Tropospheric Chemistry: A Review

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1. Introduction

Two trace greenhouse gases, ozone (O_3) and methane (CH_4) are very important in the chemistry and radiation balance of the troposphere. Other greenhouse gases, such as CFCs and nitrous oxide (N_20), have a negligible role in tropospheric chemistry, but become very important in the stratosphere where their activity is generally to the detriment of the ozone layer. Some of the other halocarbons, such as methyl chloroform (CH_3CCl_3) and HCFCs, are greenhouse gases of varying degrees of importance that, play small but significant roles in tropospheric chemistry as sinks for the hydroxyl (OH) radical.

Other trace gases are important because they affect the concentrations of gases which are radiatively active, though they are not so themselves. The active nitrogen oxides NO and NO_2, collectively labelled as NO_x, regulate the formation of ozone, while carbon monoxide (CO) and to a lesser extent volatile organic compounds (VOCs) play important roles as sinks for OH, with some of the by-products subsequently reacting to produce ozone.

The hydroxyl radical is the most important of the trace gases because it reacts with practically everything, and in a sequence of reactions the one(s) involving OH are the rate-limiting ones as often as not. It is also the most difficult to study, because its average concentrations are simply too low and its lifetime is too short to measure easily. Attempts to indirectly estimate OH concentration are made with models which use a "tracer" gas such as methyl chloroform (e.g. Prinn et aI, 1992), but uncertainties in the tracer data such as sinks of unknown magnitude make for uncertain results.

All of these species exist in an intricate, interdependent photochemical balance governed by a plethora of non-linear checks and feedbacks which are still not fully understood or quantified. Study of these processes is made more difficult by a lack of definition of their budgets and increasing anthropogenic influences upon them. The purpose of this paper is to summarize current knowledge of the chemistry, sources and sinks of these non-CO_2 trace gases in the troposphere.

2. Tropospheric Ozone

Tropospheric ozone is a health hazard to humans and animals, causing lung and eye irritation and possible damage upon prolonged exposure, damages trees, crops and other plants, and is part of what makes exposure to smog so unpleasant. It also acts as a greenhouse gas, though its short lifetime makes it more of a regional factor, with net global effects that are difficult to assess. Most important of all its high reactivity means that it plays a pivotal role in tropospheric chemistry, largely as a source of OH radicals. Much effort continues to be devoted to the study of ozone, as many of its interactions with other species remain poorly understood.

2.1 Radiative Effects

Although articles in the popular press always stress the importance of stratospheric ozone's role as an absorber of harmful ultraviolet radiation, little if any mention is made of tropospheric ozone's equally important role as a greenhouse gas. The solar and longwave effects of ozone in the troposphere and lower stratosphere act together to increase surface temperature, while in the middle and upper stratosphere they oppose each other. As a result, surface temperatures are much more sensitive to changes in tropospheric than stratospheric O3. (Ramanathan et aI, 1987; Lacis et aI, 1990; Schwartzkopf and Ramaswamy, 1993)

2.1.1 Short-Wave Effects

Rayleigh and particle scattering of UV-B radiation by dust and air molecules occurs throughout the atmosphere, greatly increasing the length of the light path and hence the chances for absorption by ozone. This suggests that tropospheric ozone could be a more efficient UV-B absorber than stratospheric ozone. Model studies (Bruhl and Crutzen, 1989) show that in spite of a decrease in stratospheric O_3, surface UV-B radiation decreases as tropospheric ozone increases, apparently confirming the above hypothesis. The diffusion of the UV-B radiation was shown to be especially important for small solar zenith angles, in summer and in low latitudes.

2.1.2 Long-wave Effects

The greenhouse efficiency of tropospheric (and stratospheric) O_3 is greatest near the tropopause and decreases as one moves away from it in either direction, and thus radiation model results are most sensitive to changes in ozone concentration near this level. (Lacis et al, 1990; Schwartzkopf and Ramaswamy, 1993) This variation in efficiency is attributed to the difference between the temperature of the emitter (i.e. the ground) and the temperature of the absorbing ozone molecules, and it follows that a change in O_3 vertical distribution would likely cause a change in climate forcing, even if the total ozone column were not to change. (Lacis et al, 1990)

2.2 Chemistry

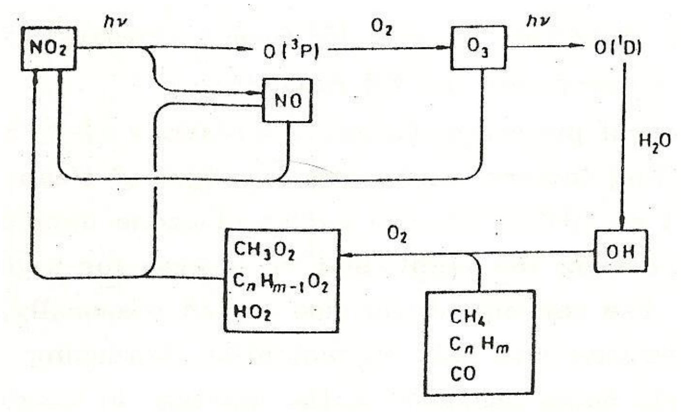


Figure 1: Summary of tropospheric ozone chemistry. The processes are explained in the text. (From Johnson et al, 1992)

2.2.1 Ozone Production and Loss Processes in Clean Air

The only known process which produces ozone is the photolysis of NO_2: (Rodhe et al, 1982; Wayne, 1991)

$$NO_2 + h\nu \rightarrow O + NO \tag{1}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{2}$$

NO_x concentrations are thus the limiting factor in ozone production. With $[NO_x]$ greater than a threshold value of about 30 pptv (parts per' trillion by volume) in relatively clean air, ozone generation by Equations (1) and (2) will exceed its consumption through the reactions:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{3}$$

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{4}$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{5}$$

because the reaction rates of (3-5) are all almost three orders of magnitude smaller than that for reaction (18) (see section 4), which regenerates NO_2. (Atkinson et al, 1990)

In very clean air which has little or no NO_x at all, such as marine boundary layer air, the destruction of ozone can be increased through its interactions with water vapour, as in the following:

$$O_3 + h\nu_{(\lambda<310\ nm)} \rightarrow O_2 + O(^1D) \tag{6}$$

$$O(^1D) + H_2O \rightarrow OH + OH \tag{7}$$

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{8}$$

(Ayers et al, 1992) Note that (4) and (5) form a catalytic cycle and are very efficient because (7) produces two OH radicals.

The photochemical processes following equations (4-7) have been identified as the controlling factors in the ozone budget of clean marine boundary layer air (Ayers et aI, 1992). Diurnal cycles of ozone depletion during the day and replenishment during the night, and vice versa for hydrogen peroxide H_2O_2, were found. The concentrations also varied seasonally, with average ozone content decreasing and H_2O_2 concentration increasing with the approach of summer, with this being ascribed to the increase in moisture content of the air along with enhanced solar intensity.

Dry deposition has been identified as a loss mechanism in the rural nocturnal boundary layer, though it is still not certain how significant it is. Shepson et al (1992) found that the ratio of the deposition velocity of O_3 to PAN, $V_d(O_3)/V_d(PAN)$, was 0.42 ± 0.19, smaller by a factor of 5-6 than that found in previous studies. This finding illustrates the need for more research in this area, because PAN (peroxyacetyl nitrate) is an important factor in the transport of NO_x and the change will influence results of the boundary-layer .concentrations of PAN in numerical models.

2.2.2 The Effects of Pollutants

The addition of methane, VOCs and CO to the "clean" atmosphere affect the concentration of ozone in a complex, often non-linear, manner which is not yet fully understood, but appear to increase the ozone concentration. The most important effect of these is the production of the HO_2 (hydroperoxy) and CH_3O_2 (methyl peroxy), which occurs as follows:

$$OH + CO \rightarrow CO_2 + H \tag{8}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{9}$$

$$CH_3 + O_2 \rightarrow CH_3O_2 \tag{10}$$

RO2 (alkyl peroxy) and peroxy radicals formed by other VOCs operate in the same manner as the methyl peroxy radical does. These radicals then react with NO to form NO_2 (see section 4), which produces ozone as shown above.

