

STRATOSPHERIC OZONE  
DEPLETION – AN OVERVIEW  
OF THE SCIENTIFIC DEBATE

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**Stratospheric Ozone Depletion - An overview of the scientific  
debate**

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## Abstract

For almost half a century it was widely believed that the photochemistry of the stratosphere and hence ozone distribution were well understood. As observations revealed a gap between observed and predicted values it was recognised that a number of substances acted as catalysts thereby increasing the destruction of ozone and that man could augment those catalysts and affect the ozone layer.

Initial concern focused on nitrogen oxides from the exhausts of supersonic transport, but attention switched in the mid-seventies to chlorofluorocarbons (CFCs). Although the theory of anthropogenic ozone depletion by CFCs found widespread scientific support the perceived threat was minimised in particular by successive model predictions downgrading the amount of depletion. The appearance of the ozone hole over Antarctica in the mid-eighties reopened the debate as to whether such depletion was anthropogenic or natural in origin. It also highlighted the model's inadequate treatment of the processes occurring in the stratosphere and the importance of dynamics and radiative transfer in stratospheric ozone destruction. Scientific consensus again favours the anthropogenic depletion of the ozone layer. In conclusion it is considered that the degree of consensus outweighs the image of scientific uncertainty that is often portrayed in relation to the issue of stratospheric ozone depletion.

Keywords: Stratospheric ozone Chlorofluorocarbons Ozone hole

## Stratospheric Ozone Depletion - An overview of the scientific debate

### Introduction

The debate surrounding the likely impact of human activity on the stratospheric ozone layer has its origins in the early 1970s with concern over the effect of supersonic transport (SST) on the ozone layer. This was followed in the mid-seventies by the realisation that man-made chemicals, chlorofluorocarbons (CFCs), could also deplete ozone.

The aim of this paper is to provide an overview of the scientific debate. The importance, known distribution and fluctuations of the ozone layer will be discussed before going on to consider the physical processes which affect stratospheric ozone. These sections will present current understanding and will not consider uncertainty, this is left to the section on the debate. Although the scientific debate concentrates on the photochemical processes involved, atmospheric dynamics and radiative transfer also play vital roles. Indeed the debate highlights the interdependency of these processes and the difficulty of proving an anthropogenic variation in stratospheric ozone given the high degree of natural variability. The conclusion places the scientific debate within the wider context of policy issues and the need

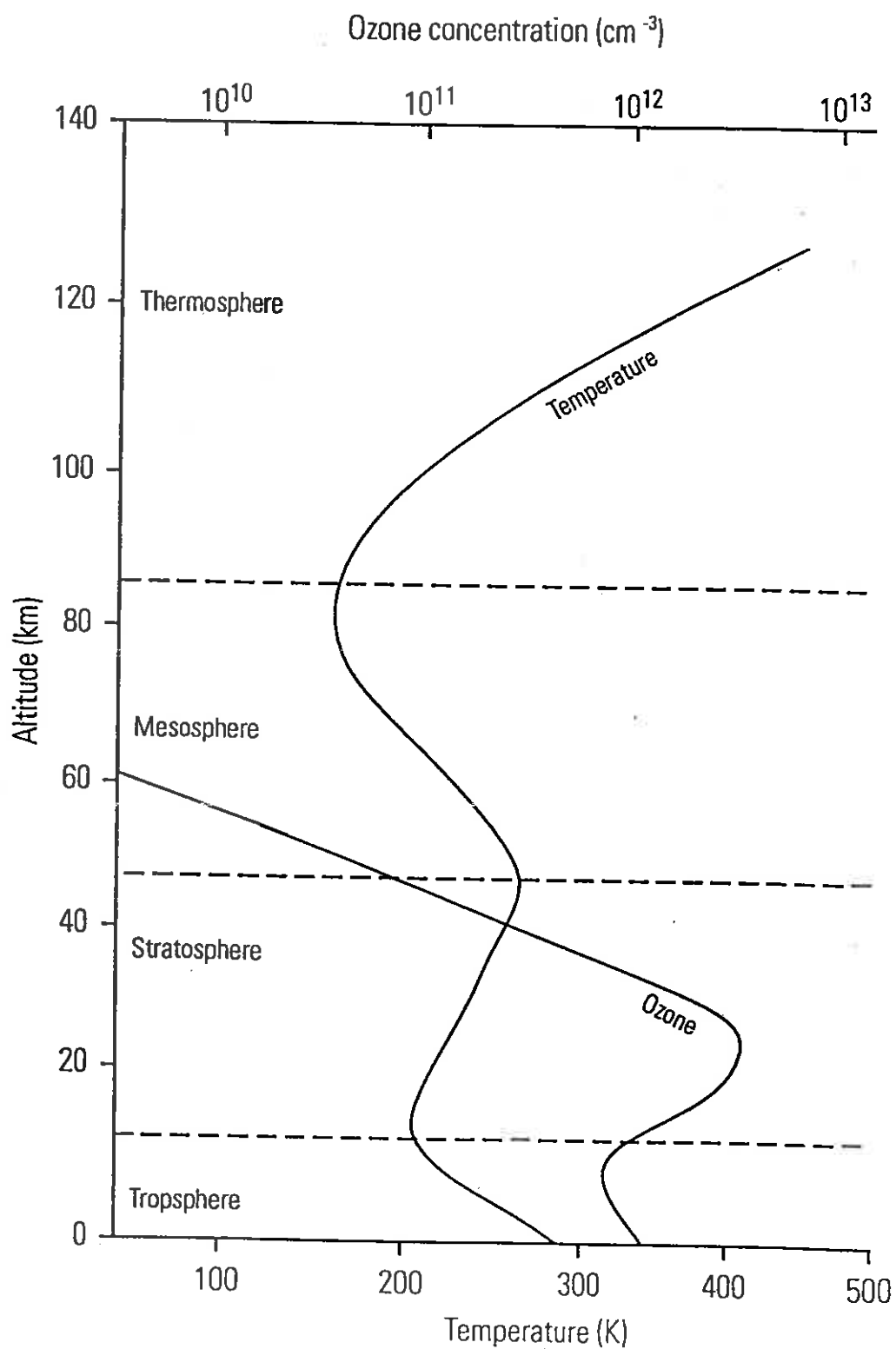
for scientific certainty.

### **The Importance of the Stratospheric Ozone Layer**

Ozone ( $O_3$ ), a gas containing three oxygen atoms, is measured using Dobson units (1 Dobson Unit = 1 milli-cm atm of column ozone). The average global abundance of ozone is 300 Dobson Units (Gribben, 1989) and it occurs in trace amounts throughout the vertical extent of the atmosphere. However ozone is most important and abundant in the stratosphere where, between 15 km and 40 km altitude, a thin layer occurs with a peak concentration at about 25 km (Figure 1). It is important because the ozone absorbs ultraviolet radiation, which is known to be harmful to life (Solomon, 1988). The ozone, combined with small amounts of oxygen, is so efficient at absorbing ultraviolet radiation that no radiation with a wavelength less than 298 nm penetrates into the troposphere. Ultraviolet radiation in the wavelength range 280 to 315 nm is commonly called UV-B radiation. If the ozone layer is depleted the intensity of UV-B will increase and proportionately more radiation at shorter wavelengths will penetrate to the lower atmosphere (Madronich et al., 1991).

