

## Ozone: Pollutant and Protector

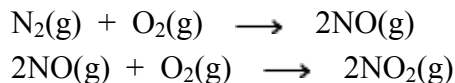
Current concerns about ozone in the Earth's atmosphere, which seems to be constantly finding its way into the news, present some excellent examples of the relationship between energy and chemical changes. One day you might read about an ozone alert in Los Angeles triggered by the concentration of ozone in the air rising to *too high* a level. This causes schoolteachers to keep their students off the playground to avoid damage to their lungs. You might then turn the page in the same newspaper and discover another article that describes the problems associated with *decreasing* ozone levels in the ozone layer that protects us from harmful radiation. *So, which is it? ...too much or too little?* Is ozone a pollutant or a protector? What is this stuff, and why are we so worried about it?

There are two forms (allotropes) of the element oxygen found in nature, the life-sustaining oxygen in the air, O<sub>2</sub>, and ozone, O<sub>3</sub>, which is a pale blue gas with a strong odor. The concentrations of ozone in the air around us are usually too low for the color and the odor to be apparent, but sometimes when we stand next to an electric motor, we notice ozone's characteristic smell. This is because an electric spark passing through oxygen gas creates ozone.

Ozone is a very powerful oxidizing agent. Sometimes this property can be used to our benefit, and sometimes it is a problem. Ozone mixed with oxygen can be used to sanitize hot tubs, and it is used in industry to bleach waxes, oils, and textiles, but when the levels in the air get too high, ozone's highly reactivity becomes a problem. For example, O<sub>3</sub> is a very strong respiratory irritant that can lead to shortness of breath, chest pain when inhaling, wheezing, and coughing. Anyone who has lived in a smoggy city will recognize these symptoms. Not only can ozone oxidize lung tissue, but it also damages rubber and plastics, leading to premature deterioration of products made with these materials. According to the Agricultural Research Service of North Carolina State University, ozone damages plants more than all other pollutants combined.

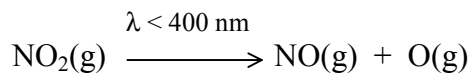


The highest concentrations of O<sub>3</sub> in the air we breathe are found in large industrial cities with lots of cars and lots of sun. The explanation for why this is true begins with a description of the source of nitrogen oxides. Any time air (which contains nitrogen and oxygen) is heated to high temperature (like in the cylinders of our cars or in many industrial processes), nitrogen oxides are formed (NO and NO<sub>2</sub>).

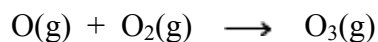


Nitrogen dioxide, NO<sub>2</sub>, is a red-brown gas that contributes to the brown haze associated with smog.

