United States
Environmental Protection
Agency

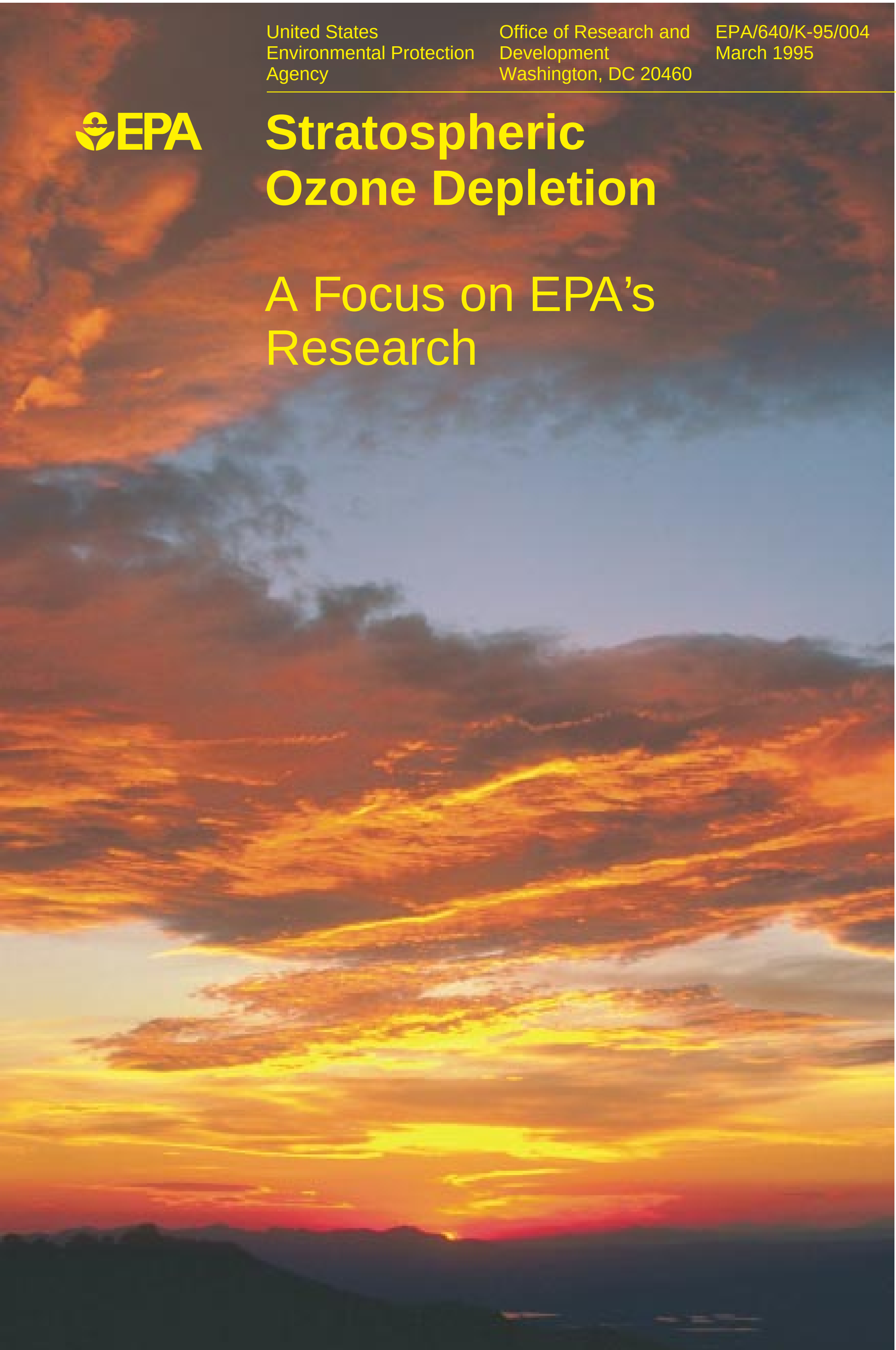
Office of Research and
Development
Washington, DC 20460

EPA/640/K-95/004
March 1995

EPA

Stratospheric Ozone Depletion

A Focus on EPA's Research



EPA's Office of Research and Development

The Office of Research and Development (ORD) conducts an integrated program of scientific research and development on the sources, transport and fate processes, monitoring, control, and assessment of risk and effects of environmental pollutants. These activities are implemented through its headquarters offices, technical support offices, and twelve research laboratories distributed across the country. The research focuses on key scientific and technical issues to generate knowledge supporting sound decisions today, and to anticipate the complex challenges of tomorrow. With a strong, forward-looking research program, less expensive more effective solutions can be pursued and irreversible damage to the environment can be prevented.

"It is important to recognize that by the time it is possible to detect decreases in ozone concentrations with a high degree of confidence, it may be too late to institute corrective measures that would reverse this trend."

(*U.S. EPA's Science Advisory Board*, March, 1987)

In September of 1987 the United States, along with 26 other countries, signed a landmark treaty to limit and subsequently, through revisions, phase out the production of all significant ozone depleting substances. Many researchers suspected that these chemicals, especially chlorofluorocarbons (CFCs) and halons, were depleting the protective stratospheric ozone layer and allowing increased levels of solar radiation to reach the Earth's surface. What made this treaty — the *Montreal Protocol on Substances that Deplete the Ozone Layer* — so significant is that consensus was reached and action taken based upon scientific theory. Although the causes and effects of stratospheric ozone depletion are still not completely understood, these countries (joined by 106 more as of 1994) agreed that the potential risks were significant and that environmentally safe alternatives to ozone depleting substances (ODSs) could be developed.

The Protocol was not ratified without considerable debate. One significant concern was that economic alternatives would be difficult to find. The highly-engineered compounds in question included refrigerants (refrigerators and freezers), coolants (air conditioning), synthetic foams (insulation, life vests, pads), propellants (aerosol spray cans), cleaning solvents, fire extinguishers, and sterilizers. Typically, these compounds were nonflammable, noncorrosive, nonreactive, low in toxicity and efficient in heat absorption and transfer . . . a vital combination of traits considering their applications. Would use of alternatives present an even greater threat to human health and the environment? Would alternative compounds require replacement or expensive conversion of current equipment? Would developing nations be provided the necessary technology and financial assistance to accommodate the phaseout? Were fluctuations in the stratospheric ozone layer simply natural phenomena?

As asserted by EPA's Science Advisory Board several months prior to Protocol ratification, delaying global action until every facet of the ozone depletion issue was com-

The stratospheric ozone layer should heal through reduced emissions of ozone depleting substances. However, due to the long life span of these chemicals and their gradual migration to the stratosphere, we have yet to face the time of greatest solar radiation levels and the potential consequences.

*90% of the ozone present in the Earth's atmosphere can be found in the stratosphere. This **stratospheric ozone** is considered to be beneficial because of its ability to screen out potentially harmful solar radiation. Much of this ozone is created over the equator (where the sun's rays are most direct) and is transported by global air currents toward the poles.*

***Tropospheric ozone** is a component of smog – and quite often part of the air we breathe. This harmful "layer" of ozone, formed when sunlight reacts with certain pollutants, can damage lung tissues, crops and other plants.*

pletely understood might have allowed irreparable damage to the stratospheric ozone layer. Strategies to effect the phaseout as mandated by the Protocol were devised and key areas of needed research and development were identified. Amendments to both the Montreal Protocol (1990 and 1992) and in the U.S., the Clean Air Act (1990), have further accelerated the phaseout schedule.

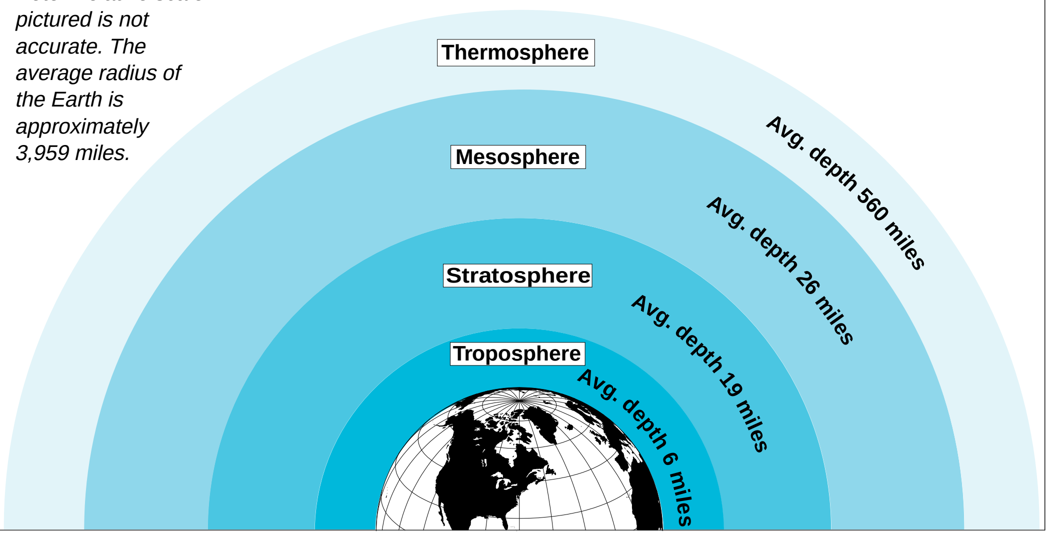
The mission of EPA's Office of Research and Development (ORD) includes identifying and quantifying the risks associated with stratospheric ozone depletion; working cooperatively with the private sector to catalyze development of safe alternative chemicals and technologies; and studying both natural and human-induced effects on the Earth's atmosphere. Through an orderly phaseout of ozone depleting substances and a thorough understanding of the potential effects of increasing levels of solar radiation, policy makers and citizens alike can remain aware of the risks while effecting solutions to the problem.

