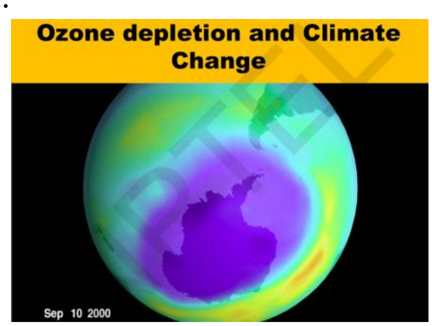
Climate Change Science
Prof. J. Srinivasan
Department of Environmental Science
Indian Institute of Science, Bengaluru

Lecture 17
Ozone Depletion

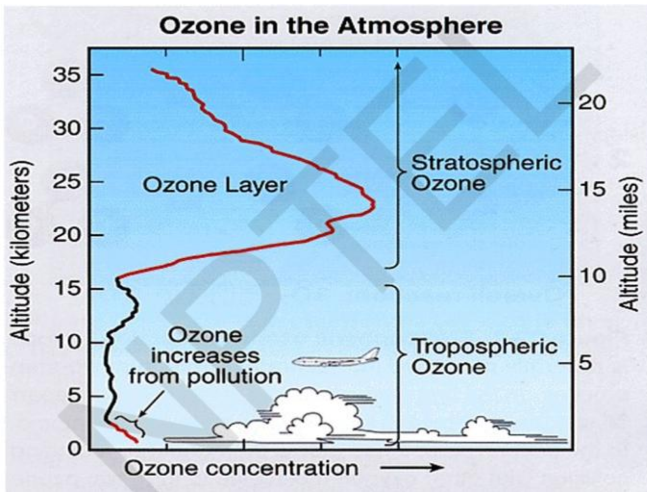
In the previous lecture, the contrasting temperature structures of the troposphere and stratosphere were discussed. In the troposphere, temperature decreases with altitude because most solar radiation is absorbed at the Earth's surface. This heat is then transferred upward via radiation, evaporation, and turbulent fluxes. Conversely, in the stratosphere, temperature increases with altitude due to the presence of ozone, which absorbs ultraviolet (UV) radiation from the Sun. This absorption leads to heating at higher altitudes, creating a thermal inversion. These distinct temperature profiles define the structural layers of Earth's atmosphere.

A common source of confusion among the public has been the distinction between ozone depletion and global warming. Though both involve atmospheric changes, they are fundamentally different phenomena. Ozone depletion refers to the reduction of ozone in the stratosphere due to human-made chemicals, such as chlorofluorocarbons (CFCs). This affects the absorption of harmful UV radiation from the Sun. On the other hand, global warming is primarily driven by the accumulation of carbon dioxide and other greenhouse gases that trap infrared radiation emitted by the Earth, leading to a rise in surface temperatures.

Despite these differences, there is some overlap. Ozone not only absorbs UV radiation but also acts as a greenhouse gas by absorbing Earth's infrared radiation, particularly in the 9.6 micron band. Thus, while the mechanisms and consequences of ozone depletion and global warming are distinct, they are interlinked through the complex radiative processes in the atmosphere.



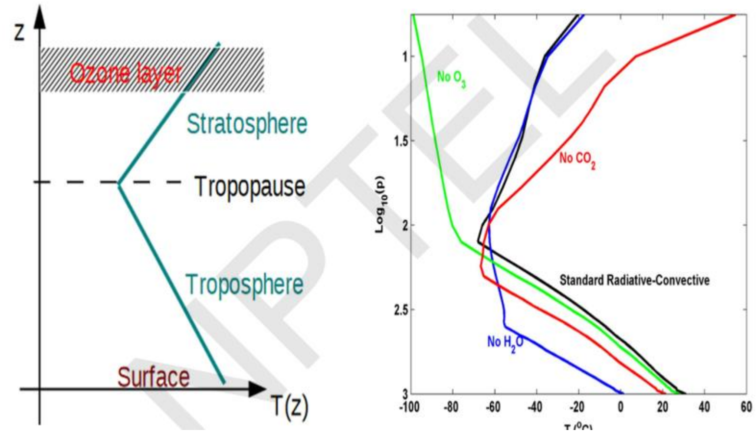
The discovery of the ozone hole over Antarctica about 40 years ago was a significant scientific event. It revealed a sharp reduction in stratospheric ozone over the region, appearing like a "hole" due to its stark contrast with surrounding ozone levels. This finding led to urgent investigations to determine whether it was a natural occurrence or caused by anthropogenic factors. Once human activities, specifically the emission of ozone-depleting substances were identified as the primary cause, the international community responded by formulating the Montreal Protocol. This landmark treaty aimed to phase out the production and use of substances responsible for ozone depletion, representing a major global effort to protect the stratospheric ozone layer.