The effect of increasing UV-B radiation on the environment is assessed every 4 years under Article 6 of the Montreal Protocol (UNEP, 1989). As this is the most carcinogenic part of the solar UV spectrum (UNEP, 1991) it is expected that the

Figure 1 - Vertical distribution of atmospheric ozone after Harries (1991). Reprinted by permission of Ellis Horwood Publishers.



incidence of skin cancers (both melanoma and non-melanoma) will increase especially amongst caucasians. Ocular damage and increasing numbers of cataracts are also predicted. UNEP (1991) reports growing evidence that UV-B suppresses the human immuno-defence system and that this occurs in both fair and dark skinned individuals. Studies of plants indicate that growth, yield and photosynthesis may all be reduced, with aquatic ecosystems being particularly badly affected. Insects which can see in the ultraviolet may also be affected (Crutzen, 1974).

### **Stratospheric Ozone Climatology**

The distribution of stratospheric ozone varies naturally in space and through time. Therefore to assess whether any anthropogenic induced changes have occurred, it is necessary to know the natural distribution and fluctuations. Ozone is predominantly produced above 25 km altitude (Figure 1) by photochemical reactions and then stored in the lower stratosphere, where it is redistributed by the atmospheric winds.

Ozone is created near the equator and then transported to the poles where it is destroyed. The column abundance of ozone is 225 DU at the equator and 600 DU at the South Pole (Salby, 1992). At the tropics, where ozone is least abundant, it varies little with the seasons. Seasonal variations become

most marked poleward of  $30^{\circ}\text{N}$ . Ozone is more abundant at higher latitudes all year round (Brasseur and Solomon, 1986) reaching maximum values during late winter and early spring (McFarland and Kaye, 1992). In the northern hemisphere the maximum is positioned close to the pole ( $70$  to  $75^{\circ}\text{N}$ ) occurring at the end of March, whereas in the southern hemisphere it is displaced away from the pole and occurs earlier in the year. This distinct difference between the two hemispheres is mostly due to changes in the amount of ozone below  $20$  km altitude, which appears to be related to the transport of ozone in weather systems that propagate into the lower stratosphere (Brasseur and Solomon, 1986).

Shorter term variations occur which are related to atmospheric wave activity in the middle and high latitudes during winter (Solomon, 1988). These are closely linked to changes in the tropopause height, the formation of weather systems and corresponding temperature perturbations. Longer term variations in the total amount of ozone are linked to variations in the zonal flow of the stratospheric wind ('quasi-biennial oscillation' or QBO) and the 11 year solar sunspot cycle. Other solar phenomenon, such as solar flares, also appear to affect ozone. An aerosol layer of sulphate, called the Junge layer, occurs in the stratosphere (Brune, 1991) and is believed to help ozone destruction. Primarily this is formed from the photodissociation of carbonyl sulphide ( $\text{COS}$ ) which originates from the troposphere (McFarland and



Kaye, 1992). However it can be augmented by direct injection of sulphate from volcanic eruptions resulting in variations in the amount of ozone.

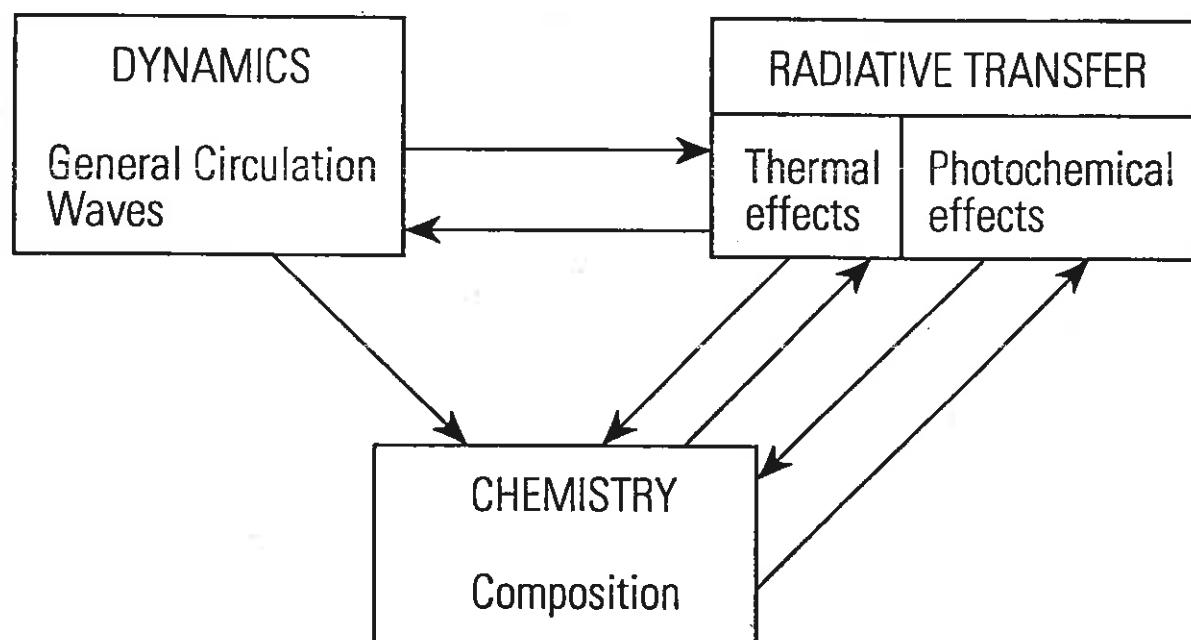
### **Processes affecting Stratospheric Ozone Distribution**

Brasseur and Solomon (1986) summarise the couplings between the chemistry, radiation and dynamics of the stratosphere as follows (see also Figure 2): Dynamics control the distribution of atmospheric constituents in space and time, and the dynamics are affected by the temperature distribution in the stratosphere. The temperature of the stratosphere is controlled by those atmospheric constituents which are radiatively active. These constituents will in turn be controlled by photochemical processes which are themselves temperature dependent. To understand the response of the stratosphere to external perturbations, whether natural or anthropogenic in origin, all the above mechanisms have to be taken into account.

### **Photochemical Processes Affecting Stratospheric Ozone**

Photochemical reactions occur frequently in the stratosphere producing free radicals which can then react with other constituents of the atmosphere (Brasseur and Solomon, 1986). Temperature can affect the reaction rate thereby determining the rate of production or destruction of a chemical. Therefore the lifetime of a chemical will depend on the reaction rates.

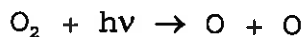
Figure 2 - Interactions between chemistry, radiation and dynamics in the stratosphere after Brasseur and Solomon (1986). Reprinted by permission of Kluwer Academic Publishers.