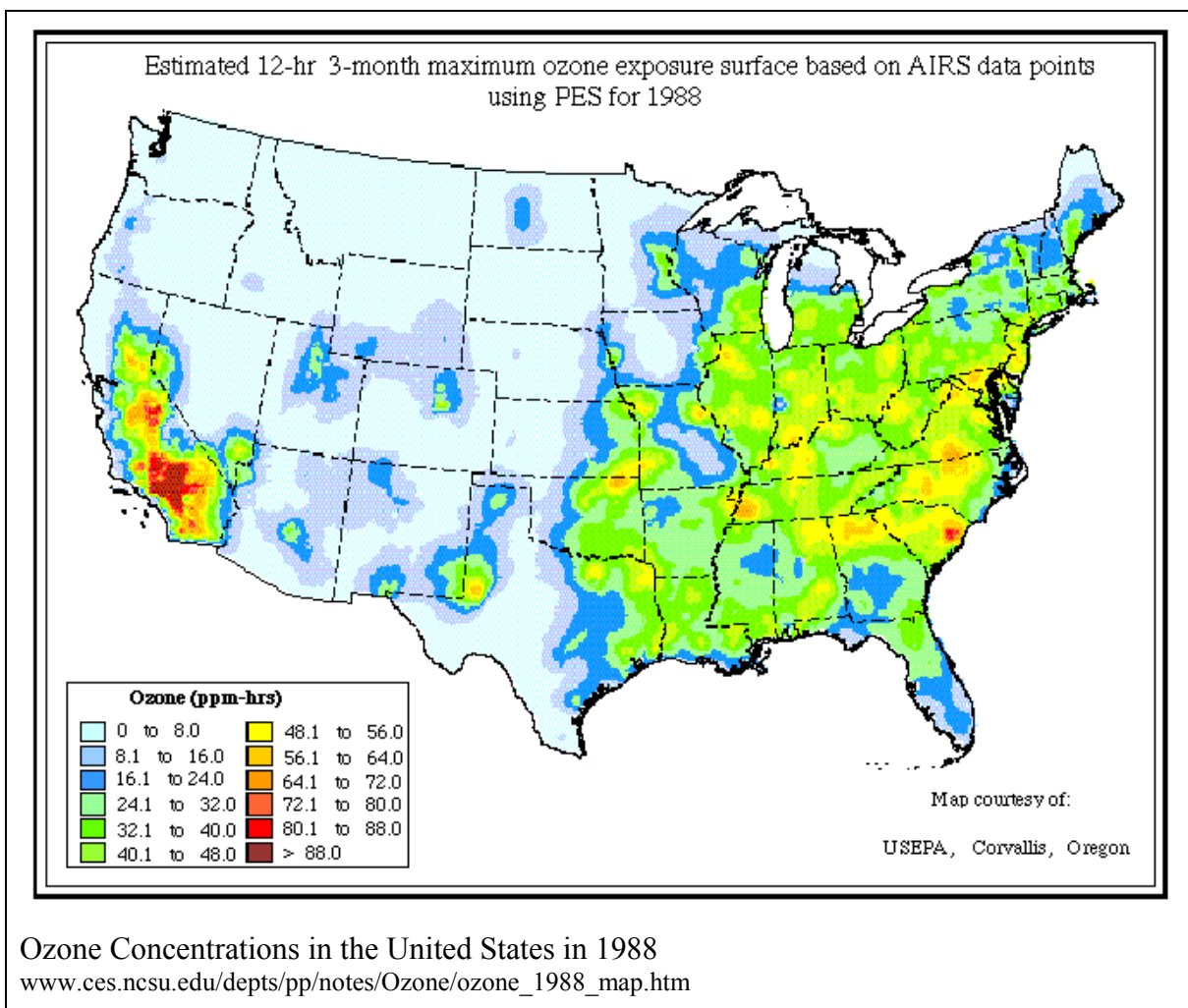
The radiant energy that passes through the air on sunny days can supply the energy necessary to break covalent bonds between nitrogen atoms and oxygen atoms in NO<sub>2</sub> molecules, converting NO<sub>2</sub> molecules into NO molecules and oxygen atoms. Remember that the shorter the wavelength of light is, the higher the energy. Radiant energy of wavelengths less than 400 nm has enough energy to break N-O bonds in NO<sub>2</sub> molecules, but radiant energy with wavelengths longer than 400 nm does not supply enough energy to separate the atoms.



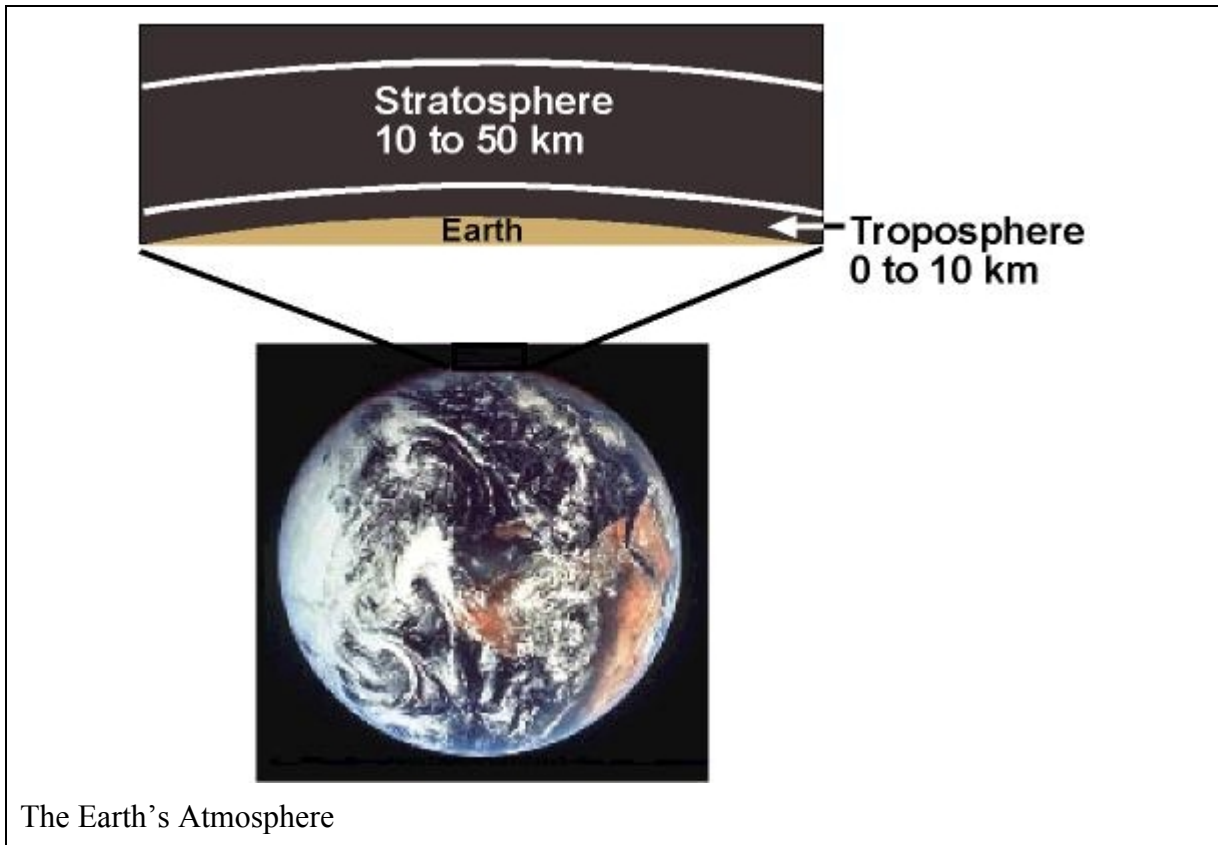
The oxygen atoms react with oxygen molecules to form ozone molecules.



