPCC (1990) remain unresolved, there have been a number of important advances.

Atmospheric Concentrations and Trends of Long-lived Greenhouse Gases:

The atmospheric concentrations of the major long-lived greenhouse gases (carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), chlorofluorocarbons (CFCs), and carbon tetrachloride (CCl₄) continue to increase because of human activities. While the growth rates of most of these gases have been steady or increasing over the past decade, that of CH₄ and some of the halocarbons has been decreasing. The rate for CH₄ has declined from about 20 ppbv/yr in the late 1970s to possibly as low as 10 ppbv/yr in 1989.

Atmospheric Concentrations and Trends of Other Gases that Influence the Radiative Budget:

Ozone (O₃) is an effective greenhouse gas in the upper troposphere and lower stratosphere. Significant decreases in total column O₃ have been observed throughout the year during the last one to two decades, and at all latitudes except the tropics, with the trends being larger during the 1980s than during the 1970s. These decreases have occurred predominantly in the lower stratosphere, below 25km, where the rate of decrease has been up to 10% per decade depending on altitude. In addition, there is evidence from the few existing ozonesonde stations that, at northern mid-latitudes, O₃ levels in the troposphere up to 10km altitude have increased by about 10% per decade over the past two decades. Also, the abundance of carbon monoxide (CO) appears to be increasing in the Northern Hemisphere at about 1% per year. There is little new information on the global trends of other tropospheric O₃ precursors (non-methane hydrocarbons (NMHC) and oxides of nitrogen (NO_x)).

Sources and Sinks of Carbon Dioxide:

The best estimate for global fossil fuel emissions in 1989 and 1990 is 6.0±0.5 GtC, compared to 5.7±0.5 GtC in 1987. The estimated total release of CO₂ from oil well fires in Kuwait during 1991 was 0.065 GtC. The United Nations Food and

Agriculture Organization (FAO), using information supplied by individual countries, recently estimated that the rate of global tropical deforestation in closed and open canopy forests for the period 1981-1990 was about 17 million hectares (Mha) per year, approximately 50% higher than that for the period 1976-1980. A comprehensive, multi-year, high spatial resolution satellite data set has been used to estimate that the average rate of deforestation in the Brazilian Amazonian forest between 1978 and 1989 was 2.1 Mha/yr, and that the rate increased between 1978 and the mid-1980s, and decreased to 1.4 Mha/yr in 1990. Despite the new information suggesting higher rates of deforestation globally, the uncertainties in estimating CO₂ emissions are so large that there is no convincing reason to revise the IPCC (1990) estimate of annual average net flux to the atmosphere of 1.6±1.0 GtC from land-use change during the decade of the 1980s.

Based on models and the atmospheric distribution of CO₂, it appears that: (i) there is a small net addition of carbon to the atmosphere from the equatorial region, a combination of outgassing of CO₂ from warm tropical waters and a terrestrial biospheric component that is the residual between large sources (deforestation) and sinks; (ii) there is a strong Northern Hemisphere sink, containing both oceanic and terrestrial biospheric components, and a weak Southern Hemisphere sink; (iii) an ocean sink of 2.0±0.8 GtC per year is still reasonable; and (iv) terrestrial biospheric processes are sequestering CO₂ due to forest regeneration, and fertilization arising from the effects of both CO₂ and nitrogen (N).

Sources and Sinks of Methane:

A total annual emission of CH₄ of about 500Tg can be deduced from the magnitude of its sinks combined with its rate of atmospheric accumulation. New information includes a revised rate of removal of CH₄ by atmospheric hydroxyl (OH) radicals (because of a lower rate constant), a new evaluation of some of the sources (e.g., from rice fields) and the addition of new sources (e.g., animal and domestic waste). Recent CH₄ isotopic studies suggest that approximately 100 TgCH₄ is of fossil origin, largely from the coal, oil, and natural gas industries. Recent studies of CH₄ emissions from rice agriculture show that the emissions depend on growing conditions, vary significantly, and are significantly lower than reported in IPCC (1990). The latest estimate of the atmospheric lifetime of CH₄ is about 11 years.

Sources and Sinks of Nitrous Oxide:

Adipic acid (nylon) production, nitric acid production and automobiles with three-way catalysts have been identified as possibly significant anthropogenic global sources of nitrous oxide. However, the sum of all known anthropogenic and natural sources is still barely sufficient to balance the calculated atmospheric sink or to explain the observed increase in the atmospheric abundance of N₂O.

Sources of Halogenated Species:

The worldwide consumption of CFCs 11, 12, and 113 is now 40% below 1986 levels, substantially below the amounts permitted under the Montreal Protocol. Further reductions are mandated by the 1990 London Amendments to the Montreal Protocol. As CFCs are phased out, HCFCs and HFCs will substitute, but at lower emission rates.

Stratospheric Ozone:

Even if the control measures of the 1990 London amendments to the Montreal Protocol were to be implemented by all nations, the abundance of halocarbons will increase over the next several years. As the weight of evidence suggests that these gases are

responsible for the observed reductions in stratospheric O₃, the rate of depletion at middle and high latitudes is predicted to increase during the 1990s.

Precursors of Tropospheric Ozone:

Little new information is available regarding the tropospheric ozone precursors (CO, NMHC, and NO_x), all of which have significant, but uncertain, natural and anthropogenic sources.

Aerosols:

Industrial activity, biomass burning, volcanic eruptions, and subsonic aircraft contribute substantially to the formation of tropospheric and stratospheric aerosols. Industrial emissions are especially important to the tropospheric burden of aerosols; the Northern Hemisphere is particularly affected but so are any regions having a concentration of industrial activity. Sulphur emissions, which are due in large part to combustion effluents, have a similar emissions history to that of anthropogenic CO₂. Estimates of emissions of natural sulphur compounds have been reduced from previous figures, thereby placing more emphasis on the anthropogenic contribution.

A1.1 Introduction

This section updates Chapter 1 of the 1990 IPCC Scientific Assessment. The key issues are to quantify the atmospheric distributions, trends, sources and sinks of greenhouse gases and their precursors, and to understand the processes controlling their global budgets in order to relate their emissions quantitatively to atmospheric concentrations.

A1.2 Carbon Dioxide

A1.2.1 Introduction

The atmospheric accumulation of CO₂ is the balance between fossil fuel and land-use change emissions, and the uptake due to oceanic and terrestrial sinks. The key issue is to understand the processes controlling the global carbon budget in order to relate anthropogenic emissions of CO₂ quantitatively to atmospheric concentrations. Two concerns have dominated scientific debate since the first IPCC Science Assessment: (a) the global rate of land-use change, especially deforestation, and (b) the fluxes of carbon and the processes controlling its release and uptake in both the terrestrial biosphere and the oceans.

A1.2.2 Atmospheric Abundances and Trends

IPCC (1990) assigned a value of 353 ppmv to the global annual average concentration of CO₂ in 1990, based on an extrapolation of the most recent measurements available at that time. For 1991, the best global estimate is approximately 355 ppmv, given the recent observed rate of increase of 1.8 ppmv/yr. There is a small, but coherent gradient in concentration from the South Pole to the Arctic basin of about 3 ppmv (Keeling *et al.*, 1989a; Heimann *et al.*, 1989), that depends on the distribution of both emissions from fossil fuel combustion and the distribution of terrestrial and oceanic sources and sinks (IPCC, 1990). The gradient implies a continuous flux of CO₂ from the Northern Hemisphere, where about 90% of the fossil fuel emissions occur, to the Southern Hemisphere, where part of the net uptake by the oceans takes place. The concentrations of CO₂ and its stable isotope ¹³CO₂ show clearly that the wide and regular seasonal variability at most stations, with substantially higher amplitudes in the Northern Hemisphere, is dominated by the activity of the terrestrial biosphere in the Northern Hemisphere, rather than by seasonal changes in ocean pCO₂ or fossil sources.