The ozone layer primarily resides in the stratosphere, at an altitude of around 20 to 25 kilometers above the Earth's surface. This "good ozone" is crucial for life on Earth, as it absorbs the Sun’s harmful ultraviolet (UV) radiation. Without this protective shield, UV rays would reach the Earth's surface in much greater intensity, damaging the DNA of living organisms and making life on land unsustainable. Though life might still persist in the deep ocean where UV radiation cannot penetrate, most terrestrial life forms, including humans, would face severe biological risks.

In contrast, ozone near the Earth's surface, often called "bad ozone," is a harmful pollutant. Though it exists in much lower concentrations compared to stratospheric ozone, this ground-level ozone has significant negative impacts on air quality and human health. It is a major component of smog and contributes to respiratory problems such as asthma and lung damage. This distinction between the beneficial ozone in the stratosphere and the harmful ozone at ground level highlights the dual role of ozone in atmospheric science - protective at high altitudes, but dangerous near the surface.

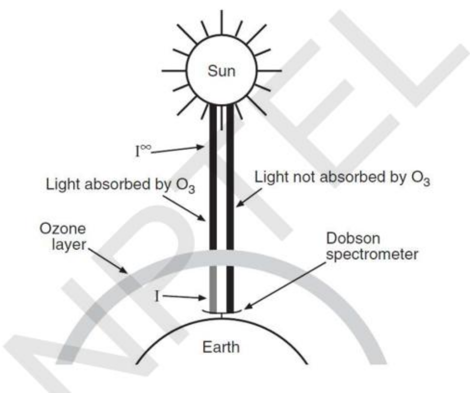
The vertical temperature structure of the Earth’s atmosphere is fundamentally shaped by the presence of ozone in the stratosphere, which absorbs ultraviolet (UV) radiation. This absorption leads to a distinct two-layer temperature profile: the troposphere, where temperature decreases with height, and the stratosphere, where temperature increases with height. The boundary between these two layers is known as the tropopause, where the temperature levels off briefly. Climate models clearly illustrate this structure. In the absence of ozone, the temperature would continue to decrease throughout the atmosphere, as shown by the green line in the model. The lapse rate, the rate of temperature decrease with height, varies between these layers. In the troposphere, water vapour significantly influences the lapse rate, whereas in the drier stratosphere, the lapse rate behaves differently.

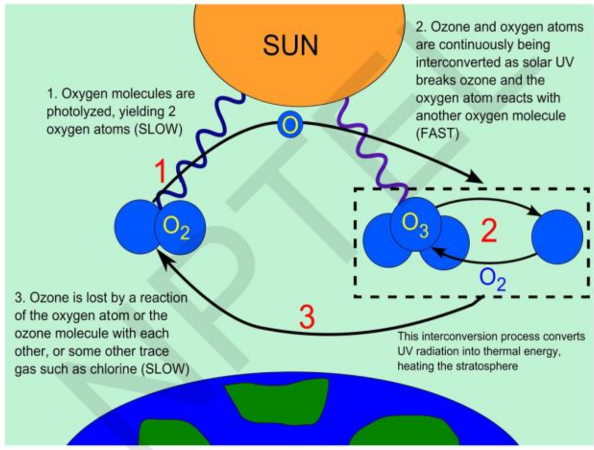


The presence of CO_2 and water vapour further modifies this temperature profile. Removing CO_2 leads to a cooler Earth (red line), and eliminating water vapour leads to even greater cooling, but the overall shape of the temperature profile remains. Both gases are vital to maintaining Earth’s habitable climate through the greenhouse effect, which keeps surface temperatures above freezing and conducive to life. Despite their importance, an excess of CO_2 primarily from human activities like burning fossil fuels has led to abnormal warming. While atmospheric CO_2 levels naturally fluctuated between 200–280 parts per million over the past 3 to 4 million years, industrial activities have pushed these levels far beyond their natural range, causing a 1.5°C rise in global temperatures over the past 150 years. This rapid warming threatens many life forms, particularly mammals, and underscores the urgency of controlling CO_2 emissions despite its natural role in climate regulation.

The amount of ozone in the Earth's atmosphere is measured using an instrument called the Dobson spectrometer, invented over a century ago by G. M. B. Dobson. The measurement unit derived from this instrument is known as the Dobson Unit (DU). One Dobson Unit represents a layer of ozone that would be 0.01 millimeters thick if compressed to the Earth's surface at standard temperature and pressure. Typically, the Earth's atmosphere contains about 300 Dobson Units, meaning that if all atmospheric ozone were brought down to the surface, it would form a layer approximately 3 millimeters thick.