Understanding Ozone and the Atmosphere

As seen in the diagram below, the Earth's atmosphere consists of four layers (listed respectively from closest to furthest away from the Earth's surface): troposphere, stratosphere, mesosphere, and thermosphere. Regions between each of these layers where temperature remains constant (isothermal) tend to reduce mixing between layers. However, since temperature in the troposphere (where our weather occurs) normally decreases with increasing height, a great deal of turbulence occurs. This turbulence and instability allows upward movement of air currents that may contain the heavier-than-air ozone depleting substances. While ozone can be found in the troposphere as a chief component of smog (see box at left), a great deal of effort is being devoted to reduction of this "ground-based" ozone.

The next layer — stratosphere — is much more stable than the troposphere and has little influence on the weather. The stratosphere does, how-

Note: Relative scale pictured is not accurate. The average radius of the Earth is approximately 3,959 miles.



ever, contain high levels of ozone gas (referred to as the "ozone layer") that absorb much of the sun's ultraviolet radiation (including ultraviolet-B — a type of solar radiation that has been linked to skin cancer, eye disease, immune system disorders, and damage to various marine and terrestrial ecosystems). Since the outer two layers (mesosphere and thermosphere) have much lower concentrations of ozone (and other atmospheric components), they do not significantly affect the incoming ultraviolet radiation.

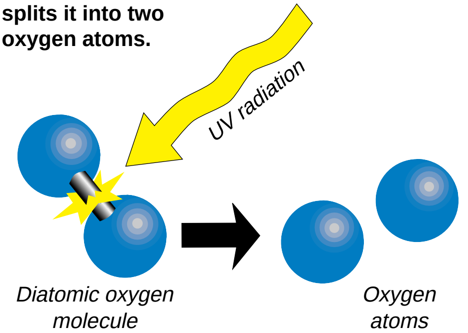
Ozone (O_3) molecules are made up of three oxygen atoms while the diatomic oxygen molecules we need to breathe consist of only two oxygen atoms (O_2). Ozone molecules are created and broken down continuously in our atmosphere…essentially maintaining a balanced oxygen to ozone budget.

Ozone concentration is a balance of processes that produce ozone and those processes and reactions that remove ozone. Natural formation of stratospheric ozone involves two steps: 1) the sun's rays strike and

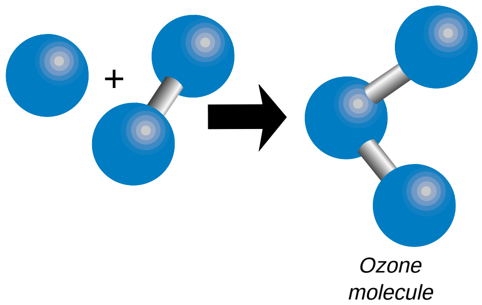
According to NASA, of the incoming short-wave solar radiation, only 50% hits the Earth's surface—24% as direct sunlight and 26% as scattered sunlight. The rest of the incoming short-wave radiation gets caught up in the Earth's atmosphere, where it is either scattered back into space (25%) or simply absorbed (25%).

Natural Ozone Production in the Stratosphere

Ultraviolet radiation from the sun strikes a diatomic oxygen molecule and splits it into two oxygen atoms.

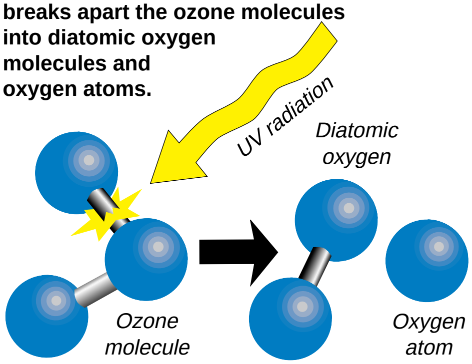


The free oxygen atoms react with diatomic oxygen molecules to form ozone.

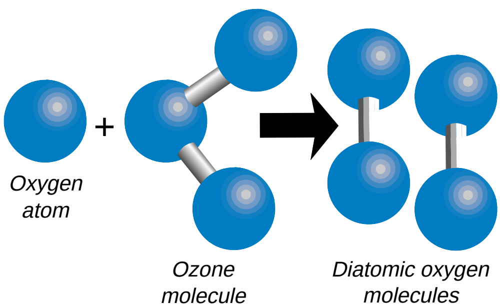


Natural Ozone Destruction in the Stratosphere

Ozone absorbs ultraviolet light in the range of 290-320 nanometers. This solar energy breaks apart the ozone molecules into diatomic oxygen molecules and oxygen atoms.

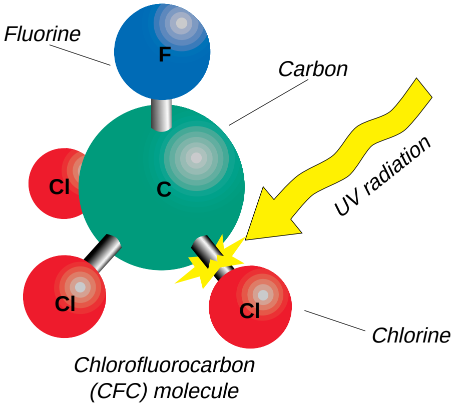


The free oxygen atom can react with an ozone molecule and form two molecules of diatomic oxygen.

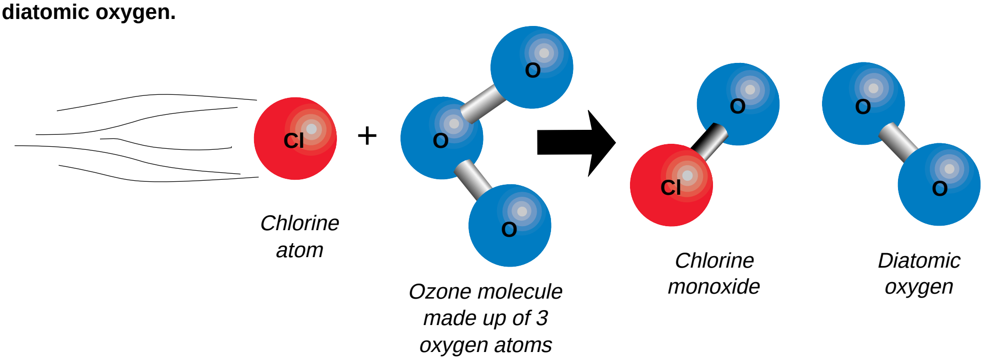


Ozone Destruction Caused by Manmade Compounds (e.g., CFCs)

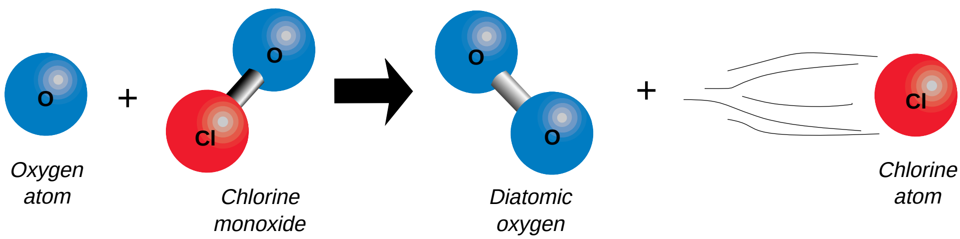
Ultraviolet radiation from the sun strikes the CFC molecule and causes a chlorine atom to break away.



The chlorine atom reacts with an ozone molecule to form chlorine monoxide and diatomic oxygen.



When a free atom of oxygen reacts with a chlorine monoxide molecule, diatomic oxygen is formed and the chlorine atom is released to destroy more ozone.

