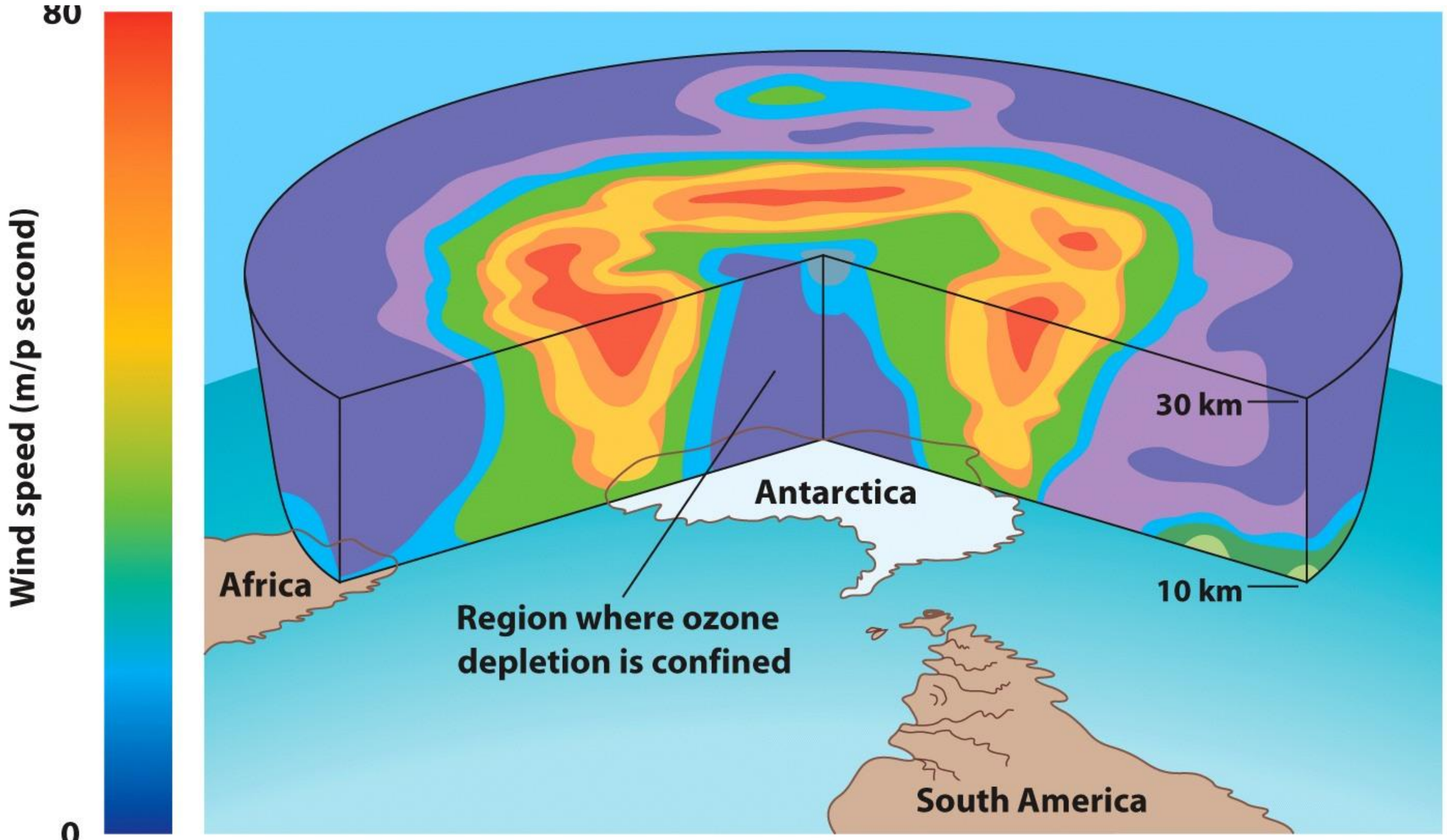
Chapter 21: Closer Look (21.2)

High-Altitude (Stratospheric) Ozone Depletion



(*Source:* Based on O.B. Toon and R.P. Turco, "Polar Stratospheric Clouds and Ozone Depletion," *Scientific American*, 264, no. 6 [1991]:68–74.)

