

Chlorine blamed for growing 'ozone hole'

Like acid on lace, chlorine from man-made chemicals appears to be eating away the tenuous fabric of our protective ozone layer, at least over Antarctica in spring. That's the nearly inescapable conclusion from the most recent set of stratospheric measurements made last year by more than 150 scientists, who flew their most sophisticated instruments into the centre of the now-renowned 'ozone hole'.

They found that the diffuse ozone layer, spread out between 12 and 20 km above the icy continent, registered in August a thickness equivalent to 3.0 mm at sea level, but by early October — as the sun returned after the long winter night — it had been reduced to only 1.3 mm. Other instruments showed that at the heart of the ozone layer — at an altitude of 16.5 km — more than 97% of the ozone had been consumed.

Fortunately, within a further month or so, the 'hole' had been repaired, as air with normal ozone levels swept in from lower latitudes (just as has happened every year since the springtime ozone hole apparently first came into being 9 years ago). The filling-in of the hole results from the natural changeover between winter and summer circulation patterns in the Antarctic atmosphere.

Nevertheless, the phenomenon has scientists worried, because the hole is getting progressively deeper and wider each year (apart from a slight turnaround in 1986). Last year's hole had 15% less ozone than the previous minimum in 1985, and represents a thinning of ozone of more than half.

Furthermore, last year the filling in of the hole occurred later than it ever had (mid December). This could be the first observed result of the ozone hole having an impact on climate.

Because ozone shields living things from the sun's damaging ultraviolet radiation, the possibility that the Antarctic ozone hole is the forerunner of thinning elsewhere in the stratosphere has profound implications for future life on earth. Thankfully, the hole is presently confined to an isolated air mass (the very cold vortex of air that swirls in constant darkness around the South Pole every winter), and the chemistry of its formation is different from that governing

the stratospheric ozone sheltering the rest of the globe.

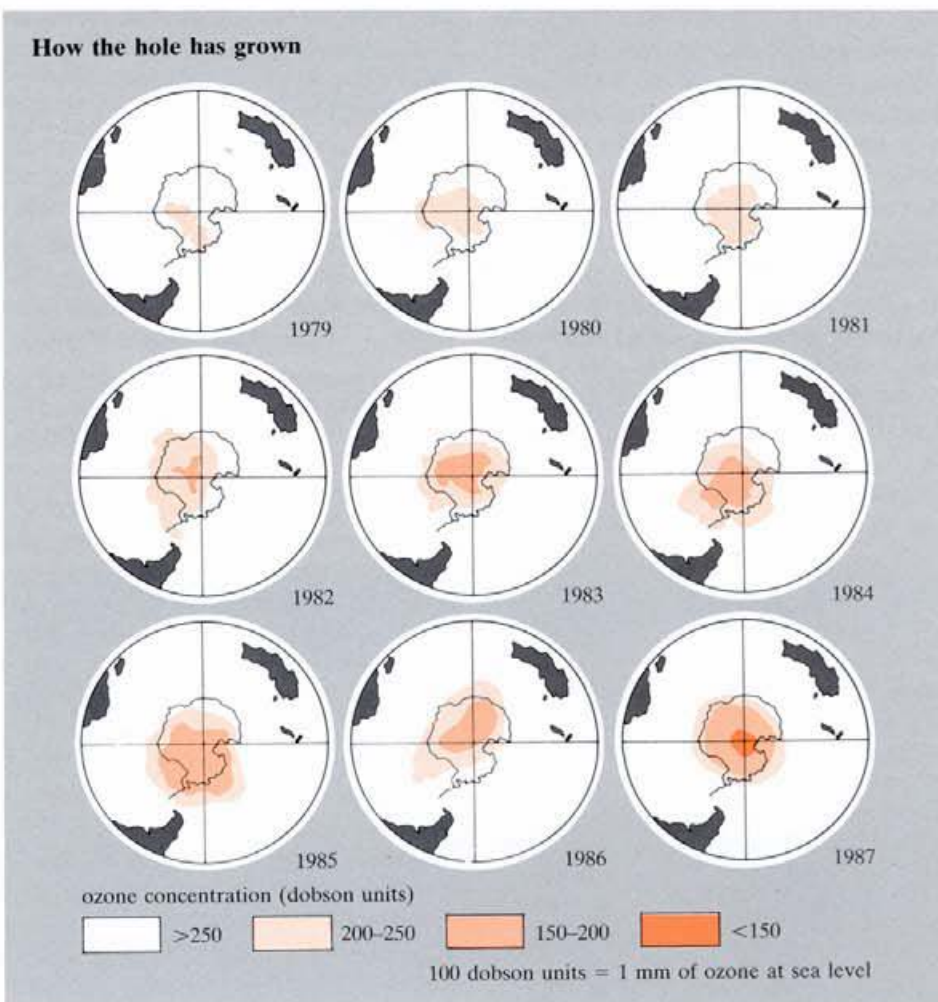
However, if ozone at temperate latitudes were to disappear at a similar rate, we'd really have something to worry about (more skin cancer, reduced crop yields, diminished phytoplankton activity, and so on). An unrestrained growth in the release of man-made chlorofluorocarbons (CFCs) to the atmosphere could bring this about, scientists warn.

