HUMAN IMPACTS ON ATMOSPHERIC CHEMISTY

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■ **Abstract**   An overview is given of the main anthropogenic influences on the chemistry of the atmosphere. Industrial and agricultural activities have altered the chemical composition of the atmosphere in many important ways, which is reflected especially in the distribution and concentrations of ozone in the troposphere and stratosphere. On one hand, as a result of industrial chlorofluorocarbon emissions, ozone has been depleted in unexpected major ways in the polar stratosphere. On the other hand, especially as a result of NO emissions, tropospheric ozone has increased both in the industrial mid-latitude regions and at low latitudes, in the latter mostly because of tropical biomass burning. In the future, growing anthropogenic emissions by developing nations will have an additional effect on the climate and the self-cleaning (oxidation) power of the atmosphere.

INTRODUCTION

Although the earth's atmosphere consists largely of N_2 and O_2, these gases do not play a significant direct role in the Earth's climate. Because of the abundance and long lifetimes of these gases, which are measured in many millions of years, human activities cannot significantly affect their atmospheric concentrations. This is in contrast to many less abundant but chemically much more reactive gases that are discussed in this review. The atmosphere's chemical and radiative properties are to a large extent determined by trace amounts of gases and aerosol particles that have increased markedly in the twentieth century as a result of human activities (Brasseur et al 1999). For example, the abundance of the greenhouse gas carbon dioxide (CO_2) has increased by about 30%, from 280 to 360 parts per million by volume (ppmv), whereas that of methane (CH_4) has more than doubled, from 0.7 to 1.8 ppmv, since preindustrial times. There is no doubt that these changes are caused by the use of fossil fuels and by agricultural emissions. Although CO_2 plays a major role in the earth's climate and as a carbon source in photosynthesis, it does not significantly influence the chemistry of the atmosphere, which is the main topic of this review. However, many other gases, even those much less abundant than

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CO_2, do influence atmospheric chemistry. This review focuses on those anthro-
pogenic gases that affect ozone (O_3), a greenhouse gas and a key component in
atmospheric chemistry that is also largely responsible for the protection of the bio-
sphere against harmful UV radiation and for the production of hydroxyl (HO), the
"detergent" of the atmosphere. Thus, we especially consider the different impacts
of anthropogenic emissions of nitrogen oxides, NO_x ($NO + NO_2$), on stratospheric
and tropospheric O_3 and HO as well as destruction of O_3 in the stratosphere by
industrial chlorine-containing gases, particularly $CFCl_3$ and CF_2Cl_2.

Owing to the presence of O_2 as a major atmospheric constituent, the earth's
atmosphere stands out as an oxidizing environment, although the main oxidizing
agent is not O_2, but O_3, and even more importantly, HO. In general, reduced and
partly oxidized gases, of both natural and anthropogenic origin, are oxidized to
form species, which are more easily removed from the atmosphere by rain or uptake
by soils and vegetation. The time scale of these events critically determines the
abundance of gases and their global distributions. It is quite conceivable that the
efficiency of these oxidation processes has changed in the past century, in particular,
as increasing emissions and decreasing lifetimes of gases can act in parallel. We
therefore focus on atmospheric compounds that are chemically reactive and for
which the atmospheric concentrations have changed significantly as a result of
human action in the twentieth century. We are especially interested in feedbacks
between processes, because these can give rise to nonlinear system responses that
are difficult to predict, while they hold the key to potential surprises in the future
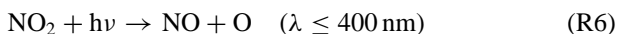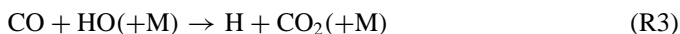development of earth's atmosphere.

TROPOSPHERIC OZONE CHEMISTRY

The 1970s were a decade that saw many key advances in our understanding of
both stratospheric and tropospheric chemistry (see review in Crutzen 1979). Dur-
ing that period it also became clear that human activities affect the chemistry of
the atmosphere in several ways, and that these effects occurred not only on local,
but also on regional and even global scales. Levy (1971) proposed that for almost
all gases the reaction with HO radicals in the troposphere constitutes the main
removal process, despite a very low globally averaged volume mixing ratio of
$<10^{-13}$. HO radicals are formed by the action of solar ultraviolet radiation on
ozone, producing electronically excited oxygen atoms, $O(^1D)$ (indicated hereafter
by O^*), followed by reaction of a small fraction of these excited atoms with water
vapor

$$O_3 + h\nu \rightarrow O^* + O_2 \quad (\lambda \leq 420\,\text{nm}) \tag{R1}$$

$$O^* + H_2O \rightarrow 2HO. \tag{R2}$$

The great importance of ozone in tropospheric chemistry was also realized dur-
ing this period. Crutzen (1973) showed that tropospheric ozone does not origi-
nate mainly from the stratosphere, as was generally assumed, but that it is largely

produced and destroyed within the troposphere. Special attention was drawn to the catalytic role of NO_x in the production of ozone, for instance during the oxidation of carbon monoxide (CO) to CO_2:
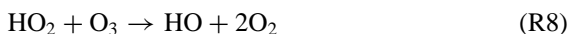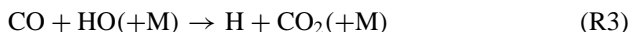
Sequence 1

$$CO + HO(+M) \rightarrow H + CO_2(+M) \tag{R3}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{R4}$$

$$HO_2 + NO \rightarrow HO + NO_2 \tag{R5}$$

$$NO_2 + h\nu \rightarrow NO + O \quad (\lambda \leq 400\,nm) \tag{R6}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{R7}$$

net: $CO + 2O_2 \rightarrow CO_2 + O_3$.

Note that in reaction Sequence 1, several catalysts participate to produce ozone: H, HO_2, HO, NO, NO_2, O, and even M, the third body (an air molecule N_2 or O_2), with, as a net result, the oxidation of CO to CO_2 and the formation of O_3. Such catalytic chain reactions are very typical for atmospheric chemistry. A critical step in the above chain of reactions is Reaction 5. If too little NO is present in the troposphere [less than $\sim$10 pmol/mol, pptv in US units (parts per trillion by volume)], then HO_2 reacts with O_3 instead, leading to loss of O_3:
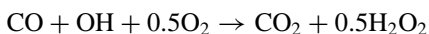
Sequence 2

$$CO + HO(+M) \rightarrow H + CO_2(+M) \tag{R3}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{R4}$$

$$HO_2 + O_3 \rightarrow HO + 2O_2 \tag{R8}$$

net: $CO + O_3 \rightarrow CO_2 + O_2$,

or HO_2 can also react with other HO_2 radicals, with the following net result:

Sequence 3

$$CO + OH + 0.5O_2 \rightarrow CO_2 + 0.5H_2O_2$$

In similar, but much more complex ways, CH_4 and other hydrocarbons are also oxidized. In NO_x-rich environments, the oxidation of CH_4 to CO follows several sequences of reactions, with the following possible net result:
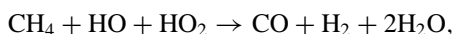
Sequence 4

$$CH_4 + 8O_2 \rightarrow CO + H_2O + 4O_3 + 2HO,$$
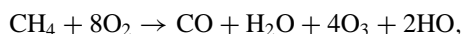
implying net production of O_3 and HO.

On the other hand, in NO_x-poor environments the net result may be

Sequence 5

$$CH_4 + HO + HO_2 \rightarrow CO + H_2 + 2H_2O,$$

with loss of HO_x (HO + HO_2) radicals.

Further oxidation of CO to CO_2, accompanied by production or destruction of O_3 and HO_x radicals, proceeds through the reaction Sequences 1, 2, or 3, given above. As a result, the global mean tropospheric ozone loading is $\sim$350 $\pm$ 50 teragram (Tg) ozone production is 4000 $\pm$ 500 Tg year^{-1}, whereas ozone destruction is 3800 $\pm$ 400 Tg year^{-1}. Net ozone production thus amounts to $\sim$200 $\pm$ 300 Tg year^{-1}, transport from the stratosphere is 600 $\pm$ 250 Tg year^{-1}, and dry deposition at the earth's surface completes the ozone budget by the removal of 800 $\pm$ 300 Tg year^{-1}. These estimates, which indicate substantial uncertainty, are based on a series of numerical calculations with global chemistry transport models by different groups (World Meteorological Organization/United Nations Environment Programme 1999).