OZONE

About 21% of the air we breathe at sea level is *diatomic* oxygen (O_2), which is two oxygen atoms bonded together.

Ozone (O_3) is a *triatomic* form of oxygen in which three atoms of oxygen are bonded. Ozone is a strong oxidant and reacts chemically with many materials in the atmosphere.

Approximately 90% of the ozone in the atmosphere is in the stratosphere, ranging from about 15 km to 40 km in altitude, with peak concentrations of about 400 ppb.

In the lower atmosphere, ozone is a pollutant produced by photochemical reactions involving sunlight, nitrogen oxides, hydrocarbons, and diatomic oxygen.

In the stratosphere, however, ozone plays an entirely different role, protecting us from ultraviolet radiation

Ultraviolet Radiation and Ozone
UVA, UVB & UVC - 0.1 and 0.4 µm

The ozone layer in the stratosphere is often called the **ozone shield** because it absorbs most of the potentially hazardous ultraviolet radiation that enters Earth's atmosphere from the sun.

Ultraviolet radiation with a wavelength of less than about 0.3 µm can be very hazardous to life.

Ultraviolet C (UVC) has the ***shortest wavelength*** and is the ***most energetic*** of the three types.

It has enough energy to break down diatomic oxygen (O_2) in the stratosphere into two oxygen atoms, each of which may combine with an O_2 molecule to create ozone.

Ultraviolet C is strongly absorbed in the stratosphere, and negligible amounts reach Earth's surface.

Ultraviolet A (UVA) radiation has the longest wavelength and ***the least energy*** of the three types.

UVA can cause some damage to living cells, ***is not affected by stratospheric ozone***, and is transmitted to the surface of Earth.

Ultraviolet B (UVB) radiation is ***energetic and strongly absorbed*** by stratospheric ozone. **In fact, ozone is the only known gas that absorbs UVB**.

Thus, depletion of ozone in the stratosphere allows more UVB to reach the Earth.

Because UVB radiation is known to be hazardous to living things, this increase in UVB is the hazard we are talking about when we discuss the problem of ozone depletion in the stratosphere

Processes that produce ozone in the stratosphere

- *Photodissociation*—intense ultraviolet radiation (UVC) breaks an oxygen molecule (O2) into two oxygen atoms.

- These atoms then react with another oxygen molecule to form two ozone molecules. Ozone, once produced, may absorb UVC radiation, which breaks the ozone molecule into an oxygen molecule and an oxygen atom.

unit (DU) is still commonly used to measure the ozone concentrations; 1 DU equals a concentration of 1 ppb O_3.

Ozone Measurements

- Ground-based measurements first identified ozone depletion over the Antarctic.
- The data are taken during October of each year—the Antarctic spring—and show that the concentration of ozone hovered around 300 DU from 1957 to about 1970, and then dropped sharply, t approximately 140 DU by 1986.
- The depletion in ozone was dubbed the *ozone hole*.

Ozone Depletion and CFCs

(carbon, chlorine, and fluorine)

- The major features of the Molina and Rowland hypothesis

1- CFCs emitted in the lower atmosphere by **human activity are very stable** and nonreactive in the lower atmosphere and therefore have a very long residence time (about 100 years).

No significant sinks for CFCs are known, with the possible exception of soils, which evidently do remove an unknown amount of CFCs from the atmosphere at Earth's surface

2- Because of their long residence time in the lower atmosphere, and because the lower atmosphere is very fluid, the **CFCs eventually disperse, wander upward, and enter the stratosphere**.

Once they reach altitudes above most of the stratospheric ozone, they may be destroyed by the highly energetic solar ultraviolet radiation.