So far, the only significant long-term ozone change found outside Antarctica has been a 2-3% loss since 1970 in the mid to high latitudes of the Northern Hemisphere. This loss was revealed in March this year by NASA's Ozone Trends Panel. (Dr Alan Plumb and Dr Paul Fraser, of the CSIRO Division of Atmospheric Research, belong to the Panel, and they have contributed to its recent comprehensive report on atmospheric ozone.)

With the current ozone-observing network, such an ozone change is barely detectable because many processes affect global ozone levels, often in opposite directions. The gas is constantly created (by sunlight from ordinary oxygen, mostly above the Equator) and destroyed (by various atmospheric constituents, natural and man-made) as winds distribute it in the upper atmosphere. Cyclical changes in atmospheric motion and variations in solar activity with the solar cycle can have a big influence on these processes.

Reports last year of large decreases in total ozone since 1979 (and of the appearance last year of a small Arctic ozone hole)

Satellite measurements have shown a progressive decline in springtime ozone levels over Antarctica. How long can the decline continue?





The ER-2 high-flying aircraft that went into the Antarctic stratosphere to take samples and analyse the chemical content of the air there.

have now been shown to be incorrect; they were due to satellite data that failed to allow for drifts in sensitivity of the on-board detectors.

The key question is whether the Antarctic ozone hole is a symptom of something far more drastic — is it an early warning sign of what may happen over the whole planet if increased quantities of CFCs are released to the atmosphere?

Another worry, voiced by Dr Plumb, is that Australia may already be feeling some effects from the loss in Antarctic ozone. Last spring, the Antarctic hole covered 15% of the Southern Hemisphere, and when it filled in it most likely did so at the expense of neighbouring regions. Dr Plumb suspects that an early summer depletion in Australian ozone levels may now be detectable, and he is keen to see if analysis of surface and satellite ozone data for the Australian region confirms his suspicions.

Montreal Protocol

As *Ecos 52* pointed out, atmospheric concentrations of CFCs — used as refrigerants, blowing agents in plastic-foam production, propellants in some spray cans, degreasers of electronic assemblies, and so on — are rapidly increasing. Inert in the lower atmosphere, these gases slowly migrate to the stratosphere where ultraviolet radiation breaks them down, creating very reactive radicals of chlorine and chlorine monoxide (Cl^* and ClO^*) and starting a chemical chain reaction. The radicals act as catalysts, with each one formed leading to the destruction of thousands of ozone molecules (O_3) into oxygen (O_2). The most common CFCs in the atmosphere have an effective lifetime of 75–110 years.

