

WHAT'S HAPPENING TO THE OZONE LAYER?

The gradual thinning now occurring is likely to continue for some time despite international agreement to phase out emissions of ozone-depleting substances

The Antarctic ozone 'hole' and a smaller deficit over the Arctic have been big news in recent years. So far, the fact that some depletion has also occurred in the stratospheric ozone right above us has received less attention. But it has occurred and, unfortunately, the chances are high that the ozone layer above Australia will continue to thin for some decades.

To help assess the extent of our local problem, Dr Paul Fraser and Dr Willem Bouma, of the CSIRO Division of Atmospheric Research, have examined the satellite data on ozone changes at our latitudes. They've also calculated how the recently revised Montreal Protocol, concerning the control of ozone-depleting substances

and signed by most nations in 1990, will affect our exposure to ultraviolet light in the coming decades.

The total 'package' of radiation that we receive from the Sun includes some in the ultraviolet region of the spectrum, which lies between X-rays and the violet end of visible light. Ultraviolet rays are divided, on the basis of wavelength, into UV-A, B and C. Their harmfulness to biological molecules — and hence to living things — depends on their wavelength, the shortest (UV-C) being the worst. Luckily, almost none of this can penetrate to ground level, even with a thinned ozone layer. UV-B is also damaging, but the ozone layer screens out most of it. UV-A occurs in sufficient quantity that much of it reaches us despite the ozone layer. It

causes sunburn — which, although many people believe otherwise, can occur regardless of whether it is a hot day, as skiers well know. Ozone depletion is likely to cause a significant increase in both UV-A and UV-B reaching ground level; the latter is the most serious cause for concern because it is far more effective than UV-A at inducing skin cancer and damage to the retina.

Ozone (O₃) in the upper atmosphere is an important gas precisely because it absorbs UV-B. It is the presence of the gas in trace amounts in the stratosphere between about 10 and 50 km above sea level that we mean by the 'ozone layer'. We must distinguish this from ozone near the ground, a common feature of air pollution in cities. This lower-atmosphere ozone



Australian Overseas Information Service

does not find its way to the stratosphere in any abundance. It is a noxious pollutant that can damage the lungs.

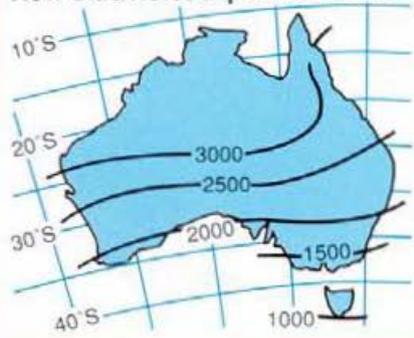
(Incidentally, ozone is also a greenhouse gas; it allows heat from sunlight to pass through but absorbs the longer-wavelength reflected heat that comes up from the Earth, thus acting to trap heat.)

Rather than migrating to the stratosphere from below, ozone is produced there naturally — by the action of ultraviolet light on oxygen existing as molecules. It can also be broken down by UV radiation and by reacting with atomic oxygen, both of which return it to molecular oxygen. The reaction with atomic oxygen is catalysed by the hydroxyl radical (OH), derived from water, and the reactive nitric oxide radical (NO), which comes from nitrous

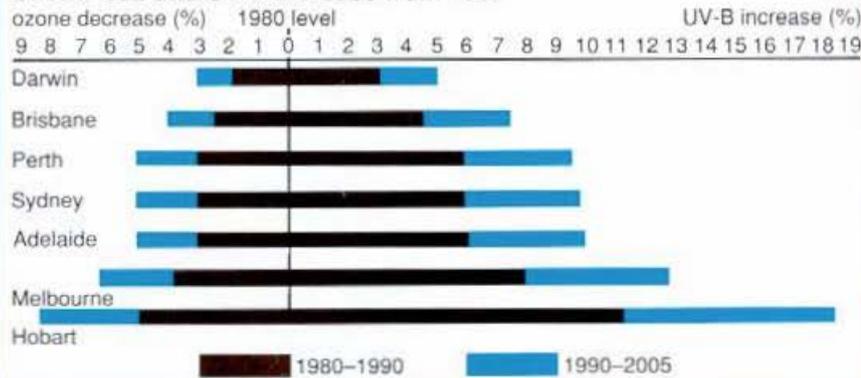


Although ozone thinning will cause bigger percentage increases in UV exposure in southern Australia than further north, northern Australia will continue to receive much more UV than the south. The figures on this map, from the late 1970s, are annual mean radiation doses expressed in erythemal units — a measure of sunburning power.

