The ozone layer

an overview of the threats posed to it, and likely consequences for Earth

The sun reflected in polar stratospheric clouds outside Kiruna, Sweden[1].

Contents:

Introduction

In an altitude band some 15 to 50 kilometres above our heads a form of oxygen present only in the tiniest of amounts is doing a quite remarkable service to us all on this planet. Ozone, or O_3, a triatomic derivative of the ordinary diatomic oxygen molecule, denoted O_2, is constantly being formed and broken down by the effect of the sun's rays on our atmosphere. This process strongly absorbs ultraviolet (UV) radiation that otherwise would be lethal to any organism that had to endure the sun's rays unshielded from it (**Figure 1**). Ordinarily ozone, a pale blue gas, is poisonous to human life, even in small quantities. Formed from electric discharges such as lightning or high-voltage electrical equipment, or through the effects of sunlight acting on pollution at ground level, the gas is a hazard to be avoided close up. Strange then, that without its presence in the stratosphere, life might still be contained to 10 metre deep primeval pools of water where crude organisms once could enjoy their only respite from the mixed blessing that the sun has provided, and continues to provide, for life on Earth[1].

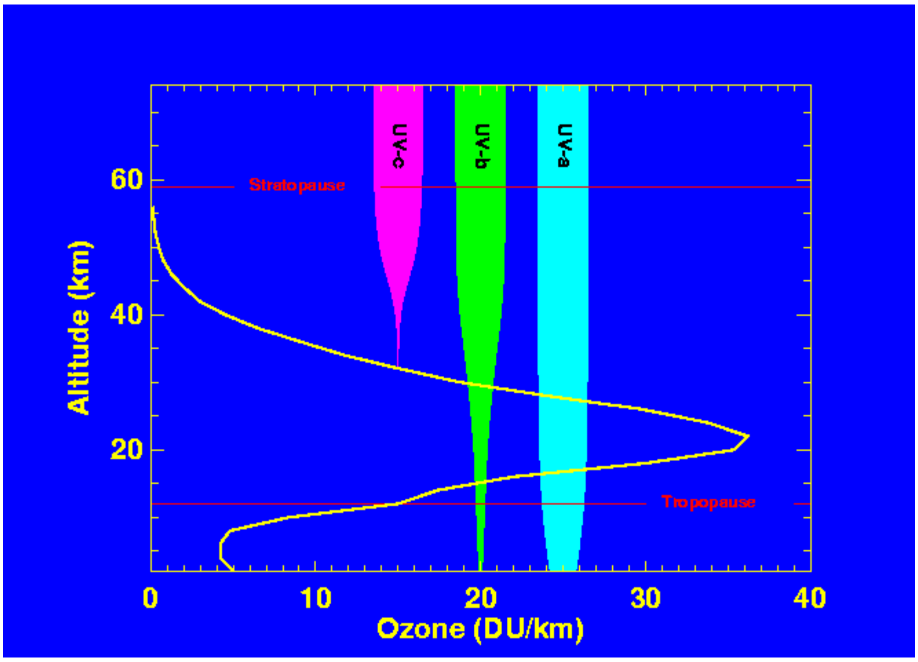


Figure 1. *The above vertical profile is typical for ozone density in the midlatitudes of the northern hemisphere[2]. UV-a denotes UV radiation in the wavelength band between 320-400nm (cyan), UV-b in the range 280-320nm (green), and UV-c in the range 40-280nm (magenta). The tropopause denotes the stratosphere's lower boundary to the troposphere, and the stratopause denotes the stratosphere's higher boundary to the mesosphere. The width of the bars indicates the amount of energy reaching through the atmosphere at any given altitude. UV-c is absorbed entirely as it starts to hit denser parts of the ozone layer, while some UV-b does penetrate to the surface. UV-a is only weakly absorbed by the ozone layer as it nears the surface.*
DU denotes Dobson Units and is equivalent to all the ozone over a given area being brought down to one atmosphere pressure and a standard temperature of 0°C, and the corresponding thickness of ozone being expressed in thousandths of a millimetre –thus, for instance, 25DU/km is equivalent to 0.025mm ozone / km.

Formation of the Atmosphere

The story begins with the formation of the earth in the early years of our solar system. At this time Earth was little more than a hot and glowing, often violent, pile of interstellar rubble and in fact possessed no atmosphere at all. As the Earth cooled and compressed inwards from the force of gravity, the interior was, in conjunction with natural radioactivity, at the same time kept hot and molten by this same force. An atmosphere was gained from the large amount of gases released as a result of the extensive volcanic and other geological activity that characterised the planet especially in its early days. These processes released a steady stream of gases that has continued to supply our atmosphere right up to our present day. From what we know of the emissions of present-day volcanoes, which are not considered to behave substantially differently to those of the early history of the Earth, volcanic gases were comprised of mostly water (about 80%) –which went to supply the oceans–, carbon dioxide (12%), significant amounts of sulphur dioxide (7%), and some nitrogen (1%)[2]. Trace amounts of related compounds such as hydrogen sulphide, ammonia and methane were also emitted. A run-away greenhouse effect due to a predominantly carbon dioxide atmosphere was avoided thanks to the ability of the oceans (which they themselves only existed thanks to the planet being at just the right distance from the sun to enable the water to be present in liquid form, rather than as gas or ice) to absorb and lay down as carbonate-rich sediments large quantities of carbon dioxide.

Those wavelengths of solar UV radiation that today the ozone layer protects us from sterilised the surface of the earth and life could only then begin to have evolved underwater. Some UV radiation is however, still thought to have been necessary in order to catalyse the reactions that eventually led to the evolution of life, and it has been suggested that a depth of approximately 10 metres of water would have provided an optimal amount of UV radiation for life to have evolved successfully, while not at the same time being snuffed out too easily (dissolved organic matter in the water would have been able to filter out UV radiation[3]). At first, organisms simply fed off the chemical riches of the 'primordial soup' and built up complex molecules with the aid of UV energy in a variety of fermentation processes. As the supply of this chemical soup began to be used up, the need for the development of alternative sources of energy led to the emergence of photosynthesis as a viable life process. Using visible wavelength sunlight primitive plant life began to strip carbon dioxide molecules (denoted CO_2) of carbon in order to construct their cells, and thus released ordinary O_2 into the atmosphere. Because of its vigorous reactivity with other substances, including those important to life that contain hydrogen and carbon, O_2 was poisonous to the earliest forms of life on earth. Some organisms though, soon began to lock O_2 up in other compounds and thus gained an evolutionary advantage over those organisms that could not cope with the new environment that was rapidly emerging. At first, the small amounts of O_2 that were released into the atmosphere had only a modest effect on the environment, chiefly becoming bound up in oxidised surface rocks. First appearing some 2.7 billion years ago, photosynthesis was firmly established by about 2.6 billion years ago as can be witnessed from the huge deposits of iron oxide found in geological formations of this age[4].

Figure 2. *It is thanks to photosynthesis that we today have significant concentrations of O_2 in the atmosphere*[3].

The environment could only absorb so much O_2 however and, once saturated, further emissions of O_2 built up in the atmosphere. After a concentration of about 1% O_2 in the air had been achieved, a new life process –respiration– could evolve. This involved utilising the energy available from reacting O_2 with carbon, and thus releasing CO_2 back into the atmosphere. Respiration provides more energy at a faster rate than photosynthesis and it is from the life forms that began to favour this form of lifestyle that we are evolved. This line of evolution could, of course, only start to progress once photosynthesis had laid the groundwork towards beginning to change the Earth's atmosphere from one predominantly rich in CO_2 into one rich in O_2. Thanks to processes instigated by photosynthesis we thus today have an atmosphere that on average across all altitudes contains about 75% nitrogen (N_2), 23% O_2, 0.05% CO_2 and about 1.28% argon, with trace amounts of other gases (despite the low amounts involved in its initial release, N_2 nevertheless became the dominant gas in the atmosphere because such vast quantities of CO_2 that O_2 was derived from were dissolved in the oceans[5]). Without the presence of O_2 in the atmosphere respiration would not be possible and what is more, as we shall see, the formation of the ozone layer would not have been possible either, in which case the evolution of life on Earth as we know it today would not have occurred.

Atmospheric dividing lines

The atmosphere may be divided into layers that are separated primarily by the manner in which temperature changes with altitude. The boundaries are seldom sharply defined, but instead describe regions over which gases travel frequently in both directions. The region closest to the ground, the troposphere, contains approximately 85% of the atmosphere's mass and describes a region of air that experiences a decline in temperature up to an altitude that varies between approximately 8km at the poles and approximately 16km at the equator (the global average is about 11km[6]).

