

Formation of the Ozone Layer

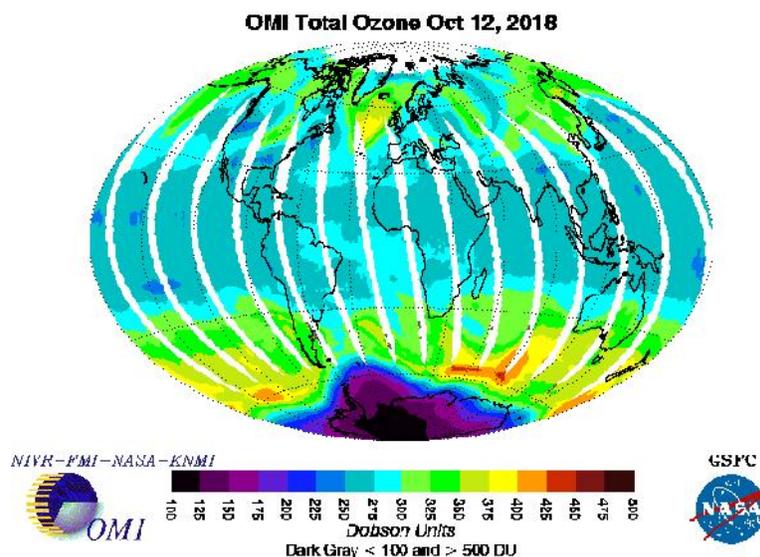
Over two billion years ago, early aquatic organisms called blue-green algae began using energy from the Sun to convert molecules of water (H_2O) and carbon dioxide (CO_2) and recombine them into organic compounds and molecular oxygen (O_2). This solar energy conversion process is known as photosynthesis. Some of the photosynthetically created oxygen began to accumulate in the atmosphere, touching off a massive ecological disaster with respect to early existing anaerobic organisms. As oxygen in the atmosphere increased, CO_2 decreased.

High in the atmosphere, some oxygen (O_2) molecules absorbed energy from the Sun's ultraviolet (UV) rays and split to form single oxygen atoms. These atoms combined with molecular oxygen (O_2) to form ozone (O_3) molecules, which are very effective at absorbing UV rays. The thin layer of ozone that surrounds Earth acts as a shield, protecting the planet from irradiation by UV light.

The amount of ozone required to shield Earth from biologically lethal UV radiation, wavelengths from 200 to 300 nanometers (nm), is believed to have been in existence 600 million years ago. At this time, the oxygen level was approximately 10% of its present atmospheric concentration. Prior to this period, life was restricted to the ocean. The presence of ozone enabled organisms to develop and live on the land.

Science of the Ozone Layer

Image of the latest global distribution of ozone



A little closer to home, you can find the [ozone overhead](#) as measured by satellite if you know your latitude and longitude. For the U at Albany Uptown Campus, the latitude is 42.7 degrees and the longitude is -73.8 degrees. The minus sign is needed for West longitudes. If you forget the minus sign, you'll find the overhead ozone for Kara-Balta, KYRGYZSTAN which is about 200 miles south of Lake Balkhash where my wife used to vacation with her family as a child

September 16th is the "International Day for Preservation of the Ozone Layer" as designated by the United Nations

Here are a few internet resources for reading related to course material.

[United Nations Environment Programme Slide Show](#). A rather detailed and well documented four-part description in the format of [frequently asked questions](#) posted in 1997. [FAQ 2010 update](#) (Strongly recommended if you missed something in class) [The U.S. Environmental Protection Agency](#) (EPA) has a nice site with lots of interesting links. (For the surfer at heart) [Electronic Textbook on Stratospheric Ozone](#) is a thorough and technical resource [Scientific Assessment of Ozone Depletion: 2010](#)

Because sometimes it's easy to get tangled up in the web and because I'm paranoid (some internet sites are here today and down, gone, changed, or moved tomorrow), I have copied some basic points here to assist you.