The Dobson spectrometer measures ozone by analysing ultraviolet (UV) radiation at two specific wavelengths: one where ozone strongly absorbs UV light, and another where absorption is minimal or negligible. By comparing the UV radiation intensity at these two wavelengths, the instrument estimates the amount of ozone present. This differential absorption technique is now a standard method used not only for measuring ozone but also for detecting other atmospheric gases. By selecting appropriate absorption and non-absorption wavelengths, scientists can deduce the concentration of various trace gases in the atmosphere.



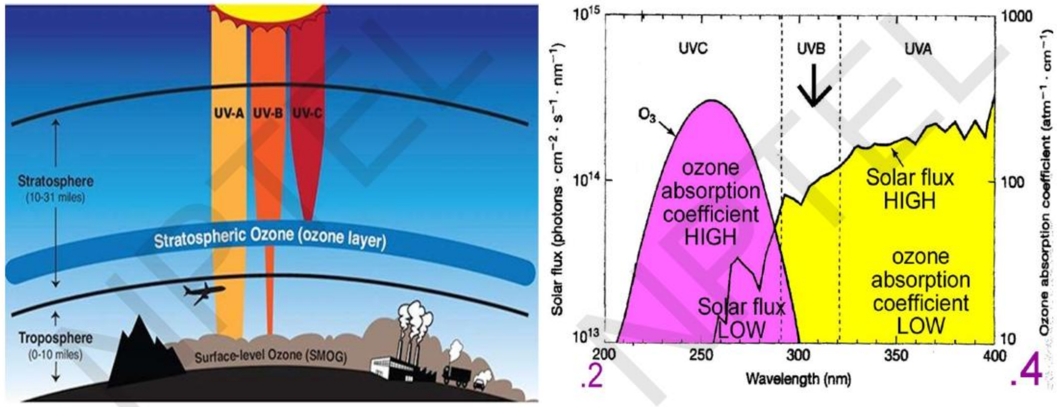


Ozone occurs naturally in the Earth's atmosphere through a well-established photochemical process involving oxygen and ultraviolet (UV) radiation from the Sun. For over a billion years, molecular oxygen (O_2) has been present in the atmosphere. When exposed to high-energy UV radiation, an oxygen molecule splits into two separate oxygen atoms (O). These highly reactive oxygen atoms can then collide with other oxygen molecules (O_2) to form ozone (O_3). This reaction has been continuously occurring for billions of years, leading to the formation of the ozone layer in the stratosphere.

The establishment of the ozone layer was a crucial development for life on Earth, particularly for life on land. Before the ozone layer formed, life existed primarily in the deep ocean, where it was shielded from the Sun’s harmful ultraviolet radiation. The formation of the ozone layer allowed life forms to colonize land, as it protected them from DNA-damaging UV rays. This protective function of the ozone layer continues to be essential for sustaining life on Earth’s surface.

Ultraviolet (UV) radiation from the Sun is divided into three regimes based on wavelength: UV-A, UV-B, and UV-C, and each interacts differently with the ozone layer and affects life on Earth in distinct ways.

UV-A radiation (wavelengths from approximately 0.325 to 0.4 microns) is not strongly absorbed by the ozone layer and thus reaches the Earth's surface in significant quantities. This type of UV radiation is beneficial in moderate amounts, as it helps the human body synthesize vitamin D through skin exposure. Because of this, medical professionals often recommend regular but limited sunlight exposure.



UV-B radiation (wavelengths between roughly 0.3 to 0.325 microns) is only partially absorbed by the ozone layer. It is more energetic than UV-A and can be harmful to human health, especially with prolonged exposure. For people with lighter skin, excessive exposure can penetrate the skin and increase the risk of skin cancer. This is why protective measures such as sunscreen or protective clothing are advised when spending extended periods in sunlight.

UV-C radiation (wavelengths between about 0.2 to 0.3 microns) is the most dangerous of the three, but fortunately, it is completely absorbed by the ozone layer and does not reach the Earth's surface. If it were to reach the surface, it would pose a severe threat to all life, making land-based existence unviable.

Thus, the ozone layer plays a crucial protective role by filtering out the most harmful UV radiation, particularly UV-C, and limiting the damaging effects of UV-B while allowing beneficial UV-A to reach the surface.