This behaviour is observed due to the surface of the Earth receiving visible and UV sunlight and reflecting it back to space at much longer wavelengths than it is received at. This change in wavelength into the infrared (IR) spectrum (**Figure 3**) occurs since the surface, and anything at the surface, will absorb some of the incoming radiation and only reflect what is not absorbed. This IR energy is then partially absorbed by the atmosphere close to the ground, thereby keeping the ground warm, and thereafter in diminishing amounts until the tropopause is reached –the end of the troposphere. This diminishing temperature gradient reaches a minimum of about –60°C though in the Antarctic this can go down to temperatures as low as –95°C, with important consequences for the ozone layer (Arctic tropospheric/stratospheric temperatures usually hold at a minimum about 10°C above this due to differing weather systems[7]). Above the tropopause, up to an altitude of about 50km, extends the stratosphere and it is in this layer of the atmosphere that some 90% of atmospheric ozone exists[8]. Here the temperature gradient moves in the opposite direction from that in the troposphere and temperatures increase until at the upper boundary, the stratopause, the temperature is comparable to that at sea level. Above this boundary, the temperature goes down again through the mesosphere up to about 80km, where the start of the thermosphere marks a region where temperature again begins to rise with

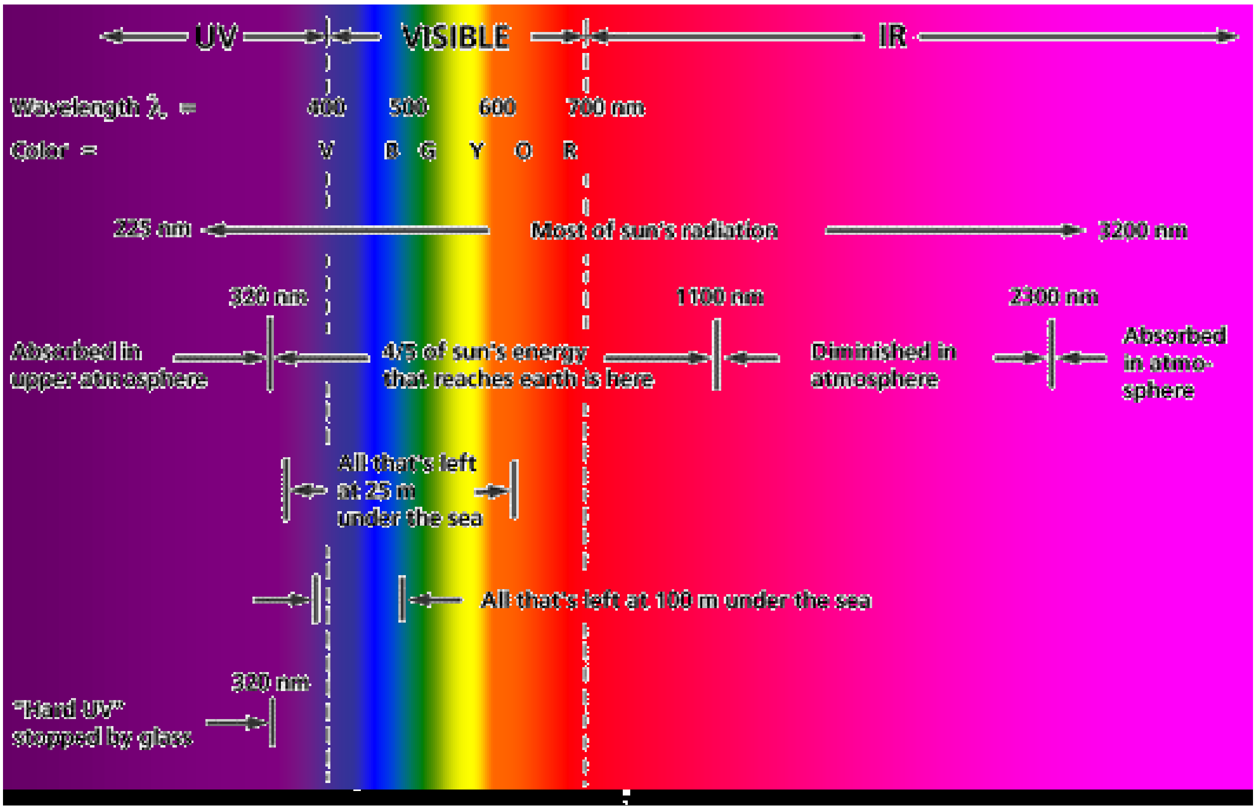


Figure 3. *Diagram depicting the region of the sun's spectrum that spans the range from UV to IR radiation wavelengths[4]. Different portions of the sun's energy are absorbed in the atmosphere, water, and glass.*

altitude. These upper atmospheric layers play little part in the process of ozone formation and destruction, however[9].

The reason the temperature gradient in the stratosphere goes in the opposite direction to that in the troposphere has much to do with the activity resultant from the ozone-forming and breaking reactions that occur predominantly about midway through the stratosphere. Air, containing O_2 molecules, seeps up from the troposphere into the stratosphere where it begins to be increasingly affected by UV radiation as it gains altitude. The initial dissociation of O_2 is dependent upon UV radiation in wavelengths below 240nm (UV-c), and proceeds particularly effectively at wavelengths below 190nm. In the next step another molecule (M), typically diatomic nitrogen (N_2) or another O_2 molecule, is present and acts to catalyse the formation of O_3 from one of the lone O atoms and a previously unaffected O_2 molecule (**Figure 4**).

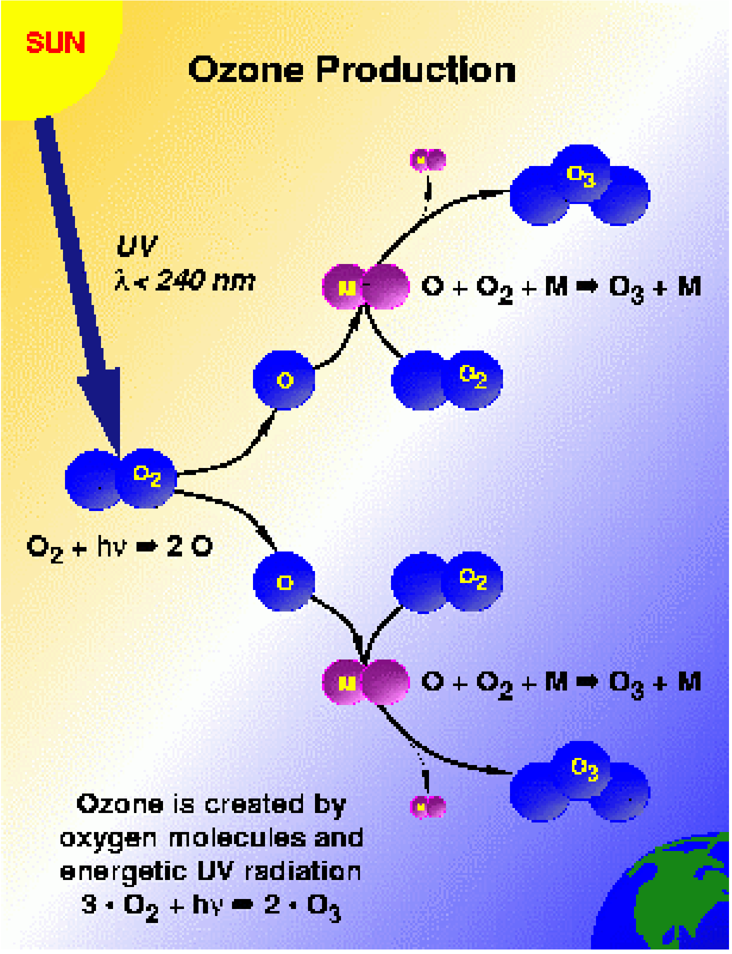


Figure 4. *UV radiation at wavelengths less than 240nm breaks an* O_2 *molecule up into two O atoms*[2]*. In conjunction with a third molecule, M,* O_3 *is then formed as one of the lone O atoms combines with a previously unaffected* O_2 *molecule.*

Since the reaction gives up energy to the catalytic molecule M, and thereby causes it to move faster, the gas of which it is a constituent increases in temperature and causes the surrounding air also to warm up[10]. UV radiation has thus been transformed into heat energy and the ozone layer has thereby accomplished the filtration of most UV radiation below 240nm. The newly formed O_3 molecules are relatively weakly bound however, and do not continue to build up but instead interact with sunlight or other chemicals present in the stratosphere. Weaker UV radiation in the range 240-320nm (UV-b) is in this way able to photodissociate O_3 back into O_2 and a single O atom (**Figure 5**, part 1), thus filtering out further radiation (though not throughout the entire UV-b range, as UV-b becomes progressively less effective at breaking up O_3 with increasing wavelength), and adding yet more thermal energy to the stratosphere. In this way essentially all UV-c and a significant amount of UV-b radiation is prevented from reaching the troposphere. Since the most intense UV radiation is absorbed in the higher reaches of the stratosphere this is also where the highest temperatures occur. Thereafter they diminish down to a minimum at the tropopause and generate the temperature profile that is characteristic of the stratosphere. Since the amount of O_3 generated is dependent on the amount of O_2 available for reaction as well as the available intensity of short wavelength UV radiation, optimum conditions for the creation of ozone are found in the middle of the stratosphere, at an altitude of around 20 to 30km[11] (**Figure 1**, page 2). The temperature inversion effects keep hot air from the troposphere from entering the stratosphere, and so a 'lid' is effectively kept on weather.

