EMISSION OF GREEN HOUSE GASES AND THEIR IMPACT ON CLIMATIC CHANGE AND OZONE DEPLETION - AN OVERVIEW


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ABSTRACT

In 1973, it is proposed that the release of chlorine in the stratosphere might lead to destruction of ozone. This hypothesis and the data just shown were used by Molina and Rowland in 1974 to claim that the CFCs were major sources of stratospheric chlorine, that their continued release would eventually severely deplete the ozone layer, and that this might threaten the very existence of life on earth. In 1984 a remarkable and totally unpredicted phenomenon was discovered by the British Antarctic Survey, the so-called “ozone hole”. In 1985 this unexpected observation was discussed at a meeting of the Vienna Convention when it was decided that world-wide regulations were required to control the production and emissions of chlorine containing gases. In 1987 governments negotiated and established the Montreal Protocol, the first international treaty to protect the global environment. Till from the discovery of ozone hole the concentration of ozone and area of the ozone hole is under watch continually. From 2002-2005 recovery of ozone layer observed, it was believed that phasing out of ODS working out well and influencing recovery of ozone hole. But shockingly the total ozone measurements from a number of individual ground-based stations show unusually low ozone columns on several days in November and December 2006, from 21-30 September average area of the ozone hole from OMI data was 27.4 million km², the largest on record since the TOMS measurements began in 1979. The report delivered by WMO reveals that the total area of ozone layer depletion is being much larger than the periods (1974-1986), were we had use large amount of ODP substances. One of the main reasons for this catastrophic effect is due to the formation of PSC (polar stratospheric clouds) clouds in the stratospheric region. In this paper a critical review of atmospheric concentration of green house gases and ODS, their impact on climate change and ozone depletion is presented. Under the Kyoto protocol, usage of GWP substances has been restricted and it continues its role in a slow manner which causes large emission of green house gases in the atmosphere that could trigger the formation of PSC clouds. The total climatic change and ozone depletion factors seems interconnected to one another. It is observed that the refrigerants contribute nearly 45% of green house gases and increases in a very rapid manner, could produce adverse effect on the environment. Because of R134a contains no chlorine and thus presumably will not lead to the catalytic destruction of stratospheric ozone, it has been suggested as a replacement for the CFC refrigerants, and today it is the most widely used refrigerant in worldwide with very highest growth rate besides its GWP contribution (GWP of HFC-134a relative to CO₂ is 1300 and ODP relative to CFC-11 is 0) which need to be controlled. Possible alternate refrigerants with low ODP and GWP have been identified and presented.

Key Words : Ozone depletion, Global warming, Green house gases, ODP substances, Stratosphere

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INTRODUCTION

Successful absorption of sun’s high energy ultraviolet rays by stratospheric ozone protects both humans and other living things from exposure to ultraviolet radiation. Results from many researches during 1970’s reveal that this ozone layer is being depleted\(^1,2\). The general consensus for the cause of this event is that free chlorine radicals remove ozone from the atmosphere, and later, chlorine atoms continue to convert more ozone to oxygen. The presence of chlorine in the stratosphere is the result of the migration of chlorine containing chemicals. The chlorofluoro carbons (CFCs) and hydrochlorofluorocarbons (HCFCs) are a large class of chemicals that behave in this manner\(^3\). The possibility that chlorine may deplete stratospheric chlorine has received considerable attention recently. During the past few years, there has been much debate on the effects of refrigerants, chlorofluorocarbons (CFCs) in particular, on the depletion of the stratospheric ozone layer. In addition, it has been recognized that refrigerants also absorb infra-red radiation. Over the last decade, CFCs, HCFCs and HFCs have been receiving increasing attention because of their potential contribution to greenhouse warming\(^4,5\). The impacts of the refrigerants in the ozone layer and global warming and the international scenario on regulating these refrigerants are discussed in this review.

The role of refrigerants in Ozone depletion

Chlorofluorocarbons (CFCs) as a class of chemicals where developed in the 1930s. It was quickly recognized that the physical and thermodynamic properties of these compounds make them ideal fluids for refrigeration, like they are nonflammable, non-toxic and extremely stable. Thus they replaced other less desirable refrigeration fluids and faster the development of safe, long-lasting refrigerators and refrigeration units. Almost all the refrigeration and air conditioning equipments operated with CFCs as working fluid till two decades ago around the world.