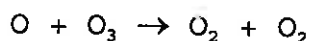
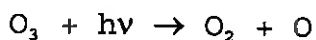
If the lifetime is short compared to the time necessary for the atmospheric winds to move the chemical in the atmosphere (transport time) then the effects of transport are negligible and photochemical equilibrium can be reached. For ozone, photochemical equilibrium occurs above 25 km (Crutzen, 1972).

Ozone is constantly being created and destroyed by these photochemical reactions and the first attempt to describe this cycle of formation and destruction was made by Chapman (1930a and 1930b) as follows:

#### Formation



#### Destruction



M is any other energy-removing air molecule, which acts as a catalyst.

This model remained unchanged until the 1950s when Bates and Nicolet (1950) suggested that there were additional cycles of destruction due to the catalytic action of atomic hydrogen (H), hydroxyl (OH) and perhydroxyl ( $\text{HO}_2$ ). These catalysts form

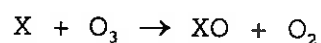
predominantly from the dissociation of methane, the photodissociation of water vapour, mainly above 60 km, and the destruction of molecular hydrogen. Monitoring of the ozone layer (Gribben, 1989) had revealed that the amount of stratospheric ozone predicted by the Chapman equations (Schiff, 1969) was far larger than that observed (Hunt, 1966). These additional cycles were still too slow to account for the observed concentrations of ozone (Crutzen, 1970) meaning that further cycles required identification.

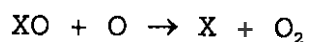
Bates and Hays (1967) suggested that nitrous oxide ( $\text{N}_2\text{O}$ ), produced by microbes in the soil, might move into the stratosphere where it could be photodissociated into nitrogen oxides ( $\text{NO}$  and  $\text{NO}_2$ ). Crutzen (1970) proposed that these could then catalytically enhance the destruction of ozone. A potentially large source of nitrogen oxides are the exhaust gases of supersonic aircraft (Johnston, 1971; Crutzen, 1971). Other anthropogenic sources of nitrogen oxides are the atmospheric testing of nuclear weapons (Crutzen, 1974) and the use of nitrogen based fertilizers (McElroy et al., 1976). Solar flares emit high energy particles which enter the upper atmosphere producing nitrogen oxides which may then enter the stratosphere and affect ozone (McFarland and Kaye, 1992).

Stolarski and Cicerone (1974) and Molina and Rowland (1974), suggested that stratospheric ozone could be destroyed by oxides of chlorine. Stolarski and Cicerone (1974) noted that

there were many potential sources of chlorine. Some, such as volcanic eruptions and solid fuel rockets, would eject chlorine straight into the stratosphere. Others, such as fumaroles, sea salt spray and industrial processes, would emit chlorine into the troposphere from where it would have to be transported into the stratosphere. However, Molina and Rowland (1974) drew attention to CFCs, a potentially large anthropogenic source of chlorine in the stratosphere. CFCs photodissociate under ultraviolet light (190-225 nm) which can penetrate into the middle stratosphere, though not into the troposphere (Rowland, 1974). Therefore if CFCs were transported into the stratosphere, above 25 km, they could break down to release chlorine atoms which could then destroy the ozone layer.

Present understanding suggests that ozone is destroyed in the stratosphere mainly through catalytic cycles involving four active free radical families, namely Hydrogen Oxides ( $\text{HO}_x$ ), Nitrogen Oxides ( $\text{NO}_x$ ), Chlorine Oxides ( $\text{ClO}_x$ ), and Bromine Oxides ( $\text{BrO}_x$ ) (WMO, 1985). These families are often referred to in the literature as odd oxygen (e.g. atomic oxygen (O) and ozone ( $\text{O}_3$ )), odd nitrogen (e.g. nitric oxide (NO), nitrogen dioxide ( $\text{NO}_2$ )), odd chlorine etc (see Crutzen (1972) for more details). The destructive reaction for all the families can be described by





where the catalyst X can be H, OH, NO, Cl or Br.

The relative importance of each catalytic cycle varies with altitude. Above 40 km odd hydrogen cycles dominate the destruction of ozone. Between 35 and 45 km the most efficient destruction cycle is nitrogen but chlorine is also efficient at these altitudes. At lower altitudes the efficiency with which ozone is destroyed by these compounds is restricted by the lack of atomic oxygen. However there is some destruction of ozone by odd hydrogens and odd chlorine at the tropopause and at 20 km altitude, respectively. Several of these cycles are temperature dependent, more ozone destruction occurring with increasing temperature (McFarland and Kaye, 1992). There are also other 'secondary' catalytic cycles which compete for the chlorine and result in no change in the amount of ozone.

Ozone production occurs predominantly in the upper stratosphere and is independent of temperature (McFarland and Kaye, 1992). There are catalytic cycles occurring in the lower stratosphere which form ozone. These involve methane (CH<sub>4</sub>) and carbon monoxide (CO) together with hydroxyl (OH) and nitric oxide (NO) (Brasseur and Solomon, 1986).

### ***Dynamical Processes Affecting Stratospheric Ozone***

To a large extent the distribution of ozone in a vertical column can be explained by the photochemistry. However work in the late 1920s showed that the amount varies with weather patterns, season and latitude. Later observations revealed large geographical variations in total ozone (London and Park, 1974). These variations can arise because in the lower stratosphere the lifetime of ozone is comparable to the rate at which it is transported by physical processes and so ozone can be transported by the atmospheric winds. Therefore an accurate description of the stratospheric ozone distribution requires an understanding of atmospheric dynamics.

The increase of temperature with height in the stratosphere greatly reduces vertical mixing and consequently gases injected into the stratosphere have long residence times. This is enhanced by the extreme dryness of the stratosphere which is due to the very cold temperatures. Gases that would be washed and rained out of the troposphere will remain in the stratosphere and large concentrations can accumulate. The meridional wind, like the vertical motions, is weak. However the zonal flow is intense and in the winter hemisphere it has a wavelike structure at high latitudes owing to large scale planetary waves (Brasseur and Solomon, 1986). A polar vortex forms over the pole of the winter hemisphere, effectively isolating the stratospheric air over the polar region during the polar night. This feature will now be discussed in some

detail because it is believed to be of fundamental importance in explaining the depletion of stratospheric ozone at polar regions, observed in recent years.

The dynamics of the stratospheric polar vortex are described by Schoeberl and Hartmann (1991). The vortex forms poleward and above the subtropical jet and is considerably more intense in the southern hemisphere owing to the unique geographical position of Antarctica. Centred at the pole and isolated from the surrounding land masses a circumpolar ocean current essentially cuts off Antarctica from the influence of warmer surface water. In the atmosphere the subsiding air over the high plateau of Antarctica leads to circumpolar westerlies. In the northern hemisphere Rossby waves propagate into the stratosphere owing to the mountain ranges of North America and Asia. In contrast the atmosphere over Antarctica is rarely disrupted as only the Andes have any major topographic effect on the east-west flow.