Because the process that produces the ozone is initiated by light photons, the pollutants created are called photochemical smog. The Figure below shows the ozone concentrations in the United States in 1988. Notice that the concentrations are highest in southern California. Cities like Los Angeles, with its sunny weather and hundreds of thousands of cars, have ideal conditions for the production of photochemical smog. This smog is worst from May to September when the days are long and the sunlight intense.



Now we see how we can get *too much* O<sub>3</sub> in the air we breathe and why that is a problem. We next want to know why depleting the ozone in the upper atmosphere, creating *too little* ozone there, can be a problem. Let's start with a little information about our atmosphere. Atmospheric scientists view the atmosphere as divided into layers, each with its own characteristics. The lowest layer, which extends from the surface of the earth to about 10 km (about 6 miles) above sea level, is called the troposphere. For our discussion of ozone, we are more interested in the next lowest layer, the stratosphere, which extends from about 10 to about 50 km (See Figure below.).



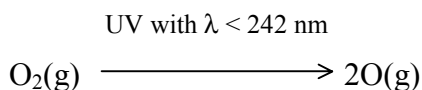
The stratosphere contains a mixture of gases, including oxygen molecules, O<sub>2</sub>, and ozone molecules, O<sub>3</sub>. These gases play a very important role in protecting the earth from high-energy ultraviolet radiation from the sun. The ultraviolet portion of the sun's energy spectrum can be divided into three parts: UV-A, UV-B, and UV-C. Not all UV radiation is harmful. UV-A, which includes radiant energy of wavelengths from about 320 to 400 nm, passes through the stratosphere and reaches us on the surface of the earth. We are glad it does, because UV-A radiation provides energy that our bodies use to produce vitamin D.

The shorter-wavelength UV-B radiation (from about 290 to 320 nm) has higher energy than the UV-A radiation. Some UV-B radiation is removed by the gases in the stratosphere, but some of it reaches the surface of the earth. Radiation in this portion of the spectrum has high enough energy that excessive exposure can cause sunburn, premature skin aging, and skin cancer.

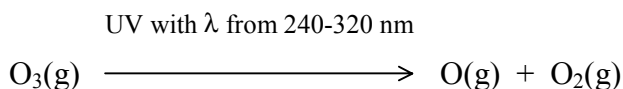
The highest-energy ultraviolet radiation is UV-C, with wavelengths from about 40 to 290 nm. We are very fortunate that this radiant energy is almost completely removed by the gases in the atmosphere. UV-C has high enough energy to cause serious damage not only to us but to all life on earth. DNA, the substance that carries genetic information in living cells, absorbs UV radiation of about 260 nm. Proteins, which are vital structural and functional components of living systems, absorb radiation with wavelengths of about 280 nm. If these wavelengths were to reach the earth in significant quantity, the changes they would cause by altering DNA and protein molecules would lead to massive crop damage and general ecological disaster.