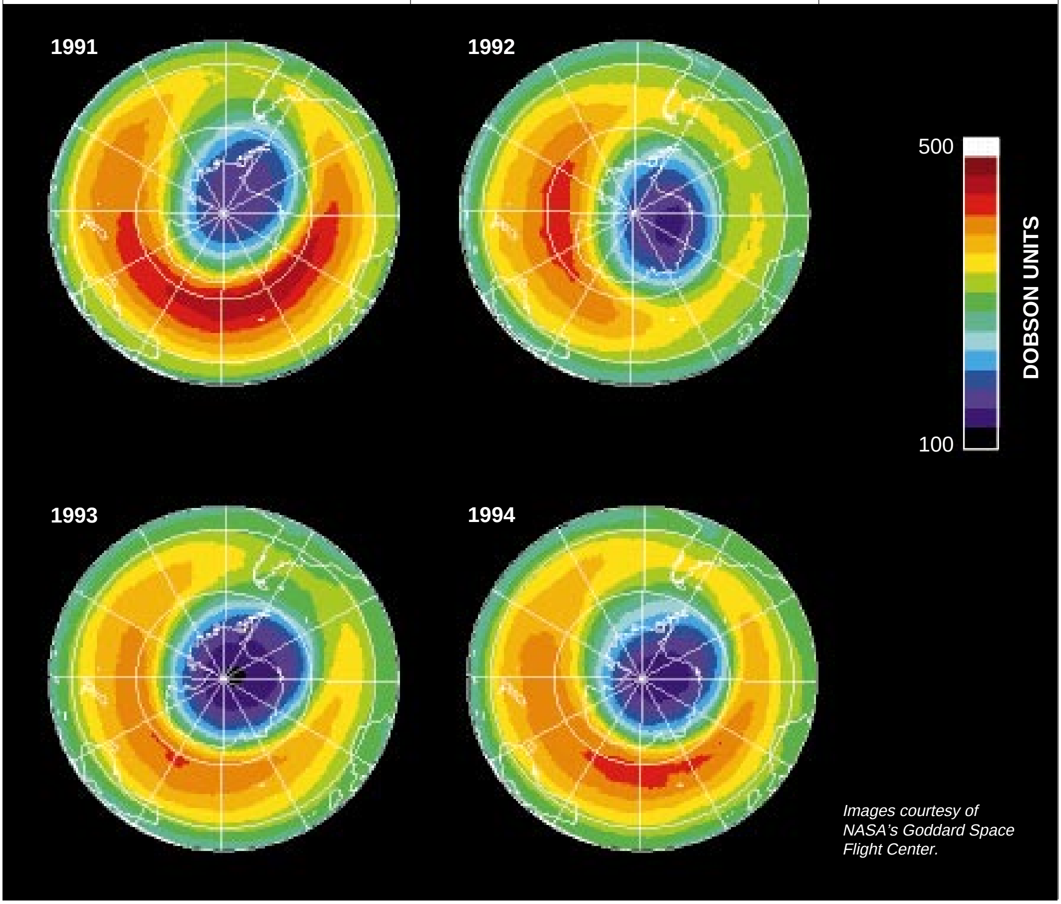


split apart oxygen molecules (O_2) into single oxygen atoms (O); 2) these single atoms are very unstable and will react readily with nearby atoms or molecules to become more stable. When O atoms combine with nearby O_2 molecules, ozone is formed.

Stratospheric ozone levels fluctuate periodically. Under some circumstances, the fluctuations are extreme. For instance, atmospheric conditions can at times isolate a portion of the stratosphere . . . effectively keeping it from mixing with surrounding ozone-rich and warmer pockets of air. Should there be a high concentration of ozone depleting substances in the isolated pocket, ozone destruction can outpace ozone replacement and result in a sharp decrease in ozone concentration (an "ozone hole") and consequently, less screening out of the sun's ultraviolet-B rays.

This extreme depletion occurs during the southern spring (September through November) . . . creating the Antarctic "ozone hole." Atmospheric conditions there clearly favor the annual phenomenon (extremely cold winter temperatures support the formation of a "polar vortex" — an impenetrable core in the atmosphere) where ozone depleting substances accumulated throughout the winter can be activated by springtime solar radiation to

October mean concentrations of ozone in the stratosphere over Antarctica during the years 1991 to 1994. Reds and greens indicate high ozone concentrations while blues and purples indicate low ozone concentrations (see color index). The "ozone hole" typically breaks up in mid-November.



Images courtesy of NASA's Goddard Space Flight Center.

Concentrations of ozone depleting substances in the stratosphere are not expected to peak until the year 2000.

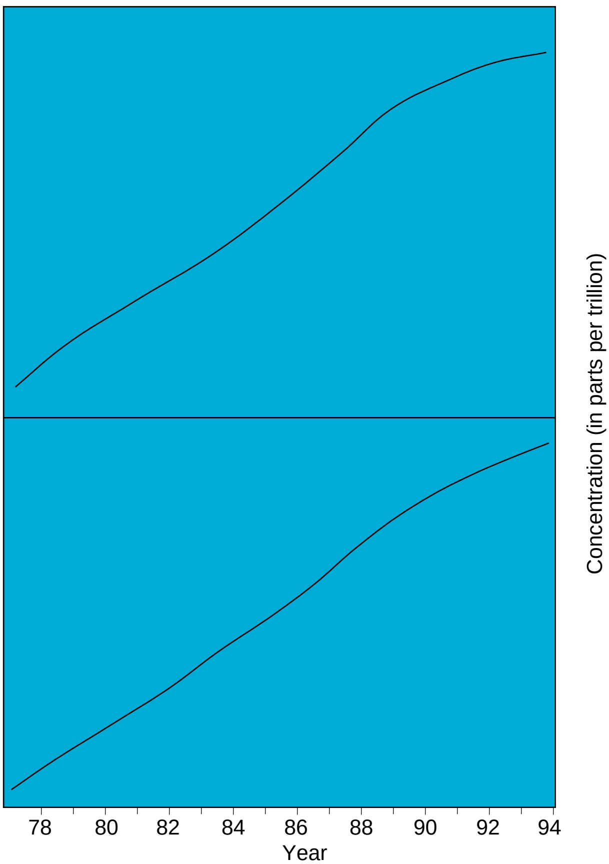
break down ozone. Additionally, ice crystals present in this region of the stratosphere act as reaction "platforms" for enhanced ozone breakdown.

The stable ozone depleting substances don't just destroy one ozone molecule; a chain reaction occurs. Using chlorofluorocarbons (CFCs) as an example, solar radiation breaks down the CFCs which in turn releases chlorine atoms. A series of reactions takes place, with chlorine acting as a catalyst, that results in destruction of ozone (O_3) and the formation of diatomic oxygen (O_2). The chlorine from the CFCs is available to begin the ozone destruction cycle again.

Antarctic Ozone Deficit: Why Should We Care?

Even knowing that the Antarctic ozone hole has gotten larger since 1979, most people might not be concerned. After all, few people live in the Antarctic (e.g., international scientific teams); additionally, shouldn't decreasing CFC production eventually shrink the ozone hole to its natural size?

Recent findings (Elkins et al., 1993) do indicate that the increasing rate of emissions of two significant ozone depleters (CFC-11 and CFC-12) has slowed (see figure below). EPA's Office of Air and Radiation has successfully implemented regu-



Monthly mean measurement curves of CFC-11 and CFC-12 from 7 monitoring sites for the period from 1977 to 1993 (adapted with permission from Elkins et al., 1993).

How Everyone Can Help

Car Air Conditioning

Have your car air conditioning system properly serviced. *Only certified technicians using approved recovery or recycling equipment may work on car air conditioners. Ask your service company if its technicians and equipment meet EPA requirements before agreeing to service.*

Check for leaks. *Have leaks repaired before more refrigerant is added. Some states may require this by law.*

Ask about retrofitting. *Many of today's car air-conditioning systems will soon be able to use an alternative refrigerant that does not destroy ozone.*

Old Refrigerators and other Appliances

Dispose of appliances responsibly. *CFC or HCFC refrigerant must be removed from an appliance before it is discarded. The public works or solid waste department in your town or a home appliance dealer can help. Ask about home appliance recycling or CFC recovery programs.*

Help start a refrigerant recovery and recycling program in your area. *Contact EPA's Stratospheric Ozone Information Hotline to hear about innovative steps some communities have already taken. The number is 800-296-1996.*

The New Clean Air Act

The Clean Air Act of 1990 contains many measures to protect the ozone layer. Most important, the law requires an end to the production of chemicals that deplete the ozone layer. CFCs will not be produced after 1995. HCFCs can replace CFCs in some air conditioning systems and may be produced until 2030.

In addition, the Clean Air Act bans the release of CFC and HCFC refrigerants during the service, maintenance, and disposal of air conditioners (and all other equipment that contains these refrigerants). Individuals who work on such equipment must follow EPA regulations for ozone-safe service practices, including the recovery and recycling of refrigerant.

Home Air Conditioners

Ensure that refrigerant is recovered. *The intentional release or "venting" of refrigerant during service, maintenance, and disposal is prohibited. Used refrigerant can be recycled. Before agreeing to service, ask whether the technician will use refrigerant-recovery equipment if the refrigerant needs to be removed. Also, ask if the technician is or plans to become certified by an EPA-approved organization. After the job has been completed, ask if the equipment was used.*

Repair leaks. *Ask the service technician to locate and repair leaks before refilling (or "recharging") your system with more refrigerant.*

Violation Reports

Call the Hotline. *If you suspect or witness unlawful refrigerant releases, you can file a report easily and anonymously by calling the Stratospheric Ozone Information Hotline at 800-296-1996.*

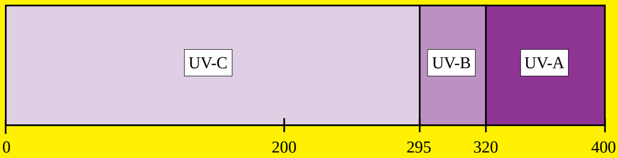
Other Actions

Become active in your community. *Speak with your neighbors and friends about ozone depletion and their air conditioners.*

Be an informed consumer. *Look for labels identifying products manufactured with or containing ozone-depleting substances. Consider alternatives that do not damage the ozone layer.*

(Adapted from the publication EPA/430/F-93/006)

Ultraviolet Region of the Electromagnetic Spectrum



Wavelength in Nanometers (one-billionth of a meter)

Energy is transferred from the sun to the earth in the form of electromagnetic energy. Electromagnetic energy can be divided into a spectrum, in which photons that transfer energy have both a wavelength and energy level. The electromagnetic spectrum is divided into ultraviolet, visible, and infrared regions. The ultraviolet (UV) region, shown above, is composed of UV-C, UV-B, and UV-A. Ozone differentially removes wavelengths of UV-B between 295 and 320 nm; UV-A in wavelengths above 350 nm is not removed, nor is visible light (400-900 nm). Ozone removes all UV-C. Wavelengths between 295 and 300 nm are generally more biologically effective (i.e., able to cause damage) than other wavelengths in UV-B and even more so than UV-A radiation.