A few points of clarification are needed regarding the significance of the stratospheric flux of ozone to the troposphere. Although substantially more ozone is produced and destroyed in the troposphere than the amount supplied from the stratosphere, the supply of stratospheric ozone remains very important and is, in fact, a prerequisite for initiation of the photochemical reactions in the troposphere that can lead to ozone production or loss. Furthermore, the amount of ozone in the troposphere is substantially more determined by the influx from the stratosphere than might be expected from the budget numbers presented above. This effect is associated with the fact that O_3 transport from the stratosphere occurs at relatively high latitudes and altitudes, whereas the chemical budget of O_3 is dominated by reactions in the lower part of the troposphere. These points are more thoroughly discussed by Crutzen et al (1999) and Lelieveld & Dentener (2000).

In the global background troposphere, most HO radicals react with CO or CH_4 and its oxidation products. Because the lifetime of most other hydrocarbons is much shorter than that of CH_4, oxidation of those hydrocarbons mainly causes regional production of O_3, provided again that sufficient NO_x is present. Summarizing, we note that in NO_x-rich environments, the oxidation of CO and CH_4 leads to O_3 production; otherwise O_3 and HO_x destruction takes place via Reactions 1, 2, and 8. This sequence of reactions was already known in principle in 1979; however, since then the budget of O_3 has become significantly better quantified, also taking into account the effects of other, more-reactive, hydrocarbons than CH_4.

Because of its great importance as a catalyst in ozone formation, it is important to know the sources, sinks, and distribution of NO_x in the troposphere. Remarkably, quantitative knowledge about some of the sources of NO, for example, NO production from lightning and soil exhalation, is nearly as uncertain today as it was in 1979. The contribution to increased NO_x of fossil-fuel burning, which was already well known, was estimated at 20 Tg N year^{-1} in 1979, compared with 22 Tg N year^{-1} today (Bradshaw et al 2000). Since 1979, an important, additional source of NO as a result of biomass burning, mostly in the tropics and subtropics during the dry season, has been identified. Current estimates of the global sources of NO are summarized in Table 1.

The main chemical sink of NO_x that was known in 1979 was the recombination of NO_2 with HO, leading to the formation of highly water-soluble and

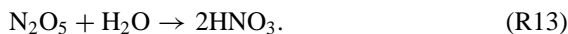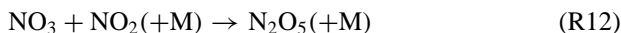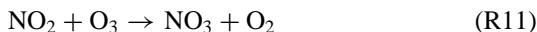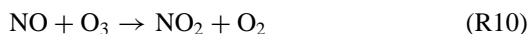**TABLE 1** Estimated global NO_x sources, including uncertainty ranges

Sources	Amount (Tg N year^{-1})
Natural	
Soils (small part anthropogenic)	7 (5–12)
Lightning	5 (2–20)
Stratospheric (from $N_2O + O^* \rightarrow 2NO$)[a]	0.6 (0.4–1)
Total ($\sim$30%)	12.6 (7.4–33)
Anthropogenic	
Fossil fuel use	22 (20–24)
Biomass burning	8 (3–13)
NH_3 oxidation (small part natural)	0.9 (0.1–1.6)
Aircraft	0.5 (0.2–1)
Total ($\sim$70%)	31.4 (23.3–39.6)

[a] O^* represents excited oxygen atoms, $O(^1D)$.

photochemically relatively long-lived nitric acid (HNO_3):

$$NO_2 + HO(+M) \rightarrow HNO_3(+M). \tag{R9}$$
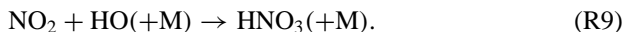
We now know, however, that NO_x can also be removed during darkness by gas-phase reactions that produce N_2O_5, which subsequently reacts with H_2O on aerosol surfaces such as sulfate, sea-salt, or soil dust particles to produce HNO_3, which may be removed from the gas phase by incorporation into aerosols:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{R10}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{R11}$$

$$NO_3 + NO_2(+M) \rightarrow N_2O_5(+M) \tag{R12}$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3. \tag{R13}$$

Following some early incorrect laboratory measurements, the potential significance of heterogeneous reactions in atmospheric chemistry had been neglected, a view that had to be abandoned after the discovery of the stratospheric "ozone hole," which demonstrated the great potential of such reactions.

In polluted air, oxidation reactions that involve the more reactive hydrocarbons can sequester part of the NO_x through the production of peroxy-acetyl-nitrate (PAN), a thermolabile gas. The potential importance of PAN as a reservoir species of NO_x under low-temperature conditions (Crutzen 1979) has since been confirmed by many atmospheric measurements [for an up-to-date review of NO_x chemistry, see Bradshaw et al (2000)]. In contrast to HNO_3, which owing to its high solubility, is rather efficiently removed from the atmosphere by rainfall, PAN is hardly affected by precipitation and can therefore be transported over long distances

through the low-temperature upper region of the free troposphere. Thermal dissociation of PAN can thus become a significant source of NO_x, especially in NO_x-depleted, warm environments. Other organic nitrates may likewise play a significant role in NO_x chemistry, requiring further investigation.

STRATOSPHERIC OZONE CHEMISTRY

Major advances in knowledge about stratospheric chemistry were also made in the 1970s. Through careful laboratory measurements of the optical cross sections of O_2 and rate coefficients of reactions in the classical "Chapman chemistry" scheme (Chapman 1930), it had become clear that production of ozone via
Sequence 6

$$O_2 + h\nu \rightarrow 2O \quad (\lambda \leq 240\,nm) \tag{R14}$$

$$O + O_2 + M \rightarrow O_3 + M(2x) \tag{R15}$$
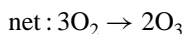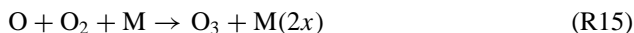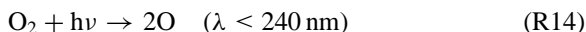
$net : 3O_2 \rightarrow 2O_3$
is substantially greater than ozone destruction by the following reactions:
Sequence 7

$$O_3 + h\nu \rightarrow O + O_2 \quad (\lambda \leq 1140\,nm) \tag{R1}$$

$$O + O_3 \rightarrow 2O_2 \tag{R16}$$
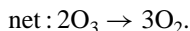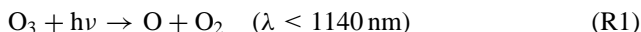
$net : 2O_3 \rightarrow 3O_2$.
To achieve mass balance of O_3, Crutzen (1970) proposed that, under natural conditions, reactions involving NO and NO_2 as catalysts, for example,
Sequence 8

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{R17}$$

$$O_3 + h\nu \rightarrow O + O_2 \tag{R1}$$

$$O + NO_2 \rightarrow NO + O_2 \tag{R18}$$
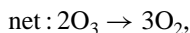
$net : 2O_3 \rightarrow 3O_2$,
could provide much of the missing ozone sink, with Reaction 18 being rate controlling.

The oxidation of N_2O by reaction with a small fraction ($\approx 4 \times 10^{-7}$) of the O^* atoms, produced by ozone photolysis via Reaction 1, was identified as the main stratospheric source of NO (McElroy & McConnell 1971, Crutzen 1971):

$$N_2O + O^* \rightarrow 2NO. \tag{R19}$$

Because N_2O is largely produced by microbiological activity in waters and soils, including that produced by agricultural activities, it was realized for the first time that the biosphere could have a substantial influence on the stratospheric ozone layer.
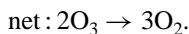
One of the discoveries of the 1970s was that, through catalytic destruction of ozone, human activity could affect stratospheric ozone. Independently, Johnston (1971) and Crutzen (1971) suggested that the large fleets of supersonic aircraft whose construction was planned in the United States, France/Great Britain, and the Soviet Union, would inject NO in the lower stratosphere (between 18 and 21 km) in an amount similar to that produced naturally by Reaction 19 (Crutzen 1971). Furthermore, several authors proposed that the growing use of nitrogen fertilizers could increase the emissions of N_2O to the atmosphere, leading to an enhancement in stratospheric NO production. The growth in atmospheric N_2O by 0.2%–0.3% year^{-1}, which is still ongoing, has been confirmed by many observations, starting from Weiss (1981).