Ozone is constantly being produced and destroyed in a [natural cycle](#). However, the overall amount of ozone is essentially stable. This balance can be thought of as a tub with a tap and a drain. As long as the tap adds water as fast as the drain removes water, the water level in the tub remains constant. Similarly, while ozone production and destruction are balanced, ozone levels remain stable. This was the situation until the past several decades.

Large increases in stratospheric chlorine and bromine have upset that balance. In effect, they have added another drain to the tub, removing ozone faster than natural ozone is created. Therefore, ozone levels are beginning to fall towards a lower level until a new balance can be achieved; analogous to the tub in which water drains out more slowly as the water level goes down and eventually the tap again adds water at the same rate that water drains out but now the water level is lower.

The [ozone depletion process](#) begins when CFC's and other ozone-depleting substances (ODS) leak or are released from equipment. Winds efficiently mix the troposphere and evenly distribute the gases. CFC's are extremely stable, and they do not dissolve in rain. After a period of a few years, ODS molecules reach the stratosphere. Strong UV light

breaks apart the ODS molecule. CFC's release chlorine atoms and halons release bromine atoms. It is these atoms that actually destroy ozone, not the intact ODS molecule. It is estimated that one chlorine atom can destroy over 100,000 ozone molecules before finally being removed from the stratosphere.

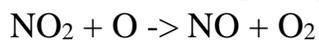
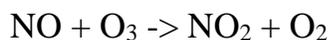
Chlorofluorocarbons (CFC's) are a class of compounds that have been used as refrigerants (the fluid used in compressors for air conditioners and refrigerators), aerosol propellants (for spray cans), foam blowing agents (for manufacture of styrofoam and insulation), and as solvents (for cleaning in the electronics industry). They are chemically very unreactive, and hence safe to work with. The CFC's have lifetimes of 50-200+ years in the atmosphere and their major "sink" is photolysis by UV radiation. CFC's were [invented in 1928](#), but only came into large-scale [production](#) after 1950.

The most important CFC's for ozone depletion are:
Trichlorofluoromethane, CFCl_3 (usually called CFC-11 or R-11)
Dichlorodifluoromethane, CF_2Cl_2 (CFC-12 or R-12) and
Trichlorotrifluoroethane, $\text{CF}_2\text{ClCFCl}_2$ (CFC-113 or R-113)

"R" stands for "refrigerant". Sometimes CFC-12, for example, is called "F-12"; the "F" stands for "Freon", DuPont's trade name for these compounds. CFC's as well as related compounds such as HCFC's (Hydrochlorofluorocarbons) and Halons (Chlorofluorobromocarbons) are identified by a particular [numbering scheme](#). More info on [uses and alternatives](#).

NO_x and the SST

In 1969, Paul Crutzen discovered that oxides of nitrogen NO_x (NO and NO₂) could be an efficient catalyst for the destruction of stratospheric ozone:



Harold S. Johnston made the connection to Supersonic transport (SST) emissions. Until then it had been thought that the radicals H, OH, and HO₂ (referred to collectively as "HO_x") were the principal catalysts for ozone loss; thus, investigations of the impact of aircraft exhaust on stratospheric ozone had focussed on emissions of water vapor, a possible source for these radicals. It had been argued - correctly, as it turns out - that

water vapor injection was unimportant in affecting the ozone balance. The discovery of the NO_x cycle again threw open the question of SST's and the ozone layer.

The natural source of stratospheric NO_x is from nitrous oxide N₂O, popularly known as laughing gas which is very unreactive - it has an atmospheric lifetime of more than 150 years - so it reaches the stratosphere, where most of it is converted to nitrogen and oxygen by UV photolysis. However, a small fraction reacts instead with oxygen atoms and this is the major natural source of NO_x in the stratosphere. This natural source would have been matched by 500 of the SST's, designed by Boeing in the 1960's, each spending 5 hours per day in the stratosphere. (Boeing was intending to sell 800 of these aircraft.) The Concorde, a slower plane, produces less than half as much NO_x and flies at a lower altitude; since the present Concorde fleet is small, its contribution to stratospheric NO_x is not significant. In the meantime, there has been a great deal of progress in developing jet engines that will produce much less NO_x - up to a factor of 10 - than the old Boeing SST. The most recent model calculations indicate that a fleet of the new "high-speed civil transports" would deplete the ozone layer by 0.3 to 1.8%.