Contrary to first impressions, however, the reactions (8-10) are in fact non-linearly dependent on the ozone and OH concentrations through reaction (7). It is the attack by OH on CH_4 the VOCs, and CO (see sections 3, 5 and 6 respectively) which initiates the formation of the peroxy radicals which then form ozone, which reacts with water vapour to form more OH radicals to continue the process in a quasi-catalytic cycle. It is thus no surprise that smog-induced misery is at its highest in urban areas polluted by anthropogenic NO_x and VOC emissions on hot, sunny and humid summer days, when the OH recycling becomes highly efficient.

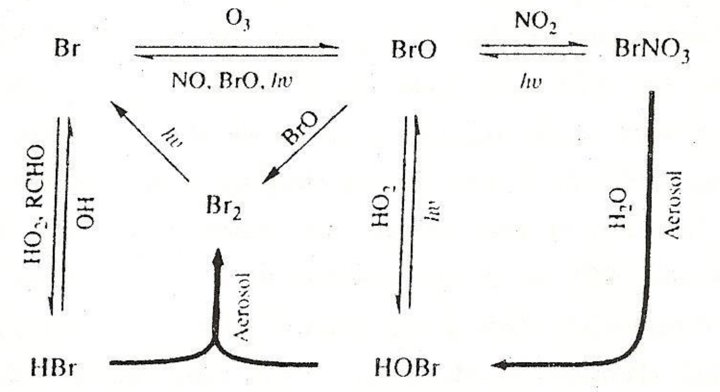
2.2.3 Sensitivity of Ozone to Precursors

It is well known that several types of VOC have natural sources, the most important of these being isoprene and monoterpenes that are emitted by foliage. (See section 5) Natural VOCs have been shown to be significant contributors to ozone production, accounting for 56% of all VOC contributions in a reference case and 88% in a case where natural background VOC concentrations were quadrupled. (McKeen et al, 1991) In urban/suburban regions during midday, it was found that biogenic hydrocarbons accounted for a significant fraction of the ambient HC reactivity, while in rural areas they contributed almost 90% of it. (Chameides et al, 1992) The background CO and CH_4 concentrations also play a significant role in the regionally averaged net ozone formation (McKeen et al, 1991), confirming the previous discussion.

The sensitivity of O_3 to reductions in either NO_x or VOCs at a given location depends on the extent of urban influence. The ozone in urban regions is more sensitive to VOC concentrations, while that in rural regions is more sensitive to anthropogenic NO_x. (McKeen et al, 1991; Chameides et al, 1992) Ozone in rural areas is less sensitive to rural isoprene emissions than ozone in urbanized areas, because the latter are highly sensitive to O3 which arrives from rural areas that are upwind. Overall, it appears that (at least in the Eastern United States) NO_x rather than VOCs is the limiting factor in ozone production. (McKeen et al, 1991; Chameides et al, 1992) Hence, NOx control appears to be the most effective way to reduce ozone concentrations over a whole area, as opposed to just the urban centres, with the added benefit that it reduces the average O_3 levels over a higher vertical extent.

Research for this paper did not uncover any information concerning the variation of tropospheric ozone chemistry with altitude. It is reasonable to assume, however, that the same reactions will occur at all levels, at rates and with results which depend on the concentrations of the reacting species and the temperature.

2.3 Heterogeneous Processes



Chemical cycling of inorganic bromine in the troposphere. Thin lines indicate gas-phase reactions; data for these reactions can be found in ref. 8. The aerosol reactions (1) and (2) discussed in the text are shown as heavy lines. The sequence of reactions $Br + O_3 \rightarrow BrO + O_2$ followed by $BrO + BrO \rightarrow 2Br + O_2$ represents a catalytic loss mechanism for ozone.

Figure 2: Chemical cycling of inorganic bromine in the troposphere
(From Fan and Jacob, 1992)

It has long been recognized that heterogeneous processes (that is, those occurring in gas and liquid phases) can play important roles in atmospheric chemistry (see Granier and Brasseur, 1992). The sulphuric acid aerosols which occur in the Arctic spring have been shown to provide a means of accelerating the destruction of tropospheric ozone by bromine by enabling the radicals Br and BrO to be rapidly recycled. (Fan and Jacob, 1992) Figure 2 illustrates this cycle.

Modelling tests indicate that the proposed mechanism is much more efficient at destroying ozone than is the gas-only reaction set, especially at high initial Br_x and low NO_x concentrations.

It has also been found that the addition of aqueous phase chemistry creates a significant effect upon O_3 and H_2O2 distributions in a modelled troposphere. (Jonson and Isaksen, 1993) Ozone levels were found to be reduced by 10-30%, with the largest reductions in the remote middle troposphere, but the peroxide changes were not readily predictable, depending strongly upon the pH of the cloud droplets.

2.4 Trends

There is general agreement that tropospheric ozone has been increasing, especially in the northern mid-latitudes, and will continue to do so, due to increases in CH_4, NO_x, CO and NMHCs. The exact amount of the increase continues to elude researchers, as it is dependent on the assumed values of its aforementioned precursors, on losses of stratospheric ozone, and water vapour concentrations, but it is likely on the order of 0.5-1.0% per year. (Thompson, 1992) Surface O_3 measurements in Antarctica have decreased, however, likely due to the depletion of the stratospheric ozone layer. (Thompson, 1992)

3. Tropospheric Methane

Methane is one of the most important trace components of the atmosphere. It is an effective greenhouse gas, causing approximately 15% of the greenhouse effect (Anastasi et aI, 1992, and others) and its final oxidation products are CO_2 and water vapour, both of which are also important greenhouse gases. Ozone is the most important by-product, and CO is a prominent intermediate product because it is a major sink for OR. Because the primary removal mechanism of CH_4 is oxidation by OH, any increase in the amount of methane present will decrease the OH concentration, thus increasing the concentrations of a host of other species which react with it, including ozone.

3.1 Methane Chemistry

The main reaction pathway for the oxidation of methane in the presence of NO_x is:

$$CH_4 + OH \rightarrow CH_3 + H_2O \tag{11}$$

$$CH_3 + O_2 \rightarrow CH_3O_2 \tag{12}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{13}$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \tag{14}$$