The publication by Johnston (1971) especially led to major stratospheric research programs, initiated in the United States, Great Britain, and France. As an outcome of these programs, it was concluded that supersonic transport could indeed substantially diminish stratospheric ozone (e.g. National Academy of Sciences 1975). An excellent review of the initially often tense interactions between industry, representatives of environmental groups, policy makers, and scientists in the early 1970s is given by Johnston (1992). However, the large fleets of supersonic aircraft were never built. Until recently, only a few of these aircraft are flying at about 18 km altitude in the stratosphere, too few to significantly affect ozone. In fact, additional knowledge about the role of NO_x in the O_3 budget has shown that additions of NO_x below $\sim$25 km in the stratosphere may actually lead to an increase in O_3 (Hidalgo & Crutzen 1977), both via the photochemical smog reactions already discussed and by counteracting the O_3 depletion that would result from ClO_x and HO_x catalysis, as will be discussed next.

Just at the conclusion of the aircraft impact research programs (National Academy of Sciences 1975), a major and already pertinent danger to stratospheric O_3 was identified by Molina & Rowland (1974)—the catalytic destruction of O_3 by Cl and ClO produced by the photolysis of CCl_4 and especially the chlorofluorocarbon (CFC) gases, $CFCl_3$ and CF_2Cl_2:

$$CF_xCl_{4-x} + h\nu \rightarrow CO_2 + xHF + (4 - x)ClO_x, (x = 0, 1, \text{ or } 2). \quad (R20)$$
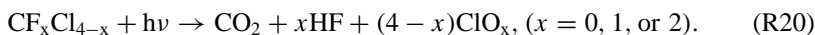
The only partially natural source of ClO_x in the stratosphere is the reaction of HO with methyl chloride (CH_3Cl), which is present in the atmosphere at about 0.6 nmol/mol of air, or parts per billion by volume (ppbv) in US units. Analogous to the catalytic NO_x cycle, Cl and ClO destroy O_3 by the following set of reactions: Sequence 9

$$Cl + O_3 \rightarrow ClO + O_2 \quad (R21)$$

$$ClO + O \rightarrow Cl + O_2 \quad (R22)$$

$$O_3 + h\nu \rightarrow O + O_2 \quad (R7)$$

net : $2O_3 \rightarrow 3O_2$.

Model calculations showed that the largest relative loss of ozone would take place

between 35 and 45 km altitude. However, most stratospheric ozone is located below 25 km, where the ClO_x catalytic Sequence 9 is rather ineffective owing to low concentrations of atomic oxygen.

Fortunately, not all ClO_x produced by Reaction 20 remains in the active radical forms. Under most circumstances, especially below 30 km, the largest fraction of the inorganic Cl exists as HCl and $ClONO_2$, which do not react with O_3:

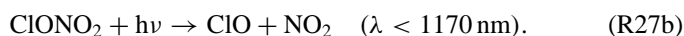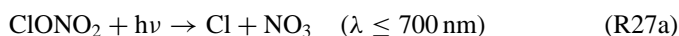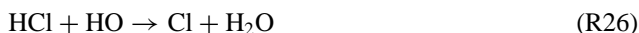$$ClO + NO \rightarrow Cl + NO_2 \qquad \text{(R23)}$$

$$Cl + CH_4 \rightarrow HCl + CH_3 \qquad \text{(R24)}$$

$$ClO + NO_2 + M \rightarrow ClONO_2 + M. \qquad \text{(R25)}$$
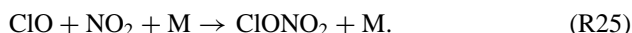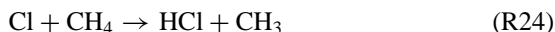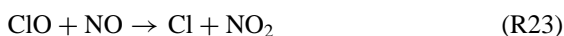
Consequently, relatively slow decreases in total O_3 were estimated by model calculations to result from reaction Sequence 9.

The return flow of HCl and $ClONO_2$ to ClO_x occurs mainly via

$$HCl + HO \rightarrow Cl + H_2O \qquad \text{(R26)}$$

$$ClONO_2 + h\nu \rightarrow Cl + NO_3 \quad (\lambda \leq 700 \, \text{nm}) \qquad \text{(R27a)}$$

$$ClONO_2 + h\nu \rightarrow ClO + NO_2 \quad (\lambda < 1170 \, \text{nm}). \qquad \text{(R27b)}$$

As shown in Figure 1, many complex interactions take place within and between the O_x, HO_x, NO_x, and ClO_x families of reactants. In general, although NO and NO_2 can destroy O_3 by the catalytic reaction chain Sequence 8 via Reactions 23–25, they also promote the conversion of reactive ClO_x radicals into the inactive reservoir species HCl and $ClONO_2$. On the other hand, Reaction 26 between HCl and HO leads to ClO_x activation, quite in contrast to the case with NO_x, in which reaction of HO with NO_2 leads to the conversion of the catalytically active NO_x to much less reactive HNO_3.

All reactions in the gas phase discussed above or shown in Figure 1 were already known in principle by the end of the 1970s. What has changed in our fundamental understanding of stratospheric chemistry over the past 2 decades is the importance of heterogeneous reactions that can take place on or in particles in the stratosphere. These reactions are particularly important below ∼25 km, that is, in the region of the stratosphere where most ozone is located. The importance of heterogeneous reactions became especially clear after the discovery of the "ozone hole" over Antarctica.

STRATOSPHERIC OZONE DEPLETION OVER POLAR REGIONS: The "Ozone Hole"

In 1985 a shocking set of environmental observations was published by scientists of the British Antarctic Survey (Farman et al 1985) that showed a dramatic springtime (September–November) loss of total ozone by ∼30% over Antarctica compared with natural conditions (Figure 2). Since then, the vertical column ozone
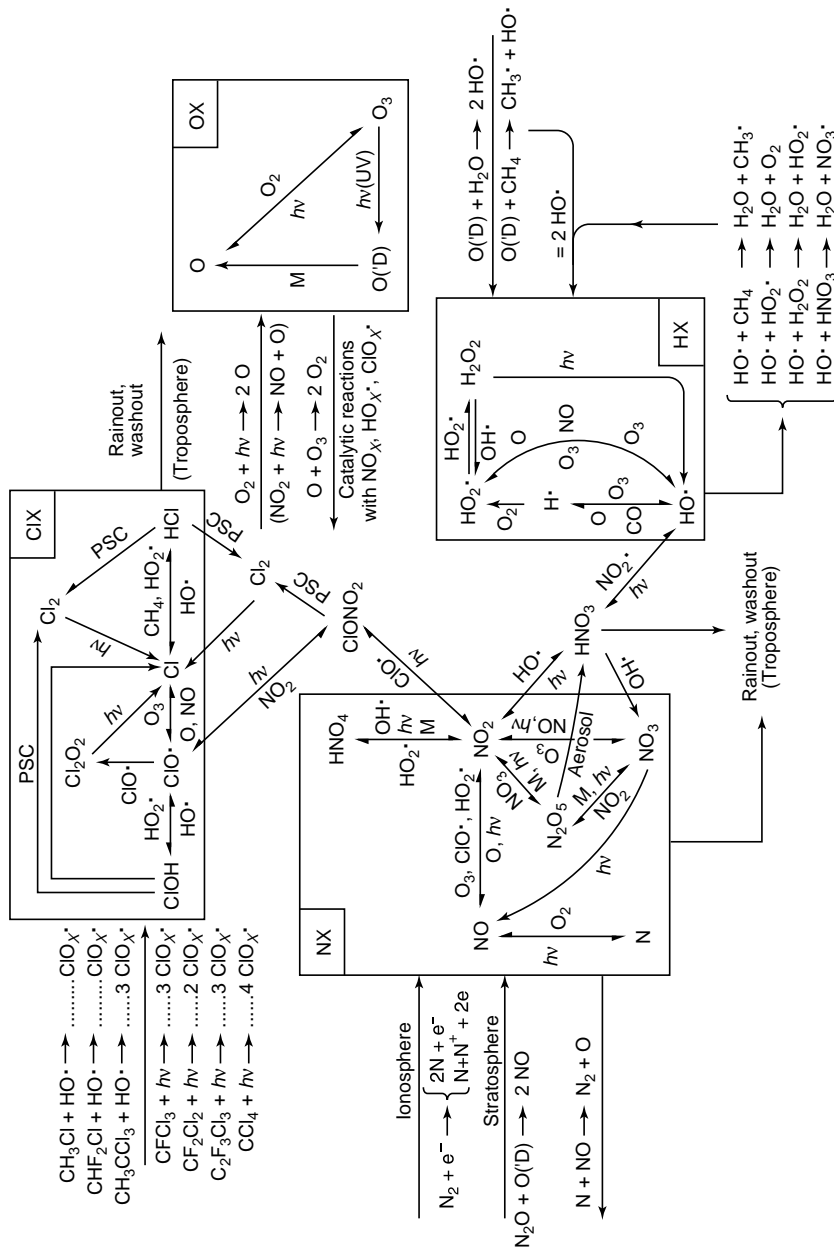
Figure 1 Chemical interactions within and between the oxygen, reactive nitrogen, hydrogen, and chlorine families in the stratosphere. The small box labeled OX shows the oxygen-only Chapman scheme, which until the mid-1960s was believed to describe satisfactorily the stratospheric ozone chemistry.
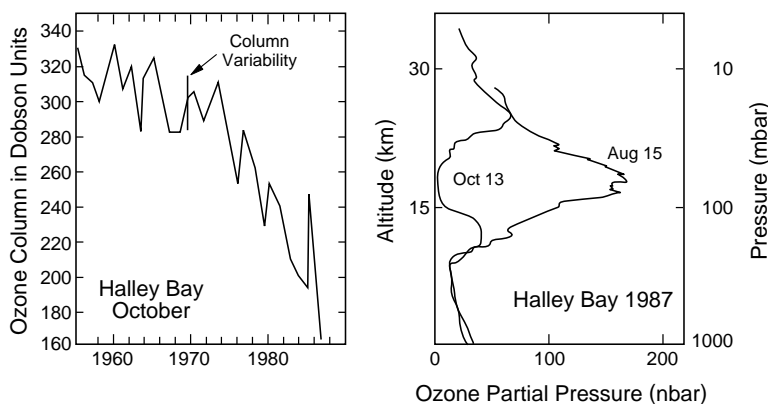
Figure 2   The left-hand panel shows the decrease of total ozone in October over the Halley Bay station of the British Antarctic Survey (Farman et al 1985). The right-hand panel shows the conversion of maximum ozone concentrations to the "ozone hole" over the short period of only 2 months (Hofmann et al 1987).