One sometimes hears that the US government killed the SST project in 1971 because of concerns raised by H. S. Johnston's work on NO_x. This is not true. The US House of Representatives had already voted to cut off Federal funding for the SST when Johnston began his calculations. The House debate had centered around economics and the effects of noise, especially sonic booms, although there were some vague concerns about "pollution" and one physicist had testified about the possible effects of water vapor on ozone. About 6 weeks after both houses had voted to cancel the SST, its supporters succeeded in reviving the project in the House. In the meantime, Johnston had sent a preliminary report to several professional colleagues and submitted a paper to *Science*. A preprint of Johnston's report leaked to a small California newspaper which published a highly sensationalized account. The story hit the press a few days before the Senate voted, 58-37, not to revive the SST. (The previous Senate vote had been 51-46 to cancel the project. The reason for the larger majority in the second vote was probably the statement by Boeing's chairman that at least \$500 million more would be needed to revive the program.)

The Effects of Ultraviolet-B (UVB) Radiation

- **Effects on Human Health** ([more detail](#))

Laboratory and epidemiological studies demonstrate that UVB causes nonmelanoma [skin cancer](#) and plays a major role in malignant melanoma development. In addition, UVB has been linked to cataracts and weakening of the immune system. All sunlight contains some UVB, even with normal ozone levels. The [UV Index](#) provides a forecast of UV intensity. [Current forecast](#)

[map](#) (showing 58 U.S. cities). Satellites are also monitoring [UV intensity](#). It is always important to limit exposure to the sun. However, ozone depletion will allow an increase in the amount of UVB that reaches the ground, which will then increase the risk of health effects.

- **Effects on Plants**

Physiological and developmental processes of plants are affected by UVB radiation, even by the amount of UVB in present-day sunlight. Despite mechanisms to reduce or repair these effects and a limited ability to adapt to increased levels of UVB, plant growth can be directly affected by UVB radiation. Indirect changes caused by UVB (such as changes in plant form, how nutrients are distributed within the plant, timing of developmental phases and secondary metabolism) may be equally, or sometimes more, important than damaging effects of UVB. These changes can have important implications for plant competitive balance, herbivory, plant diseases, and biogeochemical cycles.

- **Effects on Marine Ecosystems**

Phytoplankton form the foundation of aquatic food webs. Phytoplankton productivity is limited to the euphotic zone, the upper layer of the water column in which there is sufficient sunlight to support net productivity. The position of the organisms in the euphotic zone is influenced by the action of wind and waves. In addition, many phytoplankton are capable of active movements that enhance their productivity and, therefore, their survival. Exposure to solar UVB radiation has been shown to affect both orientation mechanisms and motility in phytoplankton, resulting in reduced survival rates for these organisms. Scientists have demonstrated a direct reduction in phytoplankton production due to ozone depletion-related increases in UVB. One study has indicated a 6-12% reduction in the marginal ice zone. Solar UVB radiation has been found to cause damage to early developmental stages of fish, shrimp, crab, amphibians and other animals. The most severe effects are decreased reproductive capacity and impaired larval development. Even at current levels, solar UVB radiation is a limiting factor, and small increases in UVB exposure could result in significant reduction in the size of the population of animals that eat these smaller creatures.

- **Effects on Biogeochemical Cycles**

Increases in solar UV radiation could affect terrestrial and aquatic biogeochemical cycles thus altering both sources and sinks of greenhouse and chemically-important trace gases e.g., carbon dioxide (CO₂), carbon monoxide (CO), carbonyl sulfide (COS) and possibly other gases, including ozone. These potential changes would contribute to biosphere-atmosphere feedbacks that attenuate or reinforce the atmospheric buildup of these gases.