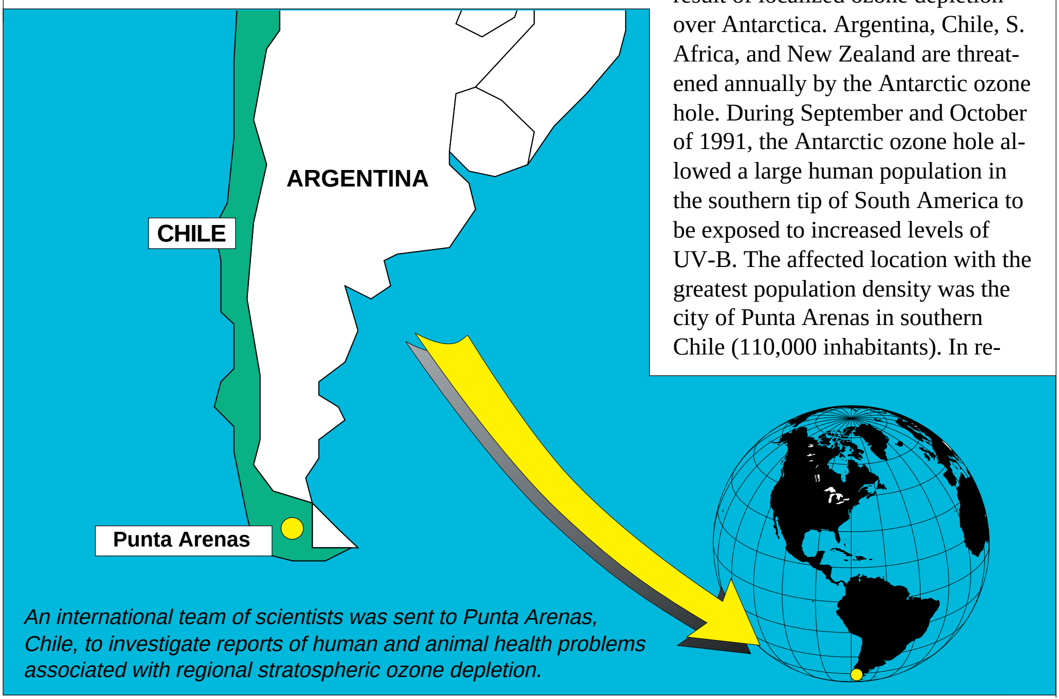
(Adapted from the publication EPA/400/1-87/001D)

lations (under Title VI of the amended Clean Air Act) limiting production, sales and imports of these and other ozone-depleters. Additionally, standards and requirements regarding servicing air conditioners and recycling refrigerants are now in place in the U.S. (see available publications listed on page 23).

Given the stability of the ozone depleting substances already in the atmosphere, the continued (yet decreased) release of these substances, and the anticipated emissions of temporary alternatives (that deplete ozone to a lesser extent), most scientists believe that the lowest levels of worldwide stratospheric ozone (and the greatest potential effects of UV radiation exposure) are yet to come.

Interest Rises in S. America

In some countries, potential adverse consequences do exist as a result of localized ozone depletion over Antarctica. Argentina, Chile, S. Africa, and New Zealand are threatened annually by the Antarctic ozone hole. During September and October of 1991, the Antarctic ozone hole allowed a large human population in the southern tip of South America to be exposed to increased levels of UV-B. The affected location with the greatest population density was the city of Punta Arenas in southern Chile (110,000 inhabitants). In re-



An international team of scientists was sent to Punta Arenas, Chile, to investigate reports of human and animal health problems associated with regional stratospheric ozone depletion.

sponse to numerous reports from that region of acute (i.e., damage caused by a short-term exposure) eye and skin disease in both humans and animals, ORD's Health Effects Research Laboratory joined a multidisciplinary international team to investigate these reports in November of 1992 (that month was purposefully chosen to capture any effects of similar ozone depletion in September and October of that year).

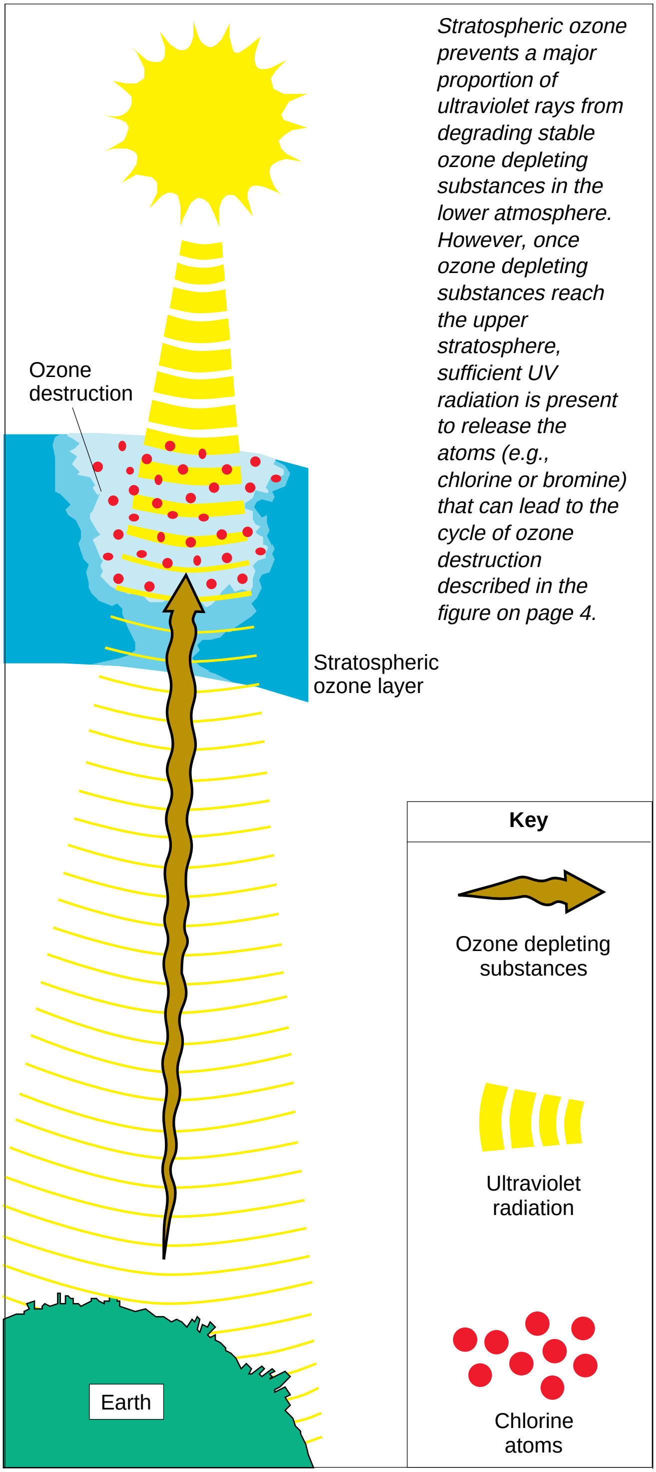
Human Health Findings

Though UV-B exposure increased in the vicinity of Punta Arenas by approximately nine percent in September and four percent in October, a review of area medical records showed no associated increase in reports of eye disease or skin irritation. A greater frequency of dermatologic visits for warts did occur yet the significance of this finding remains uncertain.

Three occupational groups (fishermen, shepherds, and hospital workers) were given standard eye and skin exams to discover if any trends could be related to the amount of time spent outdoors. No health differences by occupational category could be associated with increased UV-B exposure.

Animal Health Findings

Eye exams of sheep from the Punta Arenas region revealed an abnormally high rate of infection caused by the microorganism *Chlamydia psittaci*. However, no known relationship exists between this infection and solar exposure. A 13 percent rate of cataract was found in the studied sheep but comparison statistics for the breed of sheep common to the region do not exist. In a small sample of Hereford cattle, the team found a 17 percent incidence of



Stratospheric ozone prevents a major proportion of ultraviolet rays from degrading stable ozone depleting substances in the lower atmosphere. However, once ozone depleting substances reach the upper stratosphere, sufficient UV radiation is present to release the atoms (e.g., chlorine or bromine) that can lead to the cycle of ozone destruction described in the figure on page 4.

Viewing the Earth from the South Pole, it is easy to see why residents of S. America, Africa, Australia, and New Zealand are interested in the gradual expansion of the annual Antarctic ozone hole. At the end of each southern spring as polar temperatures increase and the ozone hole breaks up, large segments of ozone-deficient atmosphere can migrate over heavily populated areas before dispersing completely.

In describing disease and physical disorders, the term "acute" refers to effects caused by a single or short-term elevated exposure. Effects resulting from constant or long-term exposure are considered to be "chronic." As an example, sunburn may be considered an acute effect of solar radiation while certain types of skin cancer are potential chronic effects.

conjunctival squamous cell carcinoma — an eye condition related to long-term UV-B exposure.