The atmospheric adjustment time (IPCC, 1990) of CO₂ depends on the different time constants of many processes. A rather rapid adjustment takes place between the atmosphere, the surface layer of the oceans, and the terrestrial biosphere when anthropogenic CO₂ is added to or removed from the atmosphere. However, the long-term response of the atmospheric concentration of CO₂ to anthropogenic emissions depends primarily on the processes that control the rate of storage of CO₂ in the

deep ocean and in forest biomass and soil organic matter, which have characteristic time-scales of several decades to centuries.

A1.2.3 Sources

Updates of emissions from fossil fuel combustion, including oil wells set alight in Kuwait, and changes in land-use are summarized below.

A1.2.3.1 Combustion

Marland and Boden (1991) have recently updated their estimates of CO₂ industrial emissions to include data through 1989. The updated best estimate for the global emission in both 1989 and 1990 is 6.0±0.5 GtC, compared to 5.7 GtC in 1987 (IPCC, 1990); (GtC: 1 Gt = 10⁹t = 10¹⁵g; 1 ppmv CO₂ of the global atmosphere = 2.12 GtC and 7.8 Gt CO₂). The estimates rely primarily on energy data published by the United Nations with supplemental data on cement production from the US Bureau of Mines and on gas flaring from the US Department of Energy.

In recent months, concerns have been raised over the possible magnitude of emissions from oil well fires lit at the end of the war in Kuwait. About 600 naturally pressurized oil wells were set alight in Kuwait in late February 1991, but by the beginning of November all the wells had been capped. The pre-war production rate of Kuwait was about 1.6 million barrels per day (MBd⁻¹). Airborne measurements of the chemical composition of the plumes were made in late March 1991 (Johnson *et al.*, 1991); the major pollutants observed were particulates (smoke), CO₂, sulphur dioxide (SO₂), nitrogen oxides (NO_x), and unburnt hydrocarbons. Based on the sulphur composition of the oil, the oil burning rate was estimated to be equivalent to 3.9±1.6 million barrels per day. The estimated total emissions of carbon (C) as CO₂ during 1991 was 65Tg, or about 1% of the estimated annual global fossil fuel emissions; uncertainty in this figure is approximately ±50%.

A1.2.3.2 Land-Use Changes

The net flux of C to the atmosphere from land-use change (primarily, though not exclusively due to deforestation in the tropics) depends on the area converted, carbon density per ha, the fate of the altered land and the ecosystem processes that control fluxes of carbon. The IPCC (1990) estimate for the flux in 1980 was 0.6-2.5 GtC, with suggestions that the annual flux was higher in 1990 than in 1980. Houghton (1991) has recently calculated that the release of C to the atmosphere from land-use change in 1990 was 1.1-3.6 GtC, somewhat higher than the 1980 estimate of 0.6-2.5 GtC. The IPCC (1990) estimate of net average annual emissions for the decade 1980-1989 was 1.6±1.0 GtC, which is consistent with Houghton's figure within the limits of uncertainty.

Table A1.1: Summary of Global Annual Deforestation Estimates (10^6 ha)

Reference	Myers 1980	FAO/UNEP 1981	Myers 1989	FAO 1991	WRI 1990
Year of Deforestation	1979	1976-1980	1989	1981-1990	late 1980's
Closed Canopy Forest Only	7.3	7.3	13.9	14.0	16.5
Closed and Open Canopy Forests	-	11.3	-	17.0	20.4

Table A1.2: Summary of Brazilian Annual Deforestation Estimates (10^6 ha)

Reference	FAO/UNEP 1981	Myers 1989	WRI 1990	Fearnside et al. 1990	INPE 1991	
Year of Deforestation	1976-1980	1989	late 1980s	1978-1989	1987-1988	1989
Estimate	1.4	5.0	8.0	2.1	1.9	1.4

A1.2.3.2.1 Recent estimates of deforestation rates

The increase in Houghton's net flux estimate was primarily due to the use of Myers' (1989) new estimate of global deforestation in closed canopy forests in the late 1980s (13.9 Mha/yr for 1989), which is 90% higher than the earlier estimate (Myers, 1980) of 7.3 Mha/yr for the late 1970s. In addition, the World Resources Institute (WRI, 1990) estimated global deforestation in closed canopy forests in the late 1980s at 16.5 Mha/yr, and there is a preliminary estimate of 14.0 Mha/yr during the 1980s by FAO (1990, 1991) based on country estimates. The Myers (1989) value assumed that the rate of deforestation in Brazil was 5.0 Mha/yr, while the WRI (1990) value assumed a rate of deforestation in Brazil of 8.0 Mha/yr. The assumed rates of deforestation in Brazil were based on work of Setzer and Pereira (1991), who used saturated thermal infrared AVHRR Channel 3 data to estimate the rate of deforestation in 1987 (8.0 Mha/yr) and 1988 (5.0 Mha/yr). However, the results of Setzer and Pereira (1991) are now thought to be incorrect (Fearnside *et al.*, 1990) because of inadequate spatial resolution, and questionable assumptions about the relationship between the rate of forest clearing and the incidence of fires. Fearnside *et al.*, (1990) used comprehensive LANDSAT high-spatial resolution data sets from 1978, 1987, 1988, and 1989 to estimate that the mean rate of deforestation in the Brazilian Amazonian forest was 2.1 Mha/yr between 1978 and 1989, and that the rate from 1987 (1/3 data)/1988 (2/3 data) to 1989 was 1.9 Mha/yr. INPE (1991) has recently included data for 1990 and concluded that the rate of deforestation from 1989 to 1990 was 1.4 Mha/yr. It appears that the rate of deforestation in Brazil reached a peak sometime in the

second half of the 1980s. An ongoing analysis of "wall-to-wall" LANDSAT data for 1975, 1978, 1985, and 1988-1991 should provide a much improved historical record of deforestation in Brazil. In addition, similar data for the period 1985 to 1991 is currently being analysed for all of tropical South America. The Myers (1989) and WRI (1990) global estimates of deforestation could both be revised downward to approximately 10.5 to 11.0 Mha/yr assuming that the actual rate of deforestation in Brazil was close to 2 Mha/yr for the late 1980s. Tables A1.1 and A1.2 summarize estimates of deforestation globally and in Brazil. Each of these studies used different methodologies, covered slightly different time periods, and the difference in the estimated increase in rates between the late 1970s and late 1980s is unresolved.

FAO (1990, 1991) has released a preliminary estimate, based on country submissions, of global deforestation in closed and open canopy forests for the period 1981-1990 of 17 Mha/yr, 50% higher than their estimate of 11.3 Mha/yr for 1976-1980. However, FAO acknowledges that some of the apparent increase may be due to underestimates of deforestation in the earlier time period. FAO has indicated that a rate of 6.8 Mha/yr has been estimated for tropical South America, and that the rate assumed for the Brazilian Amazonian forest was that reported by Fearnside *et al.*, (1990), i.e., 2.1 Mha/yr. This seems to ascribe a very high proportion (about 70%) of the total deforestation in South America in the late 1980s to the region outside of the Brazilian Amazonia, even though this region accounts for very little of the total amount of forest on the continent.

