

## Other Trace Gases and Atmospheric Chemistry

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# CONTENTS

<b>Summary</b>	77	<b>2.7 Tropospheric Nitrogen Oxides</b>	99
<b>2.1 Introduction</b>	79	2.7.1 Sources of Tropospheric NO <sub>x</sub>	99
<b>2.2 Atmospheric Chemistry</b>	79	2.7.2 NO <sub>x</sub> Removal Processes	100
2.2.1 Chemical Processes and the Removal of Trace Gases	79	2.7.3 Tropospheric Distribution of NO <sub>x</sub>	100
2.2.2 Atmospheric Adjustment Times of the Trace Gases	82	2.7.4 Trends of NO <sub>x</sub>	103
2.2.3 Current Tropospheric OH	83	<b>2.8 Carbon Monoxide and Volatile Organic Compounds</b>	103
2.2.4 Other Atmospheric and Surface Removal	84	2.8.1 Sources and Removal Processes of CO	103
2.2.5 Lifetimes from Stratospheric Removal	84	2.8.2 Atmospheric distribution and trends of CO	103
2.2.6 Examples of Chemical Feedbacks Affecting Greenhouse Gases	85	2.8.3 Volatile Organic Compounds	104
<b>2.3 Methane</b>	85	2.8.3.1 Introduction	104
2.3.1 Methane Sources	85	2.8.3.2 Sources of volatile organic compounds	104
2.3.2 Removal of Methane	87	2.8.3.3 Sinks of the volatile organic compounds	105
2.3.3 Atmospheric Distribution	87	2.8.3.4 The role of volatile organic compounds	105
2.3.4 Trends and Sensitivities	87	<b>2.9 Inter-Comparison of Tropospheric Chemistry/Transport Models</b>	105
<b>2.4 Nitrous Oxide</b>	89	2.9.1 Intercomparison of Transport: A Case Study of <sup>222</sup> Rn	106
2.4.1 Sources of Nitrous Oxide	89	2.9.2 Intercomparison of Photochemistry: O <sub>3</sub> Production and Loss	109
2.4.2 Removal of Nitrous Oxide	91	2.9.3 Conclusions	111
2.4.3 Atmospheric Distribution	91	<b>2.10 Global Tropospheric Ozone Modelling</b>	111
2.4.4 Trends and Sensitivities	91	2.10.1 Tropospheric NO <sub>x</sub> : Surface Combustion and Aircraft	112
<b>2.5 Halocarbons</b>	92	2.10.2 CH <sub>4</sub> Increases: A Case Study	113
2.5.1 Atmospheric Distributions and Trends	92	2.10.2.1 The current atmosphere	113
2.5.1.1 CFCs and carbon tetrachloride	92	2.10.2.2 O <sub>3</sub> perturbations	113
2.5.1.2 Methylchloroform and the HCFCs	93	2.10.2.3 Adjustment time of CH <sub>4</sub> emissions	115
2.5.1.3 Other chlorinated species	93	2.10.3 Conclusions	116
2.5.1.4 Methylbromide, halons and other brominated species	93	<b>2.11 Stabilisation of Atmospheric Chemical Composition</b>	116
2.5.1.5 Other perhalogenated species	94	2.11.1 Methane	116
2.5.2 Industrial Production, Use and Emissions	94	2.11.2 Nitrous Oxide	117
2.5.3 Natural Sources	95	2.11.3 Halocarbons	117
2.5.4 Halocarbon Removal Processes	95	2.11.4 Ozone	117
<b>2.6 Observed Ozone (O<sub>3</sub>) and Tropospheric UV</b>	95	<b>References</b>	118
2.6.1 Stratospheric Ozone	96		
2.6.2 Tropospheric Ozone	98		
2.6.3 Tropospheric UV	99		

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## SUMMARY

### Methane (CH<sub>4</sub>)

Atmospheric CH<sub>4</sub> concentrations have increased from about 700 ppbv in pre-industrial times to a global mean of 1714 ppbv in 1992. The 1980s were characterised by declining methane growth rates which were approximately 10 ppbv/yr by the end of the decade. The average growth rate of 13 ppbv/yr corresponds to an imbalance between sources and sinks of about 37 Tg(CH<sub>4</sub>)/yr. If emissions were frozen at this level, CH<sub>4</sub> would rise to about 1900 ppbv over the next 50 years. If emissions were cut by 37 Tg(CH<sub>4</sub>)/yr, then CH<sub>4</sub> concentrations would remain at today's levels. Current estimates of the CH<sub>4</sub> budget assign 20-40% to natural sources, 20% to anthropogenic fossil fuel related sources and the remaining 40-60% to other anthropogenic sources.