## Removal of UV Radiation by Oxygen and Ozone Molecules

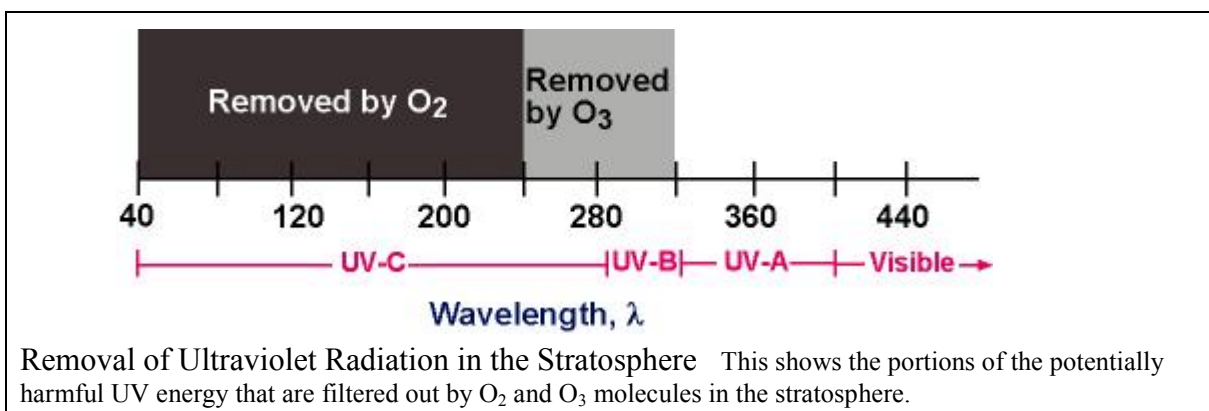
Some of the dangerous radiation removed in the stratosphere is absorbed by the  $O_2$  molecules there. Radiant energy wavelengths must be shorter than 242 nm to have enough energy to break the O-O bond, and UV-C radiation has wavelengths in the proper range.



UV radiation can also provide the energy to break a bond between oxygen atoms in ozone molecules. Because less energy is needed to break a bond in the  $O_3$  molecule than to break the bond in  $O_2$ , the UV photons that break the bond in  $O_3$  are associated with longer wavelengths. The  $O_3$  molecules will absorb UV radiation of wavelengths from 240 nm to 320 nm.

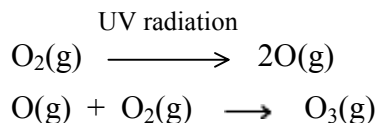


Thus, oxygen molecules,  $O_2$ , and ozone molecules,  $O_3$ , work together to absorb high-energy UV radiation.  $O_2$  molecules absorb UV radiation with wavelengths less than 242 nm, and  $O_3$  molecules absorb radiant energy with wavelengths from 240 nm to 320 nm (See Figure below). Wavelengths in the range of 240 to 320 nm can cause problems that include skin aging, skin cancer, and crop failure. Because  $O_2$  does not remove this radiation from the atmosphere, it is extremely important that the ozone layer be preserved.

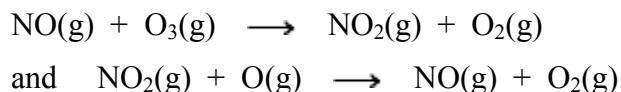


## The Natural Destruction of Ozone

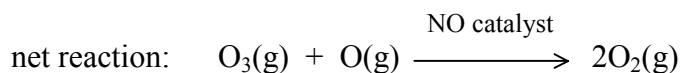
In the following reactions, ozone is constantly being generated and destroyed in the stratosphere as part of a natural cycle.



There are several natural processes that destroy ozone in the stratosphere other than the UV-initiated reaction described above. Perhaps the most important of these are:



The first reaction destroys one ozone molecule directly. The second reaction destroys an oxygen atom that might have become an ozone molecule. (Because oxygen atoms can collide with oxygen molecules to form ozone molecules, the ozone concentration is depleted indirectly through the removal of oxygen atoms.) The main reason that this pair of reactions is so efficient at destroying ozone molecules is that the NO(g) that is destroyed in the first reaction is regenerated in the second reaction. In the overall reaction, an ozone molecule and an oxygen atom are converted into two oxygen molecules with no change in the number of NO molecules. This makes NO(g) a catalyst for the reaction. A catalyst is a substance that speeds a chemical reaction without being permanently altered itself. The equation for the net reaction is below.