It seems likely that the area deforested globally in 1990 was higher than the area deforested in 1980, since the major global estimates show increases in rates of 50% (FAO, 1990, 1991) to 90% (Myers, 1989). However, the data quality for southern Asia and Africa are poor, and the results for tropical South America, which strongly influence the global estimates, are at the same time the most intensively studied and yet still uncertain. There are no global estimates of deforestation in the peer-reviewed scientific literature derived from studies using common methodologies, especially using high spatial resolution satellite data, such as LANDSAT and SPOT, which have the most potential for resolving this issue.

A1.2.3.2.2 Carbon density and ecosystem processes

Critical variables to take into account for calculating the net carbon released from deforestation and its distribution among CO₂, CO and CH₄ include the relative contribution of above-ground and below-ground carbon; the distribution between immediate releases and the effects of deforestation on the processes controlling the subsequent fluxes of carbon; the fate of deforested land; and the final carbon density of the land compared to its original carbon density. Several of these factors are poorly known locally, and depend on the sampling methods used. For example, carbon density values based on ecological data from small plots generally provide higher estimates than those from forest inventories (e.g., 328 Mg biomass/ha versus 175 Mg/ha for tropical closed forests, Brown and Lugo, 1984). All the factors are poorly known globally. Such problems must be reconciled in order to make reasonable estimates on global scales (Brown and Lugo, 1991).

In situ degradation of forest stands by selective removal of the largest or most valuable trees also affects net flux from deforestation, since the biomass at deforestation is lower than for undisturbed stands (Lugo and Brown, 1992). Other environmental factors have the potential to influence carbon density or ecosystem processes controlling carbon fluxes. For example, recovery from fires is accompanied by increasing biomass, but damage from air pollution may decrease biomass and reduce carbon fixation. However, there is no strong evidence to suggest that the frequency, intensity, or global significance of these factors has changed over the past several decades.

A1.2.3.2.3 Annual average fluxes

The estimates of average annual net flux of carbon released to the atmosphere from land-use change still appear to be among the most uncertain numbers in the carbon cycle. Houghton's (1991) estimate for 1990 suggests that the average annual net flux for the 1980s is higher than the IPCC's previous estimate. However, measurement uncertainties in the total area deforested and its average carbon density prevent accurate estimates of

changes in average annual net fluxes from being made.

The conclusion is that there is no strong evidence to revise the IPCC (1990) estimate of annual average net flux to the atmosphere from land-use change during the decade of the 1980s. The likeliest scenario is that annual fluxes increased during the early part of the decade, peaked in the middle years, and may have fallen since, based on our best understanding of deforestation rates in closed forests. While this state of affairs is unsatisfying, it is within the range of measurement error, and is representative of the present degree of scientific uncertainty.

A1.2.4 Sinks

This section summarizes new information on sinks of carbon in the oceans and the terrestrial biosphere.

A1.2.4.1 Oceans

The IPCC (1990) estimate of the global annual ocean sink, 2.0 ± 0.8 GtC, is still reasonable. Global ocean sinks in the neighbourhood of 1.0 GtC/yr or smaller (Tans *et al.*, 1990) appear less likely, but are still within measurement error. Estimates of the strength of the ocean sink depend on air-sea exchange, which is a function of wind speed and temperature, the difference in the partial pressure of CO₂ between the water and the air ($\sim p\text{CO}_2$), and on the initial assumptions of the ocean models. A quantitatively significant role for carbon transport by rivers would imply that ocean uptake estimates based primarily on $\sim p\text{CO}_2$ will be underestimates.

Direct measurements of the relative decline in ¹³C/¹²C ratios in dissolved inorganic carbon in ocean waters and in atmospheric CO₂ yield an estimate of 2.3 GtC/yr for the global ocean sink for the period between 1970 and 1990 (Quay *et al.*, 1992).

While widespread episodes of coral bleaching are of regional concern for the integrity of marine ecosystems, there is no evidence that they are influencing the ocean's carbon budget in any significant way. Their abundance and distribution in the world's oceans compared to the total amount of carbon stored in the ocean is far too small to be significant.

A1.2.4.2 Terrestrial Biosphere

A major issue reported in IPCC (1990) was due to the Tans *et al.* (1990) analysis, which suggested a terrestrial sink in the north temperate latitudes, of the order of 1.6-2.4 GtC/yr during the decade of the 1980s. This result was obtained through inversion of the observed atmospheric CO₂ distribution combined with an atmospheric tracer model from which was derived a distribution of sources and sinks of carbon at the surface, constrained by oceanic $p\text{CO}_2$ data. The IPCC analysis used a value of 1.6 ± 1.4 GtC/yr as the net imbalance in the carbon cycle during the decade of the 1980s, but did not specify whether it might

be found in the terrestrial biosphere or in the oceans. The Tans and IPCC analyses have received considerable attention over the last year, primarily because of the difficulty of accounting simultaneously for very large carbon sinks in the terrestrial biosphere in northern temperate latitudes and a very small global oceanic sink.

Keeling *et al.* (1989a,b), Heimann *et al.* (1989), Heimann and Keeling (1989), Heimann (1991), Enting and Mansbridge (1991), and Tans *et al.* (1990) agree that a strong Northern Hemisphere sink and an apparently weak Southern Hemisphere sink must exist. The Northern Hemisphere sink must contain both oceanic and terrestrial biospheric components. The models disagree on the meridional distribution of total sources and sinks, and the allocation of those sinks to oceans and the terrestrial biosphere (Heimann, 1991). Tans *et al.* (1990) partitioned the northern sink of carbon between land and ocean, based on the data compiled on $p\text{CO}_2$ in surface waters. Recent measurements have shown large CO_2 drawdown in spring blooms in the North Atlantic (Watson *et al.*, 1991; Kempe and Pegler, 1991). On the other hand, Murphy *et al.* (1991) found less CO_2 flux into the South Pacific Ocean in austral spring than estimated by Tans *et al.* (1990). How these regional estimates combine to give an improved globally and annually averaged net flux between the atmosphere and ocean is still to be resolved. Keeling *et al.* (1989b) concluded that a large fraction of the Northern Hemispheric sink is due to a natural imbalance in the oceanic carbon cycle, consisting of a net transfer from the Northern to Southern Hemispheres, balanced by a return flux through the atmosphere, suggesting a much smaller northern terrestrial sink than calculated by Tans *et al.* (1990).

Models and atmospheric CO_2 concentration data suggest that there is a relatively small net addition of carbon to the atmosphere from the equatorial region, which is a combination of outgassing of carbon from warm tropical waters and a biospheric component. While land-use change in the tropics is an increasing and significant source of CO_2 to the atmosphere, Keeling *et al.* (1989a,b) conclude that about 50% of the terrestrial sink due to CO_2 fertilization may occur in this region, thus reducing the net flux of CO_2 from this region. These conclusions need to be tested, but it is clear that the net carbon added to the atmosphere in the tropics is less than expected simply from deforestation.