$$HCHO + h\nu \rightarrow H + HCO \tag{15}$$

$$HCHO + OH \rightarrow H_2O + HCO \tag{16}$$

$$HCO + O_2 \rightarrow HO_2 + CO \tag{17}$$

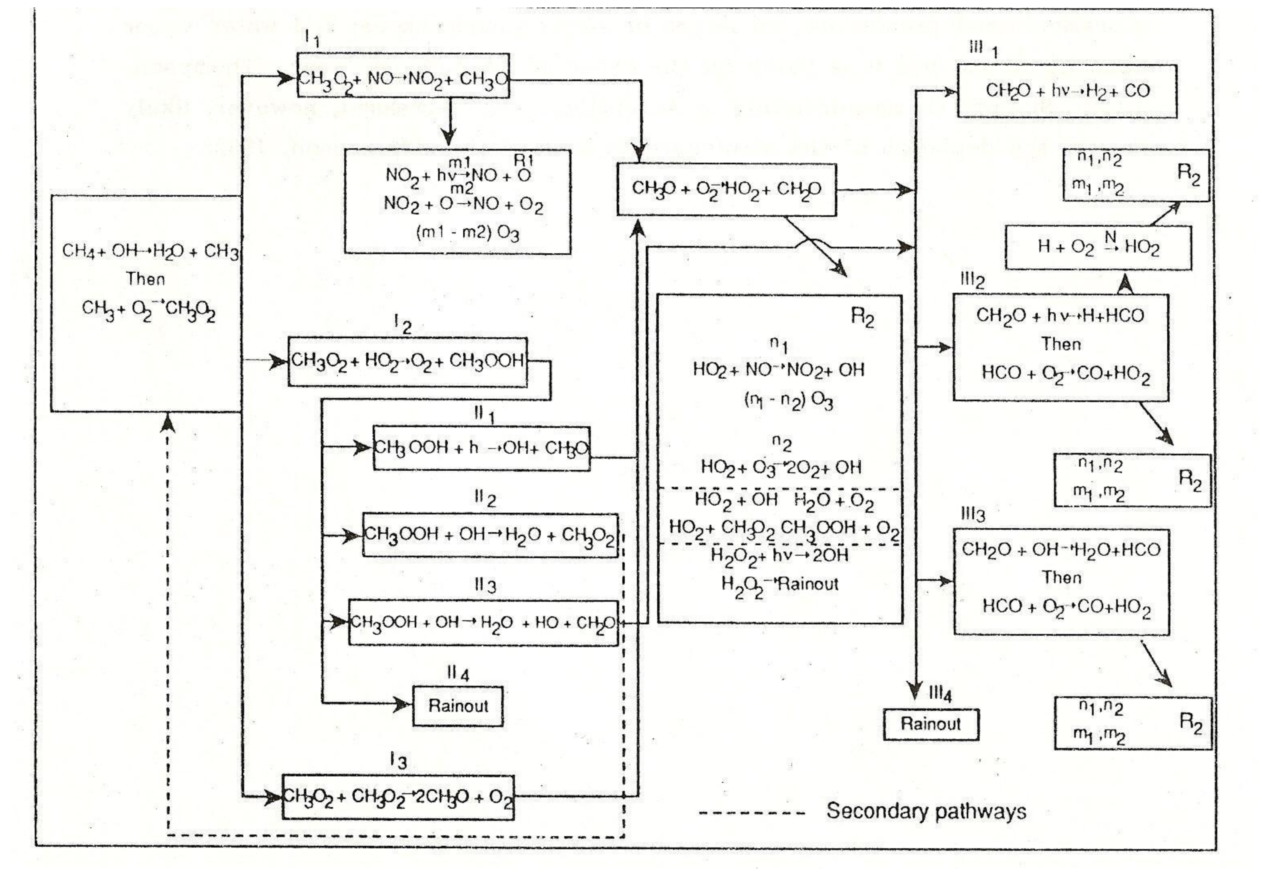


Figure 3: The Methane Reaction Pathways (From Tie et al, 1992)

The oxidation of CO is discussed in section 6. Figure 3, shown above, is a more complete illustration of the Methane Oxidation Cycle (MOC). The free H will react with O_2 as shown in equation (9). The HO_2 radicals created in (14) and (17) and the NO_2 created in (13) are likely to react further to create ozone, especially in polluted air (see section 2).

A numerical study of the MOC revealed that an average annual loss of 0.22 molecules of OH, and an average gain of 0.82 molecules of CO and 1.53 molecules of O_3 occur for each molecule of methane that is destroyed. If the new OH+CH_4 reaction rate coefficient of Vaghjiani and Ravishankara (1991) is used, the global annual average production rates of CO and O_3 are reduced by up to 23%. (Tie et al, 1992) It was also found that the seasonal cycles, spatial distributions and even the signs of the yield coefficients of OH, CO and O_3 were sensitive to the initial distributions of NO_x, HO_2 and OH. The MOC was shown to produce OH when HO_2 concentrations were relatively low, and destroy it when they were relatively high due to the favouring of different pathways (none was specifically mentioned). High NO_x and low HO_2 concentrations in winter tend to increase ozone and decrease CO production, when the MOC favours pathway I_1 (see Figure 3), while summertime low NO_x and high HO_2 have the opposite effect, when pathway I_2 and scavenging process II_4 are favoured.

Because of its short lifetime, the NO_x which catalyzes the methane oxidation is located mainly in the lower troposphere, and hence most of the decomposition and ozone formation will occur there. It is known that ozone is more effective as a greenhouse gas near the tropopause than near the surface (see section 2), but the IPCC's 1990 report did not take this into account, resulting in an overestimation of the indirect effects of CH_4 on global warming. (Lelieveld and Crutzen, 1992)

3.2 Methane Concentration Trends

The atmospheric lifetime of methane is about 10.5 years (IPCC, 1992). This has been called into question, though, by Vaghjiani and Ravishankara (1991), whose experiments revealed that the accepted value of the reaction rate for CH_4 and OH in the troposphere may be too large, with the result that methane's real lifetime may be up to 25% greater, and the flux smaller (by about 100 Tg CH_4 per year) than previous estimates. Even with the revised figures, it appears that the loss of 75 Tg per year of CH_4, needed to balance the budget, has yet to be explained.

It is generally accepted that the amount of CH_4 in the atmosphere has approximately doubled since pre-industrial times (e.g. Jacob, 1991; IPCC, 1992), but that the rate of increase has slowed in recent years (e.g. Madronich and Granier, 1992; Steele et aI, 1992). The rate of increase in methane has dropped from 14-27 ppb/year in 1978-1983 to 8-20 ppb/year (or about 1% per year; see Crutzen, 1991) since 1984 (Madronich and Granier, 1992). A possible cause for this is an increase in global OH concentrations, caused in turn by the change in the dissociation rate for ozone. (Madronich and Granier, 1992)

Because methane is oxidized only by OH, less OH is left to react with further CH_4 emissions, thus enhancing its lifetime and creating one of many atmospheric chemistry feedback mechanisms. Increasing CH_4 emissions contribute only 70% to the observed methane increase, with the remaining 30% attributed to decreased OH concentrations. (Lelieveld and Crutzen, 1992)

Switching from coal and oil to natural gas would reduce climate forcing, so long as the gas leakage could be kept under 4.3-5.7% for coal and under 2.4-2.9% for oil over a ten-year period. Over 100 years, a more frequently used time scale for estimating effects, the ranges increase to 10.5-12.0% for coal and 6.7-7.2% for oil. Since studies have revealed that gas losses are much less than 1% for several Western countries, switching to natural gas would be beneficial, but for places like the former USSR which have unknown, but probably large, losses, this may not be the case. (Lelieveld and Crutzen, 1992)

3.3 Sources and Sinks

CH_4 is emitted from biogenic sources such as wetlands, ruminants, rice paddies and biomass burning (i.e. forest or grassland fires), as well as by purely anthropogenic sources like coal mines, landfill sites, and oil and gas wells (Crutzen, 1991, and others). Since the methane oxidation cycle is fairly well understood, much of the current research on tropospheric methane involves attempts to quantify in better detail and accuracy its various sources and sinks to formulate better estimates of the global budget.

3.3.1 Desert Soils

Desert soil uptake, so far excluded from soil uptake estimates of CH_4, has been recently estimated to be 7 Tg per year. (Streigl et aI, 1992) It was found that increasing soil moisture causes a marked increase in CH_4 consumption, while lower soil temperatures were found to inhibit uptake. It was also found that if near-surface conditions are unfavourable for decomposition, methane will diffuse down to depths of up to two metres where it will be consumed under better circumstances. This finding was suggested as a reason for difficulties in relating CH_4 consumption to soil moisture and/or temperature at some fixed depth. (Streigl et aI, 1992)

3.3.2 Grasslands

Semi-arid grasslands could contribute 0.5-5.6 Tg per year to the global methane sink (Mosier et aI, 1991). Experiments conducted in the Colorado shortgrass steppe revealed that fertilization and cultivation decrease CH_4 uptake. (Mosier et aI, 1991) Methane absorption has far less diurnal and spatial variation than nitrous oxide emissions, but the two appear to be inversely related with moisture content. N_20 flux from the soil of all sites was highest immediately after precipitation, while CH_4 absorption was "at its lowest levels, but during very dry conditions both processes declined until it rained again. (Mosier et aI, 1991)

3.3.3 Rice Paddies

Although there is considerable uncertainty to the contribution, it is currently estimated that up to 20% of the global CH_4 flux is from rice paddies. (Anastasi et aI, 1992) A model incorporating 1989 per capita rice production and population increase statistics in 94 rice-producing countries predicts that the flux will increase from the 1990 level of 97 Tg per year to 145 Tg per year in 2O25. The uncertainties are large, however, due to questions about geographical variations in release rates and factors such as fertilization and soil temperatures. (Anastasi et aI, 1992)

3.3.4 Tropical and Boreal Wetlands

An estimate of the total methane emission from the flooded forest region of the Congo river basin was made as 1.6-3.2 Tg per year, (Tathy et aI, 1992), but overall, soils in tropical forest regions are net sinks of methane in spite of intense, but size-limited, sources. (Delmas et aI, 1992) Emission from termite nests appeared to be only a minor component of the flux in this case, which may be due to the presence of methane-oxidizing bacteria.