Ozone in the Earth's atmosphere is formed through a continuous photochemical reaction cycle driven by ultraviolet (UV) radiation from the Sun. This process primarily occurs in the stratosphere, where sufficient UV radiation is available to initiate the reaction.

$$O_2 + h\nu \rightarrow O + O$$

$$O_2 + O + M \rightarrow O_3 + M$$

$$O_3 + h\nu \rightarrow O + O_2$$

$$O_3 + O \rightarrow 2O_2$$

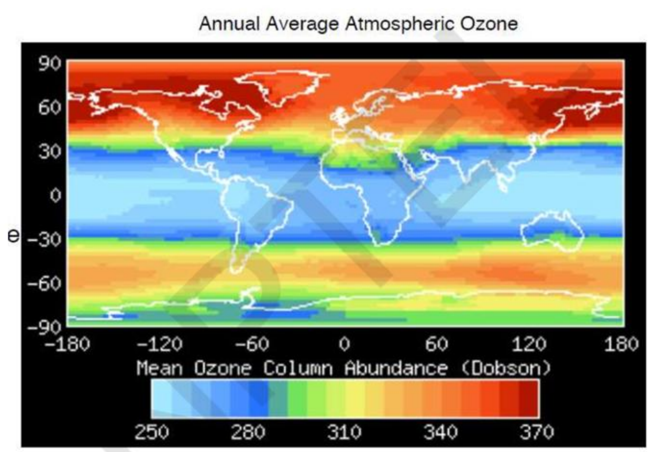
The cycle begins when a high-energy UV photon strikes a molecule of oxygen (O_2), causing it to dissociate into two individual oxygen atoms (O). These highly reactive oxygen atoms then collide with another oxygen molecule (O_2) in the presence of a third molecule such as nitrogen or another oxygen molecule, which serves as a collision partner to carry away excess energy. This results in the formation of ozone (O_3).

The ozone produced can again absorb UV radiation, which causes it to decompose back into an oxygen molecule (O_2) and a free oxygen atom (O). This free oxygen atom can then recombine with another O_2 to form ozone again.

This dynamic cycle of formation and destruction maintains a stable concentration of ozone in the stratosphere under natural conditions.

Ozone in the stratosphere plays a crucial role in shielding life on Earth from harmful ultraviolet (UV) radiation. Although UV-A was once considered harmless, recent research shows that it contributes to skin aging, wrinkles, and even skin cancer. UV-B, which is partially absorbed by ozone, is more dangerous; it causes sunburn, skin cancer, and various other health issues. UV-C is the most harmful of all, as it can severely damage DNA, but fortunately, the ozone layer completely absorbs this radiation.

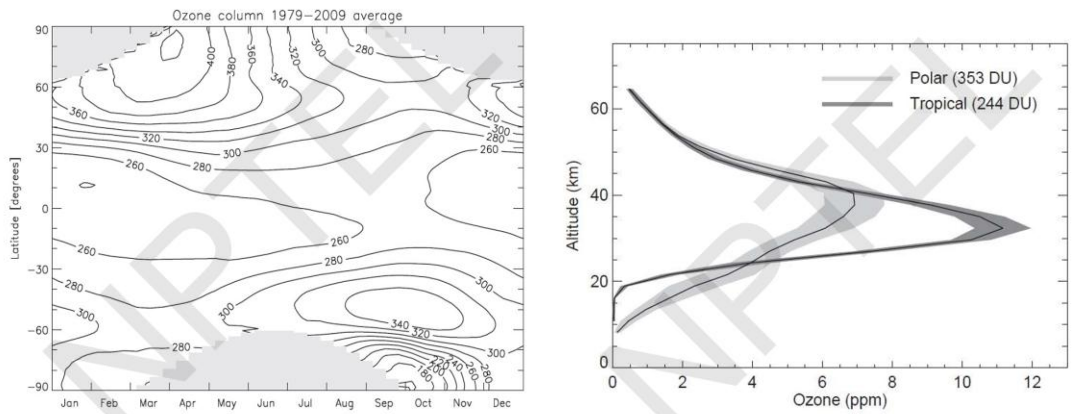
Exposure to UV radiation is associated with a range of health problems including skin cancer, sunburn, eye damage, and cataracts, particularly among the elderly. Scientific studies indicate that even a 10% reduction in the ozone layer can lead to a 25% increase in non-melanoma skin cancer in temperate regions by the year 2050. This highlights the immense significance of the ozone layer. Historically, before the ozone layer formed, life was restricted to the oceans where UV radiation could not penetrate. Only after the formation of this protective layer was it possible for life to thrive on land. Therefore, preserving the ozone layer is essential for sustaining life on the Earth's surface.



http://isccp.giss.nasa.gov/products/browsed2.html

The distribution of ozone in the Earth's atmosphere varies with latitude, and this has important biological and evolutionary implications. According to NASA, ozone concentration is highest in the higher latitudes and relatively lower in the tropics. As a result, regions near the equator receive more ultraviolet (UV) radiation. This higher UV exposure in the tropics is one reason why people native to these regions typically have darker skin. Melanin in darker skin offers protection against UV damage. In contrast, people who evolved in higher latitudes have lighter skin, which allows more UV penetration necessary for the synthesis of vitamin D, since UV levels are lower in these areas due to higher ozone concentrations.