The likeliest terrestrial biospheric processes contributing to large sinks are enhancement in productivity due to atmospheric CO_2 increases, N fertilization from atmospheric deposition, and forest regrowth. Enhancement of photosynthesis, reduction in respiration, and increased water-use efficiency due to enhanced CO_2 concentrations have all been found in laboratory and field experiments (Bazzaz, 1990). Quantifying a net ecosystem response in

terms of carbon storage is more difficult, and no field studies of natural forests have yet been done. Experiments in wetlands (Drake and Leadley, 1991) show net C accumulation. Analogous experiments in Arctic tundra show contrasting results, from acclimation due to the variability of the effects of CO_2 on individual species (Prudhomme *et al.*, 1984; Oechel and Strain, 1985; Tissue and Oechel, 1987) to a small net accumulation (Grulke *et al.*, 1990). The conclusion is that while the individual effects of CO_2 enhancement on plant growth and physiology are well-documented, the net ecosystem consequences of CO_2 increases under natural conditions depend on many other factors and cannot currently be quantified. Nevertheless, in models with active biospheres, global estimates of net carbon accumulation from the physiological effects of increased CO_2 are often made in order to account for a missing sink.

Fertilization of the northern temperate latitudes through increased N deposition due to air pollution and increased fertilizer use is possibly of sufficient magnitude to sequester an additional 1.0 GtC/yr during the decade of the 1980s (IPCC, 1990; Thornley *et al.*, 1991). However, the N deposition data are poorly known, and the extent of any increase in growth rates of forests and grasslands must be weighed against the possibility of other pollutants adversely affecting physiological processes, either directly (e.g., O_3 pollution) or indirectly (acid deposition affecting soil nutrients over decades). The possible adverse effects, while suspected to be important on regional scales in eastern North America and Europe, are insufficiently quantified to provide global estimates.

Forest regrowth in temperate latitudes may currently be responsible for net C accumulation in the terrestrial biosphere. Regeneration seen in such areas as the eastern US, Europe and China often reflects recovery of land previously deforested or degraded in the late nineteenth to mid-twentieth centuries.

A1.2.5 Models and Predictions

While there are a variety of carbon cycle models, including 3-D ocean-atmosphere models, 1-D ocean-atmosphere box-diffusion models, and box models that incorporate a terrestrial biospheric sink, all such models are subject to considerable uncertainty because of an inadequate understanding of the processes controlling the uptake and release of CO_2 from the oceans and terrestrial ecosystems. Some models assume a net neutral terrestrial biosphere, balancing fossil fuel emissions of CO_2 by oceanic uptake and atmospheric accumulation; others achieve balance by invoking additional assumptions regarding the effect of CO_2 fertilization on the different parts of the biosphere. However, even models that balance the past and contemporary carbon cycle will not predict future atmospheric concentrations accurately unless they represent the proper

mix of processes on land and in the oceans, and how these processes will evolve along with changes in atmospheric CO₂ and climate. For a given emissions scenario, the differences in predicted changes in CO₂ concentrations, neglecting biospheric feedbacks, are up to 30%, but this is unlikely to represent the major uncertainty in the prediction of future climate change compared to uncertainties in estimating future patterns of trace gas emissions, and in quantifying physical climate feedback processes. Future atmospheric CO₂ concentrations resulting from given emissions scenarios may be estimated by assuming that the same fraction remained airborne as has been observed during the last decade, i.e., 46±7%.

Great strides have been made in developing models that adequately simulate the terrestrial carbon budget. Regional models that simulate the response of ecosystems to CO₂ and N fertilization now exist and are being implemented for global studies (Raich *et al.*, 1991; Parton *et al.*, 1987; Thornley *et al.*, 1991). The current challenge lies more in the development of data sets adequately describing the heterogeneity of natural ecosystem types and land use, and of techniques for validation over large areas. Improvement in the estimates of present and future global ocean uptake will require better understanding of the contribution of high-frequency pCO₂ fluctuations to the global mean and a better description of the vertical mixing rate in the ocean.

A1.3 Methane

Methane (CH₄) is an important greenhouse gas. Chemical reactions involving CH₄ in the troposphere can lead to ozone production, and reaction with the hydroxyl radical (OH) in the stratosphere results in the production of water vapour. Both tropospheric ozone, especially in the upper troposphere, and stratospheric water vapour are significant greenhouse gases. The final oxidation product of CH₄ is CO₂ which is also a greenhouse gas. One of the major removal mechanisms for OH is reaction with CH₄, therefore, as the levels of CH₄ increase the levels of OH could decrease. This could lead to increased lifetimes of CH₄ and other important greenhouse gases, e.g., hydrochlorofluorocarbons (HCFCs).

A1.3.1 Atmospheric Concentrations and Trends

The present atmospheric concentration of CH₄ is 1.72 ppmv globally averaged, more than double its pre-industrial value of about 0.8 ppmv. The abundance in the Northern Hemisphere is almost 0.1 ppmv greater than in the Southern Hemisphere. Recent data, which were carefully reviewed in WMO (1992), verify that the rate of growth of the atmospheric concentration of CH₄ slowed during the last decade or so from a rate of about 20 ppbv per year (about 1.3% per year: Blake and Rowland, 1988)

Table A1.3: Estimated Sources and Sinks of Methane (Tg CH₄ per year)

Sources		
<i>Natural</i>		
• Wetlands	115	(100-200)
• Termites †	20	(10-50)
• Ocean	10	(5-20)
• Freshwater	5	(1-25)
• CH ₄ Hydrate	5	(0-5)
<i>Anthropogenic</i>		
• Coal Mining, Natural Gas & Pet. Industry †	100	(70-120)
• Rice Paddies †	60	(20-150)
• Enteric Fermentation	80	(65-100)
• Animal Wastes †	25	(20-30)
• Domestic Sewage Treatment †	25	?
• Landfills †	30	(20-70)
• Biomass burning	40	(20-80)
Sinks		
Atmospheric (tropospheric + stratospheric) removal †	470	(420-520)
Removal by soils	30	(15-45)
Atmospheric Increase	32	(28-37)

† indicates revised estimates since IPCC 1990

in the late 1970s, to a rate of about 12-13 ppbv per year (about 0.75% per year) in the mid-1980s, to possibly as low as 10 ppbv per year (about 0.6% per year) in 1989 (Steele *et al.*, 1992). A range of 10-13 ppbv per year is reported in Table A1.3. There are no convincing explanations for this decline in CH₄ growth rates. It could be due to a decrease in emission rates from natural or anthropogenic sources, an increase in its loss rate due to an increase in the concentration of tropospheric OH, which has been suggested by Prinn *et al.*, (1992), or a combination of the two.

A1.3.2 Sinks

The main sink of CH₄ is reaction with the OH radical in the troposphere, so any estimate of the magnitude of this sink requires knowledge of the rate constant and the atmospheric abundance of OH. Current estimates of lifetime and global sources must be viewed with caution until more reliable values of the atmospheric abundances of OH are derived. Vaghjiani and Ravishankara (1991) have shown that the rate constant for CH₄ reacting with OH had been overestimated by up to 25%. Using this new rate constant data, Crutzen (1991) and Fung *et al.*, (1991) estimated the annual current removal of CH₄ by OH to be

420±80 TgCH₄. Crutzen (1991) also estimated an additional sink of 10±5 TgCH₄ due to photochemical removal in the stratosphere. Prinn *et al.*, (1992) have estimated higher atmospheric concentrations of OH using the ALE/GAGE methyl chloroform (CH₃CCl₃) data, and with the new OH + CH₄ rate constant data have deduced a lifetime for CH₄ of 11.1 (+1.4, -1.1) years and a net CH₄ source of 470±50Tg per year for the period 1978-1990. The Prinn *et al.* (1992) estimate of lifetime, and hence of source strength, includes both tropospheric and stratospheric chemical removal. The annual magnitude of an additional sink, i.e., uptake by soils, has been estimated to be 30±15 TgCH₄ (IPCC, 1990; Whalen and Reeburg, 1990). Recent CH₄ soil flux measurements indicate that changes in land use (Keller *et al.*, 1990; Scharffe *et al.*, 1990) or enhanced nitrogen fertilizer input (Mosier *et al.*, 1991) are decreasing the CH₄ uptake by soils. While the current magnitude of the soil sink is relatively small, the importance of this sink may change in the future if changes in climatic conditions result in significant changes in soil moisture. The lifetime of CH₄ is presently estimated to be about 11±2 years.