Emissions from the boreal wetlands of Canada are on the order of 0.15 Tg CH_4 per year, with beaver ponds, thicket swamps and bogs being the primary emitters. (Roulet et aI, 1992) As with the tropical and desert areas, the moisture content was the key to the amount of gas released, with peat and sediment temperature modulation. This value is about an order of magnitude less than a previous estimate, made for the entire boreal region in the northern hemisphere, would have given the Canadian wetlands.

The following values are summarized from Crutzen, 1991. The imbalance is represented by the annual increase value.

Source/sink Name	Amount
Reaction with OH	-420 ± 80 Tg
Uptake by soils	-30 ± 15 Tg
Stratosphere	-10 ± 5 Tg
Coal mines	25 ± 5 Tg
Methane	~5 Tg
Oil & gas distribution	70 ± 15 Tg
Ruminant animals	~80 Tg
Landfills	50 ± 20 Tg
Oceans and termites	~30 Tg
Biomass	30 ± 15 Tg
Wetlands & rice paddies	215 ± 50 Tg
Annual increase in CH_4	45+5 Tg

The following is a summary of findings from other papers.

Source/Sink Name	Amount	Source
Rice paddies	~100 Tg	Anastasi et al, 1992
Canadian boreal wetlands	~0.15 Tg	Roulet et al, 1992
Desert soils	~-7 Tg	Streigl et al, 1992
Semi-arid grassland	-0.5 to -5.6 Tg	Mosier et al, 1991
Flooded forests of the Congo basin	1.6 – 3.2 Tg	Tathy et al, 1992

(The net from the entire Congo forest region is actually absorption.)

4. Nitrogen Oxides (NO_x)

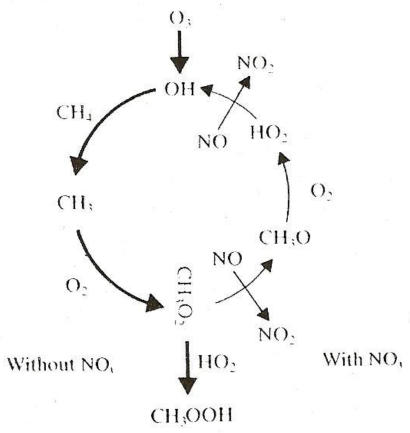
The nitrogen oxides NO and NO_2 are referred to collectively as NO_x because they are in a state of rapid photochemical equilibrium during daylight (Jacob, 1991). For ease of reference, important reactions involving NO_x are repeated below.

$$NO_2 + h\nu \rightarrow O + NO \tag{1}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{18}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{13}$$

Although not greenhouse gases themselves, they are very important because they act as catalysts in many of the tropospheric chemical reactions, including the decomposition of methane and VOCs. (Jacob, 1991) As has been mentioned in section 2, the production of ozone is dependent on the ambient concentrations of NO_x. They also control the concentration of the OH radical, with an increase in NO_x tending to cause an increase in OH.



Essential steps in tropospheric methane oxidation. The heavier arrows on the left-hand side of the diagram indicate the steps that can occur in the absence of NO_x. With NO_x present, the processes on the right-hand side can close a loop, with regeneration of OH and oxidation of NO to NO_2

Figure 4: Illustration of the Importance of NOx to the Methane Oxidation Cycle. (From Wayne, 1991)

4.1 Sources and Sinks in the Lower Troposphere

Sources and sinks of NO_x have for the most part been identified. The primary biogenic source is emission from soils, while the primary anthropogenic source is from combustion of fossil fuels and biomass. (Jacob, 1991) Creation by lightning is a possibly significant, but still uncertain, factor and transport from the stratosphere a small one (Jacob, 1991; Dignon, 1992). The primary sink is oxidation to HNO_3, which is lost by wet and dry deposition to the surface, with the wet deposition as the so-called acid rain and/or snow. Reaction with hydrocarbons to form organic nitrates such as PAN (peroxyacetyl nitrate) which are then deposited is another sink, but the stability of PAN at low temperatures allows for significant transport of NO_x away from the sources. Due to its reactivity, the generally accepted lifetime of lower tropospheric NO_x is approximately 1 day (Jacob, 1991 and others).

4.1.1 Anthropogenic Emissions

The importance of anthropogenic sources was made evident by the detection of a large gradient in NO_x concentrations between forest, rural and urban areas in a recent study. (Chameides et aI, 1992) Even though the sources are relatively well-known, the amount produced by each is still not. A global database of annual NO_x (and SO_x) emissions from fossil fuel combustion, based upon estimates of fuel consumption and population distribution of various countries, revealed that there is a large spatial variation in both emissions, with over 90% of each gas being emitted in the Northern Hemisphere. (Dignon, 1992) Not surprisingly, the United States, former Soviet Union, and China were the three largest NO_x emitters, producing an estimated 6.4, 4.4, and 1.7 Tg N respectively in 1980. The highest per capita emitters were found to be oil-producing nations, with Qatar, Netherlands Antilles, and the United Arab Emirates producing 78, 51, and 49 kg N per person respectively.

4.1.2 Lightning

In regions of very high temperature, such as a vehicle engine, nitrogen gas is oxidized to NO and NO_2, so it is also expected that the high temperatures generated by lightning discharges would also be a source of NO_x, Estimation of NO_x produced this way on a global or regional scale is very difficult, in part because the method of production is not yet fully understood. Experimental work has revealed that the NO/NO_x ratio produced by a spark varied from 0.75 to 0.95, depending on the discharge energy, that little ozone is produced except at low discharge energies, and that no HNO_3 is produced when the air is humidified. NOx production appears to occur in the hot regions of the discharge as a result of ohmic heating of the air, rather than by a shock wave. (Franzblau, 1991)

4.1.3 Soils

NO emissions from soils depend on a large number of variables, including vegetation cover, soil temperature, type, and nitrate and water content. (Williams et aI, 1992; Muller, 1992) Croplands, especially corn fields, are important NO sources, likely due to fertilization practices (Williams et aI, 1992). On the other hand, undisturbed areas emit relatively little NO to the atmosphere, with amounts from grasslands, forests and wetlands listed in decreasing order of importance. The dependence on soil temperature implies a temporal variability to add to the spatial one, thus introducing large uncertainties into any estimate of soil NO emissions. (Williams et aI, 1992; Muller, 1992)

4.1.4 Surface Fluxes

Modelling the effect of air chemistry on surface fluxes of NOx revealed that emission of NO at the surface strongly influences NO flux near the surface, but chemical reactions tend to determine the flux a few metres up. (Gao et aI, 1991) The fluxes of NO and NO_2 can vary strongly with height, but the effect of rapid reactions on O_3 was found to be small relative to its total flux. The effects of hydrocarbons on the reactants were ignored, however, which could bring the applicability of their results into question as many VOCs are highly reactive, especially the biogenic compound isoprene.