Recommendations

The Punta Arenas investigation demonstrated the feasibility of performing standardized field examinations and using local medical records to assess the possibility of acute UV-B related disorders. While documented evidence of such disorders in this region was sparse, the relatively small sample sizes studied made trend determinations difficult. No changes to the Chilean Ministry of Health's current UV-B exposure strategy (which includes public education and the recommendation of hat and sunglass use during periods of maximal exposure) were recommended.

Should the exposure in this region remain constant or decrease from the exposure levels experienced in 1992, the team agreed that the likelihood of acute ozone hole-related disease is low. However, should exposures increase over the coming years, the likelihood of chronic UV-B related health effects would increase.

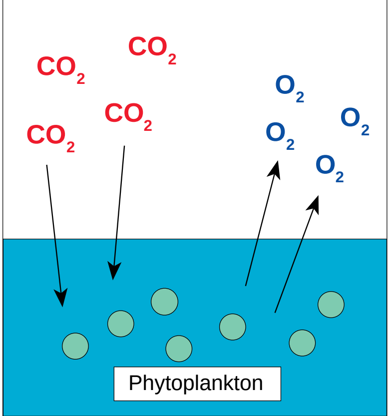
Taxing the Food Chain

In an ecosystem (the interacting system of a biological community within its environment) such as the Antarctic Ocean, plants and animals have adapted to the harsh environmental conditions. As is often the case, these species are greatly dependent upon one another for survival (see diagram on page 12). Adverse effects to one species in a food web may cause harmful effects to other species and the ecosystem as a whole.

Though injurious UV-B effects have been documented on some individual species within marine ecosystems, the nature and extent of ecosystem responses to UV stress are not well understood. Is the structure and function of the total marine ecosystem more or less sensitive than its components? Will negative effects (e.g., increased UV-B) on the base of the food web cascade through the system and reduce fish production?

To answer these questions, ORD's Pacific Ecosystem Branch based in Newport, Oregon, is studying a broad range of potential effects related to stratospheric ozone depletion and the subsequent increased UV-B at the Earth's surface. Because phytoplankton circulate in the euphotic zone (area of light penetration) of oceans where some

The Oceanic Carbon Cycle



UV-B penetrates, they are the marine species most at risk from ozone depletion.

Under one project, university and EPA scientists are studying the effects of UV-B radiation on marine ecosystems using 13,000 liter tanks as "living models" of a marine ecosystem. A set of these tanks will be exposed to a range of UV-B doses, with the effects on both primary producers (i.e., phytoplankton) and fish larvae determined. The results will be incorporated into a model of UV-B radiation effects on marine food webs and ecosystems.

Evaluating Phytoplankton

Perhaps differences in UV-B tolerances between species will be great enough to create a competitive advantage for one particular species over another. What if animals dependent upon a certain species of phytoplankton for food cannot readily adapt to feeding on other species? Will more and more species in the food web also decline? How will decreased or different, more UV-tolerant phytoplankton populations affect the carbon cycle and global climate change (see boxes above)?

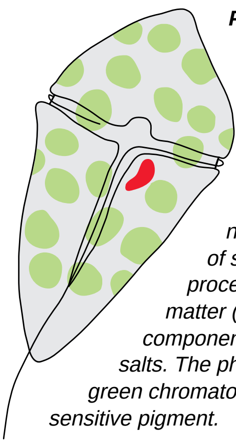
Global Climate Change: Connected to Stratospheric Ozone Depletion

Energy from the sun passes through the Earth's atmosphere relatively freely. However, the radiant heat emitted by the Earth is absorbed to some degree by gases in the atmosphere. When the concentration of these heat-absorbing gases increases, more heat is absorbed at the Earth's surface and the climate warms. Carbon dioxide (CO_2), a key heat-absorbing compound in the atmosphere, is used up by plants and phytoplankton during photosynthesis. Significant reductions in plant and phytoplankton populations due to increased levels of ultraviolet-B radiation can be expected to worsen the global warming phenomenon.

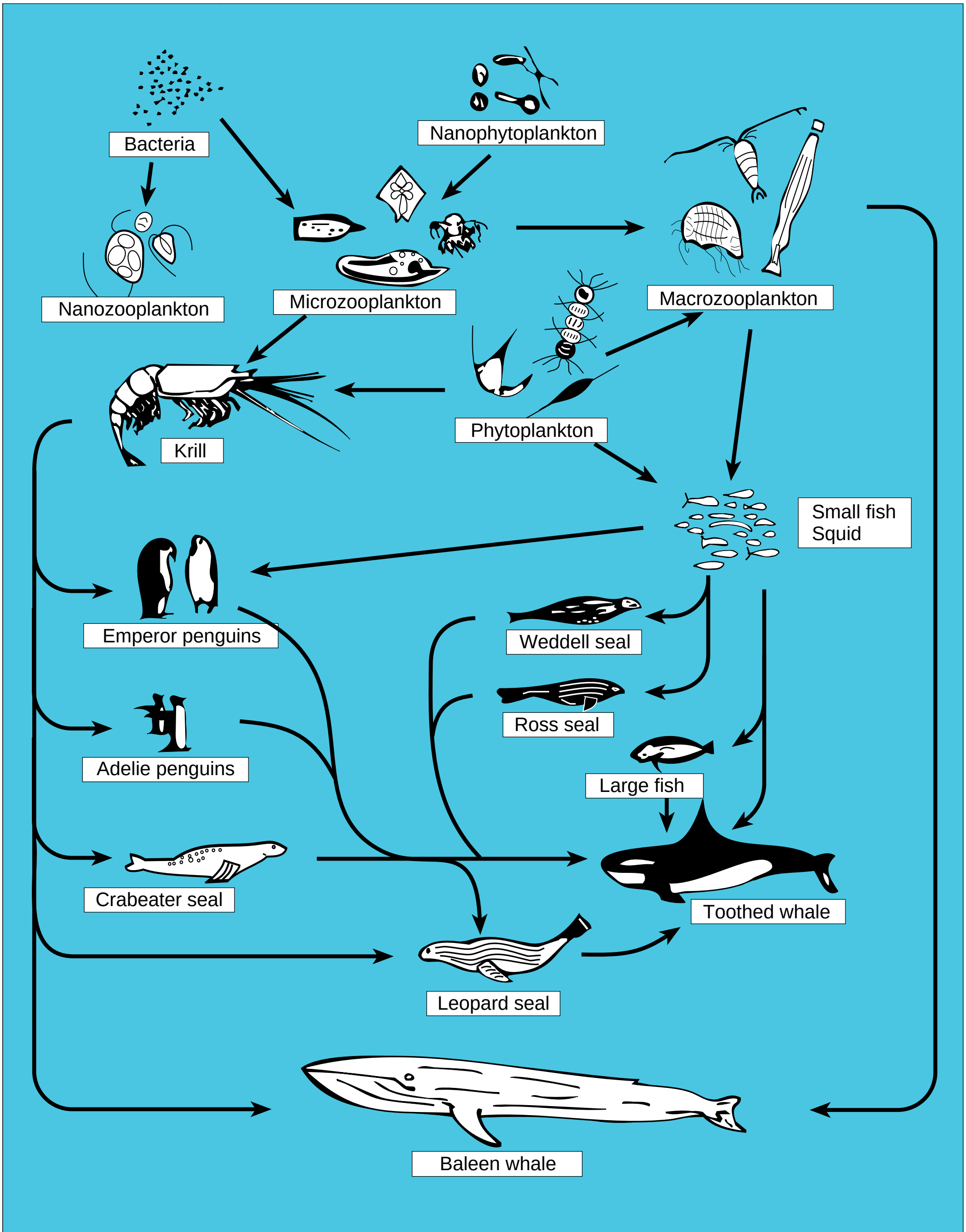
Many ozone depleting substances and proposed alternatives are global warming substances. Researchers are going to great lengths to find substitutes that minimize adverse environmental impact.

The Pacific Ecosystem Branch is studying the direct effects of UV-B radiation on long-term growth and metabolism in representative phytoplankton species. The research results will aid development of models to predict the effects of increased UV-B radiation on the structure and function of marine phytoplankton communities.

In a related project, growth rings in the shells of long-lived Antarctic bivalves (e.g., clams) are being studied much like the rings in



***Plankton**, forming the basis of aquatic food chains, are microscopic life forms inhabiting bodies of water. **Zooplankton** form the animal complement of the plankton community. **Phytoplankton**, the plant (photosynthetic) component of this community, reside most often near the surface where the presence of sunlight allows photosynthesis. In this process, phytoplankton build new organic matter (and release oxygen) using such components as carbon dioxide, water, and salts. The phytoplankton at left has many small green chromatophores and the red stigma — a light-sensitive pigment.*



A representation of the Antarctic marine food web. EPA's researchers are studying the effects of increased levels of ultraviolet-B radiation on the base of this chain and how subgroup population changes affect other organisms within this ecosystem (Source: Ambio *Vol. 19, No. 2, 1990, p. 57).*

cross-sections of trees. Fluctuations in growth ring sizes of these filter feeders (i.e., they filter phytoplankton out of water for food) may correlate well with the annual Antarctic ozone hole (first documented in 1979). If so, bivalve growth rings could be used as indicators of phytoplankton population reductions resulting from stratospheric ozone depletion.

How sensitive are phytoplankton species to changes in solar radiation? ORD scientists are studying phytoplankton pigment reactions to increased UV-B exposure. Should a measurable correlation be established, pigment change can be used as a cost-effective, ecologically relevant indicator of the extent of exposure and damage to phytoplankton.