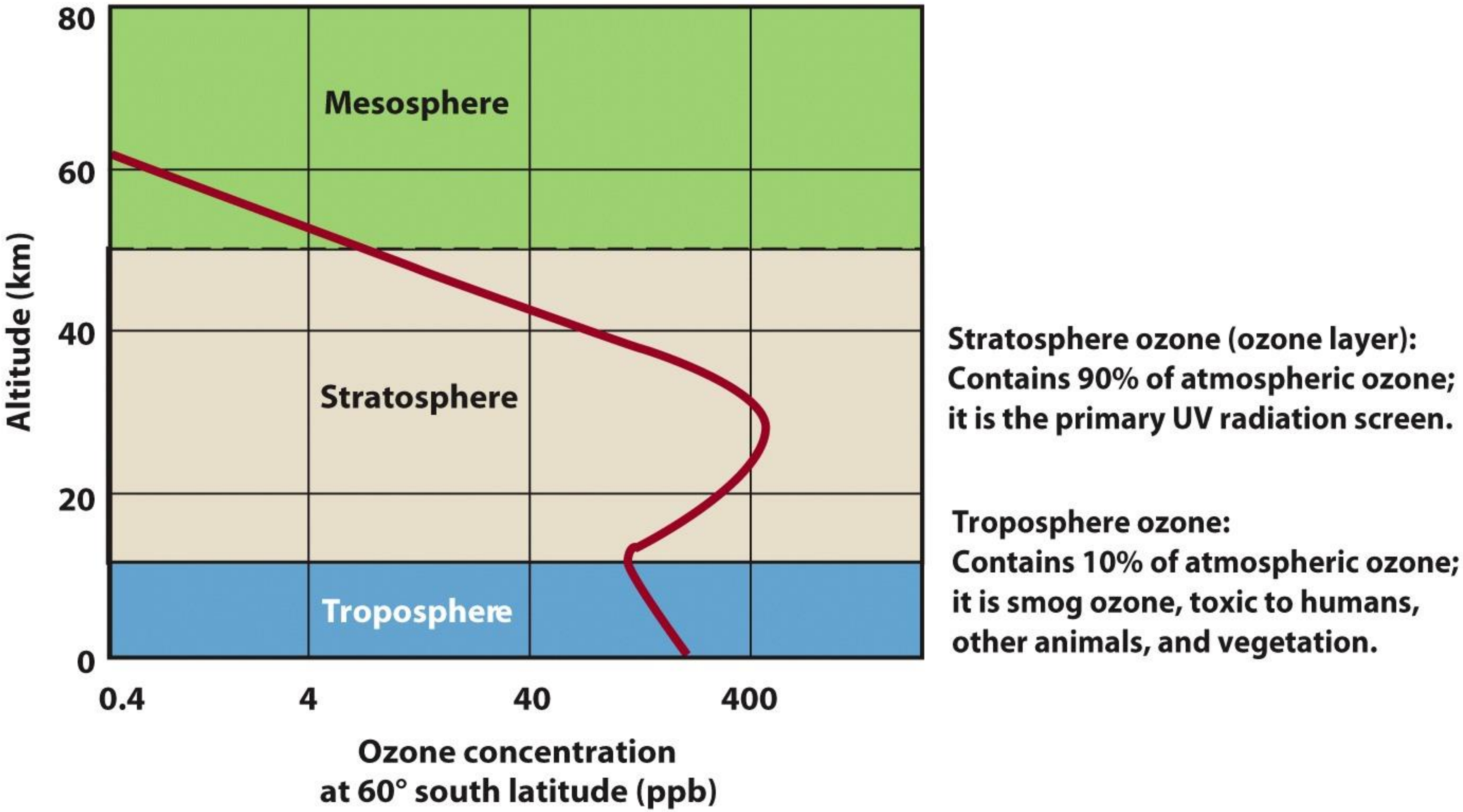
This releases chlorine, a highly reactive atom.

3- The reactive chlorine may then enter into reactions that deplete ozone in the stratosphere.