With the onset of the polar night temperatures start to decrease and may fall below 195 K ( $-78^{\circ}$  C) in the lower stratosphere (McFarland and Kaye, 1992). In the southern hemisphere the drop in temperature closely follows the decrease in sunlight but this is not the case in the northern hemisphere because the vortex is frequently disrupted by planetary waves. The low temperature in the stratosphere allows the formation of polar stratospheric clouds (PSCs). The



type of PSC formed is dependent on temperature. At temperatures around 195 K ( $-78^{\circ}$  C) clouds composed of nitric acid trihydrate ( $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ ) are believed to form whereas at temperatures of 205 K ( $-88^{\circ}$  C) water-ice clouds form. The area of low temperature is larger in the southern hemisphere than in the northern hemisphere so PSCs are more likely to form there (Schoeberl and Hartmann, 1991).

The cooling in the atmosphere leads to a downward flow of air in the polar regions and weak rising motion elsewhere. Upper stratospheric air moves down in the vortex carrying its chemical composition with it (Schoeberl and Hartmann, 1991). The downward motion in the vortex also leads to warming due to adiabatic compression. Below 30 km altitude the descent lessens due to radiative equilibrium being reached. Outside the vortex the air is warmer and as a consequence the rate of descent should be greater than that in the vortex, but this is offset by the mixing influence of the planetary waves (Schoeberl and Hartmann, 1991). The polar vortex can be viewed as a containment vessel, the boundary impermeable to inflowing air (Plumb, 1990). Winds in the polar night jet can attain speeds of up to  $60 \text{ ms}^{-1}$  near the stratopause (Salby, 1992).

In spring the sun returns to the polar regions and the meridional temperature gradient weakens. The polar vortex disappears quite suddenly, and is referred to as the final stratospheric warming event. In the final warming the

amplitudes of the planetary waves increase breaking the polar vortex into segments which drift equatorward. In the northern hemisphere the final warming usually occurs in March and in the southern hemisphere as late as early December (Schoeberl and Hartmann, 1991). In the summer hemisphere the zonal flow is easterly but also intensifies near the stratopause. At the tropopause this easterly flow may interact with the weak easterlies in the tropics (Salby, 1992). The zonal flow in summer is usually parallel to the latitude circles and no wave structure is detectable (Brasseur and Solomon, 1986).

The QBO is a reversal in the zonal flow in the tropical lower stratosphere which has a period of approximately 28 months. The strength and temperature of the polar vortex responds to the year to year changes in planetary wave activity and this activity seems to follow the phase of the QBO, with an easterly phase corresponding to greater planetary wave activity and a weakened polar vortex (Schoeberl and Hartmann, 1991). The QBO effect is strongly dependent on latitude and altitude (McFarland and Kaye, 1992) and changes the concentration of ozone in the stratosphere by as much as 5% of the mean column ozone.

### ***Radiative Processes Affecting Stratospheric Ozone***

Stratospheric ozone absorbs ultraviolet radiation and it is this which controls the temperature structure of the stratosphere. The previous two sections have shown how the

temperature is a controlling factor in both the photochemical reactions and dynamics of the stratosphere. Therefore radiative processes can affect stratospheric ozone distribution through the control of temperature. Also the chemical reactions that form and destroy ozone are dependent on the wavelength of sunlight; any change in solar output reaching the stratosphere can change the amount of stratospheric ozone. During the 11 year solar sunspot cycle the amount of ultraviolet radiation changes particularly at shorter wavelengths. It is these wavelengths that are important in the formation of ozone, so increasing solar UV can lead to increasing stratospheric ozone. However the increased UV also affects the temperature of the stratosphere, which affects ozone destruction and the transport of ozone. The recent solar maximum (1990) seems to have led to an increase in the amount of ozone (Herman et al., 1991).

It may appear that stratospheric ozone depletion will lead to a warming of the troposphere because more ultraviolet radiation will penetrate into the lower atmosphere to be absorbed there. However, the stratosphere will cool given that less radiation is being absorbed there resulting in a reduction of the radiative forcing on the surface-troposphere system and an overall cooling within the troposphere. This may have already had an important impact on the global climate because CFCs are strong absorbers of longwave radiation contributing to global warming (Houghton et al., 1990, 1992).

Current analyses imply that on a global average the decrease in radiative forcing on the surface-troposphere system by stratospheric ozone depletion is exactly offset by the increased radiative forcing due to increased levels of CFCs (Houghton et al., 1992). However the distribution of stratospheric ozone varies with latitude and region and thus the result is very uneven and could have important consequences in terms of global warming.

### **The Scientific Debate**

In order to assess the potential effect that human activity might have on the stratospheric ozone layer, computer models are frequently used to estimate the steady state change in the globally averaged total ozone column (Solomon, 1988). These models have inherent limitations (Brasseur and Solomon, 1986 and Trenberth, 1992) and many of the early studies were completed with simple one dimensional models. Although much of the controversy centred on whether these models were sufficiently accurate to make any valid predictions some objections to a man-made stratospheric ozone depletion were far more fundamental. The idea that the force of nature is greater than any man-made force is central to some of the objections.

### **The Early Issues**

The first consideration of human influence on the ozone layer

was in 1970 when a "Report of Critical Environmental Problems" (Wilson and Matthews, 1971) discussed the possible effect of combustion products from SST on the ozone layer. Only water vapour was thought to affect the ozone layer through enhanced catalytic destruction, other combustion products, namely carbon monoxide and nitrogen oxides, were considered to have negligible affect. However both Johnston (1971) and Crutzen (1971) considered that nitrogen oxides from SST might be important. The nitrogen oxides would be able to accumulate in the lower stratosphere owing to its dynamic stability and dryness (Brasseur and Solomon, 1986) and have a residence time in the order of 2 years (Crutzen, 1972).

Most of the studies into SST used as their baseline some variation of the Federal Aviation Administration estimate that, by 1985, there would be 500 supersonic aircraft cruising in the stratosphere for an average of 7 hours per day. Of these 500 aircraft 334 would have 4 engines and the remainder 2. Johnston (1971) using a simple chemical model estimated that the amount of NO emitted by the aircraft could reduce the ozone layer by a factor of 2. However the problem needed to be considered in an atmospheric model where the dynamical processes could be treated properly (Crutzen, 1971). Results from models containing a simple treatment of atmospheric motions did not differ significantly from those found by Johnston (1971) (Crutzen, 1972 and references therein).

Confidence in these results were low (Crutzen, 1972) for several reasons: It was unclear how significant man-made nitrogen oxides were because the natural level was only known to a factor of 10. The altitude of the aircraft would affect the residence time of the exhaust gases in the stratosphere. Using a two dimensional atmospheric model with an oxygen-hydrogen-nitrogen chemistry, Hesstvedt (1974) found that the amount of ozone depletion depended critically upon the altitude at which the aircraft flew. The higher the altitude the greater the ozone depletion; 0.3% for 18 km, 2% for 23 km and 5% for 28 km altitude. Furthermore the flight corridors and seasonal operation intensity of aircraft could lead to nitrogen oxide concentrations in some localities 10 times higher than the estimated global accumulations (Crutzen, 1972). This could then interact with the seasonal and geographic variations of ozone, substantially thinning the ozone layer in some localities.