However, this evolutionary adaptation becomes a concern if ozone depletion occurs, especially in higher latitudes. With reduced ozone, light-skinned individuals become more vulnerable to skin cancer and other UV-related health issues. The key takeaway is that while a certain amount of UV radiation is essential for human health, particularly for vitamin D production, excess UV especially in harmful wavelengths is dangerous. Hence, the ozone layer acts as a critical shield that maintains the balance between beneficial and harmful UV exposure.



A long-term average of ozone column data reveals distinct spatial patterns in ozone distribution. The 30-year mean column ozone, expressed in Dobson Units, shows lower values in the tropics, around 260 DU, compared to higher values in the polar and mid-latitude regions, which are generally closer to 300 DU. A notable exception to this pattern is observed over Antarctica, particularly during September and October, when the ozone hole appears. This seasonal depletion is associated with the Antarctic spring and represents a significant reduction in ozone levels in that region.

Additionally, a comparison of the vertical ozone profiles between the polar and tropical regions highlights further differences. While the tropics may show higher ozone concentrations at certain altitudes, the overall column-integrated ozone (i.e., the total amount of ozone through the atmospheric column) tends to be greater in the polar regions. This is evident from the broader distribution of ozone over a larger vertical range in the polar atmosphere, even if the peak concentration is not as high as in the tropics. These variations are important for understanding regional differences in UV exposure and the resulting impacts on climate and health.

To summarize, there are two distinct types of ozone based on their location in the atmosphere and their impact on human health and the environment:

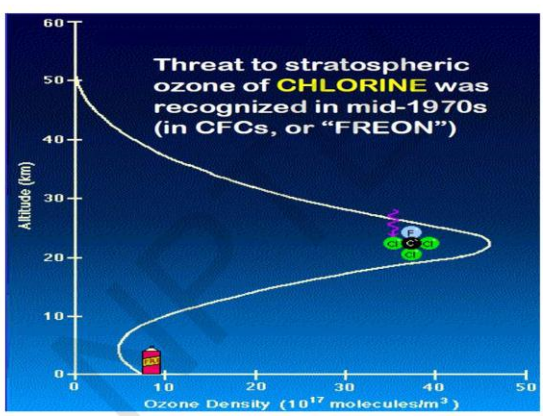
1. Stratospheric ozone is the "good ozone" found at altitudes around 20–25 kilometers. It plays a crucial protective role by absorbing the Sun's harmful ultraviolet (UV) radiation, especially UV-B and UV-C. This absorption prevents DNA damage and other harmful biological effects, making the ozone layer essential for the survival of life on Earth's surface.

2. Tropospheric ozone, in contrast, is the "bad ozone" located near the Earth's surface. It is not emitted directly, but is formed through photochemical reactions involving pollutants such as nitrogen oxides (NO_x) and volatile organic compounds (VOCs) in the presence of sunlight. This ground-level ozone is a major component of urban smog and is harmful to human health, especially affecting the lungs and respiratory system.

Thus, while ozone is beneficial in the stratosphere, it becomes a hazard in the lower atmosphere due to pollution, underscoring the importance of understanding ozone in its specific atmospheric context.

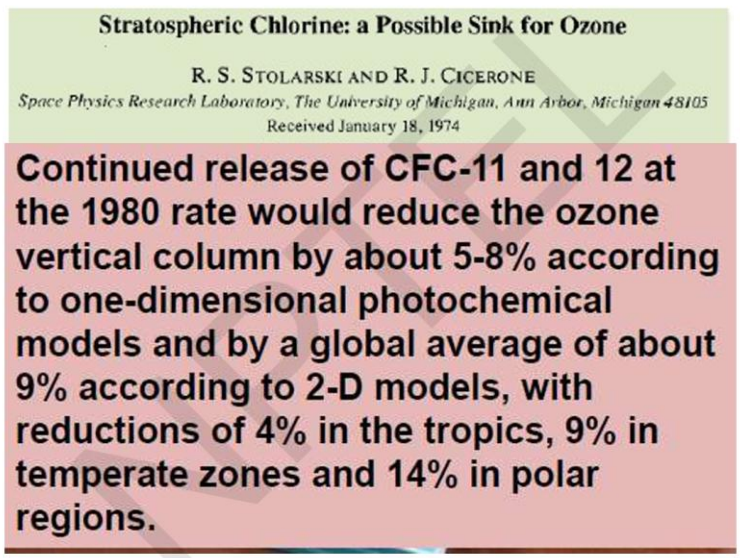
Surface ozone, often referred to as tropospheric ozone, has significant adverse effects on human respiratory health. It acts as a powerful irritant, capable of inflaming and damaging lung tissues, particularly during heavy physical activity or prolonged exposure. One of its serious impacts is the aggravation of asthma, a condition already affecting a large portion of the population.