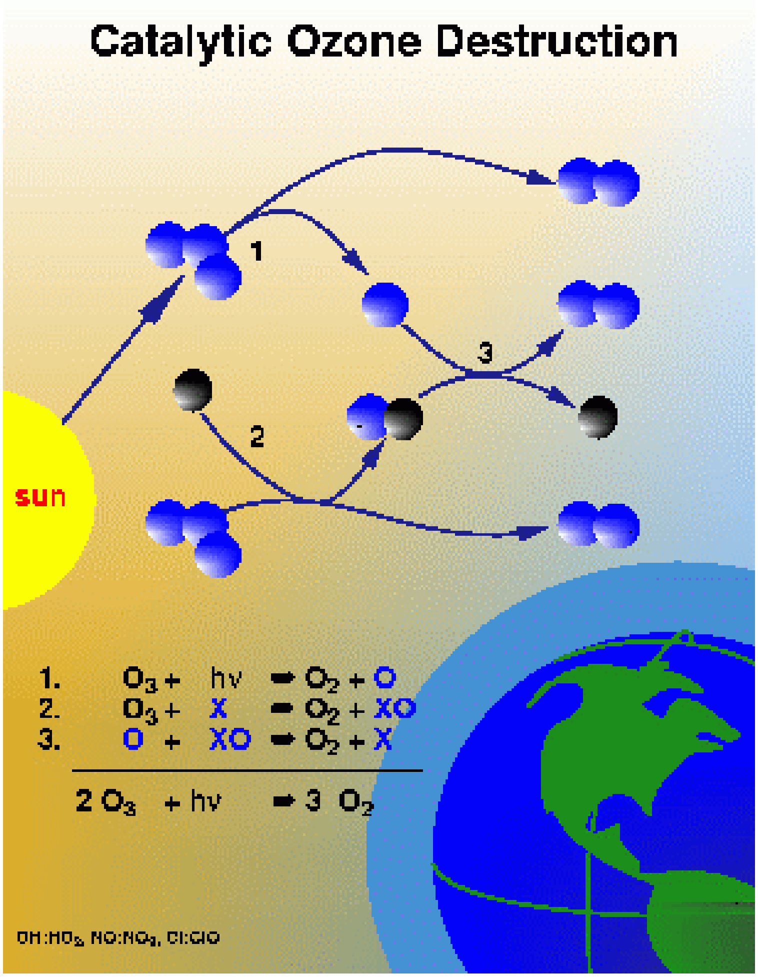


Figure 5. *In the first step UV radiation at wavelengths between 240nm and 320nm photodissociate O_3 down to O_2 and a single O atom*[2]*. At this stage the O atom may simply react with another molecule of O_3 and form two O_2 molecules. However, as step 2 illustrates, often the O_3 molecule meets up with another species such as catalytic agent X, which reacts with another O_3 molecule to form XO and a second O_2 molecule. Finally, the XO molecule reacts with the O atom to form a third O_2 molecule, allowing the catalyst X to reform. In brief, the catalyst converts 2 O_3 molecules into 3 O_2 molecules without itself being affected.*

The oxygen fragment that results from the photodissociation of O_3 can in turn react with another O_3 molecule and produce two molecules of O_2 but, since O_3 is present only in trace quantities anyway, it is more likely to encounter another O_2 molecule and re-form a molecule of O_3. Both of these reactions are however less energetically favourable than a destructive encounter with an agent such as nitric oxide (NO) or a halogen such as chlorine (Cl). If we call such an agent X, then X will react with another O_3 molecule to form XO and a molecule of O_2 (**Figure 5**, part 2). Upon encountering the lone O atom, XO will then give up *its* O atom to allow the formation of O_2, and X will revert to its original state, ready to attack another O_3 molecule (**Figure 5**, part 3). Crucially, species like these may become involved in such a cycle many times over and, as such, are termed catalytic[12]. As an example, it is estimated that a typical Cl atom may become responsible for the destruction of up to 100,000 O_3 molecules! The ozone-depleting compounds (ODCs) from which such species are derived are generally only removed from the stratosphere at a fairly slow rate, and depend on reaction with other constituents in the stratosphere. The OH species is the most important of these and is derived from water (H_2O) reacting with free O atoms. Reaction with this is, however, not as prevalent as ozone destructive reactions are (among other things, the prerequisite water molecules for the production of OH are scarce at this altitude).

Because the sources for ozone destructive agents are thought to have been relatively constant up until the 1950's[13] the ratio of O_3 production to removal is also believed to have remained constant. Since then however, worryingly large amounts of catalytic ozone-depleting species have been introduced, somewhat unwittingly, by man (these are termed anthropogenic species).

The utility of Chlorofluorocarbons

These days, ozone depletion is often popularly associated with the free chlorine atoms that are generated by such ODCs as the infamous chlorofluorocarbons (CFCs), a group of compounds that has been produced industrially in vast quantities since the 1930's. These have dominated the debate about man's threat to the ozone layer ever since their destructive impact on ozone was discovered in the 1970's by F. S. Rowland and M. Molina of the University of California, Irvine[14] (Some twenty years later, Molina being then at the Massachusetts Institute of Technology (MIT), they received the 1995 Nobel prize for Chemistry for this discovery (and subsequent research into atmospheric chemistry), together with P. Crutzen of the Max Planck Institute for Chemistry, Germany, who was among the first to highlight the ozone-depleting properties of nitrogen oxides). Their dangerous effects on the ozone layer stem from precisely the reason that they have been so popular in industry –historically; their extreme stability and highly unreactive nature. This means that the troposphere is unable to provide a sink for their disposal and, once they move beyond the tropopause, only the extreme UV radiation of the stratosphere can break these compounds up. The fragments that result are what cause such harm to O_3 molecules (**Figure 6**). Originally invented in 1928 by DuPont chemist Thomas Midgely Jr.[15] in response to a request for a better refrigerant fluid (previous refrigerants had been hampered by toxicity and flammability issues) CFCs have since found a vast range of uses.

Rowland's and Molina's pioneering investigations on the role of CFCs in the stratosphere led to much *debate* in the 1970s as to whether or not their catastrophic predictions bore up or not, but regrettably to very little *action*. Since CFCs had by this time found such a vast range of applications for which they were deemed especially convenient, politicians and industrialists were loath to act towards phasing them out. Only after extensive pressure by environmentalist lobbies, backed up by an increasingly wide retinue of scientists in many ways spearheaded by Rowland who became ever more involved in the politics of the issue, was the precautionary step of banning CFCs in spray cans implemented in the USA in 1979[16] (which at that time was by far the largest consumer and manufacturer of these cans). CFCs had previous to this been particularly valued for the low pressures at which cans could be charged and still effect a constant and uniform aerosol[17] (a fine mist of very small droplets). However, since by far and away the biggest use of propellant CFCs was essentially for luxury items such as perfumes or paints that could easily be dispensed in other ways, the largely sceptical powers-that-be decided on this occasion that since no significant socio-economic impact could reasonably be expected from banning them, that the environmentalists' concerns could be placated. After all, a number of alternatives to CFC propellants were available such as various volatile hydrocarbons, CO_2, N_2, or simply air, not to mention ordinary hand-operated pumps!