Global Ozone Deficit

The extensive Antarctic scientific efforts are well established and have been generating a broad range of data sets for years. Over time, ozone depletion trends have been recognized there and the consequences are being thoroughly investigated.

The polar regions are extremely cold for good reason—solar radiation is at its greatest angle of incidence (i.e., least direct) at these points and must penetrate more atmosphere. However, in more temperate (and populated) areas of the world, the sun's rays are more direct and intense. Even so, factors such as latitude, altitude, pollution and cloud cover can significantly affect the relative risks of UV-B radiation.

The results of a monitoring effort in Canada (Kerr and McElroy, 1993) demonstrate that UV-B exposures at the Earth's surface increased seasonally between 1989 and 1993 (more so in winter than in summer months). While Kerr and McElroy note that such short-term trends should not be used to predict future UV-B conditions, for the first time in North America increased levels of ground-based UV-B energy (at a wavelength of 300 nanometers) have been linked scientifically to stratospheric ozone depletion. Ongoing EPA effects research will provide data needed to determine the relative risks of increased UV-B exposure and whether changes in stratospheric ozone significantly affect those risks. With this information, EPA can better inform the public and policymakers should adaptation strategies against increasing UV-B radiation become necessary.

Understanding UV-B Effects on Humans

In response to the global threat of increased UV-B exposure, and in light of indicated connections of such exposure to immune system disorders, eye disease, and skin cancer, ORD's Health Effects Research Laboratory convened an expert panel in 1988 to recommend a research strategy. The panel identified the following key questions to be answered through EPA's human health research: 1) Does immune system suppression by UV-B exposure occur in humans as it does in experimental mice? 2) Does this same immune suppression lead to enhanced susceptibility to infectious diseases and UV-induced cancers? 3) Does greater skin pigmentation protect against the immunosuppressive response? 4) While sunscreens protect against sunburn, do they also prevent other effects associated with UV-B?

The following three sections highlight some of ORD's research

In his book "Earth in the Balance," Al Gore (1992) compared the phenomenon of stratospheric ozone depletion to the pouring of a sand pile: "Small changes reconfigure the sand pile and ultimately render it vulnerable to larger changes."

projects aimed at better understanding the human health effects of UV-B exposure.

Connecting UV-B to Immunity

The contact sensitivity assay is a convenient tool used to test immune responses under various conditions. Here, a compound (such as dinitrochlorobenzene or DNCB) is applied to the subject's skin. Under normal circumstances, this initial exposure results in an immune response which on second exposure to the same agent results in a rash. The rash is an expression of immune responsiveness.

When mice or humans are exposed to UV prior to the first exposure to the agent, the immune response does not develop and a rash on second exposure does not occur. Since these same types of immune responses are needed to defend the host against certain types of infections, the inability to make this response suggests that the ability to defend the host against these infections may be compromised by UV-B.

ORD's Health Effects Research Laboratory has supported research showing that prior exposure to UV-B radiation enhanced several types of infections in mice. One infection studied — leishmaniasis — is a skin disease caused by the bite of sandflies carrying the protozoan, *Leishmania major*. With simultaneous UV-B exposure (at typically-encountered levels), the sore caused by the vector's bite (usually significant due to a dermal immune response) was smaller in comparison to test animals not exposed to UV-B. An abnormally high concentration of live organisms could be found at the site of the bite and in the lymph nodes in those mice exposed to UV-B. Additionally, the UV-B-exposed mice failed to develop protective immunity against repeat infections.

Another interesting discovery was made when researchers infected test animals at one part of the body while exposing another body part to UV-B. The immune response was still suppressed (leading to an abnormally high spread of infection to other parts of the body). These data suggest that the infection does not have to occur at the same site as the UV-B exposure for the individual to experience immunological suppression. It is thought that the immune system gets programmed wrong such that there is stimulation of a different set of immune responses which actively suppress or reduce responses that would ordinarily limit certain types of infection and provide protective immunity.

Certain routine vaccinations rely on similar protective immune responses to help people (and animals) fend off disease. Future ORD work in this area may provide valuable insight on vaccine effectiveness after UV-B exposure.

Screening Out UV-B

Components of various sunscreens, though effective at preventing sunburn, may be ineffective or even enhance the possibility of other UV-B induced effects (e.g., immunosuppression). Since total avoidance of sunlight is not feasible, it is often assumed that sunscreens provide the necessary protection during times of unavoidable exposure.

Using the developed contact sensitivity assay, University of Michigan researchers under cooperative agreement with EPA have recently begun to apply various sunscreens (and sunscreen components) prior to UV-B/ contact sensitivity tests. While results

To prevent overexposure to UV-B, health officials recommend protective clothing, sunglasses, liberal use of sunscreen, and wise planning of outdoor activities during daylight hours.

of this ongoing project are as yet unavailable, ORD's efforts may help determine whether sunscreen use can protect against UV-induced immune suppression.

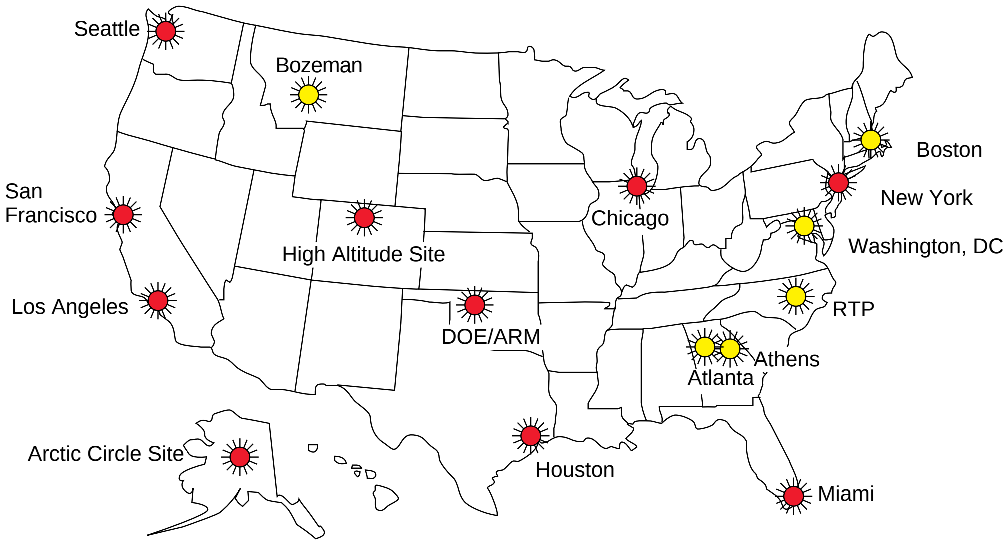
Does Skin Pigmentation Block UV-B Effects?

Fair skin is more sensitive to sunburn and skin cancer. Though ORD's research in this area is still underway, preliminary findings indicate that pigmentation does not completely protect an individual from the immunosuppressive effects of UV-B exposure. Additionally, since people with greater skin pigmentation suffer less from sunburn and are consequently less likely to take precautions against excessive exposure to solar radiation, they may be at greater risk from UV-B-related immune suppression. Information from these studies could support the added use of protective measures among all races.

Monitoring UV-B Levels

Despite models and theories suggesting that stratospheric ozone depletion should lead to increases in UV-B radiation and associated biological effects, what is actually known about increases in UV-B in the United States? What UV-B wavelengths are changing because of ozone depletion and shifts in concentrations of pollutants (including tropospheric ozone)?

ORD's Atmospheric Research and Exposure Assessment Laboratory has initiated a program to develop and operate a monitoring network, in cooperation with other federal and international agencies, to determine ultraviolet radiation changes at the Earth's surface. Data are to be compiled from 15 sites (11 urban and 4 rural) and analyzed to estimate the impact of various factors on UV radiation reaching the Earth's surface.



EPA UV-B Monitoring Sites (operational sites in yellow and proposed sites in red).

Amphibians in Decline

A recent study by A.R. Blaustein et al. (Proc. Natl. Acad. Sci., 1994), based on evidence suggesting a global environmental cause for amphibian population decline, measured the effects of increased UV radiation on the hatching success of several types of frog eggs. Species not considered to be in decline had greater hatching success when exposed to increased UV than species whose numbers are in decline. Additionally, the latter group had a greater hatch rate when shielded from UV radiation.

Informing the Public

How does EPA make the public aware of the effects of excessive exposure to UV radiation? EPA's Office of Research and Development and its Office of Air and Radiation, in cooperation with the National Weather Service, is raising public awareness of exposure to UV through the daily publication of a predictive UV "Exposure Index." The "Index," similar to the one developed in Canada in 1992, employs stratospheric ozone values derived from a National Oceanic and Atmospheric Administration satellite.

Provided along with the daily weather report, the "Index" estimates the maximum expected UV dosage for one hour centered around solar noon. Accompanying this daily value are the associated risks for various skin types — affording individuals at risk a chance to take precautions (e.g., hats, sunglasses, sun screen) as needed. The "Index" will be validated and further refined to include results from EPA's ground-based monitoring network once it is operational and the data have been analyzed.