A1.3.3 Sources

A total annual global emission of CH₄ of about 500 TgCH₄ can be deduced from the magnitude of its sinks and its rate of accumulation in the atmosphere. Although the emission rates from most of the individual sources are still quite uncertain, there is a fairly good balance between the sum of the individual sources and the deduced global emission rate. The natural and anthropogenic sources of CH₄ were discussed in detail in IPCC (1990), and in most cases the current estimated global source strengths are unchanged. Table A1.3, which summarizes the best current estimates of emissions from individual sources, clearly shows that anthropogenic sources dominate (~2:1) over natural sources, consistent with a more than doubling of the atmospheric abundance of CH₄ since pre-industrial times. There has been a reevaluation of some of the sources, particularly from rice, and the addition of new sources such as animal and domestic waste.

The proportion of CH₄ produced from sources related to fossil carbon can be estimated from studies of the carbon-14 content of atmospheric CH₄. Three independent estimates are: 21±3% (Whalen *et al.*, 1989), 25±4% (Manning *et al.*, 1990) and 16±12% (Quay *et al.*, 1991).

Table A1.4: Measured Methane Emissions During the Growing Season From Rice Paddies

	Flux mg m ⁻² h ⁻¹	Annual rate g m ⁻² yr ⁻¹	Comments
California (1)	10	25-42	1982 growing season
Spain (2) (Andalucia)	4	12	Affected by sulphate from sea water
Italy (3)	12 (6-16)	14-77	7 fertilization treatments 3 veg. periods
Japan (4) (Ibaraki-prefec.)	16.2	45	Peat soil
	2.9-15.4	8-43	Gley soil
	<0.4-4.2	<1-13	Andosol
China (5) (Tu Zu, Sczhuan Province)	60 (10-120)	170	4 rice fields, 6 plots each site, local fertilization practices; 2 veg. periods, range due, in part, to seasonal variation
China (6) (Hangzhou, Zhajiang Provinces)	28.6	55-97	Late rice
	7.8	14-18	Early rice
China (7) (Beijing)	15-50	-	Rice after wheat; 5 different methods of management; 1 veg. period
China (8) (Nanjing)	11(3-14)	-	5 different managements
India (9)	0.1-27.5	7.5-22.5	Includes irrigated and rainfed fields; acidic and non-acid soils
Texas (10)	2.5-8.7	5-16	-
Australia (11)	3.8	-	Micrometeorological measurements
Thailand (12)	3.7-19.6	8-42	-

(1) Cicerone and Shetter 1981; Cicerone *et al.*, 1983; (2) Seiler *et al.*, 1984; (3) Holzapfel-Pschorn and Seiler, 1986; Schutz *et al.*, 1989; (4) Yagi and Minami, 1990; (5) Khalil and Rasmussen, 1991; (6) Wang *et al.*, 1989; (7) Zongliang *et al.*, 1992; (8) Debo *et al.*, 1992; (9) Parashar *et al.*, 1991; Mitra, 1992; (10) Sass *et al.*, 1990; (11) Denmead and Freney, 1990; (12) Yagi, unpublished.

Thus, about 20% (100Tg) of total annual CH₄ emissions are from fossil carbon sources, primarily coal-mining operations, and oil and natural gas production, transmission, distribution and use. A very small part of this may also be due to release of old CH₄ from hydrate destabilization (0-5Tg), and a warmer climate could lead to a significant increase in the magnitude of this source. The latest estimates of global annual emissions for coal-mining range from 25 to 47Tg (Okken and Kran, 1989; Barns and Edmonds, 1990; Boyer *et al.*, 1990; Hargraves, 1990); for the gas industry from 25 to 42Tg (Okken and Kran, 1989; Barns and Edmonds, 1990); and for the oil industry from 5 to 30Tg (Okken and Kran, 1989). Emissions from these three sources are broadly consistent with a total annual emission of 100Tg.

Emissions from wetlands are the largest natural source of CH₄ to the atmosphere. Although the recent estimate is in the range of the IPCC (1990) estimate, the latitudinal distribution of the emissions has been revised. Emissions from high-latitude peat bogs are about half of that previously estimated, while inclusion of bubbling tends to enhance the estimates of emissions from tropical swamps.

The 1990 IPCC estimate of the CH₄ flux from rice paddies was based on a very limited amount of data. Table A1.4 summarizes CH₄ emission rates from rice cultivation, including a substantial amount of new information from Japan, Australia, Thailand and, in particular, India and China. Very large variations in emissions are observed between different rice paddies. These differences are probably due to several factors including irrigation and fertilization practices, soil/paddy characteristics (particularly redox potential), cultivation history, temperature, and season. While WMO (1992) decided to retain the same quantitative emission estimate of 100Tg as IPCC (1990), a detailed analysis of the available data, particularly that from India, suggests a global annual emission nearer the lower end of the range.

While the estimate of CH₄ emissions from landfills has been slightly reduced because of observed high CH₄ oxidation rates in landfill cover soils (Whalen *et al.*, 1990), two "waste" sources of CH₄ were not included in the previous IPCC assessment, i.e., emissions from animal waste (Casada and Saffley, 1990) and domestic sewage treatment (Harriss, 1991). Based on recent studies (Khalil *et al.*, 1990; Rouland *et al.*, 1991) the annual emission from termites was scaled down to 20Tg. Carbon-13 studies (Stevens, 1988; Quay *et al.*, 1991; Lasaga and Gibbs, 1991) indicate that the contribution from biomass burning is in the upper part of the range given in Table A1.3.

A1.4 Nitrous Oxide

Nitrous oxide is an important long-lived greenhouse gas. In addition, it is the primary source of the oxides of nitrogen in the stratosphere, which play a critical role in

controlling the abundance and distribution of stratospheric ozone.

A1.4.1 Atmospheric Concentrations and Trends

Numerous new data confirm that the present-day atmospheric concentration of nitrous oxide (N₂O) is about 310 ppbv; about 8% greater than during the pre-industrial era, and it is increasing at a rate of 0.2-0.3% per year (WMO, 1992). This observed rate of increase represents an annual atmospheric growth rate of about 3 to 4.5TgN.

A1.4.2 Sinks

The major atmospheric loss processes for N₂O are stratospheric photo-dissociation and stratospheric photo-oxidation. Consumption in soils may represent a small sink but, to date, this has not been evaluated. The atmospheric N₂O lifetime is about 130 (110-168) years (WMO, 1992).