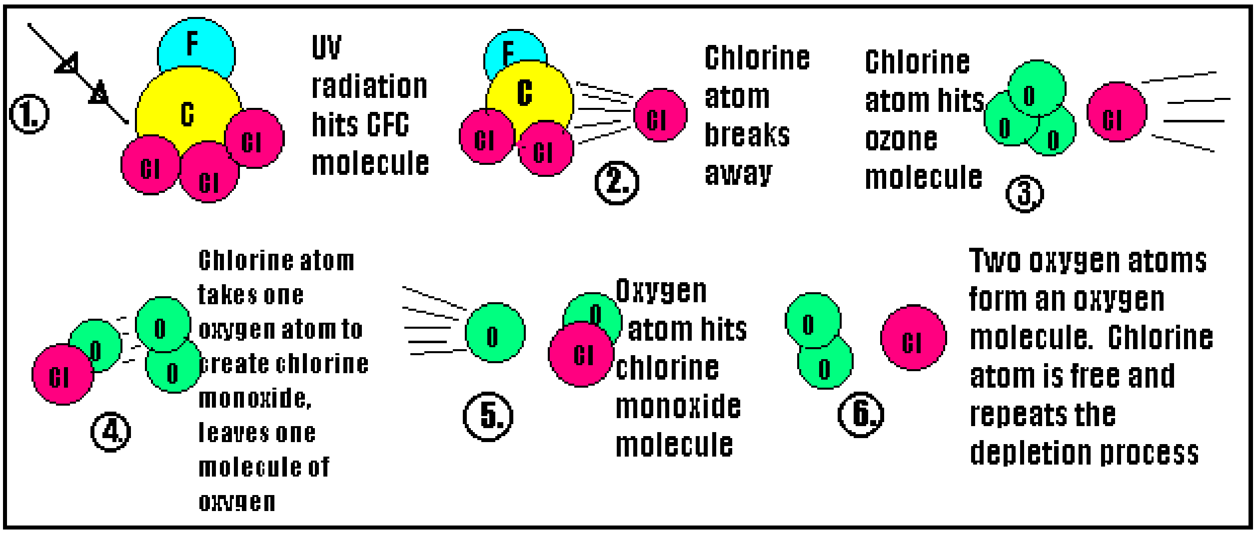


Figure 6. *CFC breakdown in stratosphere and initiation of ozone-depleting catalytic chlorine cycle*[5].

International recognition of the dangers posed by ODCs

The afore-mentioned suitability for refrigeration purposes led predictably to their use also as heat-transfer liquids for air-conditioning units. Being not only non-toxic and inert but also efficient heat-transfer agents, they have since been used extensively for this role up until the late 1980's when less harmful refrigerants became available. The emergence of severe stratospheric ozone deficiencies over Antarctica in the 1980s[18] had by this time eventually led to a consensus between atmospheric scientists on the one hand, and governments and industry on the other, that CFCs, in conjunction with a number of other anthropogenic ODCs, indeed did pose a real danger to the ozone layer. While regrettable that only a marked and detectable destructive influence on the atmosphere could achieve this consensus, this nevertheless carried the good thing with it that politicians all over the world now realised that things were going to have to change, and relatively quickly too. Thus the 1985 'Vienna Convention for the Protection of the Ozone Layer' gathered representatives of governments from all over the world to agree measures to be taken for this aim. While no specific preventative measures were at this stage recommended, the agreement did serve to encourage research, cooperation and exchange of information on ozone-related issues, and also provided for future protocols and specified procedures for amendment and dispute settlement.

With the publication of an article in the journal 'Nature' in May 1985 by British scientists led by Dr. Joe Farman[19] describing the afore-mentioned alarming events in the Antarctic, the Vienna Convention thereby paved the way forward for the 'Montreal Protocol on Substances that Deplete the Ozone Layer' to be drawn up and signed in 1987[20]. This agreement only led to limited reductions in ODCs and was characterised by a multitude of loopholes and escape clauses that had great potential to hamper the effort to protect the ozone layer. Still, the Protocol turned out to be a flexible construction in that it could be tightened or adjusted on the strength of scientific evidence, without having to be completely renegotiated. The Protocol came into force in 1989 by which time 29 countries representing some 82% of global ODC consumption had ratified it. Today 173 countries are party to the Convention and 172 to the Protocol, of which about 130 are developing countries[21]. It represented only a first step that, for a body that ordinarily isn't well known to act with expediency in the best of times, would nevertheless be expanded upon with remarkable speed and efficiency. Control provisions have been strengthened on five occasions so far, with changes made to the Protocol having been adopted in amendments agreed upon in London (1990), Copenhagen (1992), Vienna (1995), Montreal (1997) and Beijing (1999) as yet.

Indeed, the Montreal Protocol has provided considerable grounds for optimism since 1987: as a consequence of earlier undertakings the developed countries had phased out the use of CFCs and halons almost completely by 1996, and the latest amendments undertaken in Beijing[22] in 1999 aims for the same to be achieved in the developing world by 2010. The corresponding dates that have been set for the phasing out of HCFCs are 2020 and 2040. With work progressing towards the elimination of other ODCs such as MeBr, and conscious effort aimed at aiding developing countries not least financially, but also in terms of know-how, the Protocol has a real chance of achieving its aims of completely eliminating significant anthropogenic depletion of the ozone layer as a permanent global phenomenon (**Figure 7**).

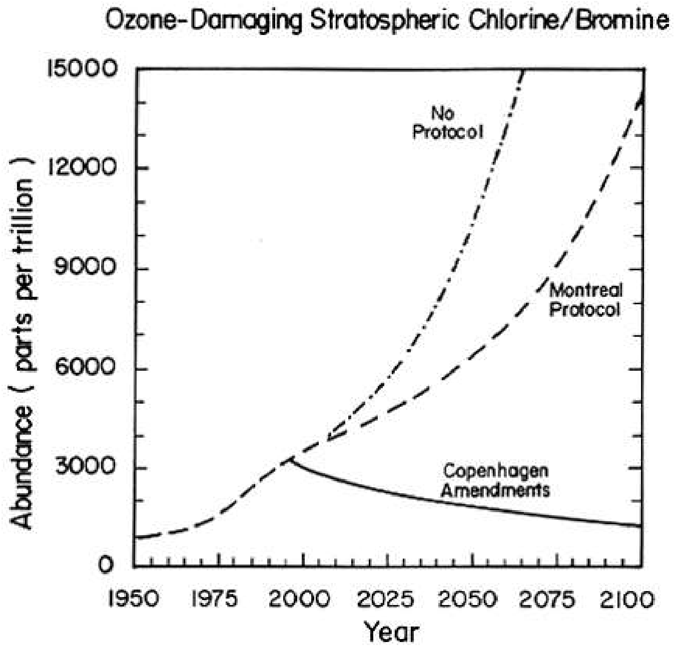


Figure 7. *Predicted future stratospheric Cl/Br concentrations as a result of the Copenhagen amendments of 1992[6].This marked one of the first ODC clampdowns of more than symbolic significance instigated as a result of the Vienna Convention.*

Alternatives to CFCs

The alternative refrigerants that would emerge as a consequence of these increasing regulatory pressures included hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) which distinguish themselves from CFCs in being only partially halogenated and bearing a number of hydrogen atoms in their structures. The presence of hydrogen tends to increase the chemical reactivity of HCFCs and HFCs and they are therefore more likely to be destroyed in tropospheric processes than the CFCs they replace. HCFCs still reach the stratosphere in significant quantities and can in fact in some cases deplete O_3 more efficiently than conventional CFCs[23], but since they have much shorter stratospheric lifetimes they are nevertheless viable alternatives. HFCs too reach the stratosphere in some quantities but, since they lack chlorine atoms in their structure, are not thought to affect O_3 levels. However, some of the most promising HFCs are also powerful greenhouse gases and so carry other environmental penalties instead.

CFCs have also been used as blowing agents for the production of a variety of foam plastics (this involves the injection of said agent into liquid plastic or plastic-forming material[24]). Their use for insulating applications has been promoted by the low thermal conductivity of some CFCs (obviously not the same ones as have found use as refrigerating agents!) that may be utilised if trapped in a porous structure. In addition, their non-toxicity and non-flammability has enabled their use in cheap manufacturing processes involving the production of packaging and cushioning foams. Again, a number of HCFCs and HFCs, with their associated advantages and disadvantages, have been developed as replacements, as have a number of non-halogenated foaming agents (such as Argon or Krypton gas, which retain the insulating properties of the CFCs they replace) and even, as regards insulating strategies, alternatives to foam. As regards the need for producing cheap packaging foams, processes involving CO_2 and volatile hydrocarbons can in most cases replace those involving CFCs.

The electronics industry long availed itself of CFC solvents to clean circuit boards in the final stages of manufacturing[25]. Left-over residue from the soldering process could relatively easily be removed from the chips in a process that posed little risk to human health or to the chips themselves. The process was widely used up until the late 1980's when, as mentioned above, growing restrictions on CFC production and usage prompted the development of alternative processes that not only spared further damage to the ozone layer, but also turned out to be cheaper and more efficient than the old processes had been[26] –quite the opposite to what the industry had grumbled would be the case when the decision to ban CFC solvent usage was taken!

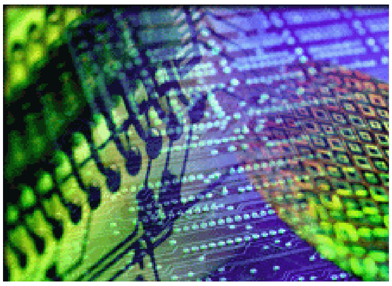


Figure 8. *The electronics industry benefited substantially from more efficient production methods when CFCs were phased out*[7].

