Freons and ozone in the stratosphere

J. Basuk
Science Council of Canada
Ottawa, Ontario

Abstract
The purpose of this note is to attempt to succinctly clarify the situation vis-à-vis Freons and ozone in the atmosphere by distinguishing between fact, supposition, and accepted theory.

1. Background
As part of an increasing public awareness (as evinced by the number of articles appearing in the scientific journals and the press), about possible deleterious changes in the natural, chemical, and physical environments by a host of activities too numerous to mention, particular attention has been given to factors that may or will be altering the ozonosphere. Specifically, it is the possible deletion of naturally occurring ozone from the stratosphere that is of concern since it is felt that a significant reduction can result in severe climatic changes, due to changes in the thermal structure of the ozonosphere, and in distressing biological changes (in the extreme, the destruction of all life on the planet) due to the introduction at the earth's surface of a portion of solar ultraviolet radiation heretofore totally absorbed by the ozonosphere.

It has been assumed, and no alternative view has been presented, that the evolution of life on the exposed surface of the planet began with the formation of the ozone screen. The removal of this screen would mean that conditions of ultraviolet illumination at the surface would become similar to those of pre-Cambrian days, and would presumably eliminate all surface life. In other words, the biosphere has adapted to the available ultraviolet illumination (Hampson, 1974).

Most of the recent concern about the ozonosphere has centered about the injection into it of oxides of nitrogen (NO) and nitrogen dioxide (NO₂) catalyze the destruction of ozone (O₃). Clear experimental evidence in favor of this hypothesis is yet lacking because no measurements have been made of nitrogen oxide concentrations in the stratosphere (Crutzen, 1972).

More recently there have been a spate of articles of an alarmist nature in both the press and in various journals about the possible depletion of the ozonosphere by Freons. (Articles in the Toronto Globe and Mail, the Montreal Gazette, Science News, New Scientist, Nature, etc.) Most of the articles are based on work done by two teams; namely Mario J. Molina and F. S. Rowland of the Department of Chemistry, University of California; and Ralph J. Cicerone, Richard S. Stolarski, and Stacy Walters of the Space Physics Research Laboratory, University of Michigan (Molina and Rowland, 1974; Cicerone et al., 1974). A third team, Michael B. McElroy, Steven C. Wofsy, and Nien Dak Sze of Harvard, have more recently still, published their own computer calculations (Wofsy et al., 1975).

2. Some facts about Freons, ozone, the ozonosphere and ultraviolet radiation
Before summarizing the three aforementioned articles, herewith some pertinent facts about the key components in any interaction between atmospheric ozone and the Freons. (Reference sources are Encyclopedias, Handbook of Physics and Chemistry, etc.)

a) Ultraviolet radiation
The ultraviolet portion of the electromagnetic spectrum includes all radiations with wavelengths from 40 to 4000 Å (1 Å = 1 Angström unit = 10⁻¹⁰ cm). Ultraviolet radiation in sunlight at the surface of the earth is restricted to the span from about 2870 Å to 4000 Å. This represents about two-thirds of the total ultraviolet radiation emitted by the sun. The remainder is absorbed by atmospheric ozone, oxygen, and other substances present in the atmosphere.

The following schematic represents a proposed mechanism indicating how nitric oxide (NO) and nitrogen dioxide (NO₂) catalyze the destruction of ozone (O₃).

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b) Ozone

Ozone is a high energy allotrope of the element oxygen. Whereas ordinary oxygen has two atoms in each gaseous molecule (O₂), ozone (O₃) has three. Although it resembles oxygen in many respects, ozone is much more reactive. Another important difference is their respective wavelength ranges of absorption in the ultraviolet spectrum. Ozone absorbs in the wavelength range of 3100 Å to 2000 Å, whereas oxygen absorbs at 2450 Å downwards.

c) Freons

Freon is a trade name for members of a group of alicyclic organic compounds containing the elements carbon and fluorine and, in many instances, other halogens (especially chlorine) and hydrogen. For the purposes of this note the two most important Freons are trichlorofluoromethane (CFCl₃) and dichlorodifluoromethane (CF₂Cl₂), also known as Freon 11 and Freon 12 respectively. The Freons are colorless, odorless, nonflammable, and of low toxicity. The low toxicity and safety of Freons is considered by some questionable (Crossland, 1974). They are usually chemically and thermally stable. Additional properties include high density, low boiling point, low viscosity, and low surface tension. This unique combination of properties has made the Freons particularly suitable for use as refrigerants and as propellants in aerosol products. While not soluble in water, Freons do serve as solvents and as such rank above the hydrocarbons and below the chlorinated hydrocarbons.