decline has continued (Jones & Shanklin 1995), reaching minimum springtime levels below 100 Dobson units (DU) compared with typical values of ∼300 DU prior to 1975. (This corresponds to a 3-mm-thick atmospheric layer if all O_3 were compressed to standard surface temperature and pressure conditions.) This huge drop in total ozone was a total surprise. It was caused by an almost complete loss of ozone between ∼12 and 21 km altitude (Hofmann et al 1987), creating a so-called "ozone hole" in the height region in which maximum ozone concentrations normally had been measured and in which it was thought that ozone would be practically inert (Figure 2). The heavy ozone losses were confirmed by satellite-based observations (Stolarski et al 1986). It soon became clear that photochemical reactions, related to the release of CFC gases to the atmosphere, had to be responsible for the precipitous loss of ozone. However, because of the low concentrations of O atoms in the lower stratosphere, reaction Sequence 9 is not effective in destroying O_3 below 25 km, so that additional chemical reactions had to be discovered. The first step to elucidate ozone-hole chemistry was taken by Solomon et al (1986), who suggested that the reservoir molecules $ClONO_2$ and HCl could react with each other on ice particles:

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \tag{R28}$$

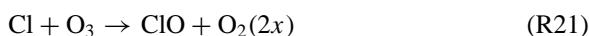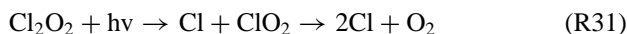$$Cl_2 + h\nu \rightarrow 2Cl, \tag{R29}$$

releasing Cl_2 to the atmosphere, where it readily photodissociates in sunlight to produce reactive Cl atoms, with the HNO_3 becoming incorporated in the ice particles. These reactions require low temperatures and sunlight, typical conditions found in early spring in the lower stratosphere over Antarctica. Thus, under cold,

sunlit conditions, the inorganic Cl species tend to be kept in their most active radical forms, Cl + ClO. The occurrence of the heterogeneous Reaction 28 on water-ice particles was confirmed by laboratory simulations (Molina et al 1987, Tolbert et al 1987).

Next, Molina & Molina (1987) proposed the catalytic ClO_x cycle, which causes rapid ozone losses of almost 0.1 ppmv day^{-1} (Solomon 1999) in the lower stratosphere:
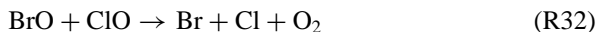Sequence 10

$$ClO + ClO + M \rightarrow Cl_2O_2 + M \tag{R30}$$

$$Cl_2O_2 + h\nu \rightarrow Cl + ClO_2 \rightarrow 2Cl + O_2 \tag{R31}$$

$$Cl + O_3 \rightarrow ClO + O_2 (2x) \tag{R21}$$

net : $2O_3 \rightarrow 3O_2$.
An additional 20% O_3 loss is caused by mixed BrO_x/ClO_x catalysis (McElroy et al 1986, Brune et al 1989):
Sequence 11

$$BrO + ClO \rightarrow Br + Cl + O_2 \tag{R32}$$

$$Br + O_3 \rightarrow BrO + O_2 \tag{R23}$$

$$Cl + O_3 \rightarrow ClO + O_2 \tag{R21}$$

net : $2O_3 \rightarrow 3O_2$.
The first proof of the validity of reaction Sequence 10 leading to the ozone hole came from ground-based microwave emission measurements by de Zafra et al (1987) that showed greatly enhanced ClO in the lower stratosphere of the order of 1 nmol/mol near 20-km altitude, about 100-fold more than the levels that would follow from gas-phase reactions alone. Furthermore, ClO can also react with BrO, producing OClO:

$$BrO + ClO \rightarrow Br + OClO. \tag{R33}$$

Spectroscopic measurements of the OClO produced by Reaction 33 over the Antarctic (Solomon et al 1988) showed unusually large column abundances under ozone-hole conditions, again indicating the presence of much higher concentrations of ClO than could be explained by gas-phase chemistry only. The measured total column of NO_2 was also very low, in accordance with the chemistry outlined above.

It is important to note that the rate-limiting step in the ozone-hole destruction cycle Sequence 10 is Reaction 30 between two ClO radicals. Thus, the rate of O_3 loss is proportional to the square of the concentrations of ClO. With the chlorine content in the stratosphere increasing by $\geq$5% year^{-1}, as was the case until the early 1990s, the ozone loss rate during spring thus goes up by ~10% from year to year. The present Cl content in the stratosphere is ~5–6 times larger

than under natural conditions, implying a 25- to 36-fold greater O_3 loss by ClO_x chemistry. Furthermore, because the heterogeneous Cl activation Reaction 28 likewise depends on the square of the Cl content in the stratosphere, O_3 loss is strongly dependent on the stratospheric Cl content, thus explaining the precipitous loss of O_3 that increases rapidly from year to year. In addition, a drop in lower stratospheric temperatures during winter/spring by about 3K decade^{-1} (World Meterological Organization/United Nations Environmental Programme 1999) is another factor that has substantially contributed to strong Cl activation and O_3 depletion. Such a drop in temperature is expected when ozone concentrations decrease and less absorption of solar radiation occurs. At reduced temperatures the growth of stratospheric particles by water vapor condensation can increase tremendously, thus enhancing heterogeneous reactions. Hence the ozone hole is caused by several strong positive feedbacks that cause a chemical instability in the stratosphere.

Initially, it was thought that Cl activation by Reaction 28 would occur on the surface of water-ice particles. However, Crutzen & Arnold (1986) and Toon et al (1986) proposed that at temperatures that were 5°–10°C higher, frozen particles consisting mainly of nitric acid trihydrate, or NAT ($HNO_3 \cdot 3H_2O$), crystals and smaller amounts of H_2SO_4, could be formed in the stratosphere at temperatures below about −75° to −80°C. This proposal was supported by equilibrium vapor measurements made by Hanson & Mauersberger (1988). Laboratory investigation showed that Cl activation by Reaction 28 also takes place on NAT particles (Abbatt et al 1992). The formation of NAT at higher temperatures than those at which water-ice can exist therefore extends in space and time the conditions under which HCl can react with $ClONO_2$, favoring ClO_x formation. It is interesting to note that although the oxides of nitrogen do not play any significant direct role in the destruction of ozone in the lower stratosphere, surface-catalyzed reactions on HNO_3-containing aerosol nevertheless are strongly involved in chlorine activation and thereby ozone depletion.