Goldsmith et al. (1973) considered the threat to the ozone layer from supersonic aircraft in comparison with nuclear weapon testing which also produces nitrogen oxide. They estimated the number of operational Concorde required to produce a quantity of NO comparable to the annual output of nuclear weapon testing from 1952 to 1972. It was concluded that during 1961 and 1962, at the height of testing, 800 Concorde would have been necessary to match the NO from nuclear explosions. Even given the differences in which the NO

would be transported and distributed in the stratosphere by the two processes stratospheric ozone would already have been subjected to a large volume of NO. However, Goldsmith et al. (1973) detected no significant downward trend in the amount of ozone which could be associated with the weapons testing, concluding that nitrogen oxides did not produce major changes in the ozone layer. This contradicted a report by Johnston et al. (1972) which had found a significant downward trend in the total ozone column associated with nuclear weapons testing.

### ***The Chlorofluorocarbon Debate***

Although both Stolarski and Cicerone (1974) and Molina and Rowland (1974) identified chlorine in the catalytic destruction of ozone it was the naming of CFCs, a widely used aerosol propellant, in the latter paper which captured media and public attention (Roan, 1986). As it became clear that large fleets of SSTs would not be built, much of the scientific debate focused on CFCs. Owing to their long lifetime in the troposphere, perhaps 50 to 400 years, CFCs could continue to affect ozone for many years (McFarland and Kaye, 1992). Lovelock (1971) showed that CFCs were distributed worldwide and were increasing. Molina and Rowland (1974) considered there were few natural sinks for CFCs and at stratospheric temperatures the catalytic destruction of ozone by chlorine would be far more efficient than by its nitrogen oxide counterparts (Molina and Rowland 1974). Their simple one dimensional model indicated that chlorine released from CFCs

would result in stratospheric ozone destruction.

Many of the objections raised to this theory were based on doubts as to whether laboratory and model studies were reliable enough to apply in the real atmosphere (Scorer, 1974). The chemical reaction rates used to calculate stratospheric ozone depletion had only been observed in the laboratory. It was argued that the models failed to represent the stratospheric chemistry realistically enough to make any prediction valid and that the one dimensional models using vertical diffusion to represent transport were wholly inadequate (Scorer, 1974, 1975). Indeed large local fluctuations in total ozone due to weather systems would prohibit the accurate modelling of the variability of total ozone except in three dimensional models (Brasseur and Solomon, 1986).

Models which failed to include all the chemical reactions providing temporary sinks for ozone depleting substances would overestimate the amount of ozone depletion (Eggleton et al., 1976). During 1975 and 1976, Lazarus et al. (1976) measured the amount of hydrogen chloride (HCl) in the stratosphere, because this is a temporary sink of free chlorine. Although model calculations suggested that HCl concentrations should be independent of solar intensity and the seasons, the measurements showed a marked seasonal variation meaning there was another temporary sink for chlorine which was dependent on



solar intensity. This was identified by Rowland et al. (1976) as Chlorine Nitrate ( $\text{ClONO}_2$ ) and this reduced the estimate by which ozone would be depleted by a factor between 0.7 and 0.85. By considering its effect on the nitrogen oxide destruction cycle as well, Eggleton et al. (1976) found the threat to the ozone layer was further reduced and depending on the actual rate of formation of chlorine nitrate might even lead to ozone increasing.

Apart from the dynamical and chemical uncertainties another major objection to the theory of ozone depletion was that the ozone layer was not significantly affected by chlorine from natural sources and therefore was quite capable of coping with chlorine from CFCs. It was not even clear that CFCs were the main source of chlorine in the stratosphere, as implicitly assumed by the proponents of CFC-induced stratospheric ozone depletion (Gribben, 1979). This was due to a lack of global monitoring of both man-made and natural sources of halocarbons. Lovelock (cited in Gribben, 1979) favoured methyl chloride as the main source of chlorine. Methyl chloride is released from natural sources into the atmosphere as well as being produced by some agricultural practices (Lovelock cited in New Scientist, 1975). Again the argument was presented that if the ozone layer could cope with chlorine from this source, which could potentially deplete ozone by 4% per year (Gribben, 1979), then it could cope with the chlorine from CFCs. In keeping with the Gaian philosophy of James Lovelock, it was

ozone layer but due to uncertainty over the scale of the problem did not recommend banning CFCs immediately (Gwynne, 1976). Successive reports of NAS, the World Meteorological Organisation (WMO) and the United Nations Environmental Program (UNEP) found the depletion theory to be without major flaws (WMO, 1985; Roan, 1989) but the perceived threat diminished because as the models increased in sophistication so the estimates of the extent of stratospheric ozone depletion dropped. In 1974 the predicted decrease in the total ozone column in 50 to 100 years was 13%, this increased to 19% in 1979 but had fallen to less than 5% in 1982 (Solomon, 1988). The use of CFCs in propellants continued to decline, but by the early nineteen eighties the production and use of CFCs had begun to increase again through increased use in other applications (McFarland and Kaye, 1992).

The dynamic and chemical effects of increasing carbon dioxide and methane were thought to reduce the impact of CFCs even further and by 1984 the threat to the ozone layer was seen as minimal (Solomon, 1988). In an article entitled '*Spray cans: the threat that never was*' (Allaby and Lovelock, 1980) the authors note with irony that in Lovelock (1971) the author anticipated "an emotional over-reaction" to the presence of CFCs in the atmosphere. It is perhaps doubly ironic that the article also contains the statement "Should there be any destruction of atmospheric ozone because of CFCs, therefore, the effect would be most pronounced in very high latitudes

during winter".

### ***The Antarctic Ozone Hole***

Continuous monitoring of the ozone layer had been carried out by the British Antarctic Survey team at Halley Bay (76° S and 27° W) and the Argentine Islands (65° S and 64° W) since 1957. Farman et al. (1985) published results which indicated that in the previous few years there had been considerable thinning of the stratospheric ozone layer over Antarctica during southern hemisphere springtime. They noted that "the annual variation of total O<sub>3</sub> at Halley Bay has undergone a dramatic change". None of the models had predicted this, neither had this been detected from satellites.

NASA had been monitoring the vertical ozone column since 1971 using various satellite instruments. In processing the raw data it had been assumed that total column ozone amounts below about 250 Dobson Units were erroneous, as these had never been observed anywhere in the world, and the processing routines rejected data which fell below that threshold value (Harries, 1990). The raw data were still available and were reprocessed without the threshold. The results published by Stolarski et al. (1986) confirmed the Farman et al. (1985) findings.