How ultraviolet exposure varies



Ozone loss and UV-B increase from 1980



Observations show that each 1% loss of ozone results in almost a 2% increase in UV-B at ground level. The ozone decreases shown here are measurements in 1988 extrapolated to 1990, and predictions to 2005 based on forecast atmospheric chlorine levels (assuming the revised Montreal Protocol takes effect) and the present observed relation between chlorine rise and ozone loss.

oxide (N_2O), a gas naturally present in the atmosphere in small quantities. A dynamic balance therefore exists between ozone's continuous formation and continuous destruction, and so, in the normal course of events, its concentration should not change significantly over time.

It so happens that chlorine and bromine, in reactive forms, can also catalyse ozone breakdown. In an unperturbed stratosphere they occur in very small quantities. Although chlorine, in a number of forms, is released naturally in large amounts from the planet's surface — mainly from sea water, volcanic eruptions and rotting or burning vegetation — much of it is removed in the lower atmosphere and only a very small percentage reaches the stratosphere.

But this natural supply is now dwarfed by synthetic compounds, such as the chlorofluorocarbons (CFCs), that are currently responsible for 80% of the stratosphere's chlorine. When these chemicals break down due to exposure to UV, their fluorine is generally not a problem for the ozone layer, but the chlorine is.

As well as CFCs, common industrial chemicals such as carbon tetrachloride and methyl chloroform contribute to the build-up of unwanted stratospheric chlorine. Other compounds, termed halons, contain ozone-destructive bromine.

Not all the chlorine that finishes up in the stratosphere directly catalyses the break-down of ozone. About 90% of it is locked away in the form of various compounds, such as hydrochloric acid and chlorine nitrate, that are not, themselves, reactive against ozone. However, under certain conditions these inactive compounds can release an active form of chlorine — the pure chlorine molecule Cl_2 . This happens during the Antarctic winter and early spring when unique weather conditions allow the build-up of clouds in the stratosphere (see *Ecos* 52 and 56.) The particles, mainly ice crystals, in the clouds seem to catalyse the reactions that release the chlorine.

The molecular chlorine accumulates but remains innocuous until the sun rises in spring after the long, dark polar winter. Then, energy in the ultraviolet light breaks up the chlorine molecule into its constituent atoms. Atomic chlorine is very reactive and

immediately attaches to ozone, breaking away one of the oxygen atoms in its molecule. The reaction produces chlorine monoxide (ClO) and molecular oxygen (O_2). Two chlorine monoxide molecules may combine to form a compound that breaks down under the influence of ultraviolet light to release more atomic chlorine, and the ozone-destructive cycle starts all over again.

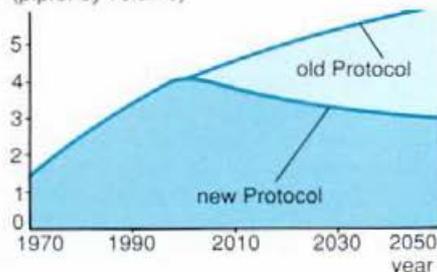
Chlorine-catalysed ozone destruction is going on now all around the world; it doesn't just take place at the Poles. However, the crucial difference between ozone destruction levels above Antarctica and above the mid latitudes where we live is the speed of the reaction. Polar stratospheric clouds provide an enhancing catalytic effect. Where they don't exist, ozone destruction continues, but at a far slower pace. A natural aerosol of droplets of sulfuric acid that occurs throughout the stratosphere at all latitudes may possibly also provide a catalytic effect — but, fortunately for us, nothing like as effectively as the clouds that grace the polar stratosphere.