# Chlorofluorocarbons: A Chemical Success Story Gone Wrong

In 1972 the chemical industry was producing about 700,000 metric tons (about 1.5 billion pounds) of chlorofluorocarbons (CFCs) per year. A chlorofluorocarbon is a compound composed of just carbon, chlorine, and fluorine. Most of the CFCs produced in the early 70's were either CFC-11, which is  $\text{CFCl}_3$ , or CFC-12, which is  $\text{CF}_2\text{Cl}_2$ . The development of these chemicals was considered a major success for the industry because they seemed to be perfect for use as propellants in aerosol cans, as solvents, as expansion gases in the production of foams, as the heat-exchanging fluid in air conditioners, and as the temperature-reducing fluid in refrigerators.

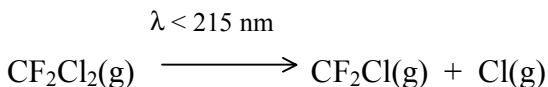
One of the reasons CFCs were so useful is that they are extremely stable compounds; very few substances will react with them. As a result, they are nontoxic and nonflammable. Another important characteristic is that they are gases at normal room temperatures and pressures, but they become liquids at pressures just slightly above normal. These were just the characteristics needed for the applications listed above.

## CFCs and the Ozone Layer

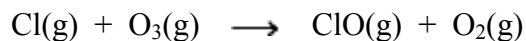
*“The announcement today, suggesting a worse situation than we thought, affirms the warning I issued last Spring: Upper atmosphere ozone depletion remains one of the world’s most pressing environmental threats.”*

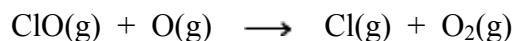
William K. Reilly,  
Administrator of the U.S. Environmental Protection Agency  
1991

Gases are removed from the lower atmosphere in two general ways. They either dissolve in the clouds and are rained out, or they react chemically to be converted into other substances. Neither of these mechanisms is important for CFCs. Chlorofluorocarbons are insoluble in water, and they are so stable that they can persist in the lower atmosphere for years. For example, CFC-11 molecules have an average life of 50 years in the atmosphere, and CFC-12 molecules have an average life of about 102 years. During this time, the CFC molecules wander about, moving wherever the air currents take them. They can eventually make their way into the stratosphere, where they encounter radiant energy with enough energy to break them down. For example, radiant energy of wavelength less than 215 nm will break the covalent bond between a chlorine atom and the carbon atom in  $\text{CF}_2\text{Cl}_2$ .

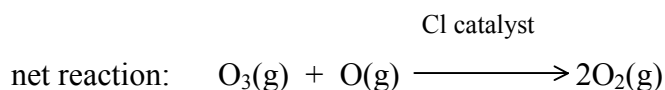


The chlorine atoms released in this sort of reaction can destroy ozone molecules, in a process similar to the catalytic reactions between NO,  $\text{O}_3$ , and O described in the last section:

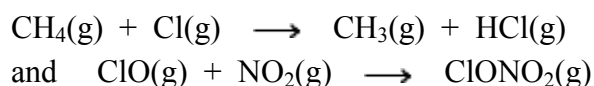




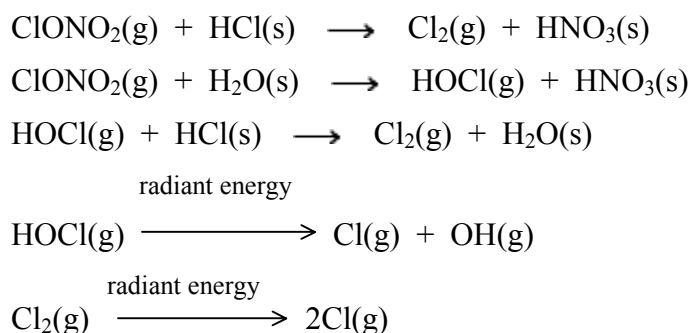
Each chlorine atom destroys one ozone molecule directly. In addition, the resulting ClO goes on to react with an oxygen atom that might otherwise have collided with an oxygen molecule to form an ozone molecule, so a second ozone molecule is prevented from forming. The chlorine atom is regenerated in the second reaction, so it is a catalyst for the reaction. The equation for the net reaction is



Each chlorine atom is thought to destroy an average of 1000 ozone molecules before being temporarily incorporated into a compound like HCl or ClONO<sub>2</sub>.