Other ODCs and their replacements

A closely related group of compounds to the CFCs are the halons. These are like the CFCs in structure but usually contain bromine, and only in some cases chlorine as well. These compounds have long been used for fire-fighting purposes, and are among the most valued of the ODCs that are to be phased out. They are capable of extinguishing fires extremely quickly and efficiently, and this has made them attractive fire safeguards for a range of applications where especially space and weight are at a premium, such as is the case aboard ships or on airplanes. Since they are non-toxic and will not affect electronic equipment or magnetic storage media –such as water might– they have also become very popular in applications where computing and data integrity are important, such as in computing and control centres, in nuclear facilities, or in banks. The military establishment especially has taken to halons as a means of providing fire-fighting capability for mission critical applications. It is thought that these compounds interrupt fires both chemically *and* physically[27] by, in the first instance, halting the reactions that are causing combustion and then, more conventionally, also by dousing the fire and thus depriving it of oxygen. Unfortunately, inert bromine compounds are an even bigger threat to O_3 than CFCs. This is because free bromine atoms in the stratosphere will not combine with other atmospheric constituents (such as free Cl atoms will into HCl or a variety of chlorine nitrates and oxides) into relatively stable 'reservoirs'[28] that can slow down O_3 degradation to some extent (although the reservoirs themselves can of course also be split apart by UV radiation and resume the destructive processes).

A number of alternatives to halons have emerged in recent years that include a variety of fluorinated alkanes and fluoriodocarbons, although these are also suspected of possessing greenhouse gas properties. In many cases, greater and sometimes novel uses of water can also offer perfectly satisfactory fire suppression capability. In particular, water systems utilising super-fine water droplets of dimensions less than 200 micrometres in diameter have shown particular promise, especially for the suppression of fires involving flammable liquids or sprays. Combinations of CO_2 and foam-flooding can be used for spaces where water might cause costly damage. New technologies that have been investigated include the deployment of fine solid and liquid particulates in aerosols that suppress fires by gas-phase cooling.

ODCs of natural *and* anthropogenic origins

A significant amount of stratospheric Cl is derived from methyl chloride (MeCl), some of which is released anthropologically as it escapes from industry during its production as a precursor for use in synthetic processes. It is also released during the burning of plant material and is emitted from natural processes in the oceans and from some species of terrestrial fungi. Since many forest fires, which rank among the largest producers of MeCl, are regularly initiated intentionally by man, significant emissions of MeCl can be classed as anthropogenic[29].

A similar ODC, methyl bromide (MeBr), also has natural and anthropogenic origins[30]. Like MeCl, MeBr is generated by oceanic biological processes and is also emitted during the combustion of biomass. It is produced industrially mainly for its exceptional effectiveness as a pesticide in soil fumigation and other fumigation processes, and is also produced as an industrial precursor chemical. Both of these chemicals have average stratospheric lifetimes of 1.5-2 years, and while some 90% of MeCl is typically removed from the troposphere by chemical reactions[31], the remaining 10% that reaches the stratosphere (natural and anthropogenic) is still estimated to contribute as much as 17% of current atmospheric chlorine concentrations[32]. MeBr is present in much lower quantities in the atmosphere but is on the other hand, because of its release of Br atoms into the stratosphere as discussed previously, a much more efficient ODC than MeCl.

Figure 9. *Large quantities of MeCl and MeBr are emitted by forest fires, many of which are started by man*[8].

There are of course, a number of sources for ODCs in the stratosphere that emanate from purely natural processes. These include the production of ODCs from lightning, a range of bacteriological decomposition processes, and volcanic emissions. Indeed, if these naturally occurring ODCs were not present the ozone layer would be about twice as thick as it is (or rather as it *was*, before the introduction of anthropogenic ODCs). In fact, the biggest source of atmospheric chlorine emissions is sodium chloride from the oceans (common salt, denoted NaCl) in the form of sea spray, and some oceanic chlorine is also released in the form of hydrogen chloride gas (HCl). These chlorine species do not generally get very far in the atmosphere though, since both forms are soluble in water and are therefore easily removed by rain within days of entering the troposphere. HCl emitted by volcanoes powerful enough to inject volcanic matter directly into the stratosphere –and thus past most cloud systems– poses more of a problem for O_3 levels[33], though even then chlorine concentrations are only affected for about two to three years, since HCl will again be removed fairly quickly by precipitation, as occurs at lower altitudes. The ozone-depleting impact of this particular source of ODCs is also limited by the comparative rarity of such powerful volcanic events.

Another ODC that emanates from natural phenomena is nitric oxide, or NO. This is emitted in small quantities by bacteria present in decomposition processes of organic material such as those typically present during the decay of dead organisms[34]. Having evolved the ability to extract oxygen from the nitrates present in such organic matter these bacteria will extract as much oxygen as they need for their respiratory processes to function normally. Since this process requires more energy than simply availing themselves of atmospheric O_2, if there *is* any free O_2 available to the bacteria they will use that in addition to any nitrate-stored oxygen they are forced by surrounding conditions into liberating. Thus while in the absence of *any* free O_2 molecules these bacteria will release normal molecules of N_2 back into the environment, if there is some O_2 around (but not enough) they will release imperfectly reduced nitrous oxide (N_2O) into the environment instead.

N_2O is sometimes known as laughing gas and is used as an anaesthetic gas. It is very unreactive and there are no known natural mechanisms that will destroy it or bind it up in the troposphere. As with CFCs though, the strong UV radiation of the stratosphere *will* break the molecule down, typically producing molecules of NO. These react with ozone as explained in **Figure 5** (page 7), although not as efficiently as a Cl atom will. Other oxides of nitrogen that can be produced will in varying circumstances combine with a range of chlorine compounds that in turn will affect O_3 levels even further (see **Figure 14**, page 19, in section entitled 'The ozone crisis over the poles'). As for MeCl and MeBr, there are a multitude of anthropogenic sources for NO and related nitrogen oxides, not least of which perhaps the biggest concern in recent years has focused on the aviation industry (although lightning flashes also have the ability to oxidise atmospheric nitrogen). In fact, before the effect of CFCs on O_3 was arrived at by Rowland and Molina in 1973-74, the modern debate over ODCs actually originated with concern over the potential for stratospheric release of oxides of nitrogen (concern was greatest over the effects of NO and NO_2, collectively known as NO_x) by a planned fleet of high-altitude supersonic aircraft[35]. Initial research concentrated on the ozone-depleting potential for oxides of hydrogen (HO_x, of which water is one such oxide) in which particularly the OH radical can act as an ODC. However, the danger of OH particles was exaggerated and research instead concentrated on the potential for NO_x particles to cause havoc in the stratosphere, with some justification.

Concerns over aviation emissions

While a certain amount of stratospheric NO is necessary as part of the natural balance of ozone-production and destruction, there is certainly the potential for anthropogenic NO to shift this balance significantly, particularly if introduced to the upper parts of the stratosphere. At the time, the projected operational altitude for the planned supersonic civil transport (SSCT) fleet –in the lower stratosphere– prompted concern that NO_x emissions would indeed be emitted at altitudes sufficiently high for this to be the case. Since then however, improved calculations and computational techniques have indicated that rather than the critical upper altitude for significant ozone damage occurring at approximately

10km, that instead this altitude actually occurs in the lower reaches of the stratosphere at around 12-15km. Thus the only SSCT to get off the drawing board, the Anglo-French Concorde, in cruising at an altitude of 15km is in fact thought to pose little threat to the ozone layer, and that even if the fleet was not as limited in operational numbers and flight time as is the case!

Figure 10. *Large-scale civil aviation NO_x emissions have been shown to increase stratospheric O_3 concentrations*[9].

Remarkably, it turns out that NO emissions at lower altitudes, within the troposphere and the lower reaches of the stratosphere, can actually *contribute* to O_3 levels, by actively producing O_3[36]. It is first oxidised to nitrogen dioxide (NO_2) and then undergoes further photochemical reactions to produce ozone (**Figure 11**). Indeed this mechanism is one of the main contributors to the ozone content of the smog pollution of many larger cities. This effect is so significant that, according to a report on 'Aviation and the Global Atmosphere' commissioned in April 1999 by the Intergovernmental Panel on Climate Change (IPCC) in collaboration with the 'Scientific Assessment Panel to the Montreal Protocol', in northern mid-latitudes ozone levels are estimated to be some 6% higher at cruise altitudes as a result of aviation NO_x emissions, than would be the case in an atmosphere without aircraft emissions!