The monitoring network will also be used to assess and improve the models for predicting the UV flux (i.e., variations in UV penetration) accounting for pollutants and other factors. Such model validation requires accurate measurements throughout the U.S. as well as consideration of the following parameters: solar angle, altitude,

Photo of EPA/IRRI cooperative study in the Philippines. Irrigated rice can be grown under a number of stressed conditions (including increasing UV-B radiation) to demonstrate potential effects of a thinning stratospheric ozone layer on growth and productivity of rice.

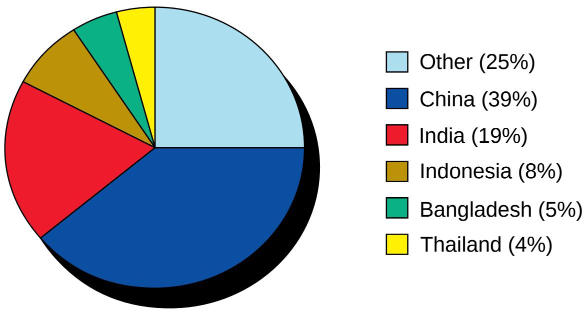
cloud coverage and density, physical parameters of the atmosphere, total column ozone, nitrogen dioxide, aerosol scattering, tropospheric ozone, and sulfur dioxide. Rigorous quality assurance/quality control procedures and comparisons with other federal and international agencies will ensure data that are compatible with other existing monitoring networks.

Understanding UV-B Effects on Crops

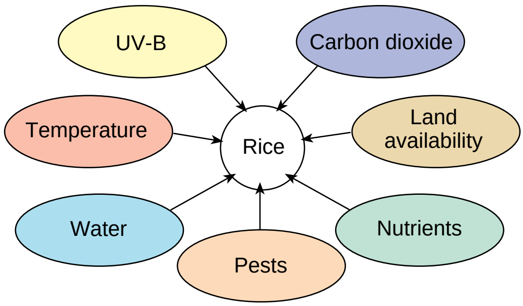
If global stratospheric ozone levels decrease, will a critical point of increasing UV-B penetration be reached that causes far-reaching environmental consequences? While human activities can be changed to minimize the direct effects of increased UV-B exposure, species of plants and other animals may be at great risk. Decreased food production through crop damage is recognized as a priority concern. Because rice is a staple food for over half of the world's population, significant failures of this crop could lead to widespread starvation and serious societal problems.

Are popular varieties of rice sensitive to increasing levels of UV-B and other changing climatic conditions? How might climate and UV-B levels change in rice-producing areas of Asia? Can a UV-B-resistant strain of rice be found or bred to replace vulnerable varieties? In 1990, EPA's Environmental Research Laboratory at Corvallis, Oregon began working with the International Rice Research Institute (IRRI) in the Philippines to learn more about rice vulnerability to changing global conditions. Additionally, mitigation/adaptation options would be explored to reduce the effect of UV-B and climate change.

The research efforts for this project include climate scoping studies, experimental studies, and how to carry out assessments. Scoping studies have used modeling to produce plausible UV-B and climate change scenarios for the tropics where the majority of world rice production occurs. The experimental studies (controlled environment and field studies) are being conducted on crop sensitivity, dose-response relationships, and other responses of rice (e.g., greater disease susceptibility)



Approximate rice productivity by country. Rice provides 2.7 billion people more than 70% of their calories.



Some key factors that can affect global rice production.

to increasing UV-B and global climate change (increased levels of carbon dioxide and higher temperature). The assessment component will develop methods to extrapolate results from the experimental studies to rice physiological and ecosystem models — which could be used to estimate regional rice yield changes. Ultimately, assessments could provide options for policymakers and rice producers when planning future agricultural strategies.

Developing Alternative Chemicals and Technologies

The rapid phaseout schedule for all ozone depleting substances has raised concern in the U.S. and abroad about the availability of environmentally-acceptable replacements. Although research by government agencies and industries has identified alternative compounds for nearly all existing systems, extensive research remains to be done.

Many of the current alternatives are only interim solutions — they still deplete stratospheric ozone to some degree (typically, the ozone depleting potential of these alternatives is only 5% in comparison to the original compounds — a lesser of two evils) and most contribute to the global warming phenomenon. Additionally, alternative compounds for some small volume applications (e.g., CFC-propelled inhalants for asthmatics) have yet to be approved.

In searching for alternative compounds and technologies, ozone depleting potential is a chief consideration. However, practicality must also be factored in. Most people care about the environment and long-term health risks — yet conversion to ozone friendly alternatives must be affordable to assure implementation on a large scale. For some developing countries, food refrigeration could save lives by allowing longer storage of food with less chance of bacterial contamination. For these countries, expensive new ozone friendly units might forever remain out of reach.

Although the Montreal Protocol will prohibit all production of ozone depleting substances, strategies are being explored to allow continued use of existing equipment until it wears out. Perhaps drop-in or near drop-in chemical replacements might be developed — requiring little or no equipment conversion. Also, successful recycling programs should ensure supplies of original compounds in the interim. For new equipment, the possibility exists that new chemicals may be used or that entirely new technologies may be developed that would satisfy the same need as the original equipment without using the old chemicals.

ORD's Air and Energy Engineering Research Laboratory (AEERL) is pursuing a wide range of research tasks to generate data on the properties of new chemicals and their performance in new and existing systems. Aiming at final (zero stratospheric ozone depletion potential) yet practical solutions, the Laboratory employs a standard series of screening tests on possible replacement chemicals — enough testing to convince private industry that the proposed alternative is potentially worthwhile. Industry then performs a more complete range of tests (taking up to 3 years) on design specific aspects, compound toxicity, and other important end effects before trying to market a product.

AEERL testing facilities include a properties laboratory where potential alternative chemicals and mixtures are analyzed. Flammability,

"Today, I am also signing an executive order that directs federal agencies to make preliminary changes in their purchasing policies, to use fewer substances harmful to the ozone layer. Here, too, we must put our actions where our values are. Our government is a leading purchaser of goods and services. And it's time to stop not only the waste of taxpayers' money but the waste of our natural resources."

Excerpt from President Bill Clinton's 1993 Earth Day speech.

oil/refrigerant miscibility (ability to remain mixed under various conditions), and materials compatibility are among the qualities measured here.

In a second area, application of potential alternatives are tested under controlled conditions (e.g., supermarket cases, refrigerator/freezers). Part of the task in this area of research is to review various equipment designs, new and old (including models that never made it to market), to see if they are somehow more compatible with alternative chemicals.

In a third laboratory area, an automobile simulator (a passenger car simulator box) has been built so that alternative air conditioning units, refrigerants, and conversion processes can be evaluated. The cost of converting automobile air conditioning systems varies by make and model year.

Applications for New Chemicals

Chillers represent one of the primary potential uses for AEERL's new chemicals. The most prevalent type of air-conditioning system uses chillers to effect cooling of the desired areas or processes. In chillers, water or a water/glycol mixture, which has been cooled in the evaporator of a vapor compression refrigeration system, moves through heat exchangers to cool and dehumidify air or to cool various processes. Chiller life spans 10 to 40 or more years.

Among AEERL's new chemicals, several HFCs (hydrofluorocarbons) have been identified with zero ozone-depletion potential, low global warming potential, and suitable thermodynamic properties for centrifugal chiller applications.

Navy Shipboard Chillers

The Navy has tentatively decided to use one of two new refrigerants (HFC-236ea and HFC-236fa) developed by EPA as replacements for ozone-depleting CFC-114 currently used in 900 shipboard chillers. Working with AEERL and a chemical producer to conduct preliminary evaluations, the Navy has concluded that these two chemicals are the most viable candidates for retrofitting existing shipboard chillers.

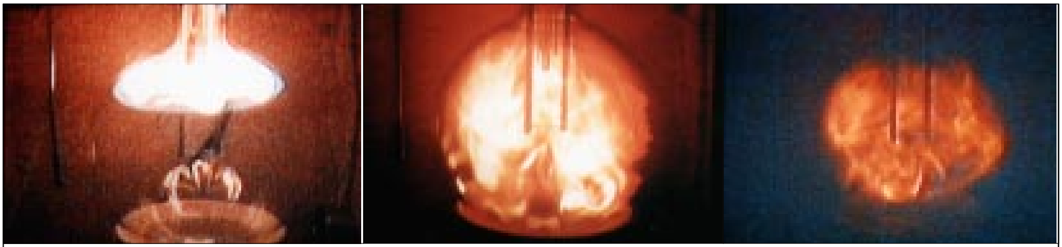
Based on data being obtained, the Navy will decide which of the two candidate EPA chemicals will be selected for long-term toxicity testing and detailed performance evaluations. These tests are necessary to justify commercial production of the chemical, for incorporation of any required design changes in the refrigeration systems, and to ensure safe occupational exposure. The tests must be completed in time to permit fleet retrofitting to commence in 1998.

Assuming HFC-236ea or HFC-236fa proves acceptable, the Navy estimates that retrofitting existing chillers with the new refrigerant would cost approximately $500 million less than replacing all of the chillers. Replacement of CFC-114 in Navy chillers with either of the candidate refrigerants could also lead to expanded use in the public refrigeration sector and would speed replacement of ozone-depleting substances.

Commercial chillers

Centrifugal water chillers are the primary means for air conditioning buildings encompassing over 40,000 square feet. They account for about 75 percent of the chiller-equipment stock and over 95 percent of the CFC emissions from chillers. They use

Once existing ozone depleting chemicals are collected, they can be dealt with in the following ways:
1) recycling;
2) chemical transformation;
3) destruction;
and 4) long-term storage.