4.2 Sources of Upper Tropospheric NO_x

Aircraft emissions (averaging about 30%) and fast, direct transport of polluted boundary layer air were found to be the major sources of NOx in the upper troposphere for the band 400N to 500N in June. (Ehhalt et al, 1992) stratospheric input was found to be significant, but not dominant, while lightning played a small part, with an emission rate estimated at $0.3x10^6$ Tg/year for the modelled region. Aircraft emissions of NO_x, though small on a global scale, were important because of the fact that they are introduced directly at the upper tropospheric level, without the potential elimination by other reactions inherent in advective processes. This model did not allow for feedback effects of NO_x on O_3 and OH, so estimates of increased emissions on the latter two species were not possible.

4.2.1 Emissions by Aircraft

The impact of increasing NO_x emissions by aircraft, which have cruising heights of 8-12 km (IPCC, 1992 and others), on tropospheric and stratospheric ozone concentrations has been of concern for some time. In the 1970's the concern was that new supersonic aircraft with cruising levels in the stratosphere would destroy ozone with their NO_x and water vapour emissions. (Johnston et al, 1989) This ozone depletion is highly altitude-dependent, and they found that the altitude at which the greatest ozone reduction would occur is 25-28 km. The latitude of injection also determines the amount of O_3 depletion, with the greatest loss occurring in tropical regions.

Concern about this source of ozone loss had declined in recent years, since high-flying passenger jets have not proliferated to any great extent, and is further reduced by the finding that a significant amount of NO_x is converted to HNO_3 by the heterogeneous reaction

$$N_2O_{5(g)} + H_2O_{(l)}(sulphate\ aerosol) \rightarrow 2HNO_{3(g)}$$

in the stratospheric aerosol layer where most of the flights would occur. (Bekki et al, 1991) The ozone column loss predicted by their model was reduced by nearly half by including this process, and increasing the background aerosol concentrations, as for a volcanic eruption, decreased NO_x and hence O_3 loss even further.

As a result, the focus has shifted to the effect of aircraft emissions on the upper troposphere. The odd-nitrogen component of these emissions has been shown to be primarily NO and NO_2, with concentrations as high as 780 and 150 ppbv. (Arnold et al, 1992)

Calculations indicate that upper tropospheric aircraft emissions could be an order of magnitude more efficient at producing ozone than surface emissions, and furthermore the increased ozone would be at levels where its greenhouse effect would be greater. (IPCC, 1992; Lacis et al, 1990) It has been estimated that radiative forcing of surface temperatures is about 30 times more sensitive to aircraft than to surface emissions of NO_x (Johnson et al, 1992). Adding the 1987 civil aircraft emissions to the atmosphere modelled by Beck et al (1992) resulted in a 12% increase in O_3, a 40% increase in NO_x and a 10% increase in OH concentrations between 8 and 12 km. Increasing the NO_x emissions resulted in nearly proportional increases in ozone at these levels. An important source of the uncertainty in these results is caused by their sensitivity to the amount of background NOx produced by lightning.

5. Hydrocarbons

Non-methane hydrocarbons (NMHC), also known as volatile organic compounds (VOCs), are important components in the chemistry of the troposphere. Because they are attacked by OH, their presence will modulate the OH concentration and hence the progress of many other reactions (Jacob, 1991). The decomposition of NMHCs produces important species like ozone, CO, and PAN when organic radicals react with NO_x. Secondary aerosols are also by-products of VOC reactions (Field et al, 1992), and many

VOCs or their by-products are considered health hazards (e.g. Jacob, 1991; Field et aI, 1992). The large number of VOCs, their widely varying reactivities, and the large number of possible products and hence reaction paths mean that much more research is required before their total effect on the troposphere can be accurately assessed.

5.1 Chemistry

The basic steps for alkane decomposition are listed below. If we define a generic alkane as RH, then:

$$RH + OH \rightarrow R + H_2O$$

$$R + O_2 \rightarrow RO_2$$

$$RO_2 + NO \rightarrow RO + NO_2$$

$$RO \rightarrow R' + R''CHO$$

$$RO + O_2 \rightarrow R'R''CO + HO_2$$

where R' and R" are daughter alkyl radicals or groups. (Wayne, 1991) Since methane is the simplest alkane, it is no surprise that its oxidation cycle (see section 5) is similar to this. The aldehydes (R"CHO) and ketones (R'R"CO) can be photolyzed or become further oxidized in thermal reactions. (Wayne, 1991)

Alkenes appear to react with OH in an addition mechanism, forming radicals which behave similarly to alkyl radicals. Wayne (1991) used the example of propene:

$$OH + CH_3CHCH_2 \rightarrow CH_3CHCH_2OH$$

$$CH_3CHCH_2OH + O_2 \rightarrow CH_3CH(O_2)CH_2OH$$

$$CH_3CH(O_2)CH_2OH + NO \rightarrow CH_3CH(O)CH_2OH + NO_2$$

$$CH_3CH(O)CH_2OH \rightarrow CH_3CHO + CH_2OH$$

$$CH_2OH + O_2 \rightarrow HCHO + HO_2$$

Ozone is produced by the above two production systems directly from the NO_2 (sections 2 and 4) and indirectly from HO_2 in the presence of NOx (section 2).

Isoprene and two of its oxidation products, methacrolein and methyl vinyl ketone, were measured in rural Alabama between mid-June and mid-July of 1990. The mixing ratios of the two products were found to be highly correlated; on average the former was the greater during the night and the latter during the day. (Montzaka et aI, 1993)

In the urban-influenced nocturnal boundary layer, it has been found that secondary production of aldehydes from alkanes and alkenes can exceed their direct emission by gasoline-powered vehicles. If a large shift in the future to vehicles powered by methanol and/or natural gas were to occur, this finding could be reversed. (Altschuller, 1993) In the early morning hours, OH reactions with alkanes make significant contributions to the higher-weight aldehydes, but overall the contribution of aldehydes from alkanes was much lower than that from alkenes. This could be of critical importance to models, because it has been shown that predictions of ozone and H_2O_2 are sensitive to the aldehyde content of the morning air. (Altschuller, 1993) It appears from studies of VOCs in urban plumes that aromatic compounds may have removal mechanisms other than OH chemistry (Blake et aI, 1993), another factor which is of importance for modelling.

5.2 Sources and Sinks

Total biogenic hydrocarbon emissions amount to about 500 Tg per year, about half of which is isoprene, 147 Tg is monoterpenes, and the rest a variety of paraffins and aromatics (Müller, 1992), while the total global anthropogenic emission rate is 110 Tg per year, a value about 10% lower than previous estimates. (Piccot et aI, 1992) Reaction with OH is the dominant pathway for decomposition for most hydrocarbons, and deposition may occur by either wet or dry processes. (Field et aI, 1992) The observed seasonal fluctuation of VOCs can be linked to the OH seasonal cycle, and reaction with the NO_3 radical may also be important, especially in the winter when OH chemistry becomes less dominant. (Penkett et aI, 1993)

5.2.1 Anthropogenic Emissions

The United States, former USSR, China, India and Japan are the biggest VOC emitters. Fuel wood combustion and savanna (i.e. biomass) burning produce the most VOCs, followed by the production and use of gasoline, refuse disposal, and organic chemical and rubber manufacturing. (Piccot et aI, 1992) Many anthropogenic sources, such as wood burning, vary widely in magnitude with the seasons. VOC levels are generally highest in the Northern Hemisphere's urban locations during winter. (Field et aI, 1992)

5.2.2 Biogenic Emissions

Although human activities, primarily related to the combustion of fossil fuels and biomass burning, are usually fingered as the primary source of VOCs, there is also a considerable biogenic source of highly reactive compounds. Isoprene, terpenes and other molecules are produced in large quantities by plants, especially coniferous trees, and possibly even their roots. (Janson, 1993) Emissions in the United States are up to 1.45 times greater than anthropogenic sources in that country, (Piccot et aI, 1992) and have been identified as important rural ozone precursors. Emissions from some coniferous trees have been found to have temperature- and humidity-independent seasonal cycles of volume and composition that appear to coincide with variations in photosynthetic activity and needle growth rate. (Janson, 1993) Wetted needles were also found to emit more terpenes, and at different ratios, than dry ones. (Janson, 1993)

6. Carbon Monoxide

Carbon monoxide is not a radiatively active gas, but it plays a key role in atmospheric chemistry because its primary sink, accounting for 80-90% of lost gas, is through oxidation by OH (Novelli et aI, 1992). Thus it, like methane, acts as a regulator of tropospheric OH and through it a host of other species. CO is also lost to the stratosphere and to soil uptake (Novelli et aI, 1992).