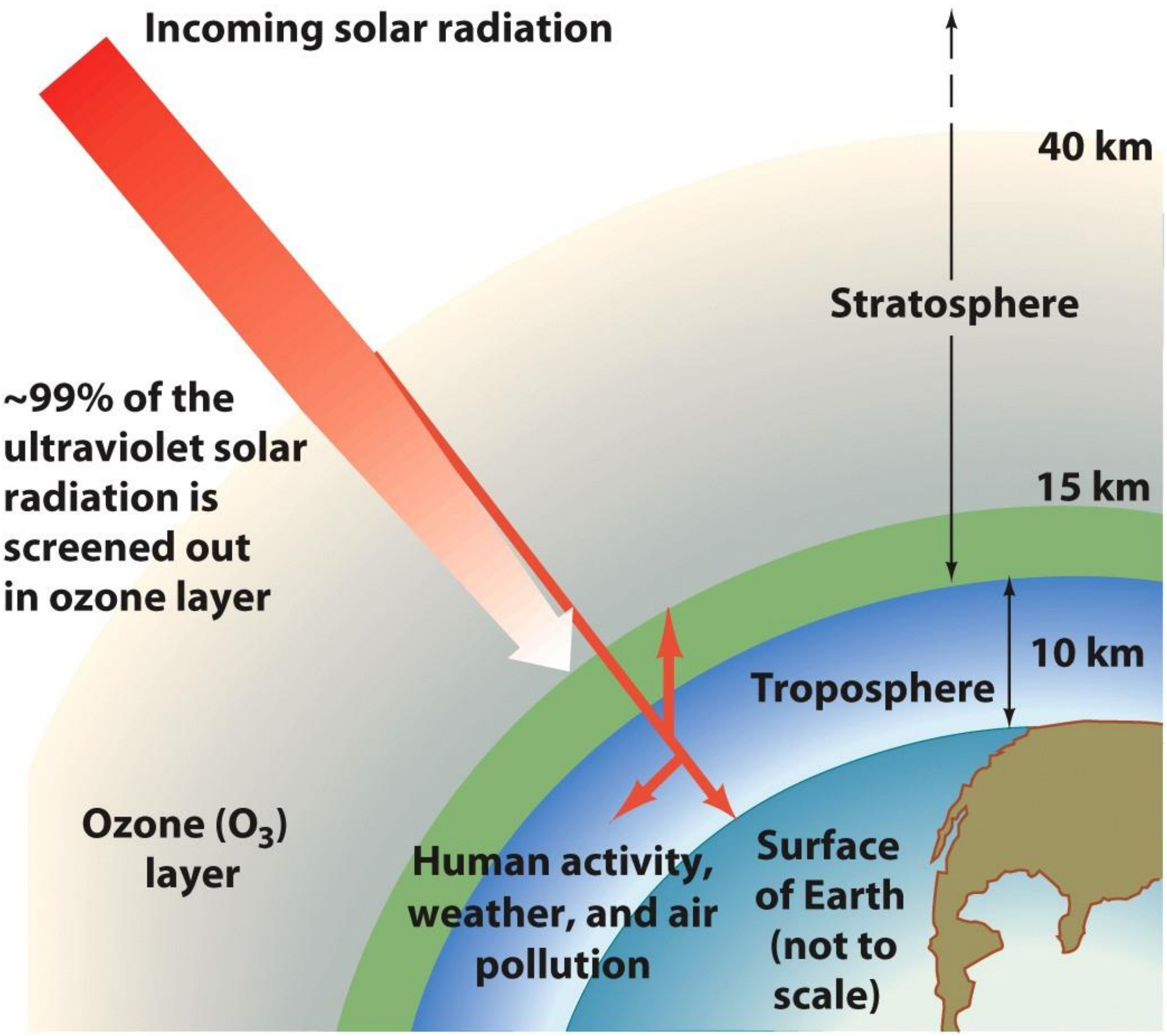
Ozone depletion allows an increased amount of UVB radiation to reach Earth. Ultraviolet B is a cause of human skin cancers and is also believed to be harmful to the human immune system.

FIGURE 21.6 (a) Structure of the atmosphere and ozone concentration.

(*Source:* Ozone concentrations modified from R.T. Watson, "Atmospheric Ozone," in J.G. Titus, ed., *Effects of Change in Stratospheric Ozone and Global Climate*, vol. 1, *Overview*, p. 70 [U.S. Environmental Protection Agency].)



(b) Reduction of the potentially most biologically damaging ultraviolet radiation by ozone in the stratosphere



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Simplified Stratospheric Chlorine Chemistry

- CFCs are responsible for most of Ozone depletion.
- No tropospheric (sunlight, rains, oxidation) sinks available; CFCs do not break down (transparent to sunlight; insoluble, non reactive in Oxygen rich lower atmosphere).