Both CFCl₃ and CF₂Cl₂ absorb radiation in the far ultraviolet and stratospheric photolysis will occur mainly in the “window” at 1750–2200 Å.

d) The ozonosphere

This is a region in the upper atmosphere between about 10 and 50 km altitude, in which the thermal structure is to a large degree determined by the radiative properties of ozone. Ozone is generated in the ozonosphere primarily as a result of shortwave solar radiation (wavelengths shorter than 2420 Å) which dissociates normal molecular oxygen (O₂) into two oxygen atoms which in turn combine with non-dissociated oxygen molecules to yield ozone with the aid of a gaseous catalyst:

\[ \text{O}_2 + \text{U.V.} \rightarrow 2\text{O} \]
\[ \text{M} + \text{O} + \text{O}_2 \rightarrow \text{O}_3 + \text{M} . \]

Ozone, once formed, is also destroyed by solar ultraviolet radiation of wavelength less than 3100 Å:

\[ \text{O}_3 + \text{U.V.} \rightarrow \text{O}_2 + \text{O} \]
\[ \text{O} + \text{O}_2 \rightarrow 2\text{O}_3 . \]

(Rate of this reaction is temperature dependent.)

From the above two sets of equations, it is evident that there naturally exists a close equilibrium between the concentrations of atomic oxygen and ozone. When photochemical equilibrium exists, the amounts of ozone present are such that the production rate is equal to the destruction rate.

Because of its capability of absorbing solar ultraviolet radiation, the presence of ozone in the earth’s atmosphere with a total variable mass corresponding to the mass of air in a 2-5 mm thin layer at the ground (STP—Standard Temperature and Pressure) is a necessary condition for the existence of present life on earth.

The ozone contained in the stratosphere has a maximum concentration $5 \times 10^{19}$ molecules per cubic centimeter at an altitude of about 25 km. The mixing ratio of ozone, which is defined as the ratio of the concentration of ozone to that of all air molecules is largest at an altitude of about 32 km and is equal to between 5 and 10 ppm. Furthermore, the absorption of solar radiation in the 2000–3100 Å wavelength region by ozone is the main source of energy in the stratosphere, with maximum heating about 10°C per day, occurring at altitudes near 50 km, thus explaining the temperature maximum at these levels.

e) Natural sinks

While the term “natural sink” is often used by the proponents of the idea that the possible interaction of Freons and stratospheric ozone is deleterious, at no place in the papers referred to previously is the term carefully defined. One proposed definition is that a natural sink is that part of the natural environment that effectively removes either some energy form or matter from the biosphere. While for those with a concern for the biosphere this definition may be adequate (and thus for the purposes of this article), some exceptions can be taken with it. It is restrictive in that it implies that the biosphere itself cannot serve as a natural sink. It appears to contain a value judgment by suggesting that such removal is beneficial when in fact it may not be. Finally, it is not clear whether the process of removal is natural or artificial. Another more general definition is that a natural sink is a natural reservoir of either a particular energy form or matter. The process by which the energy form or matter is transmitted to the reservoir is natural and thermodynamic in nature. Simplistically put, this means that if the matter or energy form in question has before it a series of competing reservoirs, it will naturally tend towards that reservoir where the increase in stability (or entropy) is greatest. There is, of course, a time factor associated with these natural reservoirs or sinks. They may be quite temporal or remain stable over a geological time period, whereupon the sink becomes a source.²

3. The concern

Between 1960 and 1972 the production rate of Freons 11 and 12 increased annually by about 22%. The production of Freons 11 and 12 in 1972 totaled approximately 500,000 metric tons. It has been suggested that a 10% growth rate would be a reasonable projection for continued world-wide production and use; some skeptics

² The author is willing to concede he may be confusing reservoirs and sinks.
doubt that growth will slow that much.\textsuperscript{3} The U.S., itself, produced and used about 400,000 metric tons in 1974.\textsuperscript{4}

While monitoring levels of other atmospheric pollutants over remote ocean sites during the 1970s, researchers noticed persistent indications of Freons in the upper troposphere. John W. Swinnerton, a chemical oceanographer at the Naval Research Laboratory in Washington, and others found that Freon concentrations in the atmosphere are climbing rapidly. In 1972 on a cruise from Los Angeles to the Antarctic he found an average of 61 parts of Freon per trillion parts of air, in 1973, 85 parts per trillion were detected over the Atlantic and in January 1974, 120 parts per trillion were detected in the Arctic air near Spitsbergen (Idso, 1974).