In the meantime, it has become clear from remote sensing (lidar) depolarization measurements that the polar stratospheric cloud particles do not generally exist in the solid phase, but also, especially in the northern hemisphere, as liquid, super-cooled, ternary mixtures of H_2SO_4, HNO_3, and H_2O. HCl is taken up in the liquid phase as well, and via Reaction 28 leads to Cl activation.

Thus, as suggested by Toon et al (1990), observations by Dye et al (1992) in the Arctic have been interpreted by Carslaw et al (1994) and Toon & Tolbert (1995) to show that there is a substantial nucleation barrier against solid NAT formation from ternary solutions and that transition to temperatures below the water-ice freezing point seem to be required before NAT particles can form. However, irrespective of the particle phase of the H_2SO_4-HNO_3-H_2O mixtures, basically the same Cl activation reactions take place (Cox et al 1994, Ravishankara & Hanson 1996, Hanson et al 1994), below ~198K at 20 km and between 200 and 210K near 13 km (Solomon 1999), causing O_3 depletion by the Molina & Molina

catalytic chain, reaction Sequence 10. These issues are discussed in much more detail by Carslaw et al (1994), Hanson et al (1994), Peter (1997), and Solomon (1999).

Although far less dramatic than the O_3 destruction over Antarctica, observations have shown that heterogeneous processes over the Arctic can also lead to significant Cl activation. However, whereas over Antarctica ozone-hole temperature conditions prevail for several months during winter/springtime, these conditions occur far less frequently over the Arctic and barely extend into springtime. Nevertheless, during cold years, substantial O_3 loss has been observed over the Arctic, although never in as large amounts as over the Antarctic, together with strongly enhanced concentrations of both ClO (Brune et al 1990, Waters et al 1993) and OClO, as well as low concentrations of NO_2 (Solomon et al 1988, Schiller et al 1990, Perner et al 1994, Mankin et al 1990, Goutail et al 1994), in agreement with theory.

Particularly during several late winter/early spring periods in the 1990s, total ozone columns were substantially reduced. Research, especially that by Von der Gathen et al (1995) and Rex et al (1997), who analyzed ozone changes in the same air parcels into which ozone sondes were launched at different times and locations, clearly indicated substantial ozone depletion during late winter/early spring periods in cold years. Correlations between O_3 and CH_4 concentrations, observed from the Halogen Occultation Experiment (HALOE) instrument on the Upper Atmosphere Research Satellite (UARS), also indicated substantial chemical O_3 loss, of the order of 60–120 DU, in the winters of 1991–1992, 1992–1993, and 1994–1995 (Müller et al 1996, Manney et al 1994). Although the basic chemistry of the ozone loss is known, model simulations seem to underestimate measured ozone depletions, an issue that has not yet been resolved (Becker et al 1998).

Since the beginning of 1996, through international agreements, the production of CFCs and several other ozone-depleting substances has largely stopped in the developed world, so that ozone recovery is expected in the future. However, because of the long residence times of the CFC gases in the atmosphere, ~50 years for $CFCl_3$ and 100 years for CF_2Cl_2, it will be the middle of this century before the ozone hole will disappear. However, because ozone depletion depends so strongly on meteorological conditions, the possibility cannot be excluded that some major ozone depletions, possibly even larger than those that have been observed so far, may still develop during single years in the future. Furthermore, because rising concentrations of CO_2 cool the stratosphere, which favors chlorine activation and ozone loss, which in turn may cause lower temperatures, etc, the recovery of the ozone layer may be substantially delayed, perhaps even beyond the middle of this century, particularly if strong denitrification (sedimentation of nitric-acid-containing particles) should occur (Waibel et al 1999) or if large-scale dynamic feedbacks lead to additional lowering of temperatures in the lower stratosphere (Shindell et al 1998). Therefore, according to these studies, years with Arctic

ozone-hole-like conditions may be possible during the long transition to an ozone-hole-free world.

PERTURBATIONS OF ATMOBIOGEOCHEMICAL CYCLES

Human-induced emissions have influenced the earth's atmosphere during the past millenium; however, these effects substantially accelerated after the industrial revolution and the strong population growth in the twentieth century. Here we discuss some important examples.

Methane (CH_4) is a gas of great importance to global atmospheric chemistry, both in the stratosphere and troposphere. Its present concentration is ~1.8 ppmv, and it has been increasing, between 1978 and 1988 by ~1% per year and at present by closer to 0.4% per year. Until ~200–300 years ago, during the recent climatic period, CH_4 concentrations were almost constant at 0.7 ppmv, ~40% of today's value. This information has been obtained from the analysis of air trapped in glaciers in Greenland and Antarctica (Delmas 1994, Legrand & Mayewski 1997). Agriculture and industry have had a considerable influence on methane concentrations. Table 2 shows the estimated CH_4 sinks and sources (Lelieveld et al 1998). The most important sink for atmospheric CH_4 is reaction with HO, which can be estimated from chemistry-transport model calculations. This can be done both for present atmospheric conditions and for those before the industrial era, the latter representing natural conditions. In this way we estimate that the current total CH_4 source is about 600 Tg year^{-1}, of which natural sources produce nearly 200 Tg year^{-1} (~33%) and anthropogenic sources add up to ~400 Tg year^{-1} (~67%). Major contributions originate from ruminants and decay of animal manure, biomass burning, landfills, rice fields, coal mines, natural gas leaks, and oil/gas extraction operations. With a present imbalance of ~20 Tg year^{-1}, only 5% of the total anthropogenic source, it is far from unrealistic to aim for a stabilization or even regression of the atmospheric CH_4 content.

A main intermediate product of CH_4 oxidation in the atmosphere is CO, which is ultimately converted by reaction with HO into CO_2. The chemistry of CO, in conjunction with NO_x, plays a dominant role in tropospheric O_3 formation. Natural CO emissions, mostly by vegetation and the oceans, amount to about 150 Tg year^{-1}, whereas human-produced CO emissions from biomass burning and fossil-fuel combustion are about 1 Pg year^{-1} (World Meteorological Organization/United Nations Environment Programme 1999). Note that the uncertainty in the estimates of natural emissions is a factor of 2 and it is ~50% for the anthropogenic emissions. Because only about one third of the CH_4 emissions is from natural sources, a large fraction of the CO derived from CH_4 oxidation is anthropogenic in origin. Global emissions of other hydrocarbons of 400–1150 TgC year^{-1}, on the other hand, largely originate from natural vegetation and may

TABLE 2   Estimates of global CH_4 sources and sinks

Sources	Amount (Tg N year^{-1})
Natural	
Wetlands	145 (115–175)
Oceans	10 (5–15)
Freshwaters	5 (1–10)
CH_4 hydrates	10 (5–15)
Termites	20 (1–40)
Natural animals	5 (1–10)
Total ($\sim$33%)	195 (128–265)
Anthropogenic	
Domestic ruminants	80 (55–100)
Rice paddies	80 (30–120)
Animal wastes	30 (15–45)
Biomass burning	40 (10–70)
Landfills	40 (20–60)
Energy use	110 (65–155)
Domestic sewage	25 (20–30)
Total ($\sim$67%)	405 (215–580)
Total sources	600 (520–680)
Methane sinks	
Troposphere (HO)	510 (460–560)
Stratosphere (HO, O*, Cl)	40 (30–50)
Soils (bacterial oxidation)	30 (15–45)
Net atmospheric increase	20 (15–25)

The total atmospheric mass of CH_4 is almost 5×10^{15} g.

have declined during the past centuries because of deforestation (Guenther et al 1995, Kesselmeier & Staudt 1999). These emissions are dominated by isoprene (C_5H_8) and monoterpenes produced by forests. This strong, though uncertain, natural hydrocarbon source substantially contributes to the global atmospheric CO loading. Nevertheless, in the northern hemisphere, human-produced CO exceeds natural tropospheric CO production by at least a factor of 2–3, whereas in the southern hemisphere this perturbation is of the order of 50% (JA Van Aardenne, FJ Dentener, CGM Klein Goldewijk, JGJ Olivier & J Lelieveld, submitted).