The annual CH<sub>4</sub> increase from 1991 to 1992 was much smaller than in the previous decade, 1992 to 1993 levels were unchanged, and in late 1993 CH<sub>4</sub> apparently started to increase again. This anomaly was largest at high latitudes in the Northern Hemisphere, and could be explained by a rapid drop, of about 5%, in global annual emissions. Longer-period variations in the growth rate of CH<sub>4</sub> have been observed for the 1920s and 1970s from air trapped in ice cores.

Methane is the only long-lived gas that has clearly identified chemical feedbacks: increases in atmospheric CH<sub>4</sub> reduce the concentration of tropospheric hydroxyl radical (OH), increase the CH<sub>4</sub> lifetime and hence amplify the original CH<sub>4</sub> perturbation. A recent analysis has shown that these feedbacks result in an adjustment time for additional emissions of CH<sub>4</sub> equal to  $14.5 \pm 2.5$  years based on a "budget" lifetime of about 10 years that reflects atmospheric chemical losses alone. It is uncertain how much the adjustment time would be affected by the small biological sink, and a range of 11 to 17 years encompasses this additional uncertainty. This lengthening of the effective duration of a CH<sub>4</sub> pulse applies also to any derived perturbations (e.g., in tropospheric O<sub>3</sub>).

Several atmospheric chemistry models have calculated the impact of a 20% increase in CH<sub>4</sub> concentrations (from 1715 to 2058 ppbv). Two important results were extracted from these simulations: (1) the chemical feedback of CH<sub>4</sub> on OH chemistry results in a reduction of the CH<sub>4</sub> removal rate ranging from -0.17% to -0.35% for each 1% increase

in CH<sub>4</sub> concentration; and (2) predicted increases in tropospheric O<sub>3</sub> varied by a factor of three or more across the models, averaging about 1.5 ppbv throughout most of the troposphere in both tropics and summertime mid-latitudes. The first result was used to derive the methane adjustment time ( $14.5 \pm 2.5$  yr or about 1.45 times the lifetime) and the latter to estimate the ratio, about 0.25, of radiative forcing from induced tropospheric O<sub>3</sub> increase to that from the CH<sub>4</sub> increase.

### Nitrous oxide (N<sub>2</sub>O)

Atmospheric N<sub>2</sub>O concentrations have increased from about 275 ppbv in pre-industrial times to 311 ppbv in 1992. The trend during the 1980s was +0.25%/yr with substantial year-to-year variations. A growth rate of 0.8 ppbv/yr corresponds to an imbalance between sources and sinks of about 3.9 Tg(N<sub>2</sub>O)/yr. If these emissions were frozen then N<sub>2</sub>O levels would rise slowly to about 400 ppbv over the next two centuries.

### Halocarbons

Tropospheric growth rates of the major anthropogenic source species for stratospheric chlorine and bromine (CFCs, CCl<sub>4</sub>, CH<sub>3</sub>CCl<sub>3</sub> and the halons) have slowed significantly in response to reduced emissions as required by the Montreal Protocol and its amendments. Total atmospheric chlorine from these gases grew by about 60 pptv (1.6%) in 1992 compared to 110 pptv (2.9%) in 1989. HCFC growth rates are accelerating as they are being used increasingly to substitute for CFCs. Tropospheric chlorine as HCFCs increased in 1992 by about 10 pptv compared to 5 pptv in 1989. Stratospheric chlorine levels are expected to peak in the next decade, and it is expected that stratospheric ozone depletion will follow this, recovering slowly in the first half of the next century.

For these long-lived, well-mixed gases, atmospheric lifetimes have been derived based on the recent re-evaluation of the lifetimes of CFC-11 ( $50 \pm 5$  yr) and CH<sub>3</sub>CCl<sub>3</sub> ( $5.4 \pm 0.6$  yr). These new lifetimes are slightly smaller than those given in previous assessments and have significantly greater certainty. The global mean lifetimes for the well-mixed gases are used to infer sources and sinks, and to predict the increase in atmospheric concentration due to specified anthropogenic emissions.