- **Effects on Materials**

Synthetic polymers, naturally occurring biopolymers, as well as some other materials of commercial interest are adversely affected by solar UV radiation. Today's materials are somewhat

protected from UVB by special additives. Therefore, any increase in solar UVB levels will therefore accelerate their breakdown, limiting how long they are useful outdoors.

- **Effects on Atmospheric Circulation**

In addition to effects due to increased UV radiation near the ground, ozone depletion alters atmospheric circulation patterns due to cooling of the stratosphere (akin to lifting a lid on a boiling pot of water). See *Journal of Climate* article "[Stratospheric Ozone Depletion: The Main Driver of Twentieth-Century Atmospheric Circulation Changes in the Southern Hemisphere](#)"

- More info on UVB effects and other [Environmental Consequences](#) of stratospheric ozone depletion.

The Montreal Protocol

A summary of the Montreal Protocol and its amendments. Those who are interested in the details are referred to the [full text](#). An excellent book on the history of the politics is **Ozone Diplomacy** by R. E. Benedick published by Harvard University Press, 1998. Ambassador Benedick was chief U.S. negotiator for the Montreal Protocol.

Terms of the Montreal Protocol ^a	
<i>Montreal Protocol of 1987</i>	
<i>Chemicals</i>	<i>Timetable</i>
CFC-11, 12, 113, 114, 115	Reductions from 1986 production levels 20% by 1995 50% by 2000
<i>London Amendments of 1990</i>	
<i>Chemicals</i>	<i>Timetable</i>
CFC-11, 12, 113, 114, 115	Accelerate 100% reductions to 1996
CFC-13, 111, 112, 211, 212, 213, 214, 215, 216, 217	Reductions from 1989 production levels 20% by 1993 85% by 1997 100% by 2000
Halons 1211, 1301, 2402	Reductions from 1986 production levels Freeze at 1986 level in 1992 50% by 1995 100% by 2000
Carbon tetrachloride	Reductions from 1989 production levels 85% by 1995 100% by 2000
Methyl chloroform	Reductions from 1989 production levels 30% by 1995 70% by 2000 100% by 2005
<i>Copenhagen Amendments of 1992</i>	
<i>Chemicals</i>	<i>Timetable</i>
CFCs, carbon tetrachloride, methyl chloroform	Accelerate 100% phase-out to 1996
Halons	Accelerate 100% phase-out to 1994
HCFCs ^b	Initial cap in 1996 35% reduction by 2004 100% by 2030
Methyl bromide	Initial cap in 1995; further action to follow
^a This schedule represents the global objectives for eliminating the production of most artificial chlorocarbons. Individual countries have established timetables that may accelerate the phase out. ^b The hydrochlorofluorocarbons are considered to be temporary, or bridging, compounds replacing CFCs until safer chemicals are developed. Source: World Meteorological Organization, 1992.	

The Multilateral Fund

- [The Multilateral Fund](#) was established by a decision of the Second Meeting of the Parties to the Montreal Protocol (London, June 1990) and began its operation in 1991. The main objective of the Multilateral Fund is to assist developing country parties to the Montreal Protocol whose annual per capita consumption and production of ozone depleting substances (ODS) is less than 0.3 kg to comply with the control measures of the Protocol. Currently, 124 of the 168 Parties to the Montreal Protocol meet these criteria. They are referred to as Article 5 countries.
- Contributions to the Multilateral Fund from the industrialized countries, or non-Article 5 countries, are assessed according to the United Nations scale of assessment.
- As at March 2007 the contributions made to the Multilateral Fund by some 49 industrialized countries (including Countries with Economies in Transition or CEIT countries) totalled over US\$ 2.2 billion.
- The Fund is managed by an [Executive Committee](#) assisted by the Fund Secretariat. Projects and activities supported by the Fund are implemented by four international implementing agencies.