The strengths of the important NO_x sources, more than 90% as NO, are shown in Table 1. It is clear that anthropogenic activities have a large impact on the NO_x budget through the burning of fossil fuels ($\sim$22 Tg year^{-1}) and biomass (3–13 Tg N year^{-1}). Biomass burning takes place mainly in the dry season in the tropics. Comparing this quantity with the estimated emissions from soils (which is also partly anthropogenic via application of nitrogen fertilizer), and from lightning, both of which are very uncertain, one recognizes that the anthropogenic

contributions to NO_x emissions are probably substantially higher than the natural contributions. We estimate that human-produced emissions contribute ~70% to the total global release of NO_x to the troposphere. Because removal of NO_x largely occurs by the deposition of nitrate, a nutrient for the marine and terrestrial biosphere, long-range atmospheric transport and deposition to N-deficient ecosystems can give rise to fertilization of natural biota. This deposition may in turn stimulate plant growth and contribute to removal of CO_2 from the atmosphere. This same effect may also result from the strong perturbation of the atmospheric ammonia-ammonium cycle caused by extensive use of nitrogen-containing fertilizers. The total ammonia release to the atmosphere is about 45 Tg N year^{-1}. Emissions from animal husbandry and fertilizer losses may contribute ~70% to this budget, a human perturbation of similar magnitude to that of NO_x (Dentener & Crutzen 1994).

As shown above, when sufficient NO is present in the troposphere, O_3 will be produced. Although production of O_3 can be beneficial in that it provides the major source of HO radicals via Reactions 1 and 2, O_3 also has unpleasant qualities in that it is an air pollutant that affects human health and plant productivity. Therefore, it is fortunate that the atmospheric lifetime of NO is only a few days. At clean-air locations, such as in the middle of the Pacific Ocean, one finds only very low volume mixing ratios of NO_x in the few pmol/mol range (e.g. Bradshaw et al 2000). In such clean-air regions, ozone decomposition takes place. The production of O_3 and HO is very nonlinear in terms of NO_x (Liu et al 1987). In regions that are already heavily perturbed, for example by fossil-fuel-related NO_x emissions, further NO_x increases have relatively small effects on levels of O_3 and HO compared with those by NO_x emissions in the pristine parts of the atmosphere. Also, the anticipated growth of fossil-fuel use and associated pollution in the developing parts of the world, especially in the tropics and subtropics, is expected to contribute importantly to future changes in the chemistry of the troposphere.

Another important example of a strong human impact on atmospheric biogeochemistry involves the sulfur cycle (Charlson et al 1992). In the ocean, sulfur is ubiquitous. Of the sulfur released to the atmosphere, some 20 Tg S year^{-1} is released as dimethyl sulfide (DMS), CH_3SCH_3 (Pham et al 1995, Chin et al 1996). The DMS lifetime, as determined by oxidation by HO, is <1 day, so its presence is largely confined to the marine boundary layer. Presently, the sulfur compound with the strongest source is SO_2, which comes mostly from the burning of coal and, to a lesser extent, of oil; together they produce ~75 Tg S year^{-1}, which is about twice the total natural sulfur source (Table 3). Of the sulfur in the atmosphere, ~15% is removed through oxidation by HO radicals; aqueous phase oxidation within clouds, mainly by hydrogen peroxide (H_2O_2) and ozone, accounts for ~60% of the SO_2 oxidation (Lelieveld et al 1997). The remaining ~25% of sulfur is removed by dry deposition. The global mean lifetime of SO_2 in the atmosphere is a few days. Both gas- and aqueous-phase oxidation yields

TABLE 3 Estimated global sources of sulfur gases[a]

Sources	Amount (Tg S year^{-1})
Natural	
Volcanic	8 (3–20)
Terrestrial	1(0.1–5)
Oceanic	20 (12–40)
Total (~33%)	35 (15.1–65)
Anthropogenic	
Fossil fuel use	75 (70–85)
Biomass burning	2.5 (1–4)
Total (~67%)	77.5 (71–89)

[a]The total mass of atmospheric non-sea-salt sulfur is 0.5–0.6 Tg S.

sulfuric acid (H_2SO_4). The gaseous H_2SO_4 rapidly partitions into already existing aerosols (or it may form new particles). Through long-range transport, H_2SO_4 deposition contributes to the widespread acidification of ecosystems (Odén 1976, Calvert et al 1985). Sulfate aerosols efficiently scatter solar radiation, hence their increase in the atmosphere exerts a cooling effect on climate that masks some of the warming caused by increased greenhouse gases (Charlson et al 1991). In the 1980s, important efforts have been devoted to the cleaning of SO_2 from power-plant exhausts, so the emissions in western Europe and the United States have decreased substantially. At present, however, the use of sulfur-containing coal in southern and eastern Asia, in particular China, represents a strongly growing contribution to the atmospheric sulfur budget with present emissions of ~25 Tg S year^{-1} (JA Van Aardenne, FJ Dentener, CGM Klein Goldewijk, JGJ Olivier & J Lelieveld, submitted).

CHANGING TROPOSPHERIC OXIDANT LEVELS

From reanalysis of historical observations at Montsouris, near Paris, a preindustrial O_3 surface level of ~10 nmol/mol has been derived (Volz & Kley 1988). Simulations of preindustrial emission scenarios with chemistry-transport models indicate somewhat higher values, ~15–20 nmol/mol (Wang & Jacob 1998, Lelieveld & Dentener 2000), in good agreement with pre–World War II ozone data in Europe, providing clear indications that average surface O_3 has increased by at least a factor of 2–3 during the past century (World Meteorological Organization/United Nations Environment Programme 1995, 1999). In the past few decades, tropospheric ozone has been monitored from several surface and ozone sounding stations (Logan 1994, Logan et al 1999, Oltmans & Levy 1994, World Meteorological Organization/United Nations Environment Programme 1999). However,

O_3 trends vary strongly in different regions, so that the lack of a global monitoring network, particularly in the tropics, hampers the assessment of global O_3 trends. In several middle- and high-latitude locations in the northern hemisphere, upward O_3 trends have been derived, varying from a few percent to 15% increase per decade. At some locations, however, notably at the South Pole, a negative surface O_3 trend has been observed. This negative trend has been associated with the Antarctic ozone hole, through which stratosphere-troposphere O_3 fluxes have decreased.

In general, observed tropospheric ozone trends have been clearly upward in the 1970s, whereas they were less so in the 1980s and 1990s, the latter associated with reductions in the growth of O_3 precursor emissions (Kley et al 1994, Fiore et al 1998). Although twentieth century O_3 trends in the troposphere have been dominated by precursor emissions in Europe, Japan, and the United States, twenty-first century O_3 trends will likely be influenced largely by developing countries, especially those in Asia. Figure 3 shows model-calculated annual average surface O_3 for the present and a projected 2025 atmosphere, according to the Intergovernmental Panel on Climate Change moderate-growth emission scenario (Lelieveld & Dentener 2000). It shows that, not only over Asia, but also throughout the northern hemisphere, surface O_3 can continue to increase in spite of NO_x-emission reductions in some western countries. A primary cause is the expected growth of Asian NO_x emissions, which will mix with pollution from other continents through long-range transport of O_3 and precursors such as CO and PAN.