6.1 Chemistry

The oxidation of CO by OH,

$$OH + CO \rightarrow CO_2 + H \tag{8}$$

is interesting from the kinetics angle because its temperature dependence is not of the Arrhenius form and because it is also pressure dependent, with the apparent rate coefficient increasing with pressure. (Wayne, 1991) The sequence

$$OH + CO \leftrightarrow HOCO^* \tag{19}$$

$$HOCO^* \rightarrow H + CO_2 \tag{20}$$

$$HOCO^* + M \rightarrow HOCO + M \tag{21}$$

$$HOCO + O_2 \rightarrow HO_2 + CO_2 \tag{22}$$

offers a pressure-dependent pathway in (21) and (22). (Wayne, 1991) The one product may be HO_2 rather than H, but reaction (9) (section 2.2.2) would likely occur to produce HO_2 anyways.

6.2 Distribution

CO mixing ratios are greatest in the high latitudes of the Northern Hemisphere and decrease as one moves southwards. Mixing ratios vary seasonally, as does the difference in CO levels between the hemispheres, with the amplitude of the cycle being greatest in the Northern Hemisphere. (Novelli et aI, 1992) The background CO concentrations in the hemispheres also appear to be increasing at different rates.

6.3 Sources and Sinks

Carbon monoxide is emitted by soils, vegetation and termites (Müller, 1992), biomass burning, and fossil fuel consumption (Jacob, 1991), as well as being produced in the atmosphere by oxidation of hydrocarbons. (Jacob, 1991) Human activities are responsible for up to 75% of surface emissions of CO, CH_4, SO_x and NO_x, and about two thirds of the total atmospheric production of CO. (Müller, 1992) CO production is dominated by biomass burning in the tropics (Jacob, 1991), and by industrial sources in the Northern Hemisphere (Novelli et aI, 1992). Production by vegetation may be locally important too, as up to 80% of the total wet-season CO source in the Amazon basin appears to be from biogenic sources (Müller, 1992).

6.4 Budget Estimates

The oxidation of biogenic NMHC contributes about 300 Tg CO to the global CO budget, which is much lower than previous estimates, Anthropogenic NMHC oxidation adds another 180 Tg. (Müller, 1992) Oxidation of methane produces about 800 Tg of CO per year, at an apparent efficiency of about 80-90%. Müller's estimate of global CO production is 2500-3000 Tg per year, in general agreement with previous findings. The total source strength in the Northern Hemisphere is approximately twice that of the Southern. (Novelli et aI, 1992)

7. Halocarbons

The term halocarbon refers to a large group of almost exclusively man-made substances. These gases are derived from hydrocarbons by partially or completely replacing the hydrogen atoms with one or more of the halogens fluorine, chlorine and bromine. Aside from their capacity to destroy stratospheric ozone, most of the halocarbons are also efficient greenhouse gases. This, in combination with their long lifetimes, gives these compounds the potential to seriously affect the Earth's radiation balance in the future. In order to better assess the potential impact, research is continuing on the rates of reaction and mechanisms of destruction of these species, as well as their effects upon the ozone layer.

Fully-halogenated chlorofluorocarbons (CFCs) have been widely used as industrial solvents, blowing agents for foam products, and in refrigeration systems. Others, which contain bromine and are known as halons, are used in fire-fighting. Efforts are being made to find substances which will perform as well as the CFCs or halons, but will have much shorter lifetimes and thus be less likely to cause harm. Partially hydrogenated compounds like hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluoroethers (HFEs) are generally believed to be excellent prospective replacements because the hydrogen atom(s) are susceptible to attack by OH radicals.

A table of CFC and CFC replacement lifetimes can be found at the end of the section, compiled from several sources. The vast number of CFCs and potential replacements has forced researchers to use models to estimate the lifetime of many gases (Cooper et aI, 1992, 1993). Their results appear to be respectable; one gas, CF_3CHFCF_3, had a numerically predicted lifetime of 63 years, compared to a lab-estimated life of 42 years. (Nelson et aI, 1993)

7.1 Hydrofluorocarbons and Hydrofluoroethers

HFCs and HFEs are of special interest because they do not contain any Cl or Br atoms, and the C-F bond is strong. Rough numerical estimates of lifetimes and reaction rates for a large number of molecules revealed that for both HFEs and HFCs, the more hydrogen atoms there are in a molecule, the shorter its lifetime, though there is no linear correlation. (Cooper et aI, 1992, 1993) Fluorinated ethers with at least 1 carbon atom attached to 2 or 3 hydrogen atoms appear to have significantly shorter lifetimes than comparable fluorinated alkanes, whereas those with carbon atoms bonded to at most 1 hydrogen have slightly longer lifetimes than their corresponding alkane HFCs. A correlation between the location of the 0 atom relative to the hydrogens and the estimated molecular lifetime was also found.

7.2 Sinks

Fully halogenated species are chemically almost inert in the troposphere, and hence are able to be transported into the stratosphere by dynamical processes. The species with some CI and/or Br are photolyzed by ultraviolet radiation, releasing these atoms which then proceed to efficiently decompose stratospheric ozone through catalytic cycles. Bromine-containing substances have large UV-absorption cross-sections and some can even be dissociated by tropospheric UV radiation. (Orkin and Khamagorov, 1993a,b) Fully fluorinated species, however, are so stable that their only significant sink is dissociation by solar Lyman-a radiation (121.6 nm wavelength in the vacuum ultraviolet region) in the mesosphere and thermosphere, and they may have lifetimes on the order of centuries. (Ravishankara et aI, 1993)

Carbonyl halides and haloacetyl halides have been identified as oxidation intermediates of HCFC molecules. (De Bruyn et aI, 1992) They are relatively inert to further homogeneous reaction, so absorption of these species by water droplets and subsequent rainout represent a tropospheric sink for their parent compounds. It was found that the uptake rates for CF_2O, CF_3CFO and CF_3CClO are low enough that the ozone depletion potential of their parent HCFCs will not be affected by the loss.

7.3 Methyl Chloroform (CH_3CCl_3)

Methyl chloroform is solely anthropogenic in origin with well-quantified sources; its primary sink is reaction with OH. These facts have been exploited to estimate the global concentration of OH radicals in the troposphere. It is also a significant source of the chlorine which destroys ozone in the stratosphere (Tie et aI, 1992) and is a minor greenhouse gas (Ramanathan et aI, 1987). A source of concern for modelling OH concentrations has been the discovery of a small ocean sink for this gas. Inclusion of the sink in a global three-dimensional chemical tracer model did not improve the simulation of the observed interhemispheric gradient of CH_3CCl_3, however. (Tie et aI, 1992) Transport was found to dominate the seasonal cycle of methyl chloroform in the Northern Hemisphere, but was less important in the Southern. The lifetime of CH_3CCl_3 is between 5.42 years (Mellouki et aI, 1993) and 5.7 years. (Tie et aI, 1992; Prinn et aI, 1992) Over the time 1978-1990, the global concentration increased at an average rate of 4.4±0.2% per year. (Prinn et aI, 1992)

7.4 Lifetime Estimates for Various Halogenated Species

The tables below list the lifetimes of various halocarbons, plus SF_6, along with the reference the lifetime came from. Some have been examined in more than one paper, in which case all values are quoted. The naming convention for CFCs and HCFCs is as follows: the hundreds digit is the number of carbons minus 1, the tens digit is the number of hydrogens plus one, and the units digit is the number of fluorenes. Anything left over (i.e. to "saturate" the CFC) is chlorine. If bromine is in the CFC molecule, Bx is added to the end of the number, where x is the number of atoms. Halons are fully halogenated (former) hydrocarbons containing at least one Br atom. The four digits in the number represent the number of C, F, Cl, and Br atoms in the molecule respectively. Note that for C_2 and greater compounds, several different molecules may have the same number.