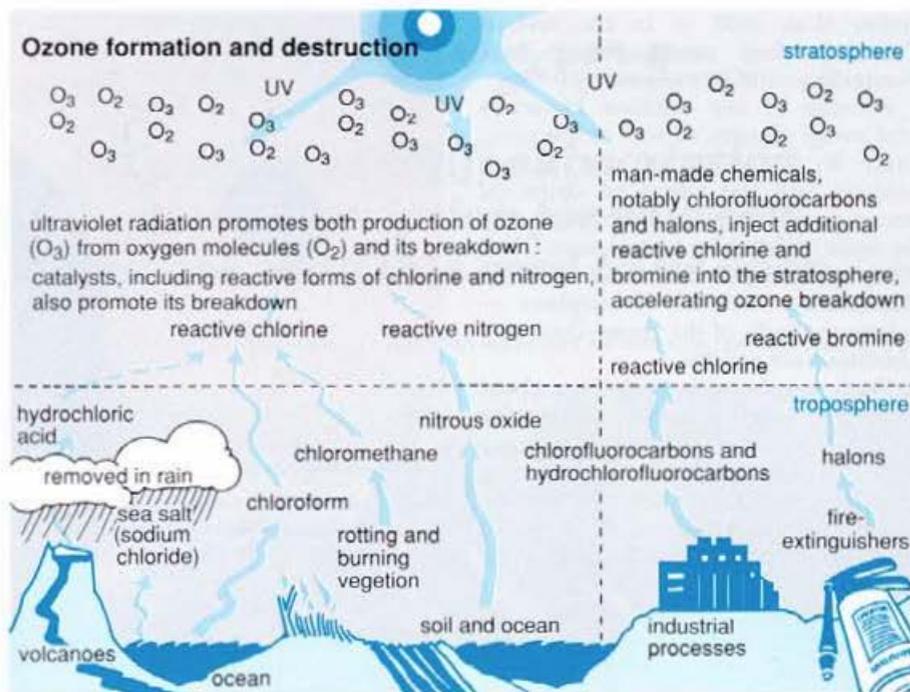
Satellites have measured the total ozone in the atmosphere beneath them since 1978. At latitudes south of $70^\circ S$ losses of total ozone of up to 50% occur in spring, in association with the Antarctic 'hole'. But total ozone (or 'column' ozone) measurements from above don't give the full picture, as they cannot pinpoint the altitude at which the loss has occurred. As some ozone is present above and below the 'layer', total figures tend to mask the seriousness of the problem within the layer.

Scientists from the United Kingdom Environment Department produced this analysis of the effects of the revised Montreal Protocol on chlorine levels in the lower atmosphere (troposphere) to the year 2050.

Future chlorine levels

globally averaged chlorine (p.p.b. by volume)





The ozone layer is the product of natural processes that both produce and destroy ozone, and the ozone concentration reflects the balance between these processes. Man-made emissions, notably of chlorofluorocarbons, can after this balance causing a decline in ozone concentration.

material like CFCs detected in the troposphere (where they are inert) to reach the stratosphere, where radiation breaks them down into potentially active compounds.

Dr Fraser measured the concentration of a number of CFCs and related compounds at the Cape Grim Baseline Air Pollution Station in Tasmania (see *Ecos* 68), and found an increase between 1980 and 1990 of just over 1 part per billion (p.p.b.). The total chlorine in the lower atmosphere sampled at Cape Grim is now about 3.5 parts per billion. Thus, during that decade, a 1-p.p.b. chlorine increase coincided with a 2.5% loss of stratospheric ozone over Australia.

In October 1987, ozone at 20 km over Halley Bay in Antarctica decreased by more than 95% in the course of just 2 months — from August to October — as spring began and the sun rose. This massive loss was particularly confined to a band at that altitude, while the small quantity of lower-atmosphere ozone remained completely unaffected, so the figure for total loss came close to 50%.

Satellite data show that the extent of the depletion of total ozone above Australia depends on the latitude, being worse further south. It seems almost certain that the loss occurs in the ozone layer, as measurements of the tropospheric (lower-atmosphere) ozone during the same period show no significant changes.

During the 8 years from 1980, the stratosphere above Darwin, at latitude 12°S, showed a small ozone loss (about 1.5%), while that above Hobart, at latitude 43°S, suffered a 4% loss. Scientists from NASA have arrived at these figures after correcting for the effect of the solar cycle, which causes changes in the energy from the Sun, and hence affects the rate of ozone formation and breakdown.

Dr Fraser and Dr Bouma have extrapolated the ozone loss to 1990 — the actual figures are not yet in — giving a 5% loss for Hobart and 1.9% for Darwin. These percentages may not appear too worrisome, until you remember that it is not ozone loss as such that concerns us, but rather the increase in dangerous UV-B radiation.