Studies have shown that 10 to 20 percent of summertime respiratory-related health problems are linked to elevated levels of surface ozone. These include coughing, throat irritation, chest pain, and reduced lung function, especially in vulnerable groups such as children, the elderly, and individuals with pre-existing respiratory conditions. This makes controlling ground-level ozone an important public health objective, especially during hot and sunny periods when its concentrations tend to rise.



The major threat to stratospheric ozone comes from chlorine, a highly reactive element that began significantly depleting ozone in the 1980s. This issue traces back to the widespread use of chlorofluorocarbons (CFCs), commonly known as Freons, which were discovered in the 1930s. These gases were extensively used in refrigerators, air conditioners, and aerosol sprays because they were non-toxic, non-flammable, non-reactive, and odourless making them appear ideal for domestic and industrial use.

However, the problem with CFCs lies in their long atmospheric lifetime. After being released at the Earth's surface, they slowly diffuse upward into the stratosphere. There, they are exposed to ultraviolet C (UV-C) radiation from the Sun, which breaks them down and releases chlorine atoms. While CFCs themselves are chemically inert in the lower atmosphere, the chlorine atoms they release in the stratosphere are highly reactive and initiate ozone-depleting reactions. This destructive process went unnoticed for decades until scientists accidentally discovered the ozone hole over Antarctica in the 1980s, revealing the severity of the problem.



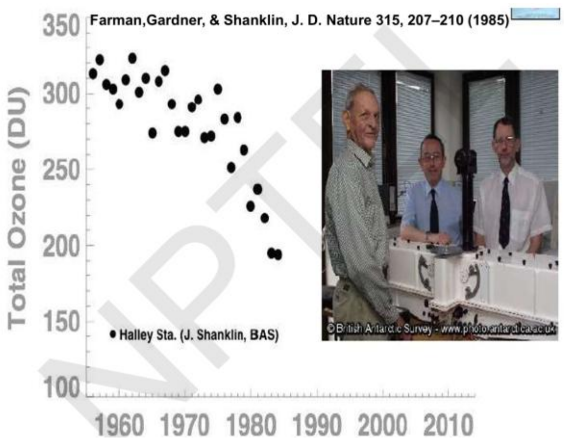
In 1974, scientists Richard Stolarski and Ralph Cicerone published a landmark paper that proposed a critical theory: chlorine in the stratosphere can destroy ozone. At the time, this idea was groundbreaking and controversial. Many scientists and policymakers were skeptical, largely because natural variations in ozone levels were well known. For instance:

- The Sun's 11-year solar cycle affects the amount of ultraviolet radiation reaching the Earth, leading to natural fluctuations in ozone production.
- Stratospheric temperature and circulation patterns also influence ozone distribution.

Because of these known natural variations, many dismissed the idea that human-made chemicals like CFCs could cause significant ozone depletion. The general sentiment was that this was an overreaction or unnecessary alarm, and any future changes in ozone levels could be addressed later if needed.

While models did predict a gradual decline in ozone due to CFCs, no one anticipated the dramatic and localized ozone loss that would later be identified as the ozone hole over Antarctica. This phenomenon, discovered in the early 1980s, took the scientific community by surprise and validated the concerns originally raised by Stolarski and Cicerone. It highlighted how underestimating seemingly small chemical effects in the upper atmosphere can lead to severe and unexpected environmental consequences.

.