Although not strictly a hole, the thinning of the ozone layer over Antarctica has become widely known as the "ozone hole". Farman et al. (1985) proposed that it was a combination of the

special meteorological conditions that occur over Antarctica with the increase in anthropogenic catalytic destructors of ozone that led to the ozone hole. Farman et al. (1985) pointed out that the catalytic destruction of ozone by chlorine would be favoured under the cold conditions which exist in the Antarctic polar vortex once spring and sunlight arrived. The eventual breakdown of the polar vortex and the penetration of warmer air over the continent would lead to a lessening of the destruction of ozone.

#### ***Post-Antarctic Hole***

Solomon (1988) sums up the change in the ozone layer as "unprecedented and unanticipated". Indeed none of the models had predicted such a change in the stratospheric ozone layer in 50 or 100 years let alone in the present-day atmosphere. It was clear that the models used to this point had an insufficient understanding of atmospheric dynamics and chemistry. The amount of research into stratospheric ozone depletion greatly increased in response to this challenge. As a consequence there are numerous reviews on the problem of the ozone hole: e.g. Schoeberl and Kreuger (1986), Solomon (1988), Brune (1991) and McFarland and Kaye (1992).

The initial debate after the discovery of the hole was framed in terms of whether the hole was a naturally occurring phenomenon or the result of increasing atmospheric pollutants. Naturally occurring phenomena included changes in the

meteorology and changes in the chemistry due to solar cycles (Solomon, 1988, and McFarland and Kaye, 1992). In November 1986 the journal *Geophysical Research Letters* devoted a special issue to ozone depletion. The overview by Schoeberl and Kreuger (1986) favoured a natural cause for the ozone hole (Roan, 1989) reporting that many investigators had noted decreases in the stratospheric temperature. It was suggested that a small climatic change in the upper atmosphere, which was caused by changes in the lower atmosphere possibly related to changes in sea surface temperature, accounted for the decrease in stratospheric temperature and antarctic ozone levels.

From satellite measurements of odd nitrogen compounds, Callis and Natarajan (1986) argued that the 1980 solar sunspot maximum was more intense than the previous two solar maxima. Because increased solar activity creates more odd nitrogen, this would lead to stratospheric ozone depletion. However other solar activity, which also drastically affected the odd nitrogen content of the stratosphere, did not appear to affect the ozone layer. Further, observational evidence showed that ozone depletion was greatest at 10 to 22 km and not at the high altitudes predicted by the solar activity theory (Solomon, 1988 and references therein). Tung et al. (1986) suggested that in spring when the sun (and radiative heating) returned to Antarctica there was an upwelling of the Junge layer, lifting the ozone layer in turn resulting in a seasonal

decrease of ozone. This upwelling, it was suggested, had increased in response to increased aerosols from recent volcanic eruptions or a general cooling of the stratosphere in winter and a resulting increase in stratospheric clouds.

The idea that chlorine from man-made pollutants was responsible for the ozone hole was soon to become accepted amongst the majority of scientists investigating the phenomenon (MacKenzie, 1987; WMO, 1988). Although the mechanisms are still not completely understood the current explanation for the occurrence of the Antarctic stratospheric ozone hole owes much to the original hypothesis of Farman et al. (1985). However it was realised that for ozone to be depleted by such large amounts at low altitudes the chlorine had to be available as reactive free radicals (Solomon, 1988).

As described earlier with the onset of winter a polar vortex is set up in the stratosphere over Antarctica and the low temperatures in the vortex allow the formation of PSCs. Most chemistry in the stratosphere occurs in the gas phase. The PSCs and Junge Layer provide a surface on which reactions occur between compounds which do not take place in the gas phase; termed heterogeneous reactions (McFarland and Kaye, 1992). Simply the presence of PSCs and aerosols allow the chlorine to be converted from a stable into a reactive form which is easily photodissociated by sunlight. The stratosphere is then said to be primed for ozone destruction. With the

arrival of the sunlight in spring the photolytic destruction of ozone can begin. Eventually the warmth of the sun destroys the polar vortex and warmer ozone rich air returns.

There are some important changes in the distribution of other atmospheric constituents as well as ozone. The concentration of ClO is greatly increased, given that it is produced during the destruction of ozone by chlorine. However the concentrations of many nitrogen compounds are decreased. It appears that odd nitrogen compounds also undergo heterogeneous reactions and are converted to nitric acid ( $\text{HNO}_3$ ) which can remain part of the PSCs. As the cloud particles get larger they move to lower altitudes and remove odd nitrogen compounds. In this case the stratosphere is said to have undergone denitrification. In some circumstances dehydration can also occur. This denitrification of the stratosphere is also an important prerequisite for ozone destruction because it stops the formation of some reservoir species of chlorine, allowing more reactive chlorine to form (Schoeberl and Hartmann, 1991).

The Antarctic ozone hole appeared to exhibit a biennial fluctuation, depletion in odd years being deeper than those in even years (Gribben, 1988). It was thought that this was linked to the QBO with the deepest holes occurring when the temperatures in the stratosphere were lowest and the polar vortex persisted well into spring (McFarland and Kaye, 1992).

In 1988 the hole was particularly small probably owing to a large amount of dynamic activity. However in recent years this biennial oscillation has been disrupted. It could be that the level of chlorine has reached such proportions that even in unfavourable meteorological conditions a hole can form (McFarland and Kaye, 1992). The hole of 1992 has been the largest so far, forming the most rapidly since measurements began at Halley Station in 1957. This might relate the volcanic eruption of Mount Pinatubo in 1991 enhancing the anthropogenic depletion of the stratospheric ozone layer.

In March 1988 the NASA Ozone Trends Panel announced a 1.7 to 3% thinning in the ozone layer in the northern hemisphere at mid to high latitudes (Roan, 1989). Although significant this is not as dramatic as that over the Antarctic. The Arctic atmosphere is primed for a hole in much the same way as the Antarctic atmosphere but the following important differences save the Arctic atmosphere (Gribben, 1989): The Arctic polar vortex is short-lived and frequently disrupted unlike the Antarctic vortex which remains undisturbed (Plumb, 1990 and Proffitt et al., 1990). Because the Arctic is less isolated than Antarctica the cold temperatures needed to form PSCs, so vital to ozone depletion, are less likely to occur. However, they can form in the lower stratosphere during the Arctic winter (Plumb, 1990). Schoeberl and Hartmann (1991) suggest that ClO formation in the Arctic vortex is most likely to be connected to PSC events rather than the continual process that



occurs in the Antarctic vortex. PSC events occur when small parcels of air are moved upwards, probably by weather systems in the troposphere, and cool by adiabatic expansion. Finally nitrogen rich air is likely to penetrate into the Arctic allowing reactive chlorine to be locked up in a stable form (Schoeberl and Hartmann, 1991).

Proffitt et al. (1990) argue that the ozone loss over the Arctic may be as great as over Antarctica but that the effect on the total ozone column appears less because ozone rich air flows in as fast as ozone is being depleted. This explanation is at odds with the idea that the polar vortex acts as a containment vessel (Plumb, 1990).