A1.4.3 Sources

The sources of N₂O were previously discussed in detail in IPCC (1990). A revised budget is given in Table A1.5 based on new information on soil fluxes from tropical ecosystems (Sanhueza *et al.*, 1990; Matson *et al.*, 1990) and temperate forests (Bowden *et al.*, 1990); detailed evaluations of cultivated soils (Bouwman, 1990; Eichner, 1990); and new estimates of emissions from biomass burning (Lobert *et al.*, 1990; Cofer *et al.*, 1991). Large tropical sources are required to explain the N₂O latitudinal

Table A1.5: Estimated Sources and Sinks of Nitrous Oxide (Tg N per year)

Sources	
<i>Natural</i>	
• Oceans	1.4-2.6
• Tropical Soils	
• Wet forests	2.2-3.7
• Dry savannas	0.5-2.0
• Temperate Soils	
• Forests	0.05-2.0
• Grasslands	?
<i>Anthropogenic</i>	
• Cultivated Soils	0.03-3.0
• Biomass Burning	0.2-1.0
• Stationary Combustion	0.1-0.3
• Mobile Sources	0.2-0.6
• Adipic Acid Production	0.4-0.6
• Nitric Acid Production	0.1-0.3
Sinks	
Removal by soils	?
Photolysis in the Stratosphere	7-13
Atmospheric Increase	3-4.5

gradient determined using 10 years of ALE/GAGE N₂O data. The analysis shows specifically that emissions into the latitude bands 90°N-30°N, 30°N-equator, equator-30°S, and 30°S-90°S, account for about 22-24%, 32-39%, 20-29%, and 11-15%, respectively, of the global total (Prinn *et al.*, 1990). The impact of tropical deforestation on the emissions of N₂O is unclear; one study indicates an enhancement after conversion of humid forest to pasture, whereas other studies conclude that forest degradation (Sanhueza *et al.*, 1990) or conversion to pasture (Keller, 1992) reduces the emissions.

Several recent publications (i.e., De Soete, 1989; Linak *et al.*, 1990; Yokoyama *et al.*, 1991) reconfirm that N₂O emissions from stationary combustion sources are very low. Fluidized bed combustion systems produce larger quantities of N₂O than the traditional coal combustors (De Soete, 1989), but because of their present limited application their contribution is negligible (CONCAWE, 1991).

Several smaller, but important, anthropogenic sources of N₂O have now been identified. Efforts should continue to identify as yet unidentified sources. Thiemens and Trogler (1991) estimate that adipic acid production (for nylon 66) results in annual atmospheric emissions of 0.4TgN per year (industrial estimates suggest that it might be as high as 0.6TgN). The annual emission from nitric acid production (mainly for N-fertilizer) is 0.1 to 0.3TgN (McCulloch, 1991). Three-way catalyst controlled vehicles have higher N₂O emissions than uncontrolled vehicles (De

Soete, 1989) and recent annual estimates of emissions vary between 0.2 and 0.6TgN.

While the estimated source strengths are quite uncertain, it appears that emissions from soils dominate the N₂O budget. Since the total annual emission rate of N₂O appears to be between 10 and 17.5TgN, deduced from the magnitude of its sinks and its rate of accumulation in the atmosphere, and the estimated annual sources are between 5.2 and 16.1TgN, it seems that the strengths of some of the identified sources have been underestimated or that there are unidentified sources. It has been suggested that agricultural development may stimulate biological production and account for the missing emissions. Although large changes in land use are occurring in the tropics no evaluation of the impact of the increasing use of nitrogen fertilizers has been made for this region.

A1.5 Halogenated Species

A1.5.1 Atmospheric Trends

The major halogenated source gases, i.e., CFCs, HCFC-22, the halons, methyl chloroform (CH₃CCl₃) and carbon tetrachloride (CCl₄), continue to grow in concentration in the background troposphere of both Hemispheres even though the consumption of most of these gases has decreased significantly in recent years (Section A1.6.2). The data are summarized in Table A1.6. The fully fluorinated species, tetrafluoromethane (CF₄), hexafluoroethane (C₂F₆), and sulphur hexafluoride (SF₆) have been measured in the atmosphere, with CF₄ being the most abundant species (70-80 pptv).

A1.5.2 Sinks

The only significant sink for the fully halogenated CFCs is photolysis in the stratosphere, whereas the primary sink for the partially halogenated chemicals is reaction with OH in the troposphere.

A1.5.3 Sources

The worldwide consumption of CFCs 11, 12 and 113 decreased by 40% between 1986 and 1991. At this rate, developed country consumption will be reduced by 50% in 1992 - a three-year advance on the requirements of the London Amendments to the Montreal Protocol on Substances that Deplete the Ozone Layer, which calls for a 50% reduction by 1995, 85% reduction by 1997, and a complete phaseout by the year 2000. Major reductions have been made by using hydrocarbons as aerosol propellants and as blowing agents for flexible foams. Solvent users are turning to aqueous and semi-aqueous systems, no-clean technologies, alcohol, and other solvents. Refrigeration and air conditioning sectors are recovering and recycling CFC refrigerants and increasing the use of HCFCs and ammonia. Insulating foams have a lower CFC content with little energy penalty.

Table A1.6: Atmospheric Concentrations and Trends of Halocarbons

Species	Annual Mean Concentration (pptv), 1989	Trend (pptv/yr)	
		1987 WMO (1989)	1989 WMO (1992)
CFC-11	255 †	9 - 10	9 - 10
CFC-12	453 †	16 - 17	17 - 18
CFC-113	64 †	5	6
CCl ₄	107 †	2	1 - 1.5
HCFC-22	110	7	5 - 6
CH ₃ CCl ₃	150 †, ¥	6	4 - 5
CBrClF ₂	1.8 - 3.5	0.2	0.4 - 0.7
CBrF ₃	1.6 - 2.5	0.3	0.2 - 0.4

† based on GAGE data (Prinn *et al.*, 1991 and references therein)

¥ the 1987 mean CH₃CCl₃ concentration was 140 pptv, not 150 pptv as reported in WMO (1989).

Table A1.7: Total Ozone Trends in Percent per Decade with 95% Confidence Limits

	TOMS: 1979-1991			Ground-based: 26°N - 64°N	
	45°S	Equator	45°N	1979-1991	1970-1991
Dec-Mar	-5.2 ± 1.5	+0.3 ± 4.5	-5.6 ± 3.5	-4.7 ± 0.9	-2.7 ± 0.7
May-Aug	-6.2 ± 3.0	+0.1 ± 5.2	-2.9 ± 2.1	-3.3 ± 1.2	-1.3 ± 0.4
Sep-Nov	-4.4 ± 3.2	+0.3 ± 5.0	-1.7 ± 1.9	-1.2 ± 1.6	-1.2 ± 0.6

Emissions of halocarbons will decrease further because reductions are mandated by the 1990 London Amendments to the Montreal Protocol. In addition, many countries and some industries have called for an even faster phase-out of the controlled substances. UNEP (1991) reported that it is technically feasible to almost completely phase out controlled substances in developed countries by 1995 - 1997 through a number of measures that are technically feasible, many either economically advantageous or at no economic cost, others at a "modest" economic cost. A more rapid phase-out depends on the extent of recycling and technical feasibility of equipment retrofit, on the availability of HCFC and HFC replacements and on their toxicological and environmental acceptability, on a regulatory regime which allows profitable investment in their production, on vigorous and effective management of the halon bank, and on the very rapid dissemination and adoption of technologies for the replacement of CH_2Cl_2 by small users.