In the 1970s Lovelock and co-workers\(^6-8\), using his newly developed electron capture detector, demonstrated that there is a strong correlation between the concentration of fluorocarbon and ozone depletion; whenever the fluorocarbon concentration rises, so does the ozone; and it is reported two compounds namely R12 and R11 convey 20% of all the chlorine entering the stratosphere from chlorocarbons generally. In 1973, Cicerone et al., (1974) anc’, Wofsy and McElroy (1974) proposed that the release of chlorine in the stratosphere might be harmful as a consequence of the well-known capacity of chlorine to catalyze the destruction of ozone. This hypothesis and the data just shown were used by Molina and Rowland in 1974 to claim that the Freon-aerosol propellants were major sources of stratospheric chlorine, that their continued release would eventually severely deplete the ozone layer, and that this might threaten the very existence of life on earth\(^9\).

Laurence w. strata (1978) reported the time for Cl atoms from an instantaneous release of CFMs to become essentially uniformly mixed in the stratosphere is 10 years, and the decay time for ozone destruction after CFC release is terminated is 80 years. The atmospheric research Programme confirmed that CFCs were likely to deplete stratospheric ozone, as predicted by Rowland and Molina, with the best computer models. It was concluded that CFCs should be phased out, but that this could occur over a sufficiently long period to minimise the economic impact of the change to CFC users. Nevertheless, several countries, most notably the USA, unilaterally banned the use of CFCs in most aerosols and by 1980 this had significantly reduced world CFC production. The company programmes identified that hydro fluorocarbons (HFCs) offered the desired combination of properties, especially HFC-134a which was reasonably similar in thermodynamic properties to CFC-12 and might therefore replace it as a
refrigerant. In 1981 the “Vienna Convention to protect the ozone layer” was signed by interested states although CFCs were only mentioned in an annexure as compounds that needed to be watched.

In 1984 a remarkable and totally unpredicted phenomenon was discovered by the British Antarctic Survey, the so-called “ozone hole”. During the Antarctic spring in October, when the sun first raises above the horizon, a major, although temporary, loss of stratospheric ozone was observed. Chlorine injected into the stratosphere by the CFCs was the prime suspect. In 1985 this unexpected observation was discussed at a meeting of the Vienna Convention when it was decided that world-wide regulations were required to control the production and emissions of chlorine containing gases. In 1987 governments negotiated the Montreal Protocol, the first international treaty to protect the global environment\(^\text{10}\). Anthropogenic ozone loss spurred policy makers to ratify a series of international agreements—the Montreal Protocol and its amendments which, beginning in 1989, led to reduced production and use of ozone-depleting substances\(^\text{11}\). Following revisions of the Protocol the complete phase-out of CFCs scheduled earlier than had been anticipated. Furthermore, the HCFCs, which had been considered as part of the long-term solution, also decided to be regulated.

The combined stratospheric abundances of the ozone-depleting gases show a downward trend from their peak values of the late 1990s; refer figure 1. The fully amended and revised Montreal Protocol is continuing to be very successful in reducing the emissions and atmospheric abundances of most ozone-destroying gases. By 2005, the total combined abundance of anthropogenic ozone-depleting gases in the troposphere had decreased by

![Fig. 1](image-url)
8-9% from the peak value observed in the 1992-1994 time period. Assuming full compliance with measures adopted under the Montreal Protocol, ozone should slowly recover. Currently, there is no unequivocal evidence from measurements in the atmosphere that the onset of ozone recovery has begun. ‘Recovery’ of the ozone layer is a complex issue: it depends not just on the extent to which the ODSs are replaced by non-ODSs, but also on emissions of gases (including ODS substitutes) that affect the climate system directly.