The amount of stratospheric ozone depletion to be expected in the future depends critically on the anticipated quantity of ozone depleters. Assuming a 95 % reduction in CFC emissions, results from 13 two-dimensional models (WMO, 1990) suggest that ozone reduction will be negligible at the Tropics but up to 4 % at high latitudes. However if chlorine levels continue to increase then the depletion could be up to 10 % at high latitudes during late winter (Brune, 1991). Recent proposals to establish a new generation of SSTs would also have a major impact on stratospheric ozone depletion. It has been estimated that the greatest damage would happen for flights at 25 km altitude occurring at high latitudes (Brune, 1991).

## Conclusions

Although it is now widely accepted by the scientific community that CFCs and other halocarbons, such as carbon tetrachloride and those containing bromine, produced by human activity are responsible for the thinning of the ozone layer (MacKenzie, 1987) there remain large holes in our understanding of stratospheric ozone depletion. Climate models can still not accurately simulate the chemistry (Brune, 1991; McFarland and Kaye, 1992), the dynamics of the polar vortex are not fully understood (Schoeberl and Hartmann, 1991) and the influence of natural perturbations still have to be resolved.

The wider debate has been called a 15 year crises (Roan, 1989). Crisis are often said to produce major advances in science and technology and the attention given to the science of the stratosphere has undoubtedly benefited from the controversy. The widespread concern generated by the scientific findings led, in 1987, to the *Montreal Protocol*, an international treaty designed to limit the production of ozone depleting substances.

This paper has concentrated on the scientific debate but the role of economics and politics in this debate must be acknowledged. Concerns about SST were short-lived partly because of the economic and political decisions to limit the number of such aircraft. Recent plans for a new fleet of

supersonic aircraft may reopen that debate (Brune, 1991; Patel, 1993). The signing of the *Montreal Protocol* is usually seen as a triumph for policy makers against a background of scientific uncertainty. However few scientific theories find immediate widespread acceptance amongst scientists and yet considerable scientific consensus was reached by 1976 in the NAS findings as well as subsequent reports. This consensus helped to make the *Montreal Protocol* happen (McFarland and Kaye, 1992). One could argue that by focusing on the uncertainty rather than the consensus it was the political and economic considerations that prolonged the debate and that influence is still being felt (Newman, 1993; Purvis 1994).

Parallels can be drawn between the processes leading to the international agreement on ozone depleting substances and possible future international legislation on global warming (Morrisette, 1989). However it could be argued that while the *Montreal Protocol* has provided a political palliative to the problem, it fails to provide a solution. Politicians, quick to emphasise their nations' adherence to the treaty, initially resisted tightening the international legislation, claiming this would deter further nations from signing the protocol. Also the *Montreal Protocol* provides for a 'technical fix'. The substances that deplete the ozone layer are to be replaced with less damaging ones. No consideration is given to changing human activity so that it impacts less upon the environment (Purvis, 1994). It is unlikely that such a quick fix approach

will provide even an interim solution to global warming.

Policy makers often cite scientific uncertainty as a reason for inaction on environmental issues. However they require a certainty that has probably never existed within science and, given the realization that deterministic science is racked with chaos, probably never will. Both the policy maker and the public have to place environmental issues within a much wider context than the scientific model. The public are clearly concerned about environmental issues and in particular stratospheric ozone depletion (Clover, 1993). But whether that concern can be translated into effective action, especially if it challenges current expectations of lifestyle, is open to debate.

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## References

- Allaby, M. and Lovelock, J. 1980: Spray cans: the threat that never was. New Scientist 87, 212-214.
- Angione, R.J., Medeiros, E.J. and Roosen, R.G. 1976: Stratospheric ozone as viewed from the Chappuis band. Nature 261, 289-290.
- Bates, D.R. and Hays, P.B. 1967: Atmospheric nitrous oxide. Planetary Space Science 15, 189-197.
- Bates, D.R. and Nicolet, M. 1950: The photochemistry of atmospheric water vapour. Journal of Geophysical Research 55, 301-327.
- Brasseur, G. and Solomon, S. 1986: Aeronomy of the Middle Atmosphere. Dordrecht, D. Reidel Publishing Company.
- Brune, W.H. 1991: Stratospheric chemistry. Reviews of Geophysics, Supplement. US National Report to International Union of Geodesy and Geophysics, 12-24.
- Callis, L.C. and Natarajan, M. 1986: The Antarctic ozone minimum: Relationship to odd nitrogen, odd chlorine, the final warming and the 11-year solar cycle. Journal of Geophysical Research 91, 10,771-10,796.

Chapman, S. 1930a: A theory of upper atmospheric ozone. Memoirs of the Royal Meteorological Society 3, 103-125.

Chapman, S. 1930b: On ozone and atomic oxygen in the upper atmosphere. Philosophical Magazine 10, 369-?.

Clover, C. 1993: Eight out of 10 are ready to pay for preserving the countryside, London: Daily Telegraph, 20 September 1993.

Crutzen, P.J. 1970: The influence of nitrogen oxides on the atmospheric ozone content. Quarterly Journal of the Royal Meteorological Society 96, 320-325.

Crutzen, P.J. 1971: Ozone production rates in an Oxygen-Hydrogen-Nitrogen Oxide atmosphere. Journal of Geophysical Research 30, 7311-7327.

Crutzen, P.J. 1972: SSTs - A threat to the earth's ozone shield. Ambio 1, 41-51.

Crutzen, P.J. 1974: Estimates of possible variations in total ozone due to natural causes and human activities. Ambio 3, 201-210.

Eggleton, A., Cox, T., and Derwent, D. 1976: Will

chlorofluorocarbons really affect the ozone shield ? New Scientist 70, 402-403.

Farman, J.C., Gardiner, B.G., and Shanklin, J.D. 1985: Large losses of total ozone in Antarctica reveal seasonal ClOx/NOx interaction. Nature 315, 207-210.

Goldsmith, P., Tuck, A.F., Foot, J.S., Simmons, E.L. and Newson, R.L. 1973: Nitrogen Oxides, nuclear weapon testing, Concorde and stratospheric ozone. Nature 244, 545-551.

Gribben, J. 1978: Ozone passion cooled by the sweet breath of reason. New Scientist 80, 94.

Gribben, J. 1979: Monitoring halocarbons in the atmosphere. New Scientist 81, 164-167.

Gribben, J. 1988: Deeper ozone hole predicted for next year. New Scientist 120, 16.

Gribben, J. 1989: Centenary unlocks the history of the ozone hole. New Scientist 121, 24.

Gribben, J. 1990: Why arctic ozone has survived - so far. New Scientist 126, 23.

Gwynne, P. 1976: Aerosols lost in the ozone. New Scientist

71, 627.

Harries, J.E. 1990: Earthwatch: The climate from Space.  
Chichester, Ellis Horwood.