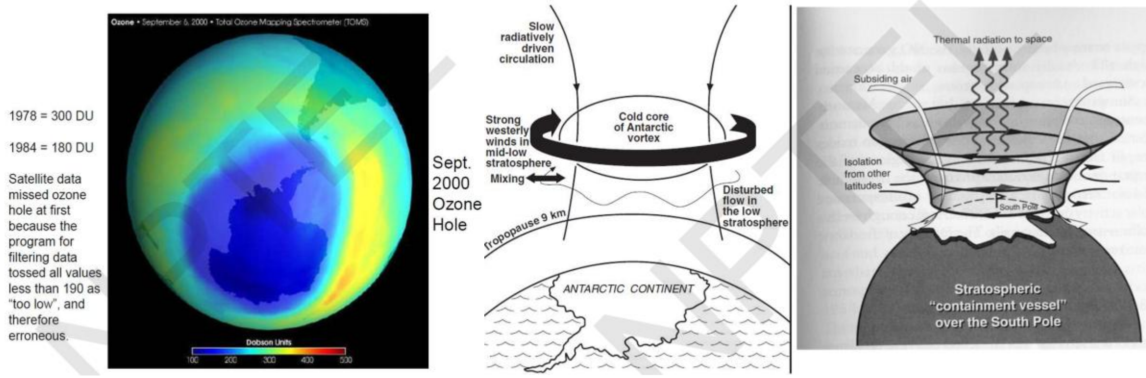


The discovery of the Antarctic ozone hole was a pivotal moment in atmospheric science. It was made by Joe Farman, Brian Gardiner, and Jonathan Shanklin, and published in *Nature* in 1985. Their measurements showed that the total column ozone over Antarctica, which had been stable around 300–325 Dobson Units since the 1960s, had dramatically declined dropping to around 200 DU and even lower during the Antarctic spring.

At first, these findings were met with disbelief. Here's how the skepticism unfolded:

- Satellite instruments had already detected signs of ozone depletion, but the data were dismissed as faulty. Scientists thought the instruments might be malfunctioning, possibly due to sensor errors or algorithm problems.
- The measurements by Farman and colleagues, taken with ground-based Dobson spectrophotometers in Antarctica, were critical because they confirmed the satellite observations with independent data. Their instruments showed a consistent and significant drop in ozone, which could no longer be explained away.

This convergence of independent ground-based and satellite data forced the scientific community to take the issue seriously. It became clear that something unprecedented was occurring in the stratosphere, and it was linked to chlorine from man-made CFCs. This discovery marked the beginning of international action on ozone protection, eventually leading to the Montreal Protocol just two years later, in 1987.



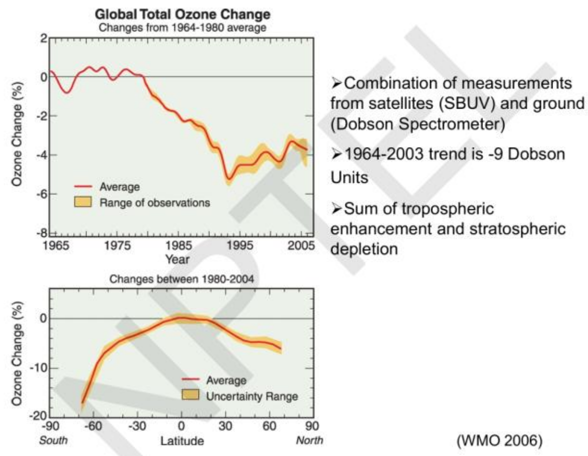
The formation of the ozone hole over Antarctica, despite chlorofluorocarbons (CFCs) being primarily released in North America and Europe, is due to unique meteorological and chemical conditions in the Antarctic region. CFCs are chemically stable and can persist in the atmosphere for decades. Over time, they spread globally and eventually reach the stratosphere. Once there, high-energy ultraviolet (UV) radiation breaks down these compounds, releasing reactive chlorine atoms that are capable of destroying ozone.

What made Antarctica particularly vulnerable was the presence of the Antarctic polar vortex. During the Southern Hemisphere winter, a strong circumpolar wind system develops, effectively isolating the air above the continent. This vortex prevents warmer, ozone-rich air from mixing in, creating an enclosed region that behaves like a sealed chemical reactor. Within this isolated vortex, extremely low temperatures allow the formation of polar stratospheric clouds (PSCs). These clouds provide surfaces on which stable chlorine compounds are converted into highly reactive forms.

As sunlight returns to Antarctica in early spring (September–October), UV radiation breaks apart these reactive chlorine compounds, releasing chlorine atoms that rapidly destroy ozone in catalytic cycles. This results in a sharp and rapid decline in stratospheric ozone, forming the so-called ozone hole. Although ozone depletion also occurs in the Arctic, the polar vortex there is less stable and temperatures are generally not as cold, which makes the ozone loss less severe and more variable than in the Antarctic.