The role of refrigerants in climate change

The principles of a natural greenhouse effect are very well understood and are not disputed. Basic physics demonstrates that CO$_2$ and other greenhouse gases trap part of the infrared radiation emitted at the surface and warm the earth’s climate. Convincing data show that greenhouse gases caused by human activities are increasing in the atmosphere and are trapping more heat. It seems reasonable to predict that continued emissions will cause global climate change. The issues are too complex to predict confidently local variations of climate and detailed effects. The important conclusion coming from the IPCC report is that global-average earth temperatures have increased over the past century, and the balance of evidence suggests a discernible human influence. The human-induced climate change occurs slowly and will be difficult to reverse. The concern that human activities may be affecting global climate has largely been focused on carbon dioxide (CO$_2$) because of its importance as a greenhouse gas and also because of the rapid rate at which its atmospheric concentration has been increasing. However, research over the last decade has shown that other gases are contributing about half of the overall increase in the greenhouse radiative forcing on climate. CFCs and other halocarbons accounted for roughly half of the direct increase in forcing from non-CO$_2$ greenhouse gases over this period. Around 1990 global warming resulting from the release of man-made gases became a major environmental issue. Although the largest contributor is carbon dioxide from the burning of fossil fuels, it was estimated that CFCs accounted for approximately 15% of global warming in the early 1980s and now it is raises up to 45% and their steady increase in usage would contribute significantly to global warming.

Since discovery of the depletion of the earth’s ozone layer and as a result of the 1992 United Nations Environment Program meeting, the phase out of CFC-11 and CFC-12, many corporations have been forced to find alternative chemicals to CFCs and HCFCs. Because the thermo physical properties of HFC-134a are very similar to those of CFC-12 and are also non-toxic environmentally safe refrigerant, the American Household Appliances Manufacturers have recommended HFC-134a as a potential replacement for CFC-12 in domestic refrigerators. However, while the ozone depletion potentials (ODPs) of HFC-134a relative to CFC-11 are very low, the global warming potentials (GWPs) are extremely high (GWP1300).

Current concentrations of greenhouse gases may cause an equilibrium surface warming which amounts to 0.8-2.4°C relative to 1880, according to recent calculations. If current trends continue, this global equilibrium surface temperature rise could reach 1.7-5.2°C by the year 2030 (Wigley, 1987; Reijnders and Kroeze, 1990). Halocarbons are calculated to be responsible for 15% of current (1990) radiative forcing. The increase of CFC forcing in the 1980s represents, 25% of the total growth in radiative forcing by trace gases (Hansen et al., 1989). The long atmospheric lifetimes contribute to the sustained increasing concentrations of these gases. From the results of various studies it can be concluded that some global warming by halocarbons during the next century is likely to be unavoidable. CFCs already in the atmosphere have long
atmospheric lifetimes (60-400 years), so that even a total cessation of production will result in only a very slow decrease of atmospheric CFC concentrations. The use of HFCs as substitutes for CFCs can enhance this problem and have an important climatic impact. HFC-134a has rapidly mostly replaced CFC-12 in several refrigeration and air-conditioning applications. As a consequence of increased emissions, the annual global mean concentration in mid-2004 was about 30 ppt, increasing at an annual average rate of approximately 3.9 ppt/yr (2000-2004)\(^{14}\). Annual emissions have been increasing at approximately 10 Gg/yr from 2000 to 2004 (Figure 2). Because so little of the HFC-134a has yet been destroyed in the atmosphere, the error bars on the annual emission estimates in 2003 are just ±6 Gg/yr. Seizing upon the perceived high GWP of HFC-134a, environmental campaigners and some governments have urged that this product and other HFCs should be regarded as transitional products and that, like the CFCs, a time-table should also be adopted for their eventual phase-out.

During the negotiations leading to the Kyoto Treaty, however, a “basket” of greenhouse gases was defined that included HFCs as well as CO\(_2\), methane, Perfluorocarbons, SF6 and nitrous oxide. Each country committed to achieving a specific level of total global warming gas emissions in 2010 based on its emissions in 1992. The restrictions upon emissions of chlorofluorocarbons (CFCs) and hydro chlorofluorocarbons (HCFCs) have been omitted from the Kyoto Protocol, because CFCs and HCFCs have already been regulated as ozone depleting substances (ODSs) under

![Fig. 2: Abundance of anthropogenic gases in the atmosphere\(^{14}\).](image-url)
the Montreal Protocol (1987). However, they are also chemically related anthropogenic GHGs and have a much larger impact on global warming than CO₂. For example, global warming potential (GWP) of CFCs per unit of weight is about 4000–12,000 times larger than that of CO₂. Furthermore, with regard to HCFCs and HFCs which are alternatives to CFCs, the GWP is about 500–3000 times larger than that of CO₂. Therefore, CFCs and HCFCs have effects on not only ozone depletion but also global warming. The important point to note is that the production of CFCs was ended by the end of 1995 in developed countries and by 2005 in developing countries.