The main sources for the fully fluorinated chemicals are not well understood. Production of aluminium and use in electrical equipment are probably some of the most important sources (Stordal and Myhre, 1991).

A1.6 Ozone

Ozone (O_3) is a particularly effective greenhouse gas in the upper troposphere and lower stratosphere, and also plays a key role in absorbing solar ultraviolet radiation. About 90% of the total column of ozone resides in the stratosphere, and the remaining 10% in the troposphere. The current scientific and policy concerns are reduction of stratospheric ozone by chlorine- and bromine-containing chemicals, and production of tropospheric ozone by carbon monoxide, hydrocarbons, and oxides of nitrogen (see Section A.2.6). This section is a summary of a very extensive international scientific assessment (WMO, 1992), which should be read for a more comprehensive discussion and for all key references.

A1.6.1 Observed Trends in Total Column Ozone

Marked Antarctic O_3 holes have continued to occur and, in four of the past five years, have been deep and extensive in

area. This contrasts to the situation in the mid-1980s, where the depth and area of the O_3 hole exhibited a quasi-biennial modulation. Recent laboratory research and re-interpretation of field measurements have strengthened the evidence that the Antarctic O_3 hole is primarily due to chlorine- and bromine-containing chemicals. While no extensive O_3 losses have occurred in the Arctic comparable to those observed in the Antarctic, localized Arctic O_3 losses have been observed in winter concurrent with observations of elevated levels of reactive chlorine.

Recent ground-based and satellite observations (Stolarski *et al.*, 1991) show evidence for significant decreases of total column O_3 throughout the year in both the Northern and Southern Hemispheres at middle and high latitudes (Table A1.7). No trends in O_3 have been observed in the tropics. These downward trends were larger during the 1980s than during the 1970s.

The observed decreases in total column ozone comprise a decrease in the stratosphere, possibly offset to some degree by an increase in the troposphere (see next section).

A1.6.2 Observed Trends in the Vertical Distribution of Ozone

Ground-, balloon-, and satellite-based measurements show that the observed total column O_3 decreases during the last one to two decades are predominantly due to O_3 concentration decreases in the lower stratosphere (between the tropopause and 25km altitude or lower). The rate of decrease at middle latitudes in both hemispheres, and high latitudes in the Northern Hemisphere has been up to 10% per decade depending on altitude. Ozone decreases exceeding 90% have been observed in the lower stratosphere within the springtime Antarctic ozone hole. In addition, there is evidence of small decreases globally in the upper stratosphere.

Measurements indicate that above the few existing balloonsonde stations at northern middle latitudes in Europe O_3 levels in the troposphere up to 10km altitude have increased by about 10% per decade over the past two decades. However, the data base for O_3 trends in the upper troposphere is sparse and inadequate for quantifying its contribution to the global radiative balance.

A1.6.3 Future Levels of Stratospheric Ozone

The weight of evidence suggests that the observed middle- and high-latitude O₃ losses are largely due to chlorine and bromine. Therefore, as the atmospheric abundances of chlorine and bromine increase in the future, significant additional losses of O₃ are expected. Even if the control measures of the amended Montreal Protocol (London, 1990) were to be implemented by all nations, the current abundance of stratospheric chlorine (3.3-3.5 ppbv) is estimated to increase during the next decade, reaching a peak of about 4.1 ppbv around the turn of the century. With these increases, additional middle-latitude O₃ losses during the 1990s are expected to be comparable to those observed during the 1980s. Hence, by the year 2000 O₃ depletions are expected to be about 6% in summer and about 10% in winter. In addition, there is the possibility of incurring widespread losses in the Arctic. Enhanced levels of stratospheric sulphate aerosols from natural (e.g., Mt. Pinatubo) or anthropogenic sources could possibly lead to even greater ozone losses by increasing the catalytic efficiency of chlorine- and bromine-containing chemicals through heterogeneous chemical processes.

A reduction in the peak chlorine and bromine levels, and a hastening of the subsequent decline of these levels, hence reducing future levels of O₃ depletion, can be accomplished in a variety of ways, including an accelerated phaseout of controlled substances and limitations on currently uncontrolled halocarbons.

A1.7 Tropospheric Ozone Precursors: Carbon Monoxide, Non-Methane Hydrocarbons and Nitrogen Oxides

Tropospheric O₃ is predicted to increase with increasing emissions of nitrogen oxides (NO_x), and with increasing emissions of carbon monoxide (CO), CH₄ and non-methane hydrocarbons (NMHC) when the atmospheric abundance of NO_x is greater than 20-30 pptv. The magnitude of ozone changes are predicted to exhibit marked variations with latitude, altitude and season. Differences between model calculations of O₃ increases from NO_x emissions are large (factor of ~3), but moderate from CH₄ emissions (~50%). The differences in the predicted spatial and temporal distributions of O₃ changes are particularly large for NO_x emissions but again moderate for CH₄ emissions. It should also be noted that increases in CH₄, CO and NMHC emissions lead to reduced OH values, while increased NO_x emissions lead to enhanced OH levels. As a result of these opposing effects, the sign of future OH changes cannot be predicted reliably. Uncertainties in present and future tropospheric OH concentrations lead to corresponding uncertainties in the lifetimes of many tropospheric species, e.g., CH₄, HCFCs and HFCs.

A1.7.1 Trends

There is little new information on the trends of these tropospheric O₃ precursors. Because of their relatively short atmospheric lifetimes, coupled with inadequate monitoring networks, the determination of their long-term trends and the spatial and temporal variability of their atmospheric distribution is very difficult. The atmospheric abundance of CO appears to be increasing in the Northern Hemisphere at about 1% per year (Khalil and Rasmussen, 1990), but there is no evidence of a significant trend in the Southern Hemisphere (Khalil and Rasmussen, 1990; Brunke *et al.*, 1990). There is also no evidence for trends in the atmospheric concentrations of NO_x or NMHC, except for ethane in the Northern Hemisphere (0.9±0.3% per year: Ehhalt *et al.*, 1991).

A1.7.2 Sources and Sinks

While it is clear that CO, NMHC, and NO_x all have significant natural and anthropogenic sources (IPCC, 1990) their budgets remain uncertain. Recent data (Leleiveld and Crutzen, 1991) suggests that the oxidation of HCHO in the liquid phase does not produce CO, but CO₂ directly, therefore the estimates of CO production from hydrocarbon oxidation may need to be revised downward. Hameed and Dignon (1992) report that NO_x emissions have increased by about 30% over the period 1970-1986. Tables A1.8 and A1.9 show both natural and anthropogenic sources of CO and NO_x.

A1.8 Sulphur-Containing Gases

Sulphur-containing gases emitted into the atmosphere through natural and anthropogenic processes affect the Earth's radiative budget by being transformed into sulphate aerosol particles that: (i) scatter sunlight back to space, thereby reducing the radiation reaching the Earth's surface; (ii) possibly increase the number of cloud condensation nuclei, thereby potentially altering the physical characteristics of clouds; and (iii) affect atmospheric chemical composition, e.g., stratospheric O₃, by providing surfaces for heterogeneous chemical processes (see Section A2.6 for a fuller discussion). Sulphate aerosols are important in both the troposphere where they have lifetimes of days to a week or so, as well as in the stratosphere where they have lifetimes of several years.