7.4.1 C_1 Compounds and SF_6

Formula	Life (yrs)	Reference	Name
CCl_4		(9)	Carbon tetrachloride
$CFCl_3$		(9)	CFC-11
CF_2Cl_2		(9)	CFC-12
CF_3Cl	400; 640	(9); (1)	CFC-13
CF_4	>500; >50,000	(9); (1)	CFC-14, carbon tetrafluoride
CF_3Br	77	(9)	Halon 1301
$CHCl_3$	0.7	(9)	HCFC-20
CHF_2Cl	12.6; 15.8	(6); (9)	HCFC-22
CHF_2Br	5.5	(7)	HCFC-22B1
CHF_3	182	(4)	HCFC-23
CH_2Br_2	0.41	(8)	HCFC-30B2
CH_2F_2	4	(4)	HCFC-32
CH_3F	2	(4)	HCFC-41
CH_3Br	1.7 – 1.9	(2)	Methyl Bromide
SF_6	3200	(1)	Sulphur Hexafluoride

7.4.2 C_2 Compounds

Formula	Life(yrs)	Reference	Name
C_2F_3Cl	110	(9)	CFC-113
CF_2ClCF_2Cl	300; 220	(1); (9)	CFC-114
CF_3CF_2Cl	1700; 550	(1); (9)	CFC-115
C_2F_6	>10,000; 550	(1); (9)	CFC-116
$CF_2ClCHCl_2$	1.05	(6)	HCFC-122
$CF_2ClCHFCl$	4.8; 1.71	(6); (9)	HCFC-123
$CF_2ClCHClBr$	1.2	(7)	HCFC-123B1
CF_3CHFCl	6.9	(9)	HCFC-124
CF_3CHFBr	3.3	(7)	HCFC-124B1
CF_3CHF_2	26; 40.5	(4); (9)	HCFC-125
CF_3CH_2Br	4.4	(10)	HCFC-133B1
CF_3CH_2F	15.5; 12.9	(4); (6)	HCFC-134
CH_3CCl_3	5.7±0.3; 6.1	(3); (9)	HCFC-140 (Methyl Chloroform)
CH_2FCHF_2	2	(4)	HCFC-143
CH_3CF_3	45	(4)	HCFC-143
CH_2FCHF_2	0.6	(4)	HCFC-152
CH_3CHF_2	1.0	(4)	HCFC-152
CH_3CH_2F	0.2	(4)	HCFC-161

7.4.3 C_3 Hydrocarbons

Formula	Life (yrs)	Reference	Name
CF_3CHFCF_3	63; 42	(5); (10)	HFC-227
$CF_3CH_3CF_3$	77	(5)	HFC-236
$CF_3CHFCHF_2$	10	(5)	HFC-236
$CHF_2CF_2CHF_2$	5	(5)	HFC-236
$CF_3CF_2CH_3$	7	(5)	HFC-245
$CF_3CH_2CHF_2$	7	(5)	HFC-245
$CHF_2CF_2CH_2F$	2	(5)	HFC-245
$CF_3CH_2CH_2F$	2	(5)	HFC-254
$CHF_2CF_2CH_3$	1.3	(5)	HFC-254
$CHF_2CF_2CH_3$	16	(5)	HFC-254
$CHF_2CH_2CHF_2$	1.3	(5)	HFC-254
$CF_3CH_2CH_3$	1.4	(5)	HFC-263
$CF_3CH_2CH_2CF_3$	12	(5)	HFC-356

7.4.4 Long-Chain HFCs

Formula	Life (yrs)	Reference	Formula	Life (yrs)	Reference
C_4F_{10}	2600	(1)	C_6F_{14}	3100	(1)
C_5F_{12}	4100	(1)	$(CF_3)_2c\text{-}C_4F_6$	2900	(1)
$c\text{-}C_4F_8$	3200	(1)	**Note:** c- means cyclic		

7.4.5 Hydrofluoroethers

Formula	Life (yrs)	Reference	Formula	Life (yrs)	Reference
$CF_3CF_2OCHF_2$	48	(5)	$CF_3CH_2OCH_2F$	0.1	(5)
$CF_3CH_2OCHF_2$	1.6	(5)	$CF_3CHFOCF_2$	38	(5)
$CF_3CHFOCHF_2$	9	(5)	CF_3CHOCH_3	< 0.1	(5)
$CF_3OCF_2CH_3$	30	(5)	$CF_3OCF_2CHF_2$	29	(5)
$CF_3OCH_2CH_2F$	0.8	(5)	$CF_3OCH_2CH_3$	0.3	(5)
$CF_3OCH_2CHF_2$	2	(5)	$CF_3OCHFCHF_2$	8	(5)
$CH_2FOCF_2CHF_2$	1.2	(5)	CH_2FOCF_3	6	(4)
$CH_2FOCH(CF_3)_2$	1.5	(4)	CH_2FOCH_2F	0.3	(4)
CH_2FOCHF_2	0.3	(4)	$CH_3OCF_2CF_3$	0.9	(5)
$CH_3OCF_2CHF_2$	0.4	(5)	CH_3OCF_3	0.7	(4)
CH_3OCH_2F	0.O2	(4)	CH_3OCHF_2	0.1	(4)
$CHF_2OCF_2CH_2F$	10	(5)	$CHF_2OCF_2CH_3$	8	(5)
$CHF_2OCF_2CHF_2$	14	(5)	CHF_2OCF_3	85	(4)
$CHF_2OCH_2CHF_2$	0.5	(5)	CHF_2OCHF_2	7	(4)

References

(1) Ravishankara et al, 1993
(2) Singh and Kanakidou, 1993
(3) Tie et al, 1992
(4) Cooper et al, 1992
(5) Cooper et al, 1993
(6) Orkin and Khamagorov, 1993a
(7) Orkin and Khamagorov, 1993b
(8) Mellouki et al, 1992
(9) IPCC, 1992
(10) Nelson et al, 1993

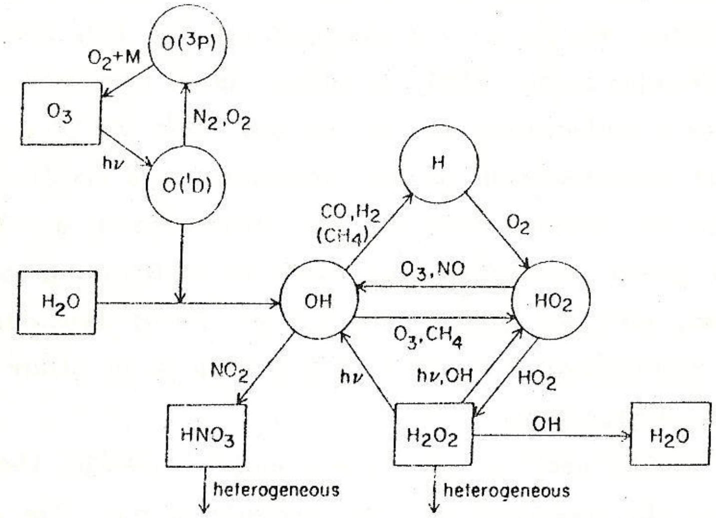
8. OH Radicals

Of all the trace gas constituents of the atmosphere, the OH radical is probably the most important because of its oxidation activity. Just as water is occasionally described as the "universal solvent", OH can be described as the "atmospheric detergent" for its capacity to attack and "clean out" a large proportion of other trace gases. The key to OH's effectiveness as an oxidant is that it is partially recycled, with the reaction $\mathrm{NO} + \mathrm{HO_2} \rightarrow \mathrm{NO_2} + \mathrm{OH}$ being the most important. (Poppe et aI, 1993) In many cases, the rate-determining step for the removal of a molecule is in its reaction with OH (Poppe et aI, 1993). Unfortunately, its concentration in the troposphere is so dilute that it is extremely difficult to measure directly with instruments, so that estimates of local, regional or global concentrations must be made using models and some sort of tracer gas, such as methyl chloroform. These methods lack the precision and certainty required for accurate predictions of other gases.