**Present and future trends of Ozone recovery**

Although much of the chemistry affecting ozone is understood, uncertainties in chemical reaction rates, along with the difficulty in estimating future levels of trace gases in the atmosphere, limit our ability to predict recovery of ozone concentrations. Total ozone measurements from a number of individual ground-based stations show unusually low ozone columns on several days in November and December 2006, in several cases the lowest columns ever measured at those sites for the time of the year. The 21-30 September average area of the ozone hole from OMI data was 27.4 million km², the largest on record since the TOMS measurements began in 1979. The meteorological conditions in the Antarctic stratosphere found during the austral winter (June-August) set the stage for the annually recurring ozone hole. Ozone levels are directly affected by the temperature of the stratosphere, which is influenced by the stability of the wintertime polar vortex circulation. Temperature declines of the past two decades

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**Fig. 3:** Ozone hole area measured from 1979

278
in the lower stratosphere are consistent with expectations of rising greenhouse gas concentrations and observed changes in stratospheric water and ozone amounts. In the upper stratosphere, colder conditions shift the balance of ozone photochemistry towards higher ozone concentrations. At high latitudes, colder conditions in the lower stratosphere promote the formation of polar stratospheric clouds which contribute to severe ozone depletion, a condition that occurred several times in the Arctic in the 1990s and as recently as the spring of 2006.

Low temperatures lead to the formation of clouds in the stratosphere, so-called polar stratospheric clouds (PSCs). The amount of water vapour in the stratosphere is very low, only 5 out of one million air molecules are water molecules. This means that under normal conditions there are no clouds in the stratosphere. However, when the temperature drops below –78°C, clouds that consist of a mixture of water and nitric acid start to form. These clouds are called PSCs of type I. On the surface of particles in the cloud, chemical reactions occur that transform passive and innocuous halogen compounds (e.g. HCl and HBr) into so-called active chlorine and bromine species (e.g. ClO and BrO). These active forms of chlorine and bromine cause rapid ozone loss in sun-lit conditions through catalytic cycles where one molecule of ClO can destroy thousands of ozone molecules before it is passivated through the reaction with nitrogen dioxide (NO₂). When temperatures drop below –85°C, clouds that consist of pure water ice will form. These ice clouds are called PSCs of type II. Particles in both cloud types can grow so large that they no longer float in the air but fall out of the stratosphere. In doing so they bring nitric acid with them. Nitric acid is a reservoir that liberates NO₂ under sunlit conditions. If NO₂ is physically removed from the stratosphere (a process called denitrification), active chlorine and bromine can destroy many more ozone molecules before they are passivated. The formation of ice clouds will lead to more severe ozone loss than that caused by PSC type I alone since halogen species are more effectively activated on the surfaces of the larger ice particles.

So, Changes in ozone concentrations at specific altitudes in both the Arctic and Antarctic will be highly dependent on temperature and resulting polar stratospheric cloud formation, as well as on the amounts of ozone-depleting substances. By the end of the century, provided the concentrations of ozone-depleting substances decrease, ozone levels are expected to be dominated by temperature, atmospheric dynamics and the abundances of trace gases. In the future, ozone levels will depend on continued compliance with the Montreal Protocol and its amendments and on climate change policies that influence atmospheric changes. Changes in the atmosphere as a result of continued anthropogenic impacts suggest that ozone will recover in an atmosphere much different from that which prevailed before the build-up of ozone-depleting substances.