IMPACTS OF AVIATION IN THE UPPER TROPOSPHERE

Considerable attention has been devoted to the atmospheric effects of aviation (Intergovernmental Panel on Climate Change 1999). Because most flights take place in the upper troposphere and lower stratosphere, the emissions of NO_x contribute to formation of O_3. The Intergovernmental Panel on Climate Change (1999) estimates an increase in ozone concentrations near cruise altitudes at northern mid-latitudes by 6% ($\sim$0.4% in ozone column), which may approximately double by the middle of this century owing to a projected growth in the fleet of sub-sonic aircraft. The ozone increases will have a warming effect on climate, which adds to the climate forcing from increasing CO_2 and CH_4. In addition, aircraft emissions of H_2O in the upper troposphere cause contrails, which likewise tend to warm the earth's surface. Currently, it is estimated that, globally averaged, line-shaped contrails cover $\sim$0.1% of the sky, a value that may grow (disproportionally, compared to fuel use), up to $\sim$0.5% by the middle of this century. The reason for this disproportionate growth in contrails compared to the growth in fuel use is that the aircraft fly in the most sensitive region for contrail formation. The greenhouse forcing caused by the CO_2 emissions from aircraft alone
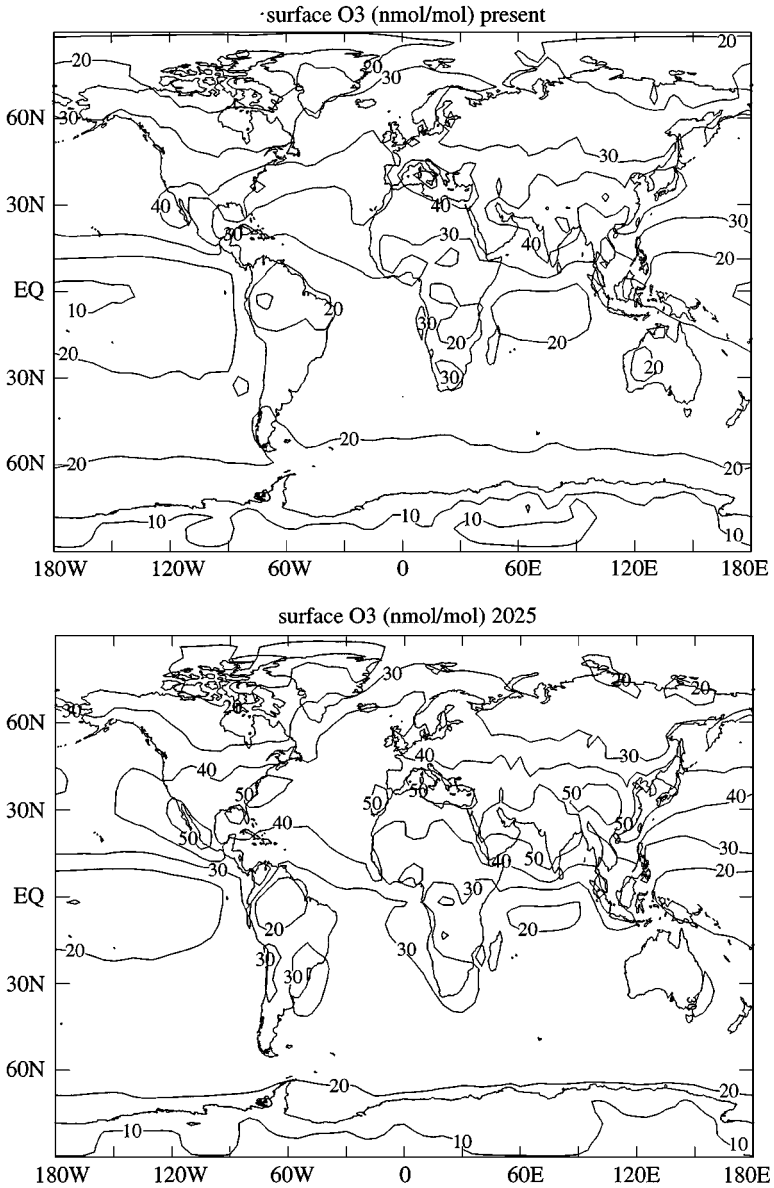
surface O3 (nmol/mol) present

surface O3 (nmol/mol) 2025

Figure 3 (Top) Model-calculated annual average O_3 mixing ratios (nmol/mol) at the surface for the present atmosphere and (bottom) for the year 2025. The future model calculations are based on the "moderate growth" scenario IS92a of the Intergovernmental Panel on Climate Change (1996) (Lelieveld & Dentener 2000).

may have to be multiplied by about a factor of 1–5 when the other factors mentioned above are included (Intergovernmental Panel on Climate Change 1999). Because of the great uncertainty and the complex nature of the problem, considerable scientific attention should continue to be given to the atmospheric effects of aviation.

Major uncertainty in estimating the impact of aviation on atmospheric chemistry arises also from the difficulty of modeling the impact of convective upward transport of ground-level pollutants, for example, NO_x, SO_2, and reactive and partially oxidized hydrocarbons, from the boundary to the upper troposphere as well as the production of NO by lightning in thunderstorms (Berntsen & Isaksen 1999). Among the ground-level emissions, photolysis of partially oxidized compounds ($(CH_3)_2CO$, CH_3O_2H, and other organic hydroperoxides may provide a greater source of HO_x in the upper troposphere than provided for by Reaction 2, which may enhance O_3 production (Singh et al 1995, Prather & Jacob 1997, Chatfield & Crutzen 1990).

IMPORTANCE OF THE TROPICS IN ATMOSPHERIC CHEMISTRY

We now address the distribution of the all-important HO radical. Figure 4 shows calculated HO concentrations, averaged over 24 hours (at night the concentration drops to near zero). Maximum concentrations occur in the tropics, with an average of only about one HO radical per 10^{13} air molecules. Towards higher latitudes and in winter, the values decrease rapidly. The reasons for the low-latitude HO maximum are high solar irradiance, a natural minimum in the vertical O_3 column over the tropics, which results in maximum penetration of HO-forming UV radiation in the troposphere, and high humidities, all of which favor higher HO concentrations through Reactions 1 and 2. Of course, the model-calculated HO concentration values in Figure 4 must be validated. Fortunately, we have a way to check the main features of the calculated HO distributions by comparing theoretical and calculated distributions of methylchloroform (CH_3CCl_3), an industrial solvent. Because there are no natural sources of CH_3CCl_3, whereas accurate information about its industrial production is available, the CH_3CCl_3 emissions to the atmosphere are well known. Because atmospheric concentrations are monitored in a global network, we can estimate how much CH_3CCl_3 is being decomposed by reaction with HO radicals, which provides a measure of the global average HO concentration (Prinn et al 1995). Even better, we can compare the extent to which the model is able to reproduce measurements of CH_3CCl_3 at different locations. Figure 5 shows that the calculated values agree very well with those observed. Thus, the calculated HO radical concentrations and latitudinal distribution, as shown in Figure 4, are indirectly confirmed. The use of chemical tracers, such as shown here for CH_3CCl_3, is the only practical way to derive globally
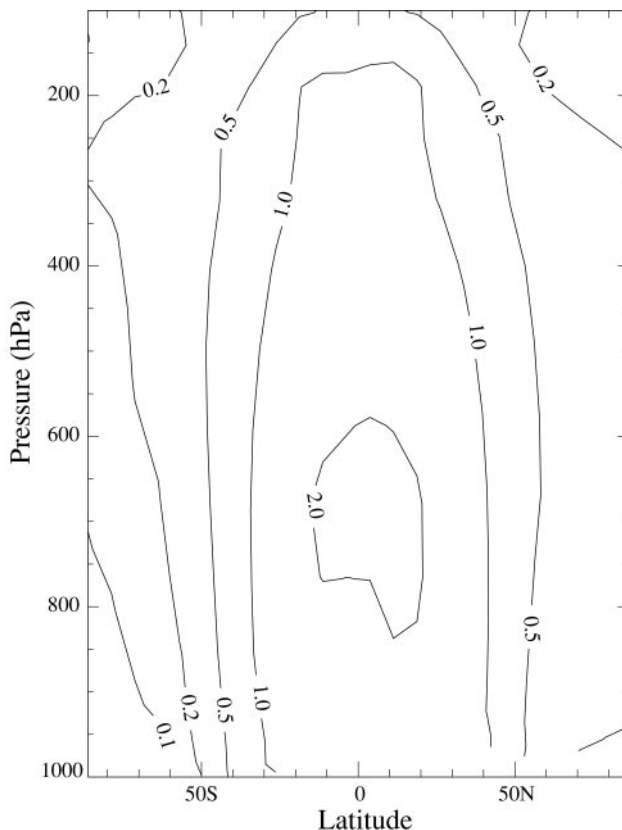
Figure 4 Model-calculated zonal and annual mean HO distribution in the troposphere (in millions of molecules cm^{-3}) (Lelieveld & Dentener 2000).

averaged HO concentrations and trends. Direct measurements of highly variable HO cannot lead to that goal, although they are important to test photochemical theory. Given the HO concentrations, we can also make estimates the decomposition rates of atmospheric trace gases, such as CH_4 and CO, yielding some of the budget results discussed above. A comprehensive discussion of tropospheric HO is presented by Spivakovsky et al (2000).

Unfortunately, we know very little about atmospheric chemistry in the tropics and subtropics. Many of the changes in atmospheric chemistry during the coming decades will probably come mainly from these regions, in which much of the world population lives and in which population growth is still considerable. Therefore, it is very important that research efforts in the tropics and subtropics be intensified. Particularly important will be the participation of scientists from these regions.