The increasing production of Freons together with their increased presence in the atmosphere has led researchers to try and identify natural sinks for these compounds. It has been assumed that because CFCl\textsubscript{3} and CF\textsubscript{2}Cl\textsubscript{2} are not very soluble in water, they are not removed by rainout in the troposphere. Because these compounds do not occur naturally, rapid biological removal appears unlikely. Also because they do not appear to be easily absorbed and adsorbed by solid materials, and because of their chemical inertness and high volatility it would appear that they can remain in the atmosphere for a long time. (Thus they may be useful as inert tracers of atmospheric motion.) If this is so, the key question then becomes, what is the atmosphere’s capacity for retaining Freons without changing some of its essential characteristics. The answer suggested by a number of researchers is that the atmosphere has a limited capacity for absorbing Cl atoms that are presumably generated by the breakdown of Freons that have diffused into the stratosphere and that important consequences, previously mentioned in this article, may result.

The proposed key reactions are—(the fact that Cl atoms can catalytically destroy ozone molecules has been confirmed in the laboratory):

\begin{align*}
\text{CF}_2\text{Cl}_y &\text{ (A Freon where } x = y = 2 \text{ or } x = 1, y = 3) \\
&+ \text{U.V. (1750–2200 A)} \rightarrow \text{CF}_x\text{Cl}_{y-1} + \text{Cl} \\
\text{CF}_x\text{Cl}_{y-1} + \text{O}_2 &\rightarrow \text{CF}_x\text{Cl}_{y-1}\text{O} + \text{ClO} \text{ (speculative)} \\
\text{CF}_x\text{Cl}_{y-1}\text{O} + \text{U.V.} &\rightarrow \text{CF}_x\text{Cl}_{y-1} + \text{Cl} \text{ (speculative)} \\
\text{Cl} + \text{O}_2 &\rightarrow \text{ClO} + \text{O}_2 \\
\text{ClO} &\rightarrow \text{Cl} + \text{O}_2 \text{ (rate determining reaction)}
\end{align*}

Reaction (5) is 6 times more rapid than the reaction between NO\textsubscript{2} and O regenerating NO and O\textsubscript{2} previously mentioned.

Reactions (1) to (3) are proposed Cl atom-producing reactions. Reaction (4) is quite rapid whereas the rate of reaction (5) is relatively slow and is dependent upon the concentration of O atoms. If the above reactions are in fact taking place in the stratosphere, the depletion of ozone would be at least partially dependent upon the concentration of Cl atoms which, in turn, is dependent upon a host of factors all related to the background chemistry and physics of the stratosphere and the interactions between the stratosphere and troposphere.

Three rather sophisticated mathematical models computing Cl production rates in the stratosphere with consequent destruction rates of ozone have been proposed\textsuperscript{5} (Molina and Rowland, 1974; Cicerone \textit{et al.}, 1974). These appear to be much too complicated to describe in this note. Some of the important parameters included in these models, where some were experimentally derived and others empirically, are (at various altitudes):

- a) Eddy diffusion coefficients to calculate the diffusion rate into the stratosphere of the Freons;
- b) Concentrations of some background substances that are most probably involved such as O, O\textsubscript{3}, CH\textsubscript{3}, OH, NO, and H\textsubscript{2};
- c) Photo dissociation rates based on photoabsorption coefficients. (Zenith and diurnal angle effects were taken into account.)