**Ozone depletion and climatic change interconnection**

The issues of ozone depletion and global climate change are linked through physical and chemical processes in the atmosphere. Gases controlled under the Montreal Protocol contribute to the Earth’s radiation balance, gases that could be controlled under the Kyoto Protocol affect the ozone layer, and climate change can have an influence on the ozone layer. Most of the ozone-depleting substances (ODSs) are also significant greenhouse gases, and increases in their atmospheric concentrations tend to have a warming effect on the Earth’s surface. At the same time, because stratospheric ozone also plays a role
in the radiation balance of the atmosphere, ozone depletion caused by increasing concentrations of ODSs tends to have a cooling effect on the Earth’s surface. Therefore, the net climate effect of an individual ODS depends on its direct global warming potential relative to its ozone depleting potential.

However, the actual implementation of the Montreal Protocol cannot mandate climate change considerations since it only controls listed substances directly involved in ozone depletion. The Kyoto Protocol has created a more immediate need to further examine the relationship between the climate and ozone treaty regimes. It includes the hydrofluorocarbons (HFCs) among the gases that are to be controlled for climate protection, and these are the principal substances chosen as substitutes for ODSs under the Montreal Protocol. Because ODSs cause depletion of the stratospheric ozone layer, their production and consumption are controlled under the Montreal Protocol and consequently are being phased out, with efforts made by both developed and developing country parties to the Montreal Protocol. Both the ODSs and a number of their substitutes are greenhouse gases (GHGs) which contribute to climate change. Some ODS substitutes, in particular hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs), are covered under the UNFCCC and its Kyoto Protocol. Options chosen to protect the ozone layer could influence climate change. Climate change may also indirectly influence the ozone layer.

Due to the environmental concerns ozone depletion potential (ODP) and global warming potential (GWP) of the existing refrigerants, industry and researchers in this field are in search of long-term solutions. With extensive work on alternatives to chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), initially Hydrofluorocarbons (HFCs) were considered to be long-term solutions. But the global warming of HFCs has become a hurdle to accept them as long-term solutions.

The refrigeration and air-conditioning industry has grown significantly over the past few decades and will continue to do so all over the world for the coming years. Thus, it is necessary to develop alternative refrigerants without ozone depletion potential and at the same time lighten greenhouse warming impact as well. In recent years, both home and foreign

Fig. 4: Interconnection of ozone depletion and global warming
researchers made great efforts to look for the more ideal refrigerant to meet synchronously the needs of the Montreal Protocol and Kyoto Protocol in order to protect human living environment.

**Alternate Refrigerant**

It is really quite remarkable that with the nearly infinite number of substances in the universe, only a handful is suitable for refrigerants. Many efforts have been made to source other families of compounds that perform as well as the group (Fluorocarbons) Thomas Midgley Jr. found in 1928. None so far have proven to be comparable. James M Calm (2002) reported “no current refrigerants are ideal even based on the partial list of requirements as ideal refrigerants”. Chemical and thermo physical analyses reveal conflicts in desired molecular makeup and properties, which virtually preclude the possibility that ideal refrigerant, exist or can be synthesized. With recognition that there are no ideal refrigerants and that none is likely to be found, users must work with available candidates.” Figure 5 summarises and compares the ODP and GWP values of available refrigerants. CFCs are phased out due to their high ODP and GWP values. HFCs have been selected because they do possess zero ODP and from fig.5 it is evident that they possess high GWP is concern for many governments now. There exist few refrigerants in the HCFC group with low ODP and working with these refrigerants will not influence either ozone depleting or global warming. They are R152a, R123, R160, R161, R600a, and R290.

It was reported that, R123 will remain as important role player in the heating, ventilation and air-conditioning industry in future. R123 unlike the majority of HCFCs has both low ODP and GWP and has an atmospheric lifetime of 1.4 years, which gives a virtual guarantee that no R123 would possibly enter the stratosphere. As R123 has high
specific volume needs a suitable combination refrigerant to work in the CFC12 system. To compensate its large specific volume, high latent heat refrigerant R290 has been identified as mixture component which can substitute the CFC-12 refrigerant. This is confirmed with simulation results done with REFPROP software.

CONCLUSION

Both ozone layer depletion and global warming issues are interrelated with each other and refrigerants are the major contributors for this problem, and it is necessary that new refrigerant should be free from ODP and GWP. Simulation results show that the mixture of HCFC-123 and HC-290 is near matching with the performance of the CFC-12. The mixture of HCFC-123 and HC-290 could be of possible refrigerant in future.

REFERENCES