Figure 5 Comparison between model-calculated (solid lines) and measured (boxes) methyl chloroform (CH_3CCl_3) mixing ratios, performed to test the model simulation of HO (Houweling et al 1998). Average values appear to be well captured by the model, although the variability, especially at Mace Head (Ireland), is underestimated.
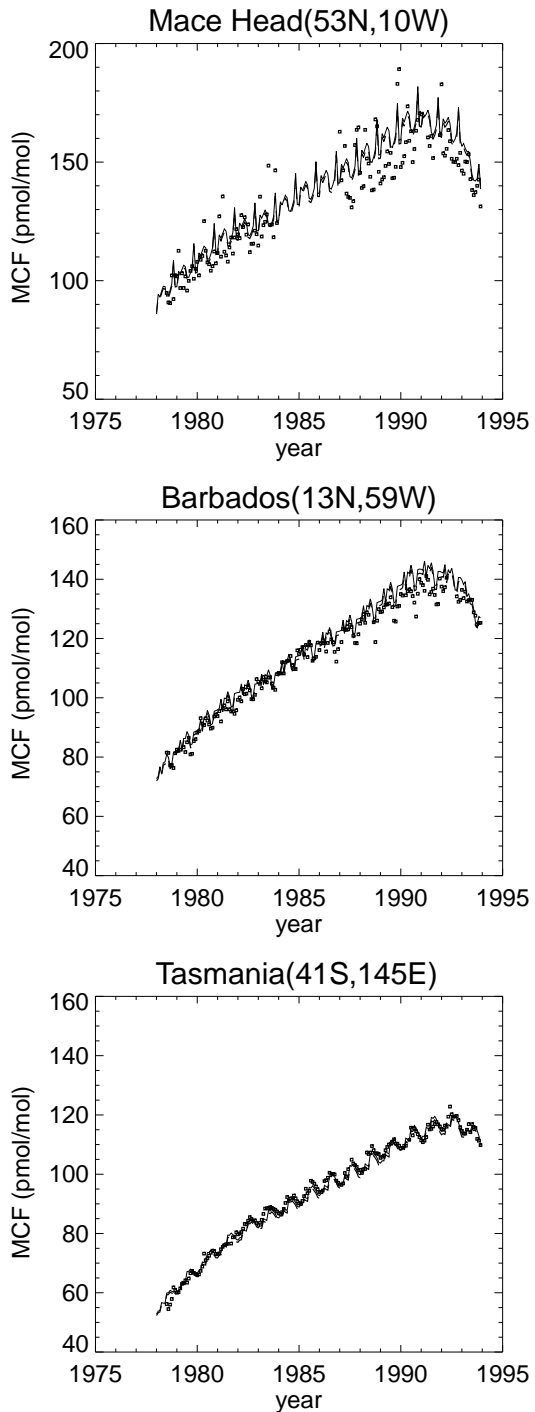
BIOMASS BURNING AS A POLLUTION
SOURCE IN THE TROPICS

Biomass burning is the principle source of air pollution in the tropics. The burning takes place during the dry season, between December and April in the northern hemisphere and shifted by 6 months in the southern hemisphere. Several human activities involve biomass burning: slash and burn agriculture, forest clearing for permanent farms and cattle ranches, burning of savanna grasses, wood burning for cooking and heating, and agricultural-waste burning. Table 4 shows quantities of

TABLE 4 Carbon emitted through biomass burning, mostly in the form of CO_2 ($\sim$90%) but with substantial contributions from CO, CH_4, and other hydrocarbons, and comparisons of emissions of several gases and particulate matter from biomass burning to the estimated total sources

Sources	Amount (Tg year^{-1})
Slash and burn agriculture	500–1000
Forest clearing	200–700
Savanna grass fires	300–1600
Wood burning	300–600
Agricultural wastes	500–800
Total	1800–4700

Compound	Amount	Emissions from Biomass Burning (Tg year^{-1})	Total Emissions by All Sources (Tg year^{-1})
All carbon		1800–4700	
CO_2		1600–4100	
CO	$43 \pm 13\%$	400–700	780–1960
CH_4	$6.6 \pm 5\%$	10–70	520–680
H_2		5–16	36
CH_3Cl		0.5–2	2
NO_x	$18.1 \pm 11.3\%$	3–13	30–73
RCN	$3.4 \pm 2.5\%$	0.5–1.7	>0.4
NH_3	$3.8 \pm 3.2\%$	0.5–2.0	20–60
N_2O	$0.7 \pm 0.3\%$	0.1–0.3	12–14
SO_2	$2.2 \pm 1.3\%$	1.0–4.0	70–170
COS	$0.01 \pm 0.005\%$	0.04–0.20	0.6–1.5
TPM	30 ± 15 g/kg C	36–154	$\approx$1500
POC	20 ± 10 g/kg C	24–102	$\approx$180
EC	5.4 ± 2.7 g/kg C	6.4–28	20–30

burned biomass estimated by Crutzen & Andreae (1990), which amount to 2–5 $\times$ 10^{15} g C year^{-1} in the tropics. For comparison, fossil-fuel burning releases about 5.5 $\times$ 10^{15} g C year^{-1}.

Biomass burning produces the same gases as the burning of fossil fuels, but generally with higher pollutant-emission factors. This means that during the dry season in the rural areas of the tropics, photochemical smog can develop, which results in the accumulation of a considerable amount of CO and O_3. This large-scale photochemical smog affects large areas of the tropical world, which can clearly be observed from space (Fishman 1991, Reichle et al 1986), especially in the southern hemisphere where emissions from fossil-fuel burning are smaller. Contrary to what might have been presumed, the tropics and subtropics and the southern hemisphere are already strongly affected by pollution caused by biomass burning (Figure 6). Note that the photochemical smog caused by biomass burning is largely a rural phenomenon, affecting large areas in the tropics and subtropics, whereas that in the industrial regions occurs more on the urban/suburban scale. The emissions of NO_x by biomass burning may thus be more efficient in O_3 production than those emitted by fossil-fuel combustion.

CONCLUDING REMARKS

Only a limited overview of the impact of human activities on atmospheric chemistry can be given here, and reference is made to the many detailed reports that are published by international organizations, such as those by the Intergovernmental Panel
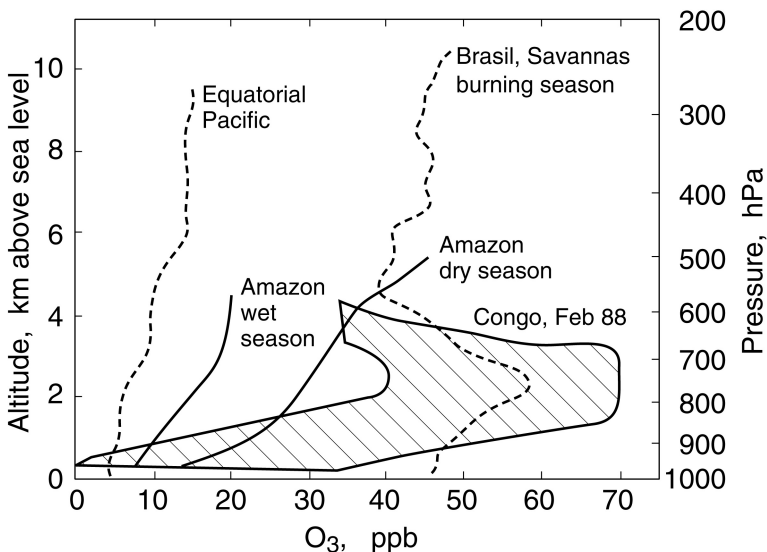

Figure 6 Typical variability of ozone profiles in the tropical troposphere, showing the contrast between continental and marine concentrations. Highest O_3 concentrations are measured during the dry season when biomass burning takes place.

on Climate Change (1996) and the World Meteorological Organization/United Nations Environment Programme (1999). General interest in atmospheric chemistry has expanded in major ways over the past 3 decades, beginning with the concern about air-pollution effects on human health and agriculture and the impact of "acid rain" on forests and inland waters, and moving thereafter to the global aspects of atmospheric chemistry, especially stratospheric ozone depletion and effects of increasing trace species on climate. Human activities now influence atmospheric chemistry in many ways, some of the most important ways having been discussed in this overview.

Because of the continuing growth in the world population and the associated technological and agricultural developments in most of the world's nations, human influences on atmospheric chemistry and the chemical composition of the atmosphere will continue to grow in future decades on all scales from the local to the global. Of particular importance in this respect are the tropics and subtropics, the regions of the earth that dominate atmospheric photochemistry because of the presence of maximum concentrations of HO radicals and strongly increasing emissions from human activities. Especially in these regions, atmospheric chemistry research needs to be accelerated, which requires a strong involvement of local scientists.

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