Dr Colin Roy and Dr Peter Gies, of the Australian Radiation Laboratory, have examined the relationship between ozone changes and UV-B at ground level. Their figures show that a 1% decrease of ozone results in approximately a 2% rise in UV-B. (Confirmation of this two-to-one ratio came during December 1987, when ozone-poor stratospheric air broke away from Antarctica and drifted for a few days across southern Australia. Satellite data showed that total ozone fell by 10%; at the same time, ground measurements of UV-B in Melbourne showed a 20% surge.) Residents of Hobart are now exposed to about 11% more UV-B than they were a decade ago, residents of Darwin about 3% more.

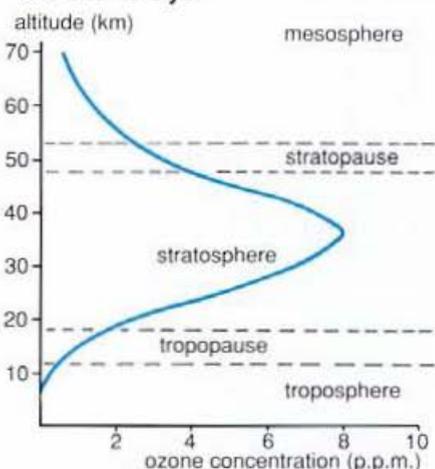
However, denizens of southern Australia can take heart. The Sun's far greater height above the horizon nearer the Equator means a much greater total dose of solar radiation per unit of ground area there. So, despite Hobart's bigger relative increase, those people enjoying the warmth and sunshine of the north still receive far more total UV-B — as the map, which makes allowance for cloud cover too, shows. Hobart still receives the least UV-B of any of our cities, although its sunshine — whether the air is warm or not — is more damaging than it used to be.

But what of the future? To predict that, we need to know the atmospheric chlorine increase that has been responsible for the measured ozone loss to date. It takes, on average, 3–5 years for

Knowing the current figures for the world's industrial production of ozone-depleting substances, and the reductions required by the Montreal Protocol, Dr Fraser and Dr Bouma have calculated future ozone losses for Australia. They have looked in detail at the terms of the Protocol signed in 1987 and, more importantly, the revised Protocol announced in London in 1990. Under the terms of this agreement, emissions of CFCs must be cut 50% by 1995, and 85% by 1997, and eliminated entirely by 2000. Halons, used as fire-fighting agents, are to be cut 50% by 1995 and phased out by 2000, except for essential

Globally averaged ozone concentration peaks in the stratosphere at an altitude of above 30 km.

The ozone layer



fire-fighting uses. Carbon tetrachloride and methyl chloroform, not covered by the original Protocol, should also be phased out completely by 2000 and 2005 respectively.

All these control measures are more stringent than those agreed on in 1987. However, the biggest single uncertainty in calculating future ozone losses is the assumption of total compliance by all nations. The scientists' calculations have assumed that targets will be met, but obviously their forecasts will have to be updated in the light of further information.

Assuming compliance, tropospheric chlorine levels will rise by 0.5 p.p.b. in the decade to 2000. They will then start to decline slowly. Because of the lag, stratospheric chlorine will continue rising until 2005 before starting its decline. Thus, stratospheric chlorine will increase by 0.6–0.7 p.p.b. over the next 14 years. On the experience of the decade to 1990, this would represent an additional ozone loss of 60–70% of the 1980–90 thinning. That means further falls ranging from 1.2% in Darwin to 3.3% in Hobart.

However, we cannot necessarily assume that the ratio that gave us a 2.5% ozone loss for a 1-p.p.b. chlorine gain will continue to hold true. Various factors could affect the balance. For example, the greenhouse effect warms the troposphere but cools the stratosphere. The lower temperature there would enhance the chemical reactions responsible for ozone formation; on the other hand it could increase the chances of stratospheric clouds forming at latitudes further from the Poles, and/or persisting for longer in the polar regions. Then, too, human activity causes the levels of methane to rise. In the stratosphere, this gas is oxidised to water vapour, which may also perhaps make stratospheric clouds more likely to form.