Comparison photos of flammability tests performed at ORD's Air and Energy Engineering Research Laboratory. Blends of some "ozone-friendly" alternatives are being used to reduce the flammability of replacement compounds without significant reduction in its overall performance.

Important factors when considering replacement chemicals include:

- *toxicity*
- *ozone depleting potential*
- *global warming potential*
- *atmospheric lifetime*
- *efficiency*
- *capacity*
- *flammability*
- *compatibility with lubricants and materials*
- *commercial producibility*
- *cost*

mainly CFC-11; however, CFC-12, CFC-114, and HCFC-22 are also used.

Among AEERL's new chemicals, HFC-245ca and HFC-245fa show promise as alternatives to CFC-11. Currently, HCFC-123 is being used to replace CFC-11, and CFC-12 is being replaced by HFC-134a (although concern about its unfavorable global warming potential stimulates the search for better alternatives).

While HFC-245ca, in its pure form, is a fitting replacement for CFC-11, it is slightly flammable, and, therefore a potential liability to industrial refrigeration manufacturers. AEERL has blended other refrigerants with HFC-245ca so that the mixture is not flammable. One blend with about 80 percent HFC-245ca eliminates the flammability problem without significantly degrading the favorable performance features of HFC-245ca alone.

Supermarket Refrigeration

For low-temperature systems, AEERL has identified HFE-125 as having the best properties for performing as a non-chlorinated refrigerant. A significant consideration is that its atmospheric lifetime is lower than industry's leading alternatives. This shorter lifetime should result in a significantly lower direct global warming potential. Recent advances in supermarket-case design technologies have lead to the possibility of using pure HFE-125 as a refrigerant. In systems with liquid subcooling, this pure ether is expected to have performance capabilities similar to current CFC refrigerants. For systems requiring a lower boiling point, blends containing HFE-125 have been identified as promising candidates.

At the high end of low temperature systems (e.g., unit freezers), another AEERL candidate, HFE-143a, has acceptable thermodynamic characteristics, and a more energy efficient operation than industry's alternatives is expected. This refrigerant is flammable, but blends using this compound may result in a non-flammable refrigerant equal or better in performance than CFC types.

Heat Pumps and Air Conditioners

Currently, no single refrigerant performs as well as HCFC-22 in heat pumps and air conditioners. A number of refrigerant blends, however, have shown promise. Important factors that must be considered include: environmental impact, capacity, efficiency, flammability, compatibility with lubricants and materials, commercial producibility, and cost. The new chemicals developed by AEERL include several that can potentially be used in blends with other commercially available chemicals to improve performance in refrigeration equipment. Initial modeling has been done and is being followed by experimental testing as the new chemicals become available in sufficient quantities.

Refrigerators/Freezers

AEERL is working to find near drop-in replacements for the CFC-12 being used in refrigerators/freezers. With a cost-effective transition to environmentally-friendly refrigerants, developing countries may choose not to use the additional ten years allotted them by the Montreal Protocol to halt the use of CFCs in refrigeration equipment. Since millions of new refrigerators will be produced or purchased by these nations over the next ten years, the need for ozone friendly refrigerants is urgent.

India, for example, produces over a million refrigerators annually; about 7.5 million presently are in service. Costly retrofitting to non-chlorine refrigerants would cause severe economic hardship. Finding near drop-in replacements that are more energy efficient will both reduce equipment modification expense and be environmentally advantageous.

The leading candidate for new refrigerator/freezers is HFC-134a. However, since HFC-134a has substantial global warming potential and may ultimately need to be replaced, other compounds are being evaluated by AEERL as potential long-term replacements.

Foam blowing

Efforts to replace CFC blowing agents in foam insulation products have resulted in the development of drop-in HCFC substitutes. While these substitutes exhibit significantly lower ozone depletion potential than CFCs, they can still only serve as interim replacements that must be phased out. Ongoing AEERL research has identified and categorized a large group of novel compounds as candidates for CFC substitutes. As a result of this effort, several new chemicals identified by AEERL (HFCs -236ea, -245ca, and -245fa) were recommended as new potential foam blowing agents and are being investigated further.

Insulation

To support the implementation of alternative refrigerants (some with lower cooling efficiencies), AEERL has focused considerable effort on development of insulation materials. Working cooperatively with the Department of Energy's national laboratories, incorporation of a polymer outer shell material into the design of refrigerator/freezer doors has shown promise in boosting insulation value.

Motor Vehicle Air Conditioning

Motor vehicle air conditioning represents one of the largest sources of ozone-depleting refrigerant emissions. AEERL's new chemicals will be evaluated as long-term replacements because, as mentioned earlier, HFC-134a may be acceptable only in the interim.

Incineration of Ozone Depleting Substances

EPA research has led to widely accepted recovery/recycling technologies for refrigerants (e.g., automobile air conditioners, refrigerators). As ozone depleting substances are phased out, however, the need for an ultimate means of disposal for the remaining supplies becomes more of a concern. In studying incineration as a possible

A "drop-in" replacement chemical is one that requires no conversion or redesign of existing equipment.

EPA's research has provided U.S. industry with a significant head start in developing and ultimately marketing new replacement chemicals.

means of disposal of these compounds, AEERL has been carefully monitoring the "products of incomplete combustion" or PICs resulting from the process.

In a small-scale study, the scientists incinerated two widely-used types of CFC refrigerants (CFC-11 and CFC-12), and analyzed the PIC emissions. A wide variety of PICs were found – including dioxins and furans.

Further testing is underway to optimize the incineration process so that such PICs can be avoided. Modifications being investigated include the injection of steam into the incinerator's flame zone as well as altering the temperature of the incinerator.

Conclusion

Progress has been made in reducing emissions of the greatest depleters of stratospheric ozone. The peak atmospheric concentration of these substances (chiefly CFCs) is not expected to be reached, however, until the end of this century. Should phaseout progress continue, a slow decline of ozone depleting substances in the atmosphere will occur thereafter. Though intermediate alternatives deplete ozone less, they continue to contribute to that problem as well as to the global warming phenomenon. For many applications, the final replacement chemicals have not yet been found.

EPA is committed to the task of finding ultimate solutions to the issue of stratospheric ozone depletion. Through its diverse research programs, the human health and ecologic effects attributable to increased UV-B radiation will be identified; UV-B radiation levels reaching the earth's surface will be monitored and reported to enable individuals at greatest risk a chance to take protective measures as needed. Cooperation from industry, private citizens, government, academia, and the international scientific community will ensure that alternative compounds and technologies are developed as quickly as possible and put to use as economically as possible.

In response to an alarm sounded by a few scientists two decades ago, the world has taken action to identify the causes and effects of a major environmental problem and is moving to solve it. With rising optimism, the work continues.

EPA Publications

The EPA publications listed below provide more detailed information on the subjects discussed in this document. These references and additional copies of this brochure can be requested at no charge (while supplies are available) from EPA's Center for Environmental Research Information (CERI) by calling 513-569-7562 or by fax at 513-569-7566. Once the CERI inventory is exhausted, clients will be directed to the National Technical Information Service (NTIS) where documents can be purchased.

Advanced insulation for refrigerator/freezers: The potential for new shell designs incorporating polymer barrier construction, EPA/600/SR-93/009.

Effects of UV-B and global climate change on rice, EPA/600/R-93/128.

Experimental investigation of PIC formation in CFC incineration, EPA/600/SR-93/078.

Manual for non-CFC aerosol packaging: Conversion from CFC to hydrocarbon propellants, EPA/600/S2-91/056.

Mobile air-conditioning recycling manual, EPA/600/SR-92/171.

New chemical alternatives for CFCs and HCFCs, EPA/600/F-92/012.

On the feasibility of using satellite derived data to infer surface-layer ozone concentration patterns, EPA/600/SR-94/081.

Stratospheric ozone protection: An EPA engineering perspective, EPA/600/J-92/005.

The refrigeration research facility at the Air and Energy Engineering Research Laboratory, EPA/600/F-92/007.

To order any of the following four publications, call EPA's Stratospheric Ozone Information Hotline at 1-800-296-1996.

Auto air conditioners and the ozone layer: A consumer guide, EPA/430/F-93/009.

Air conditioners and the ozone layer: A checklist for citizen action, EPA/430/F-93/006.

On the trail of the missing ozone, EPA/909/K-93/001.

The Federal Experimental Ultraviolet Index: What you need to know, EPA/430/F-94/016.

Cited Literature

Blaustein, A.R. *et al.* 1994. UV repair and resistance to solar UV-B in amphibian eggs: A link to population declines? *Proc. Natl. Acad. Sci. USA,* 91: 1791-1795.

Elkins, J.W. *et al.* 1993. Decrease in the growth rates of atmospheric chlorofluorocarbons 11 and 12. *Nature,* 364: 780-783.

Gore, Sen. Albert, Jr. 1992. Earth in the balance. New York, N.Y.: Houghton Mifflin Co.

Kerr, J.B. and C.T. McElroy. 1993. Evidence for large upward trends of ultraviolet-B radiation linked to ozone depletion. *Science,* 262: 1032-1034.

U.S. EPA. 1987. Ultraviolet radiation and melanoma: with a special focus on assessing the risks of stratospheric ozone depletion. PB88-231063.

Voytek, M.A. 1990. Addressing the biological effects of decreasing ozone in the Antarctic environment. *Ambio,* 19(2): 57.

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