The reason for this effect lies in the varying UV radiation levels present at different altitudes. As part 1 of **Figure 11** demonstrates, NO_2 is easily photolysed to NO, thereby generating a free O atom. This then combines with readily available O_2 to generate O_3 (**Figure 11**, part 2) in a similar manner to which high-altitude stratospheric O_3 is generated. In the third step (**Figure 11**, part 3), the NO generated initially, has the capacity to break apart the O_3 it has just aided the generation of, again as occurs high up in the stratosphere. The difference at lower altitudes is however that, because of lower UV radiation levels that high altitude O_3 screens out, the balance of equations is tilted in favour of part 2 in **Figure 11**. The generation of ozone in the upper troposphere and lower stratosphere

eq. 1 $NO_2 + h$ $NO + O$

eq. 2 $O + O_2 + M$ $O_3 + M$ *Make O_3 and O*

eq. 3 $NO + O_3$ $NO_2 + O_2$

Figure 11. *Production of O_3 at lower altitudes from photochemical degradation of NO_2. At lower altitudes the balance of equations is shifted in favour of equation 2. M represents some other neighbouring atmospheric molecule.*

does not spell all good however, since O_3 is also a greenhouse gas and will tend to contribute to global warming[37]. But, then again, NO will on the other hand also interact with atmospheric methane (CH_4) – also a greenhouse gas– (this is released from a variety of natural and anthropogenic sources) and flush this out of the atmosphere, thus decreasing the warming effects of CH_4. The effects on the climate are, to say the least, difficult to predict and are still being researched!

In consequence, the ozone-depleting potential of SSCTs therefore depends on how high an altitude they are designed to travel at. For SSCTs flying at the altitude of Concorde, NO_x emissions are thought to occur at low enough an altitude in the stratosphere for O_3 levels to be at worst only minimally affected, but at best not affected either way. Future SSCT developments may have to be watched more closely however, since many envisage higher cruise altitudes –in which case O_3 levels would be more likely to suffer.

Concerns over the Space Shuttle and satellite launchers

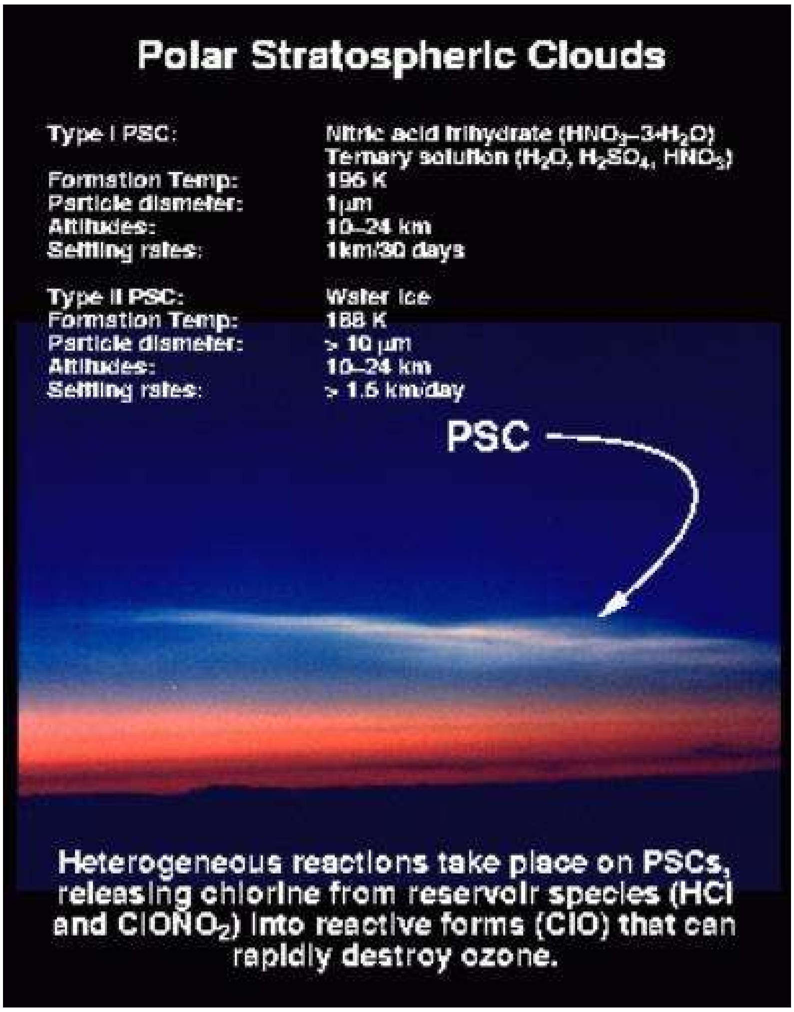
The other main field of aeronautical activity that concerned ozone scientists in the 1970's was the advent of the space shuttle (**Figure 12**). By its very nature of course, this passes through the entire stratosphere, and it belches out a vast amount of exhaust on its way out of the Earth's atmosphere. Worse still, one of the gases emitted from the solid fuel booster rockets that this craft uses is HCl, which will of course contribute to Cl levels in the stratosphere. Concern eventually died down in light of the fact that a typical yearly total of nine space shuttle launches (a somewhat optimistic target, even in the best of years) and six typical satellite launches was eventually calculated to contribute only some 0.25% of the amount of Cl to the stratosphere as is added by conventional ground-based ODCs. While local O_3 depletion in the wake of the exhaust plume has been found to be almost total, rapid horizontal mixing of atmospheric air soon dissipates the effect within hours of the shuttle passing. Total column loss from such an amount of activity has been calculated as being less than 0.1% per year[38], and so the ozone-depleting potential for this particular application has been judged to be of minimal importance. As always though, it may well pay to be prudent and keep an eye on the number of solid rocket boosters


Figure 12. *One of the gases emitted from the space shuttle's booster rockets is HCl (seen here attached to either side of the craft, with the visible flames)*[10].

making forays into the stratosphere and beyond in the future. The last five years in particular have seen an explosion in the business of launching satellites into orbit, largely due to the needs of a number of communications constellations that have been launched.

The ozone crisis over the poles

All the stratospheric ozone-depleting processes that have been discussed so far involve reactants exclusively in the gaseous phase and are thus termed homogenous reactions. In recent years a newly recognised series of reaction sequences involving reactants in *more* than one phase have been discovered. This involves gaseous atmospheric constituents utilising the surfaces of solid aerosol particles to react on, and are termed heterogeneous reactions[39]. As mentioned previously Cl atoms will between reacting with O_3 molecules become bound up into inactive 'reservoir' species that themselves will only break apart given sufficient UV radiation. It appears that if extremely low tropospheric and lower stratospheric temperatures can be achieved by some natural process, then stratospheric clouds composed of nitric acid attached to water, in turn condensed onto some background solid aerosol particle, such as solid sulphate particles (emitted by jet aircraft exhausts in limited but still significant quantities, and also by volcanic eruptions), will form[40]. As yet such extremely cold temperatures only develop over the



Polar Stratospheric Clouds

Type I PSC: Nitric acid trihydrate (HNO_3–$3H_2O$)
Ternary solution (H_2O, H_2SO_4, HNO_3)
Formation Temp: 196 K
Particle diameter: 1 μm
Altitudes: 10–24 km
Settling rates: 1km/30 days

Type II PSC: Water ice
Formation Temp: 188 K
Particle diameter: > 10 μm
Altitudes: 10–24 km
Settling rates: > 1.6 km/day

Heterogeneous reactions take place on PSCs, releasing chlorine from reservoir species (HCl and $ClONO_2$) into reactive forms (ClO) that can rapidly destroy ozone.