The predictions the three models make about future ozone depletion in the stratosphere are all ominous. The first (Molina and Rowland, 1974) suggests a 10\% decrease in the stratospheric ozone layer within 50 to 80 years; the second (Cicerone \textit{et al.}, 1974) predicts a similar decrease by 1985 or 1990; the third\textsuperscript{6} a 40\% decrease by 1995. They all agree that the Cl–ClO chain will replace the natural NO–NO\textsubscript{2} chain which is currently thought to be a key chemical factor in determining ozone concentration in the stratosphere.

\section*{4. Conclusions}

Although it is not possible to assess at this stage the real environmental consequences of Freons in the atmosphere, present knowledge indicates that there exists a possibility of serious decreases in atmospheric ozone due to the catalytic action of Cl atoms emitted when Freons are photo-dissociated. The models are, after all, only models. They contain built-in assumptions and quantitative parameters that need to be confirmed. They are useful in raising the level of concern and in identifying those areas where the “need to know” is clear. For example:

1) Natural Sinks—It appears that possible natural sinks for Freons, other than the stratosphere, have been dismissed in a rather cavalier fashion. There would appear to be a need to institute a search for other natural sinks. What about the oceans, the earth itself, various fauna and flora, and particulate matter in the troposphere (either solid or liquid)? In the latter case is it not possible the Freons contribute to an aerosol effect which, in turn, may lead to a “greenhouse effect” (Idso, 1974).

2) The diffusion rates, the dissociation rates, and re-

\textsuperscript{3} Science News, 106, 5 October 1974, p. 212.
\textsuperscript{5} Science News, 106, 5 October 1974, p. 212.
action coefficient rates previously mentioned, are all questionable.

3) Accurate determinations of solar flux intensities between 2000 A and 3500 A should be made.

4) Stratospheric concentrations of important minor constituents such as methane, nitric oxide, nitric dioxide, hydroxyl, molecular hydrogen, and carbon monoxide need to be accurately determined. Further, studies should be made of the oxidation of methane, carbon dioxide and water vapor in the atmosphere since the intermediate steps in this process probably bear heavily on the concentrations of the above mentioned constituents.

5) The meteorological aspects of the problem are of great importance because of the extensive influence of atmospheric winds on the lower half of the atmospheric ozone, thus also affecting the introduction of Freons into the stratosphere.

6) It is imperative that the weak dispersive properties of the summer stratosphere be studied in detail when the natural ozone content is nearly at its minimum and transmission through the atmosphere of hazardous ultraviolet radiation is largest.

7) Very little or nothing is known of possible heterogeneous reactions of CI atoms with particulate matter in the stratosphere.

8) The present stratospheric abundance of gaseous chlorine, natural or otherwise, should be determined.

The above is illustrative of the types of research that are needed. They should be instituted as rapidly as possible. In this particular instance, it appears essential that an anticipatory mode of behavior be adopted rather than a reactive one. As Dr. McElroy (who has been appointed to a NAS study committee which has been formed in response to the growing concern over fluorocarbons and the ozone layer) is quoted as saying "We cannot afford to wait the normal ten years that a theoretical paper usually sits on the shelf, because by that time, if the theories are correct, the effects will be pronounced."

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References


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announcements

NAS/NAE report on stratospheric pollution published


The Committee has concluded that:

... an increase in the number of stratospheric airliners with present engines will diminish the amount of ozone in the stratosphere and consequently will increase the intensity of ultraviolet light at ground level. The potential harmful biological effects of an increase in the intensity of ultraviolet at ground level are such that the burden of proof that these consequences can be accepted must lie with those proposing increased use of such aircraft. If additional aircraft are put into service in the stratosphere, one must be prepared for an increase in skin cancer unless appropriate international regulations have been formed in response to the growing concern over fluorocarbons and the ozone layer. An increase in the number of stratospheric airliners is not only to reduce the NOx emissions but also to control the sulfur content of the fuel.

In regard to climatic change and agricultural effects, the Committee concludes that:

... no clear-cut statement can be made concerning expected changes in temperature and rainfall. Nevertheless, a global change in surface temperature of a few tenths of a degree and an associated change in rainfall are not ruled out. Local changes may be larger, and the economic, social, and political effects of such changes could be substantial. To insure against this, the action required is not only to reduce the NOx emissions but also to control the sulfur content of the fuel.

For information on the availability of the report contact: the Printing and Publishing Office, National Academy of Sciences, 2101 Constitution Ave., Washington, D.C. 20418.

(More announcements on page 593)