When CFCs wander to the upper part of the stratosphere, however, reactions do occur. Highly energetic ultraviolet radiation (UVC) splits up the CFC, releasing chlorine.

Formation of chlorine monoxide and chlorine again

These two equations define a chemical cycle that can deplete ozone

$$(1)\ Cl + O_3 \longrightarrow ClO + O_2$$
$$(2)\ ClO + O \longrightarrow Cl + O_2$$

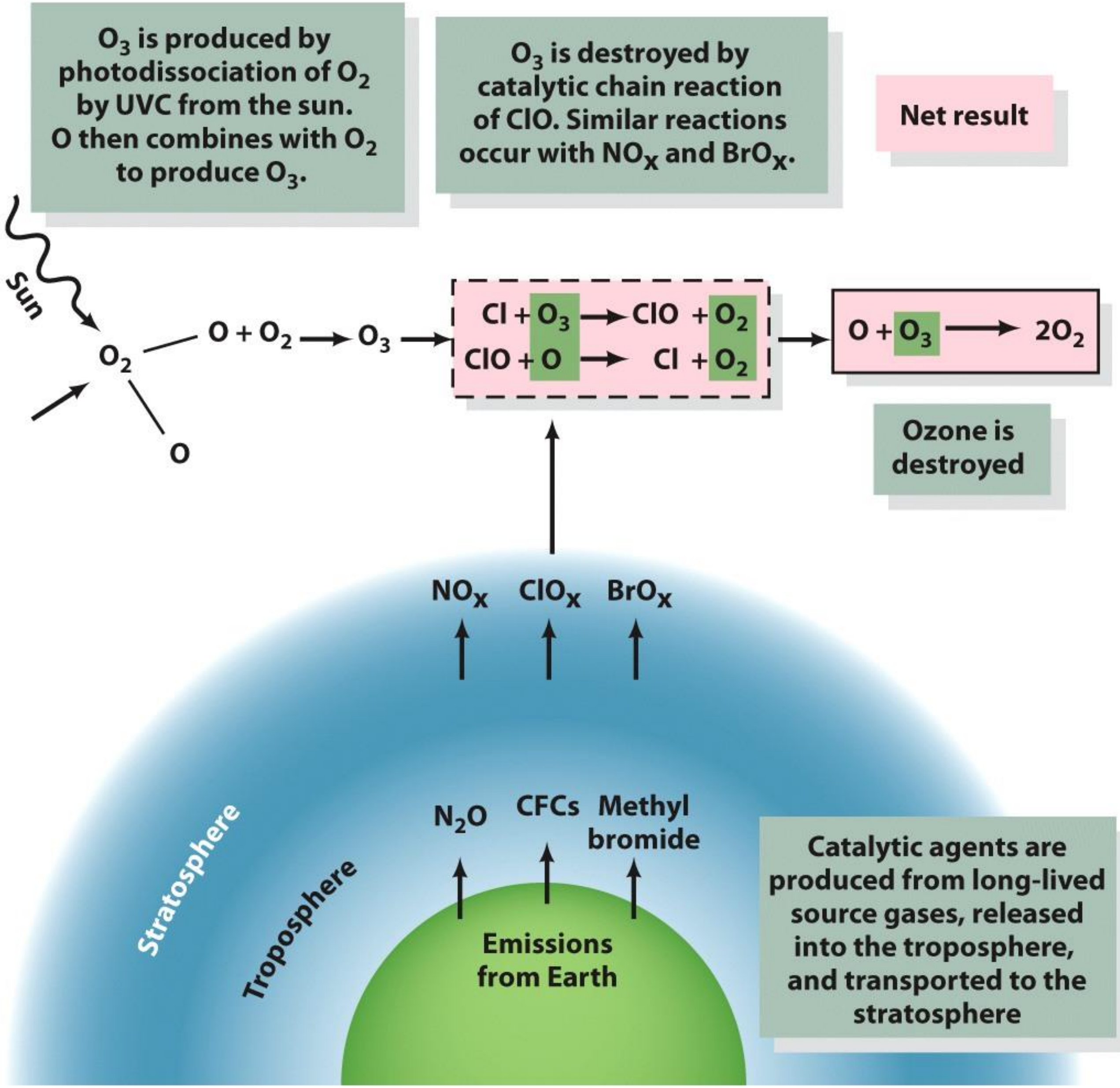
The chlorine can then enter another reaction with ozone and cause additional ozone depletion.