In 1985, scientists discovered a large decrease in the atmospheric concentration of ozone over Antarctica. This “ozone hole” could not be explained with the models used to describe atmospheric chemistry at that time, but it has since been explained in terms of an unexpectedly rapid reformation of chlorine atoms from chlorine compounds like HCl and ClONO<sub>2</sub>. The new model suggests that reactions like the following take place on the surface of ice crystals that form in the cold air of the stratosphere over Antarctica:



The chlorine atoms freed in these reactions can once again react with ozone molecules and oxygen atoms. Scientists fear that each chlorine atom that reaches the stratosphere may destroy tens of thousands of ozone molecules before escaping from the stratosphere. One way they finally escape is by migrating back into the lower atmosphere in HCl molecules that dissolve in the clouds and return to the earth in rain.

## Special Topic: Green Chemistry - Substitutes for Chlorofluorocarbons

Any television, computer, or other fragile item you have purchased in recent years has probably come packaged in polystyrene foam (Styrofoam<sup>®</sup>) for protection, the same foam likely to be serving as insulation in the cooler you take along on a picnic. It is a stiff, low-density, non-heat-conducting solid produced by blowing gas into polystyrene liquid as it solidifies. Over 700 million pounds were manufactured in 1995.

Chlorofluorocarbons have been used as the blowing agents in the production of polystyrene foam, but because of the damage CFCs can do to the ozone layer, chemists are actively seeking alternatives to do the job. In 1996, the Dow Chemical Company received the Presidential Green Chemistry Challenge Award, specifically the Alternative Solvents/Reaction Conditions Award, for developing a process that makes polystyrene foam using 100% carbon dioxide, CO<sub>2</sub>, as the blowing agent. Carbon dioxide is nonflammable and nontoxic and does not deplete the ozone layer. The process does not even increase the level of CO<sub>2</sub> in the atmosphere, because the carbon dioxide it uses comes from other commercial or natural sources, like ammonia plants or natural gas wells. This new technology reduces the use of CFCs by 3.5 million pounds per year.

## Special Topic: Other Ozone-Depleting Chemicals

Although CFCs have gotten the most attention as a threat to the ozone layer, there are other chemicals that have also been found to pose a danger to it.

Halons, which are similar to CFCs but contain at least one bromine atom, are one such group of compounds. Halon-1301 (CF<sub>3</sub>Br) and halon-1211 (CF<sub>2</sub>ClBr) have been used as fire extinguishing agents, but the bromine they release has been shown to be even more efficient at destroying ozone than chlorine is.

While governments are in general agreement that halons should be banned, the status of another bromine-containing compound is more ambiguous. This compound is methyl bromide, CH<sub>3</sub>Br. The controversy revolves around whether or not it has a significant effect on the ozone layer and whether the benefits of using methyl bromide outweigh the potential hazards. This ozone-depleting compound is different from CFCs and halons because it is not produced by humans only, but by many prolific natural sources. For example, the ocean is thought to both release and absorb significant amounts of CH<sub>3</sub>Br, and wildfires generate methyl bromide as well. The actual contribution of the various sources of methyl bromide to the atmosphere is still uncertain, but scientists agree that significant amounts do come from human activities, so-called anthropogenic sources, such as the burning of rain forests, the use of insecticides, herbicides, and fungicides, and the use of leaded gasoline that contains ethylene dibromide. One of the reasons methyl bromide has been considered less threatening to the ozone layer than CFCs or halons is that it has a much shorter lifetime. The best estimates predict its average lifetime to be 1 to 2 years compared to over 50 years for the shortest-lived common CFC and over 20 years for the most common halons. Although research on the possible effects of methyl bromide continues, experts now consider it damaging enough that steps have been taken to begin phasing it out.

With the discovery of the damaging effects of CFCs, alternatives were developed that as much as possible have the described characteristics of CFCs but are less stable in the lower atmosphere and less likely to reach the stratosphere. These chemicals, called hydrochlorofluorocarbons (HCFCs), are similar in structure to CFCs but contain at least one hydrogen atom. For example, HCFC-22 is CF<sub>2</sub>HCl, and HCFC-123 is CF<sub>3</sub>CHCl<sub>2</sub>. Although these chemicals are thought to be less damaging to the ozone layer, they too can reach the stratosphere and lead to some depletion of O<sub>3</sub>. Thus, they are viewed as transitional compounds to be used until better substitutes have been found. HCFCs, too, are being phased out over time.