The revised Montreal Protocol, if it achieves total global compliance, means that stratospheric chlorine levels, after rising to about 4 p.p.b. by the end of this century, will start a slow decline. Unfortunately, CFCs in the atmosphere have life-spans of about 100 years, so a return to 'baseline' chlorine levels will take many decades. However, under the original Protocol, the stratospheric levels would have continued to rise to beyond 6 p.p.b. during the course of the next 100 years. The CSIRO scientists calculate that if we went even further, and phased out CFCs throughout the world by 1995,

rather than 2000 as in the revised Protocol, then ozone losses over Australia would be reduced by 0.5%.

Because of our outdoor life-styles and sunny climate, as well as the proximity to Antarctica of part of our country and the worry of 'drifts' of ozone-poor spring air, Australians may be more affected by increases in UV-B than citizens of much of the industrialised Northern Hemisphere — where the bulk of the ozone-depleting chemicals are emitted.

Our capacity to do something about ozone depletion is limited by the size of our contribution. Global compliance with the Montreal Protocol is of paramount importance. If Australia alone phased out CFCs before 2000, it would have no significant effect on the time taken to recover to original levels of stratospheric chlorine around the world. Our contribution to the total damage is simply too small. Of course, that is no reason why we cannot set a good example, and hope that ultimately all nations will comply with the Protocol.

Roger Beckmann



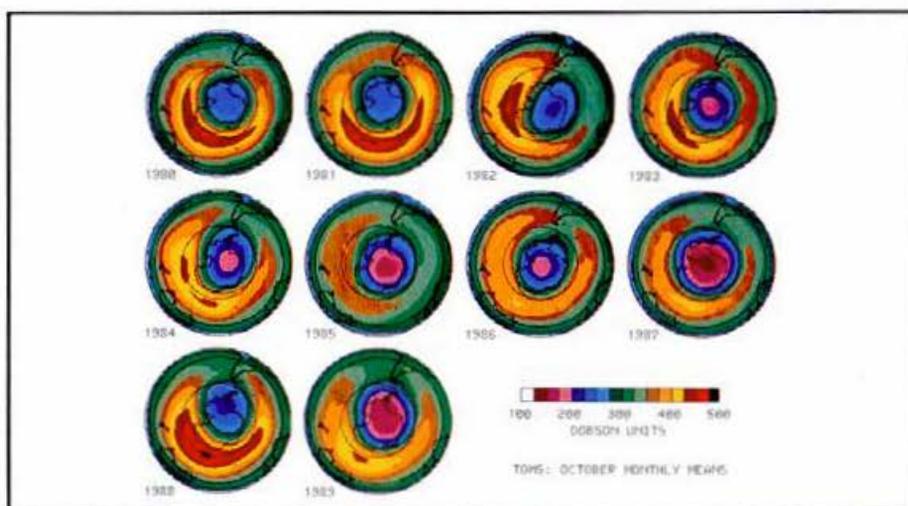
Anti-Cancer Council of Victoria

Melanoma, an often fatal form of skin cancer. Increased ultraviolet exposure increases skin cancer risk.

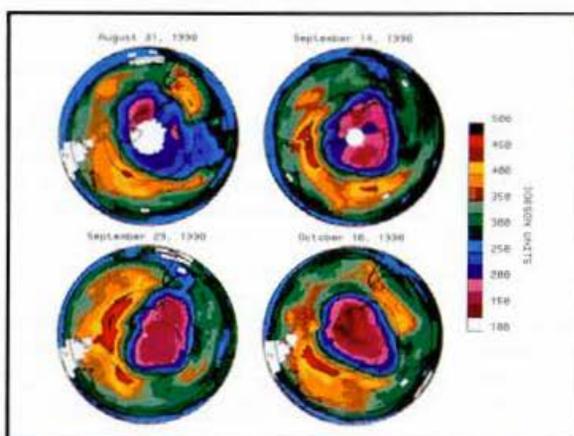
More about the topic

Chlorofluorocarbons and stratospheric ozone. P.J. Fraser. *Chemistry in Australia*, 1989, 56, 272–5.

New ozone protocol and Australia. P.J. Fraser and W. J. Bouma. *Search*, 1990, 21, 261–4.



Photos: R. Stolarski and NASA-Goddard Space Flight Center



A decade of ozone holes: these colour-coded satellite images taken over the South Pole show how the degree of ozone depletion has increased over the last decade. Dobson units are a measure of the quantity of ozone.

The development of a recent hole: the series shows how the spring 1990 ozone hole developed.