This series of reactions is what is known as a ***catalytic chain reaction***.

Because the chlorine is not removed but reappears as a product of the second reaction, the process may be repeated over and over again

Each chlorine atom may destroy approximately 100,000 molecules of ozone in one or two years before the chlorine is finally removed from the stratosphere

FIGURE 21.7 Processes of natural formation of ozone and destruction by CFCs, N_2O, and methyl bromide



(*Source:* Modified from NASA-GSFC, "*Stratospheric Ozone*," accessed August 22, 2000, at http://see.gsfc.nasa.gov.)

The catalytic chain reaction can be interrupted through storage of chlorine in other compounds in the stratosphere:

1) Ultraviolet light breaks down CFCs to release chlorine, which combines with ozone to form chlorine monoxide (ClO).

The chlorine monoxide may then react with nitrogen dioxide (NO_2) to form a chlorine nitrate ($ClONO_2$).

If this reaction occurs, ***ozone depletion is minimal.*** The chlorine nitrate, however, is only a temporary reservoir for chlorine.

The compound may be destroyed, and the chlorine released again.

2) Chlorine released from CFCs combine **with methane (CH_4) to form hydrochloric acid (HCl)**.

The hydrochloric acid may then diffuse downward.

If it enters the troposphere, rain may remove it, thus removing the chlorine from the ozone-destroying chain reaction.

This is the ultimate end for most chlorine atoms in the stratosphere.

However, while the hydrochloric acid molecule is in the stratosphere, it may be destroyed by incoming solar radiation, releasing the chlorine for additional ozone depletion.

Ozone in Polar regions

- Southern hemispheres are under natural conditions.

- Highest concentration of Ozone is in polar regions and lowest near equator! (STRANGE!)

- Because more solar energy towards equator but ozone moves from there towards poles from global air-circulation patterns.

The Antarctic Ozone Hole (October 1985 Antarctica – Spring season)

- The thickness of the ozone layer above the Antarctic in springtime has been declining since the mid-1970s, the geographic area covered by the ozone hole has grown from a million or so square kilometers in the late 1970s and early 1980s to about 29 million km2 by 1995

Polar Stratospheric Clouds

- Polar stratospheric clouds over the Antarctic appear to be one of the causes of this variation.
- They form during the **polar winter** (called the polar night because the tilt of Earth's axis limits sunlight).
- During the polar winter, the Antarctic air mass is isolated from the rest of the atmosphere and circulates about the pole in what is known as the Antarctic ***polar vortex***.
- The vortex forms as the isolated air mass cools, condenses, and descends.

Type I & II polar stratospheric clouds

- Clouds form in the vortex when the air mass reaches a temperature between 195 K and 190 K.
- At these very low temperatures, small sulfuric acid particles freeze and serve as seed particles for nitric acid (HNO_3 nitric acid).
- These clouds are called Type I polar stratospheric clouds.
- If temperatures drop below 190 K, water vapor condenses around some of the earlier-formed Type I cloud particles, forming Type II polar stratospheric clouds, which contain larger particles.
- Type II polar stratospheric clouds are the ones with the mother-of pearl color.

Reduced stratospheric ozone in the polar vortex

During the formation of polar stratospheric clouds, nearly all the nitrogen oxides in the air mass are converted to the clouds as nitric acid particles, which grow heavy and descend below the stratosphere, leaving very little nitrogen oxide in the vicinity of the clouds.

This facilitates ozone depleting reactions that may ultimately reduce stratospheric ozone in the polar vortex by as much as 1% to 2% per day in the early spring, when sunlight returns to the polar region.