8.1 Dependence on Precursors

Poppe et al (1993) used a numerical model to examine the effects of various precursors on the hydroxyl radical concentrations. The results are summarized below.

- The main source of diurnal OH variability is the solar flux, which produces the radical by photodissociation of ozone and formaldehyde.
- NO_x governs the overall behaviour of OH in a given reaction, but the competing influences of NO and NO_2 cause a relatively small increase in the [OH] with an increase of [NO_x]. As an example, a change in [NO_x] from 10 ppt to 1 ppb resulted in a modelled increase in [OH] by only a factor of four. For high [NO_x], the increase in [OH] with water vapor is linear; for low and medium [NO_x] it is weaker than linear.
- PAN indirectly influences [OH] according to its net chemical change, d[PAN]/dt, in a complex way.
- Since ozone alters the [NO]/[NO_2] balance, which in turn affects production or destruction of OH, the dependence of [OH] on [O_3] is non-linear, but in general increasing [O_3] increases [OH].
- Formaldehyde's presence acts to increase [OH], especially in the presence of high [NO_x]. In low NO_x concentrations, the recycling by radicals has its efficiency lowered, resulting in very small increases in [OH].
- Carbon monoxide and hydrocarbons act to deplete OH; as their concentration increases, that of OH will decrease. The amount of the decrease will depend on the recycling efficiency of radicals, which is greater for greater [NO]. For high enough [NO], [OH] is almost independent of [CO], and for very low [NO] it is inversely proportional to it.



. Major chemical reactions affecting odd hydrogen (OH, H, HO_2, H_2O_2) in the troposphere.

Figure 5: Chemical reactions involving odd Hydrogen in the Troposphere (From Logan et al, 1981)

8.2 Trends

Determining a trend in OH concentration is just as difficult as measuring it currently. The values reported so far are model-dependent, and also depend on assumed emissions and background concentrations of CH_4, NO_x, CO and VOCs. Other influences on OH concentration include stratospheric ozone depletion, climate warming, and perturbations near the tropopause due to aircraft exhaust. The consensus of a number of models is that OH concentrations have decreased globally since the start of pre-industrial times, with a continuing loss likely over regions of the Southern Hemisphere where NO_x concentrations are low. Two- and three-dimensional model calculations indicate OH has decreased 10-30% since the period 1200 to 1800 AD. (Thompson, 1992)

In contrast, Prinn et al (1992) deduced a 1.0±0.8% increase in global OH concentration from methyl chloroform data gathered from 1978-1990, though their weighting scheme favoured the tropical lower troposphere. An increase in the dissociation rate of ozone in the troposphere due to a decrease in stratospheric ozone will act to increase the OH concentration, perhaps by as much as 4% per decade, which could explain this finding. (Madronich and Granier, 1992) The absolute value of the change is expected to be less than 0.5% per year, though. (Thompson, 1992)

8.3 Global Distribution

Along with methyl chloroform, another trace gas used to deduce the global concentration of OH is ^{14}CO, formed by the oxidation of HC created by cosmic radiation. It is a more sensitive indicator of OH concentration than other tracer gases that are being used because it has a lifetime of about 1 month. (Brenninkmeijer et al, 1992) Southern Hemisphere ^{14}CO concentrations are up to 40% lower than those for comparable latitudes north of the equator, leading to the conclusion that, in spite of complicating factors such as ^{14}CO release from nuclear power plants and possibly uneven ^{14}CO recycling from biogenic sources, OH concentrations were lower in the Northern Hemisphere. Antarctic stratospheric ozone loss, allowing more UV radiation to create more OH, and increased aerosol concentration in the north which would decrease UV flux at the surface and affect OH, could be reasons for the distribution pattern. (Brenninkmeijer et al, 1992)

8.4 Sources of OH

When ozone reacts with some terpenes in the atmosphere, including isoprene, OH radicals are formed. The position of the C=C bond in the molecule, whether internal or terminal, appears to determine the OH yield, with the internal bond species generating the highest yields. (Atkinson et al, 1992) The reaction of O_2 $(b^1 \sum_g^*)$ the second electronically excited state of oxygen, could be an additional source of OH, especially in the upper troposphere and lower stratosphere. The radicals produced may even play a role in the Antarctic ozone hole formation, which could be rate-limited by OH concentration. (Toumi, 1993)

9. Nitrous Oxide (N_2O)

Nitrous oxide is chemically inert in the troposphere, with a lifetime of approximately 132 years (IPCC, 1992). It is of importance because it is a greenhouse gas, responsible for approximately 5% of the observed greenhouse effect (Khalil and Rasmussen, 1992; Botting et al, 1992), and because its pri¬mary sink is in the stratosphere, where it is photolyzed or decomposed by reaction with O(1D). This likely influences the ozone layer, but the extent and even the sign of this influence are uncertain. (Ramanathan et al, 1987) One estimate attributes up to 20% of the ozone depletion as being caused by N20 increases. (Botting et al, 1992) A minor sink through soil uptake is also likely to exist.

9.1 Sources

Natural sources, such as soils and oceans, account for about 15 Tg per year, or 70%, of N_2O emissions into the atmosphere (Khalil and Rasmussen, 1992; Botting et al, 1992), while anthropogenic sources account for 7-8 Tg per year. Biomass burning, nitrogen fertilizers, sewage, nylon manufacturing, cattle, irrigation, automobiles, land use change and general global warming have been listed as sources for this gas (Khalil and Rasmussen, 1992), though accurate assessments of each cannot yet be presented with confidence.

Emissions of N_2O from soils appear to depend on soil moisture, nitrate content, temperature, and organic content of the soil. (Li et al, 1992) Flux has been found to increase due to fertilization and cultivation. (Mosier et al, 1991) N_2O emissions have higher diurnal and spatial variation than methane emissions and, as mentioned above in Section 3.3.2, the latter and former are inversely related. N_2O flux is highest after a rainfall, and declines thereafter. (Mosier et al, 1991) Nitrogen fertilization increases N_2O emissions by 2-3 times at a variety of physical grassland sites, and a link between a high nitrogen turnover in soils, be it natural or due to fertilization, has been established. (Mosier et al, 1991)

10. Conclusion

Although much progress has been made, the answers to many problems remain elusive, as the phrase “more research needs to be done ... “ which appears in many papers attests. Reaction-rate constants for OH-halocarbon interactions, sources and sinks of methane, ozone and VOCs, and attempts to measure the OH radical concentration are all among the topics of current research. Many of the gases are radiatively active and/or affect gases which are so in the troposphere, so their long-term effects on the climate, and in turn the climate change's' effects on chemistry, must also be investigated. The effects of the diminishing stratospheric ozone layer upon the chemistry and radiation balance of the troposphere must be taken into account as well.

Faster and more sophisticated numerical models are required to make more accurate predictions of atmospheric change, but in turn these can be no more accurate than the data they are initialized with and to which results are compared. Development of more accurate data acquisition and analysis systems is thus underway to meet this demand.

This paper has attempted to outline the current state of knowledge of the chemistry involved with tropospheric greenhouse gases and their precursors. It is expected that progress will be made rapidly on all fronts as researchers continue to attempt to solve the mysteries of tropospheric chemistry.

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