Herman, J.R., McPeters, R., Stolarski, R., Larko, D. and  
Hudson, R. 1991: Global ozone change from November 1978 to May  
1990. Journal of Geophysical Research 96, 17297-17305.

Hesstvedt, E. 1974: Reduction of stratospheric ozone from  
high-flying aircraft, studied in a two-dimensional  
photochemical model with transport. Canadian Journal of  
Chemistry 52, 1592-1598.

Houghton, J.T, Jenkins, G.J, and Ephraums, J.J., editors,  
1990: Climate Change: The IPCC Scientific Assessment.  
Cambridge: Cambridge University Press.

Houghton, J.T, Callander, B.A. and Varney, S.K., editors,  
1992: Climate Change 1992: The Supplementary Report to the  
IPCC Scientific Assessment. Cambridge: Cambridge University  
Press.

Hunt, B.G. 1966: Photochemistry of ozone in a moist  
atmosphere. Journal of Geophysical Research 71, 1385-1398.

Johnston, H.S. 1971: Reduction of stratospheric ozone by



nitrogen oxide catalysts from supersonic transport exhaust. Science 173, 517-522.

Johnston, H.S., Whitten, G. and J. Birks, J. 1972: The effects of nuclear explosions on stratospheric NO and ozone. Report LBL 1421, Lawrence Berkeley Laboratory.

Jones, A. 1975: Ozone depletion and cancer. New Scientist 68, 14.

Kenwood, M. 1979: Ozone cautious inaction needed. New Scientist 84, 252.

London, J. and Park, J.H. 1974: The interaction of ozone photochemistry and dynamics in the stratosphere. A three-dimensional model. Canadian Journal of Chemistry 52, 1599-1609.

Lovelock, J. 1971: Atmospheric fluorine compounds as indicators of air movement. Nature 230, 379.

Lovelock, J. 1975: quoted in Hysteria ousts science from halocarbon controversy. Monitor, New Scientist 66, 643.

MacKenzie, D. 1987: Chemists unite in call for ozone protection. New Scientist 114, 25.

Madronich, S., Bjorn, L.O., Ilyas, M. and Caldwell, M.M. 1991: Changes in biologically active ultraviolet radiation reaching the Earth's surface. In Environmental Effects of Ozone Depletion: 1991 Update, Nairobi: United Nations Environment Programme (UNEP).

McElroy, M.B., Wofsey, S.C. and Yung, Y.L., 1977. The nitrogen cycle: Perturbations due to man and their impact on atmospheric  $N_2O$  and  $O_3$ . Philosophical Transactions of the Royal Society London. Biological Series B 277, 159-181.

McFarland, M. and Kaye, J. 1992: Chlorofluorocarbons and Ozone. Photochemistry and Photobiology 55, 911-929.

Molina, M.J. and Rowland, F.S. 1974: Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone. Nature 249, 810-812.

Morrisette, P.M. 1989: The evolution of policy responses to stratospheric ozone depletion. Natural Resources Journal 29, 793-820.

Newman, W. 1992: Do we have a new religion ? Crosslink: The Journal of the Bayer Group in the UK 5, 35-37.

Patel, T. 1993: Green designs on supersonic flight. New Scientist 139, 35-37.

- Plumb, A. 1990: Ozone depletion in the Arctic. Nature 347, 20-21.
- Proffitt, M.H., Margitan, J.J., Kelly, K.K., Lowenstein, M., Podlske, J.R. and Khan, K.R. 1990: Ozone loss in the Arctic polar vortex inferred from high-altitude aircraft measurements. Nature 347, 31-36.
- Purvis, M. 1994 (forthcoming): Yesterday in parliament: British politicians and debate over stratospheric ozone depletion, 1970-1990. Environment and Planning C: Government and Policy.
- Roan, S.L. 1989: Ozone Crisis: The 15-Year Evolution of a Sudden Global Emergency. New York: John Wiley and Sons Inc.
- Rowland, F.S. 1974: Aerosol sprays and the ozone shield. New Scientist 64, 717-720.
- Rowland, F.S., Spencer, J.E. and Molina, M.J. 1976: Stratospheric formation and the photolysis of chlorine nitrate. Journal of Physical Chemistry 80, 2711-2713.
- Salby, M. L. 1992: The Atmosphere. In Trenberth, K.E., editor, Climate System Modelling. Cambridge: Cambridge University Press.

- Schiff, H.I. 1969: Neutral reactions involving oxygen and nitrogen. Canadian Journal of Chemistry 47, 1903-1916.
- Schoeberl, M.R. and Hartmann, D.L. 1991: The dynamics of the stratospheric polar vortex and its relation to springtime ozone depletions. Science 251, 46-52.
- Schoeberl, M.R. and Kreuger, A.J. 1986: Overview of the Antarctic ozone depletion issue. Geophysical Research Letters 13, 1191-1192.
- Scorer, R.S. 1974: Freon in the stratosphere. New Scientist 64, 140.
- Scorer, R.S. 1975: Haze in the stratosphere. Nature 258, 134.
- Shayler, M. 1994 (forthcoming): The rise and fall of CFCs. University of Leeds: Working Paper Series.
- Solomon, S. 1988: The mystery of the Antarctic ozone "hole". Review of Geophysics 26, 131-148.
- Stolarski, R.S. and Cicerone, R.J. 1974: Stratospheric Chlorine: A possible sink for ozone. Canadian Journal of Chemistry 52, 1610-1615.

Stolarski, R.S., Kreuger, A.J., Schoeberl, M.R., McPeters, R.D., Newman, P.A., and Alpert, J.C. 1986: Nimbus 7 satellite measurements of the springtime Antarctic ozone decrease. Nature 322, 808-811.

Trenberth K.E., editor, 1992: Climate System Modelling. Cambridge: Cambridge University Press.

Tung, K.K., Ko, M.K.W., Rodriguez, J.M. and Sze, N. 1986: Are Antarctic ozone variations a manifestation of dynamics or chemistry. Nature 322, 811-813.

UNEP 1989: Environmental effects of ozone depletion panel report. Nairobi, Kenya: United Nations Environment Programme.

UNEP 1991: Environmental effects of ozone depletion: 1991 update. Nairobi, Kenya: United Nations Environment Programme.

WMO, 1985: Atmospheric Ozone 1985: Assessment of our understanding of the processes controlling its present distribution and change, Volume 1, Global Ozone Research and Monitoring Project-Report no. 16. Geneva: World Meteorological Organisation.

WMO, 1988: Report of the International Ozone Trends Panel: 1988. Global Ozone Research and Monitoring Project-Report No. 18. Geneva: World Meteorological Organisation.

WMO, 1990: Scientific Assessment of Stratospheric Ozone: 1989.  
Global Ozone Research and Monitoring Project-Report No. 20.  
Geneva: World Meteorological Organisation.

Wilson, C.L. and Matthews, W.M., editors, 1971: Man's impact  
on the global environment, Report of Critical Environmental  
Problems (SCEP). Cambridge, Massachusettes: The MIT Press.

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