Figure 13. *Illustration of a typical PSC*[2]*. Type I refers to PSCs made up of particles with little or no accumulated ice on them. Type II refers to particles* with *significant quantities of accumulated ice that thereby are much bigger than those of Type I PSCs The height of the clouds is well illustrated by the sun's reflections from well beyond the horizon.*

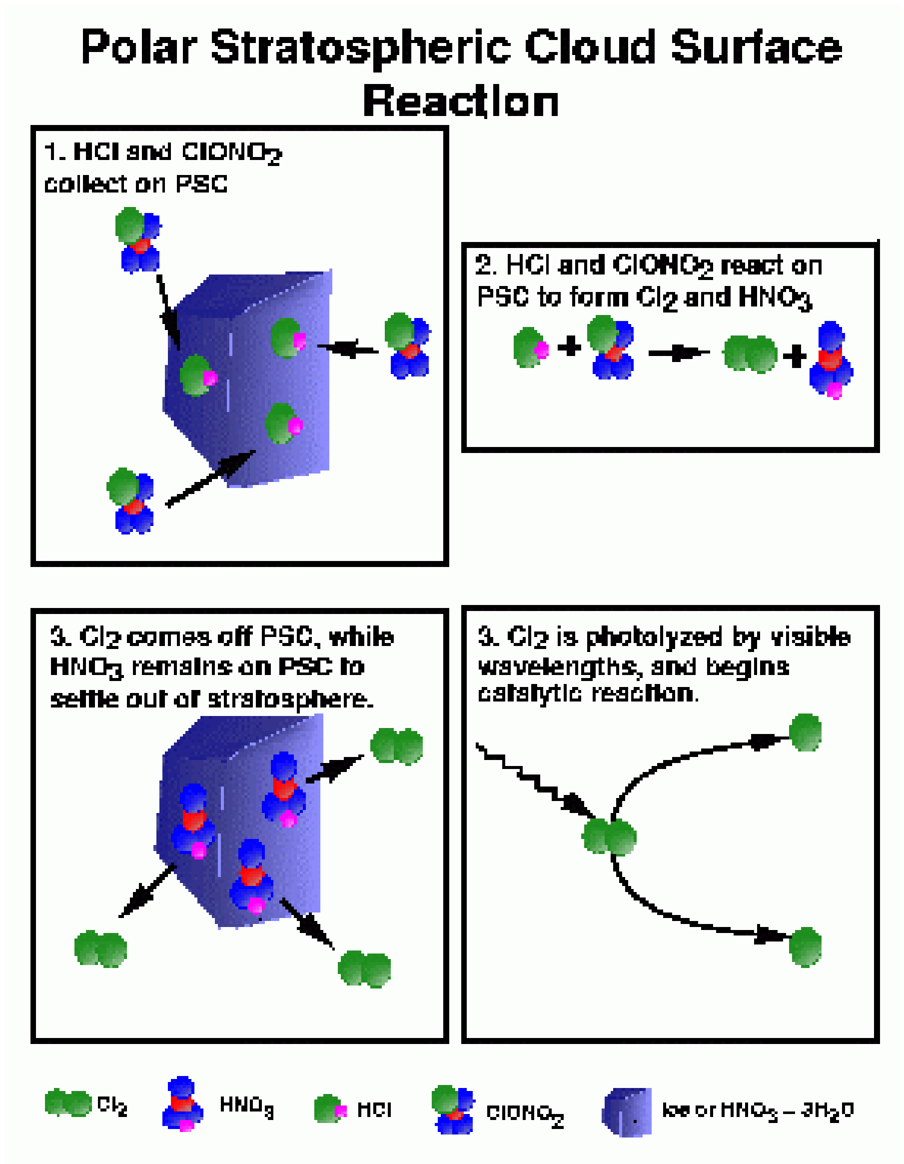


Figure 14. *Augmentation of ODC activity caused by PSCs*[2]*. Reservoir species of Cl (here HCl and* $ClONO_2$*) are converted into reactive Cl that can destroy ozone.*

North and South poles in winter as an effect of very low levels of sunlight, and these clouds are consequently referred to as polar stratospheric clouds (PSCs) (**Figure 13**). These typically form at temperatures below –70°C and begin to freeze at temperatures below –78°C. At temperatures below –83°C, despite the extremely dry conditions of the stratosphere, ice can begin to accumulate on the outside of these cloud particles (the extremely low atmospheric pressure at this altitude means that the freezing point of water is pushed down dramatically beyond 0°C), and they can grow from a size of typically 1 micrometre (a millionth of a metre) in diameter to attain diameters measurable in the tens of micrometres. Reactions such as those described in **Figure 14** follow, wherein the solid aerosol particle acts as a catalyst in service of an intensification of the stratospheric interaction between Cl compounds and O_3[41].

The chain of events that transpires over the poles begins with the disappearance of the sun in late autumn/early winter (these seasons of course occur at different times of year for either pole). This cools the air above the pole and creates a circular wind system called a circumpolar vortex, which becomes isolated from air at other latitudes. This circulates around the pole at speeds of approximately 140-

270km/h at latitudes of approximately 60°N or 60°S and beyond (inwards towards the pole). It becomes especially cold in the Antarctic where the encirclement of the continent by the Antarctic Ocean ensures that the vortex can blow unobstructed. In the Arctic large land masses and various mountain chains effect a smaller and less symmetric vortex that more easily breaks up after the emergence of the sun in spring[42].

High altitude air over the poles and high altitude air at lower latitudes that migrates towards the poles during the polar summers is subjected to a large amount of UV radiation before it is drawn down into the polar vortex during the darkness of winter. This air is consequently severely dehydrated and denitrified by the time it enters the vortex, since the anthropogenic chlorine compounds present in this air have by this stage been completely broken down, and reacted with whatever water or nitrogen containing compounds originally available[43]. When the sun returns in spring this means then, that those chlorine compounds not bound up as reservoir species are free to cause much more severe ozone depletion than would otherwise be the case, since there is nothing else for them to react with. In addition, the formation of PSCs during the winter has in any case ensured that any such reactants still available in the stratosphere are locked up. Of course, the PSCs themselves contribute further to the problem by the catalytic transformation of chlorine reservoir species to molecules of chlorine (Cl_2), which then are free to photolytically cleave and cause further damage to O_3 levels[44] (**Figure 14**).

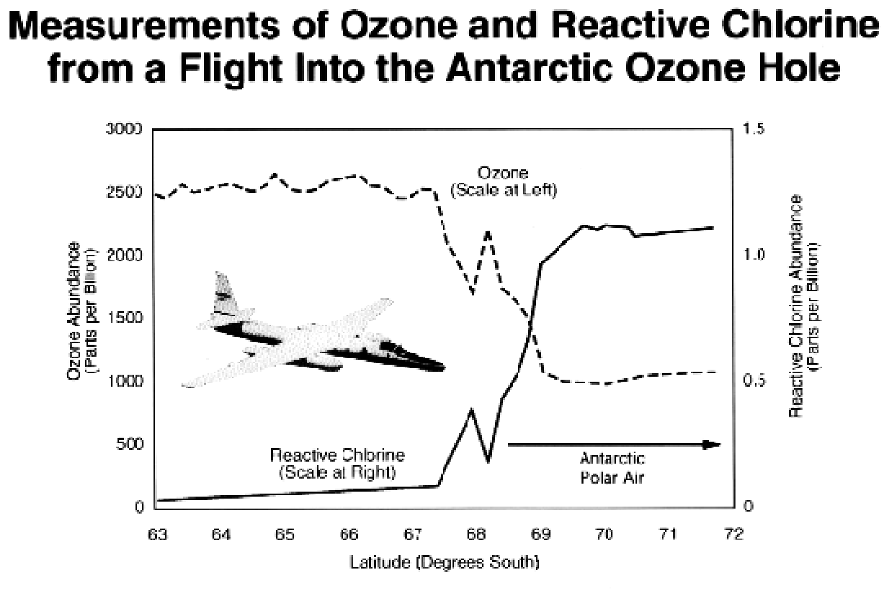


Figure 15. *Relationship between free chlorine and ozone concentrations in the Antarctic polar vortex during the Austral winter/spring of 1987*[6].

Thus O_3 levels are hit by something of a double-whammy as an already dry atmosphere is further dried out by the formation of PSCs, thereby limiting the number of non-ozone-depleting reaction routes available to anthropogenic chlorine species, *and* the catalytic enhancement of ozone chemistry by the PSCs themselves. The effectiveness of the subsequent effected ozone depletion is well illustrated by results from a NASA led expedition over the Antarctic in 1987, illustrated in **Figure 15**. Changes in concentration of reactive chlorine almost perfectly mirror opposite changes in the concentration of ozone.

The rapid loss of stratospheric ozone continues until higher sun angles of the advancing spring warm the stratosphere sufficiently to dissipate the PSCs. This releases bound nitric acid and allows again for the formation of various Cl reservoir species, thus reducing the pressure on O_3 levels, and allows for the dissipation of the circumpolar vortex. The polar air subsequently warms and mixes with relatively ozone-rich air from the middle latitudes[45].

Because the overall 'lifetime' of ozone in the lower stratosphere is about one year, and the ozone-poor air of polar winters is circulated out into the relevant hemisphere at large in summer, if the lost ozone of the winter cannot be reformed by photochemistry in these lower latitudes before the onset once again of winter, then the initial ozone depletion of the previous winter will to some extent be carried over to the next year. Indeed, continued extensive springtime polar ozone depletion in the Antarctic has already been linked with a three to four percent accumulated decline in ozone concentrations in the entire southern hemisphere. A new equilibrium will of course in the end stabilise from the permanent fixture of such events over the poles, although at what lower ozone column concentration this will stabilise at is still in question[46].