### Stratospheric ozone ( $O_3$ )

Trends in total ozone since 1979 have been updated to May 1994, and estimates of depletion since 1970, attributed to increases in halocarbons, have been made: (1) Northern Hemisphere mid-latitude loss is significantly negative in all seasons, with winter/spring cumulative losses of 10%; (2) tropical ( $20^{\circ}S - 20^{\circ}N$ ) losses are small and not statistically significant; (3) southern mid-latitude losses are significant in all seasons (4-5%/decade since 1979). Unusually low values (lower than would be expected from an extrapolation of the 1980s trend) were observed in the 1991 to 1994 period, especially at Northern mid- and high latitudes. The Antarctic ozone "holes" of 1992 and 1993 were the most severe on record; for instance, parts of the lower stratosphere contained extremely low amounts of ozone corresponding to local depletions of more than 99%.

The eruption of Mt. Pinatubo in 1991 led to a massive increase in sulphate aerosol in the lower stratosphere. Observational evidence shows that this thirtyfold increase in aerosol surface area greatly enhanced the heterogeneous chemistry and accelerated photochemical loss of  $O_3$ . Further evidence points to an additional heating of the stratosphere by Mt. Pinatubo aerosols, resulting in circulation changes that altered the distribution of  $O_3$  in the tropics immediately following the eruption, and possibly also in mid-latitudes.

### Tropospheric ozone ( $O_3$ )

Tropospheric ozone appears to have increased in many regions of the Northern Hemisphere. Observations show that tropospheric ozone, which is formed by chemical reactions involving other hydrocarbons, carbon monoxide and some nitrogen oxides ( $NO_x$ ), has increased above many locations in the Northern Hemisphere over the last 30 years. However, in the 1980s, the trends were variable, being small or non-existent. At the South Pole, a decrease has been observed; however in the Southern Hemisphere as a whole, there are insufficient data to draw strong inferences. Model simulations and limited observations together suggest that tropospheric ozone has increased, perhaps doubled, in the Northern Hemisphere since pre-industrial times.

### $NO_x$ and other short-lived tropospheric ozone precursors

Uncertainties in the global budget of tropospheric ozone are associated primarily with our lack of knowledge of the distribution of  $O_3$ , its short-lived precursors ( $NO_x$ ,

hydrocarbons, CO), and atmospheric transport. Observations of  $NO_x$  are just beginning to describe the global atmospheric distribution and they show the large variability in this ozone-producing species. Even with the observed distributions we cannot define the importance of anthropogenic sources (transport of surface pollution out of the boundary layer, direct injection by aircraft) relative to natural sources (lightning, stratospheric input) in controlling the global  $NO_x$  distribution. Current estimates of anthropogenic  $NO_x$  sources attribute 24 Tg(N)/yr to fossil fuel combustion at the surface, 0.5 Tg(N)/yr to aircraft emissions, 8 Tg(N)/yr to biomass burning and as much as 12 Tg(N)/yr release from soils, including fertilised fields. Anthropogenic emissions dominate natural sources in magnitude, but natural emissions may dominate a large fraction of the atmosphere remote from anthropogenic emissions.

Changes in ozone concentrations in the upper troposphere and lower stratosphere impact the radiative forcing. In addition to anthropogenic sources of  $O_3$  precursors from the lower troposphere, aircraft currently represent a direct anthropogenic source of  $NO_x$  in that altitude range. Research evaluating the climatic effect of the current subsonic fleet is incomplete, but initial estimates of the possible changes to  $O_3$  show that this radiative forcing is similar to, but not greater than, that of the  $CO_2$  from the combustion of aviation fuel, about 3% of all fossil fuel combustion.

For compounds with lifetimes much shorter than 6 months, mixing within the troposphere is not rapid enough to average over variations in chemical loss. For these short-lived gases (e.g.,  $NO_x$ , hydrocarbons,  $O_3$  and CO), the mean concentration cannot be accurately calculated from the product of emissions or production and a global mean lifetime, but their distribution and impacts may be evaluated in future assessments by the more advanced three-dimensional atmospheric chemistry models.

### Intercomparisons of atmospheric chemistry models

Two model intercomparison exercises have been conducted to test the ability of models to simulate (a) the transport of shortlived tracers and (b) the basic features of  $O_3$  photochemistry. More than 20 models participated. A high degree of consistency was found in the global transport of a shortlived tracer within the 3D Chemistry/Transport Models (CTMs), but distinctly different results were found amongst 2-D models. General agreement was also found in the computation of photochemical rates affecting tropospheric  $O_3$ . These are the first extensive intercomparisons of global tropospheric models.