A1.8.1 Sources

Spiro *et al.* (1991) have prepared a detailed global inventory of the geographic distribution (1° by 1°) of natural and anthropogenic sulphur emissions. The estimated emissions of sulphur dioxide (SO₂) from biomass burning and of reduced sulphur gases from soils and vegetation have been reduced (Andreac, 1990; Hao *et*

Table A1.8: Estimated Sources and Sinks of Carbon Monoxide (Tg CO per year)

	WMO (1985)	Seiler & Conrad (1987)	Khalil & Rasmussen (1990)	Crutzen & Zimmerman (1991)
Primary Sources				
• Fossil Fuel	440	640±200	400-1000	500
• Biomass Burning	640	1,000±600	335-1400	600
• Plants	-	75±25	50-200	-
• Oceans	20	100±90	20-80	-
Secondary Sources				
• NMHC oxidation	660	900±500	300-1400	600
• methane oxidation	600	600±300	400-1000	630
Sinks				
• OH reaction	900±700	2000±600	2200	2050
• Soil uptake	256	390±140	250	280
• Stratos. oxidation	-	110±30	100	-

Table A1.9: Estimated Sources of Nitrogen Oxides (Tg N per year)

Natural	
• Soils	5-20 (1)
• Lightning	2-20 (2)
• Transport from Stratosphere	~1
Anthropogenic	
• Fossil Fuel Combustion	24 (3)
• Biomass Burning	2.5-13 (4)
• Tropospheric Aircraft	0.6

(1) Dignon *et al.*, 1991; (2) Atherton *et al.*, 1991;
 (3) Hameed and Dignon, 1992; (4) Dignon and Penner, 1991

Table A1.10: Estimated Sources of Short-lived Sulphur Gases (Tg S per year)

Anthropogenic emissions (mainly SO ₂)	70-80
Biomass burning (SO ₂)	0.8-2.5
Oceans (DMS)	10-50
Soils and plants (DMS and H ₂ S)	0.2-4
Volcanic emissions (mainly SO ₂)	7-10

et al., 1991; Bates *et al.*, 1991; Spiro *et al.*, 1991). The best estimate of the magnitude of annual global anthropogenic emissions of SO₂ is between 70Tg and 80Tg (Semb 1985; Hameed and Dignon, 1988; Langner and Rodhe, 1991; Spiro *et al.*, 1991). Recent estimates of the annual global emissions of dimethyl sulphide (DMS) from the oceans

(10-50TgS) (Bates *et al.*, 1987; Bates *et al.*, 1991; Langner and Rodhe, 1991; Spiro *et al.*, 1991) are significantly lower than given by IPCC (1990). Table A1.10 summarizes known emissions of key short-lived sulphur gases.

A1.8.2 Atmospheric Gas-Particle Conversion

Oxidation of SO₂ to aerosol sulphate occurs in the gas phase and in cloud droplets (aqueous-phase oxidation). The former may generate new particles or the newly formed H₂SO₄ may add to existing particles increasing their mass but not their number. Aqueous-phase oxidation does not result in new particle formation but only adds to the mass of sulphate. The dissolved sulphate may remain in the atmosphere as an aerosol particle upon cloud droplet evaporation (this appears to be the more frequent situation) or may be removed from the atmosphere in precipitation. The rates of these atmospheric oxidation reactions depend on the concentrations of OH for the gas-phase reaction and of oxidants (hydrogen peroxide (H₂O₂) and O₃) for the aqueous-phase reactions. The rates of the aqueous-phase reactions increase with cloud liquid-water content, increase with decreasing temperature, as a consequence of temperature dependent gas solubilities, and for the O₃ reaction, decrease with decreasing cloud water pH. The decrease in pH as the reaction proceeds can lead to a self limitation of that reaction. While the extent of the H₂O₂ oxidation may be limited by the amount of H₂O₂ present, the amount of O₃ is rarely limiting to the extent of oxidation by that species. Detailed description of the rate, extent and spatial distribution of these reactions depends on knowledge of the concentrations of the reagent species and, in the case of the aqueous-phase reactions, of the pertinent cloud properties.

In addition to the mass concentration of the sulphate

aerosol it is necessary to have information about the size distribution of the aerosol particles, since this size distribution affects the radiative and cloud nucleating properties of the aerosol. The evolution of the size distribution of an aerosol (in clear air) is the resultant of new particle formation and coagulation and removal processes. These processes depend, in a complex and incompletely understood way, on the properties of the existing aerosol and the rate of generation of new condensable material. The size distribution is a strong function of relative humidity, shifting to larger sizes with increasing relative humidity (Charlson *et al.*, 1987; d'Almeida *et al.*, 1991). The size distribution is also greatly influenced by cloud processes (Hoppel *et al.*, 1990; Hegg *et al.*, 1990).

A1.8.3 Transport and Distribution

The atmospheric lifetimes of SO₂, DMS and hydrogen sulphide (H₂S) are a few weeks at most, and their atmospheric distributions are largely controlled by the distributions of their sources. The mean residence time of sulphate aerosols formed by gas-particle conversion in the troposphere is about a week. Two consequences of the short lifetimes are that the resulting distribution of tropospheric aerosols is inhomogeneous, and that these gases are not significant contributors to the stratospheric sulphate layer. To assess the climatic impact of these aerosols it is necessary to know their spatial distribution in much more detail than is the case for the longer-lived greenhouse gases, (a) because the radiative forcing due to aerosols varies spatially, (b) because cloud microphysical processes are nonlinear in the concentration of aerosol particles, and (c) because cloud forcing is nonlinear in the concentration of cloud droplets.

A1.8.4 Removal

Removal of submicrometer aerosol particles contributing to the radiative effects occurs largely by the precipitation process (e.g., Slinn, 1983). These particles are the dominant particles on which cloud particles form (cloud condensation nuclei, CCN); once a cloud droplet (of diameter of a few up to 20 micrometres) is formed, it is much more susceptible to scavenging and removal in precipitation than is the original submicrometre particle. The fraction of aerosol particles incorporated in cloud droplets on cloud formation is the subject of active current research. Earlier work has yielded a fairly wide spread in this fractional incorporation, based in part on limitations of then-existing techniques and in part on the absence of a single definition of incorporation efficiency (ten Brink *et al.*, 1987). More recent work indicates a high fractional incorporation at low concentrations of aerosol particles decreasing as the aerosol particle loading increases (Gillani *et al.*, 1992). Model calculations of the efficiency of

incorporation of aerosol particles into cloud droplets and precipitation are highly sensitive to assumptions and approach (Jenson and Charlson, 1984; Flossmann *et al.*, 1985; Hanel, 1987; Ahr *et al.*, 1989; Alheit *et al.*, 1990).

A1.8.5 Stratospheric Aerosols

Volcanic injections of sulphur are a major contributor to the stratospheric aerosol layer. Krueger (1991) used Nimbus 7 TOMS data to estimate that the eruption of Mt. Pinatubo in the Philippines in 1991 added about 20 million tons of SO₂ directly to the stratosphere, about 50% more than the eruption of Mt. El Chichon. Anthropogenic emissions add to stratospheric sulphur and their magnitude needs to be evaluated. Carbonyl sulphide (COS), a significant source, is produced by the oxidation of carbon disulphide (CS₂) in the troposphere but its origins are anthropogenic. In addition, Hofmann (1990, 1991) has suggested that the abundance of stratospheric sulphate aerosols had increased during the last decade, possibly due to aircraft emissions of SO₂.

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