Consequences for Earth

The potential for future ozone holes over the poles may increase if concerns over the potential for global warming on account of the greenhouse effect are substantiated. This is because the warmer troposphere that such a change in climate would effect would also mean a colder stratosphere[47] (since less IR radiation would be reflected past the tropopause), and this would of course also mean a greater likelihood for not only the formation of longer-lasting and more powerful polar vortexes, but also of a

Figure 16. *A warmer and wetter world would provoke the formation of more PSCs, such as these outside Kiruna, Sweden*[11].

greater number of PSCs[48]. Of even more concern is the fact that lower O_3 levels on a *global* scale would in turn have the potential to exasperate the situation even further and cause similar havoc with weather systems affecting the entire world, quite beyond the effects of greenhouse gases on their own (this on account of lower ozone levels in the stratosphere allowing for more UV radiative heating of the troposphere).

The scenario offers the possibility of a feedback effect in which ozone depletion affects tropospheric temperatures, which in turn encourages further loss of stratospheric ozone. With CFCs themselves acting as powerful greenhouse gases in conjunction with already present anthropogenic CH_4 and CO_2, there is clearly scope for a significant warming of the troposphere in a scenario that seems to bear the potential of entering into a vicious circle. Further heating of the lower stratosphere and upper troposphere may be expected by a process known as 'self-healing' of the ozone layer[49]. This occurs when ozone depletion at high altitude, in failing to filter out significant quantities of short wavelength UV radiation, allows the formation of ozone at lower altitudes instead. This effect is strongest near the equator where sunlight is strong enough to allow for enough short wavelength UV radiation to penetrate to lower altitudes and photodissociate O_2 –thus allowing for the formation of O_3– but does not occur as readily at higher latitudes. While providing some recompense for the loss of UV protection by ozone chemistry at higher altitudes, this may however be just as alarming as a straight-forward depletion of overall O_3 column concentrations, since this process will of course also warm the affected lower altitudes and contribute further to overall global warming effects.

Warming the troposphere as much as there clearly is potential for would have devastating effects on both the redistribution of global weather systems, and the associated extra energy that would go into these systems. In addition, a further effect of such events has the potential of shrinking the upper stratosphere, since the cooler stratosphere that would result would take up less space[50] (gases at cold temperatures take up less room than warmer gases). Measurements carried out by the British Antarctic Survey have indicated that this may already be occurring. There, measurements of the height of the mesosphere indicate a descent of the mesopause by some 8km over the last forty years, and this indicates in turn an underlying shrink of the stratosphere. While these measurements may as yet be the result of variations in solar activity and the Earth's magnetism rather than the result of anthropogenic influence on the climate, the medium-term trends that they are indicative of correlate with what would be expected from radiative cooling caused by global warming amplified, perhaps, by changes in atmospheric circulation. The implications of such a contracting atmosphere could have unpredictable effects, not least for satellites. Since the density of the atmosphere in some orbital altitudes could be reduced by some 50% within a few decades if these trends continue, the lesser drag that satellites would experience would disrupt their orbits and possibly require complex redesigns. In addition, and more worryingly, space debris would also last longer before burning up in the atmosphere, thus adding to the hazards for satellites and astronauts.

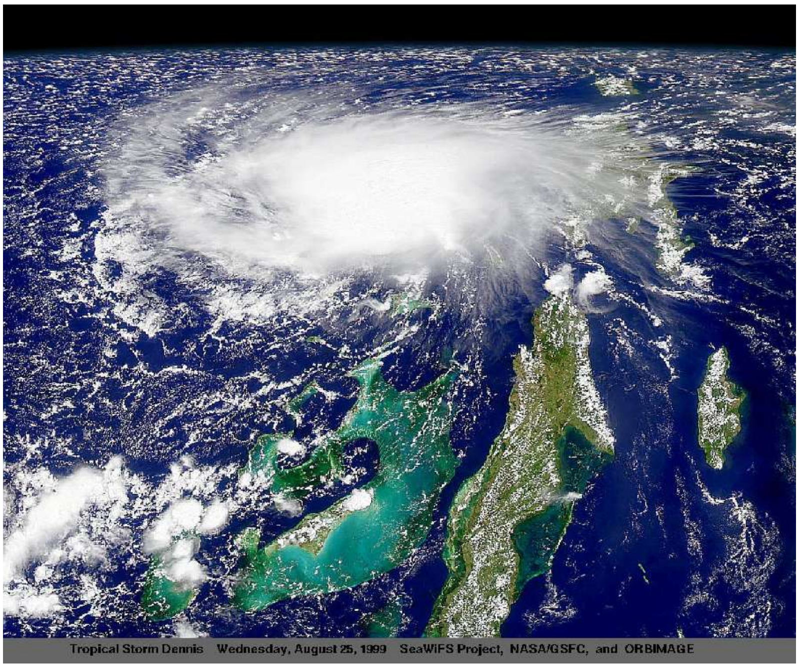


Figure 17. *Global warming may encourage stormier weather, as exemplified here by Tropical Storm Dennis in August 1999*[10].

One of the earliest implications to be highlighted by scientists of a depletion in stratospheric ozone concentrations was the increased risk for cancer that could be expected from a subsequent increase in global surface UV radiation levels (partly, this was of course a political tactic employed in order to make people take more notice of the issue and its importance for the future). This arose from the fact that living organisms are particularly sensitive to UV radiation in the UV-b wavelength band (280-320nm), which is precisely the sort of radiation a lowering of global O_3 column concentrations would let through more of[51]. Radiation in the UV-c band (below 280nm) can do much more extensive damage to living organisms, since it has the power to destroy nucleic acids (RNA and DNA) and protein structures –the basic building blocks of life. There is less scope for the penetration of UV-c radiation to ground levels however, since such radiation would activate the self-healing mechanism, mentioned above, and induce the formation of O_3 at lower altitudes if prevented from doing so higher up in the stratosphere.

The harmful effects of UV-b radiation include ordinary sunburn but, as regards more serious ailments, it particularly aids the inducement of skin cancer. In addition, there is evidence to suggest that excess UV-b radiation also acts in the suppression of the immune system, and this would entail an increased ease for the spread of other cancerous tumours. An increased incidence of a whole host of infections including herpes virus, hepatitis and various parasitic skin infections is also to be expected as a consequence[52]. Other animals than ourselves would experience similar effects, and perhaps also run a bigger risk of becoming blinded by cataracts, which are induced by increased UV radiation levels (humans may find it easier to protect their eyes from UV-b radiation). Plant life would suffer too, and we would very possibly be faced with the prospect of dramatically lower crop yields, and thereby subsequent food shortages. An expected reduction in phytoplankton numbers would also mean a reduction in the total mass of the marine food chain, with the associated risk of fish and marine mammal populations suffering as a consequence. Overall, most, if not all, ecosystems would be disrupted given a significant depletion in global stratospheric ozone concentrations, and some so with potentially catastrophic results.

Figure 18. *A decline in numbers of the minutest oceanic life –phytoplankton– will affect everything else in the oceans, including whales*[12].

Conclusions

Often, ozone is perceived as being something of a finite resource that, like coal or oil, can be exhausted and, once gone, will be gone forever. As even a rudimentary inspection of the mechanisms involved in atmospheric ozone chemistry reveals, this is of course entirely incorrect. It *is* however possible, as has been discussed, to shift the *balance* of ozone-formation and destruction towards a new equilibrium. Ozone concentrations will return to 'natural' levels once anthropogenic influences are eliminated from stratospheric chemistry, and so, while we certainly have the potential to catastrophically change the living conditions of the Earth in the short-term, in the long-term the atmosphere will recover from what ever we may throw in its way, this notwithstanding the fact that in the meantime we may nevertheless drastically alter the evolution of life on Earth. As far as the ozone layer goes, the exceptional losses of ozone over the poles that have been recorded in recent years suggests that man *has* begun to affect the environment in this way. Especially the recent emergence of an ozone hole over the Arctic is causing a great deal of concern, since much greater numbers of people stand to be affected than is the case in the vicinity of the Antarctic.

This may seem academic in light of the fact that ODCs already in the atmosphere are to all intents and purposes impossible to retract. But it is useful for planning our future management of the problem and will also aid in underlining the need for the eventual global elimination of significant ODC emissions. Recent reports by the European Space Agency indicating abnormally low ozone levels over north-western Europe suggest the importance of doing as much as possible to this end. If the Montreal Protocol continues to be as ambitious in its aims as it so far has, and is vigorously enforced, then scientists predict that the ozone layer will start to recover in the near future and will fully recover some time in the 21st century. Other potential threats that shall have to be closely monitored in future include the possible emergence of a significant high-altitude supersonic civil transport fleet, and also the predicted large increase in satellite launching activities. Time will then tell if these efforts will be enough to curb, and then turn the tide, of man's irresponsible ways with the planet.

The sun reflected in polar stratospheric clouds outside Kiruna, Sweden[13].

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