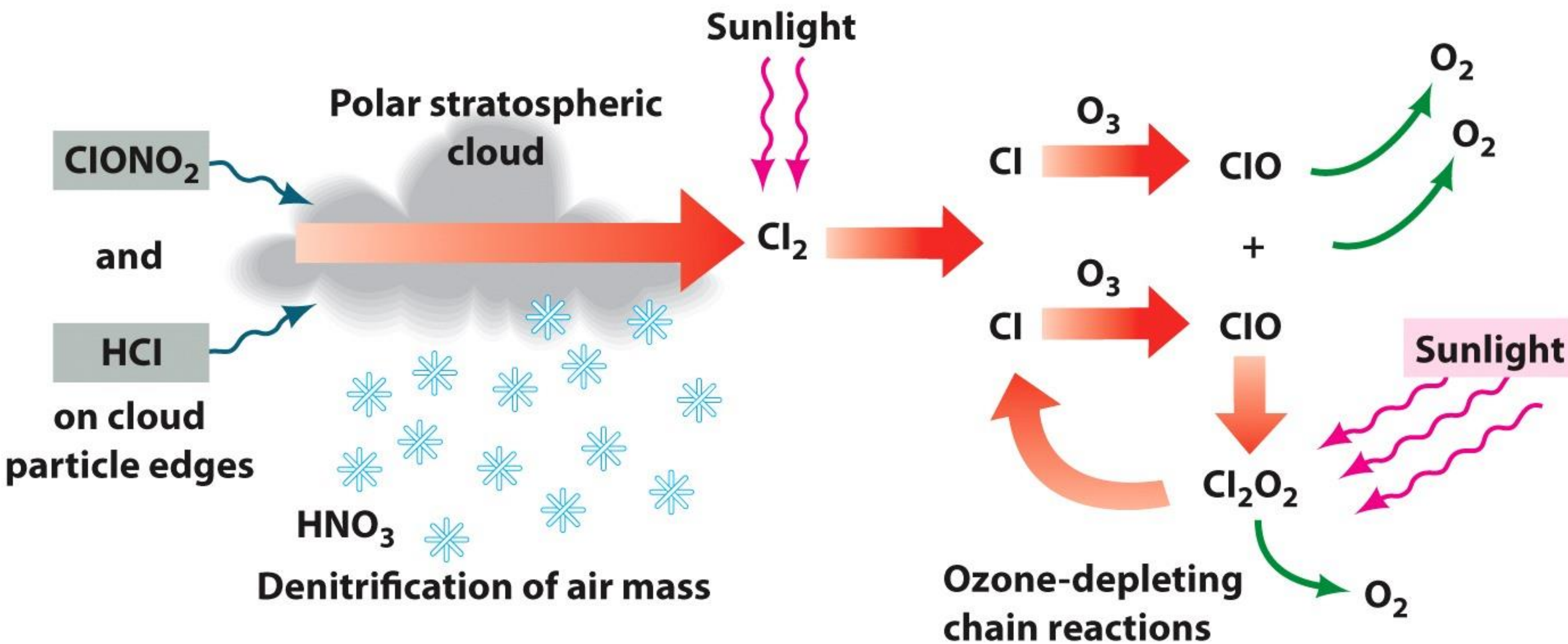
Hydrochloric acid and chlorine nitrate (the two important sinks of chlorine) act on particles of polar stratospheric clouds to form dimolecular chlorine (Cl_2) and nitric acid through the following reaction

$$HCl + ClONO_2 \longrightarrow Cl_2 + HNO_3$$

Ozone depletion in the Antarctic vortex ceases later in spring as the environment warms and the polar stratospheric clouds disappear, releasing nitrogen back into the atmosphere, where it can combine with chlorine and thus be removed from ozone-depleting reactions.

Stratospheric ozone concentrations then increase as ozone-rich air masses again migrate to the polar region

The role of polar stratospheric clouds in the ozone-depletion chain reaction



Environmental Effects of Ozone Depletion

Ozone depletion damages some food chains on land and in the oceans and is dangerous to people, increasing the incidence skin cancers and cataracts and suppressing immune systems.

You can lower your risk of skin cancer and other skin damage from UV exposure by taking a few simple precautions:

• Limit exposure to the sun between 10 a.m. and 4 p.m., the hours of intense solar radiation, and stay in the shade when possible.

• Use a sunscreen with an SPF of at least 30 (but remember that protection diminishes with increased exposure), or use clothing to cover up.

• Wear UV-protective sunglasses.

• Avoid tanning salons and sun lamps.

• Consult the UV Index before going out.