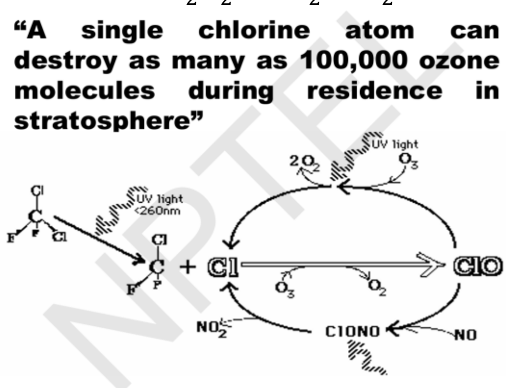
In summary, the Antarctic ozone hole appeared first due to the combination of isolated atmospheric circulation, extremely cold temperatures that facilitated key chemical reactions, and the return of sunlight that triggered ozone destruction. These unique features created the conditions for the dramatic and initially unexpected thinning of the ozone layer observed in the 1980s.

The changes in Ozone from the 1960s to the 1990s is shown in the below figure. It also shows how the changes in ozone varied at different latitudes. Most of the decline occurred in the polar region and not in the tropics.



Ozone depletion in the stratosphere primarily occurs due to the presence of man-made chemicals, especially chlorofluorocarbons (CFCs). Although CFCs are chemically inert in the lower atmosphere, they eventually migrate to the stratosphere, where they are broken down by ultraviolet (UV) radiation. This breakdown releases chlorine atoms, which are highly reactive and play a central role in ozone destruction. The chlorine atom reacts with an ozone molecule (O_3), producing chlorine monoxide (ClO) and molecular oxygen (O_2). Then, ClO can react with a free oxygen atom, regenerating the chlorine atom and producing more O_2.

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$
$$ClO + ClO \rightarrow Cl_2O_2 \rightarrow Cl_2 + O_2 \rightarrow 2Cl + O_2$$



This sequence of reactions forms a catalytic cycle, meaning the chlorine atom is not consumed in the process. It is regenerated and able to destroy many more ozone molecules. This regenerative nature of chlorine was not fully appreciated when the first scientific warnings about ozone depletion were published in 1974. The initial models predicted a slow decline in ozone levels. However, later observations revealed that a single chlorine atom could destroy up to 100,000 ozone molecules during its lifetime in the stratosphere, particularly under the special conditions found in the Antarctic.

These rapid and extensive depletions were facilitated by heterogeneous chemical reactions on the surfaces of polar stratospheric clouds (PSCs) in the Antarctic vortex. These clouds allowed for the formation of reactive chlorine species in large quantities. As the sun returned during Antarctic spring, the accumulated chlorine compounds were activated by sunlight and initiated a large-scale breakdown of ozone, leading to the dramatic ozone hole. This catalytic, self-reinforcing cycle of chlorine-induced ozone destruction was a key reason for the unexpectedly rapid depletion of the ozone layer observed in the 1980s.

The discovery of the ozone hole prompted immediate global concern due to its direct health implications, such as increased risk of skin cancer. This led to the landmark Montreal Protocol, signed on 16 September 1987, which marked the first global agreement to control substances harmful to the Earth's atmosphere specifically, ozone-depleting substances like chlorofluorocarbons (CFCs). Prior to this, no comprehensive international environmental treaty had existed. The protocol recognized that the Earth's atmosphere is a single, interconnected system, meaning emissions from any part of the world could contribute to ozone depletion elsewhere, particularly over Antarctica.

An important feature of the Montreal Protocol was its flexibility. It allowed periodic updates in response to new scientific findings. Initially, the full complexity of ozone chemistry was not understood, but as science progressed, particularly the discovery of polar stratospheric clouds (PSCs) and their role in accelerating ozone depletion via heterogeneous reactions, the protocol was amended multiple times to tighten restrictions. These PSCs provided catalytic surfaces for reactions that destroyed ozone far more efficiently than gas-phase interactions alone, a process not accounted for in earlier models.

The protocol also took into account the economic disparities between nations. Initially, developing countries were exempted due to their minimal contribution to CFC emissions. However, by 2010, all 142 developing nations had achieved a 100% phase-out of key ozone-depleting substances. This 23-year global cooperation was enabled by the evolving nature of the protocol and growing scientific evidence.

Interestingly, chlorofluorocarbons were originally celebrated as a scientific breakthrough by Thomas Midgley in the 1930s. They were seen as ideal chemicals for use in refrigeration and air conditioning due to their non-toxic, non-reactive, non-flammable, and odourless nature unlike the previously used dangerous substances like sulphur dioxide and methane. Midgley received several honours for this innovation. However, the ozone crisis demonstrated that even "harmless" inventions can have unforeseen and serious long-term consequences, underlining the critical importance of continued scientific research and environmental monitoring.