Placing a ceiling on the release of CFCs into the atmosphere is the aim of the historic Montreal Protocol, agreed to last September (2 weeks before the latest ozone hole findings became known) under the earlier Vienna Convention for the Protec-

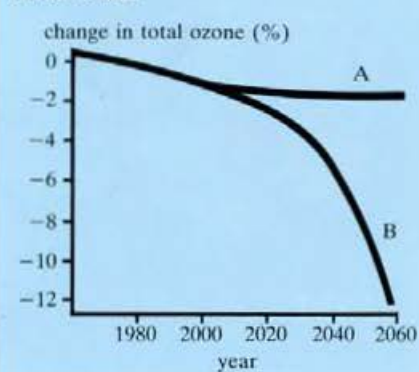
tion of the Ozone Layer. Australia is one of the countries, along with the United States, the European Economic Community, and many other nations, that have ratified the Protocol or are about to do so.

The Montreal Protocol for Substances that Deplete the Ozone Layer calls for a freeze (at 1986 levels) on the national consumption, but not production, of CFC-11, -12, -113, -114, and -115 by 1990, followed by a 20% cutback before 1994 and a further 30% cut before 1999. In addition, consumption of halons 1211 and 1301 (bromine-containing compounds used in some fire-extinguishers) will be frozen at 1986 levels by 1993. We use 40 times less halons than CFCs, but then they destroy ozone up to 10 times more effectively.

Developing countries received a 10-year period of grace, during which they would be allowed to steadily increase annual consumption of CFCs to 0.3 kg per person, which compares with a present average of about 0.8 kg in developed countries, such as Australia (this country currently consumes 12–13 million kg of CFCs each year).

Curve A models the effect on ozone if CFC emissions cease in 1997 (prior emissions detailed in text). In an alternative scenario, non-compliance with the Montreal Protocol sees one-third of the current world CFC production increasing by 2.5% per year — a path to major ozone depletion.

The outcome of two patterns of CFC use



The required reductions are measured in ozone-depleting potential, not tonnes. In other words, a country can increase its consumption of CFCs, but still reduce environmental impact, by switching to CFCs with shorter atmospheric lifetimes and lesser ozone-destroying abilities.

Of course, a big drive is now under way for companies to come up with new CFCs that possess minimal ozone-consuming side-effects (and are not too expensive to make). Normally competitive companies are co-operating to find alternatives in the shortest possible time. Nevertheless, toxicological testing of proposed substitutes will take about 5 years, and implementing changes to production facilities may take even longer.

The Protocol is a landmark achievement — the first international treaty to limit the pollution of the planet's atmospheric mantle.

Dr Fraser, a scientist with broad expertise in the effects of trace gases on ozone, believes the measures prescribed by the Montreal Protocol are probably sufficient to prevent long-term depletion of the ozone layer outside Antarctica, provided we are correct in assuming that the simultaneous release of carbon dioxide, methane, nitrous oxide, and other greenhouse-effect gases brings about a countervailing effect to that of chlorine on ozone levels.

Increased levels of these gases (that incidentally include CFCs themselves) trap extra heat low in the atmosphere, which calls for a corresponding cooling in the stratosphere to balance the energy budget. This cooling slows ozone-depleting reactions, and in addition methane acts to some extent as a chlorine 'sink'.

If we use a widely accepted model of ozone chemistry to examine the net result of these two effects, we get the ozone levels shown in the graph. Curve A shows what happens if the Protocol's provision for a 20% reduction from 1986 levels in consumption of CFCs has a compliance rate of 65%. It assumes that non-complying countries continue to emit CFCs at a growth rate of 2.5% per year until 1997, when growth stops. The final ozone depletion is less than 2% by the year 2060.

In another possible development, non-complying nations may continue to increase CFC usage at 2.5% per year indefinitely, and curve B shows the worrying result — an ozone depletion of 12% by 2060.

These predicted depletions are based on chemical processes that have been thoroughly investigated over the past 20 years, and they form the scientific basis of the Montreal Protocol. Scientists currently

believe that adherence to this Protocol will prevent future global ozone depletions from reaching unacceptable levels (outside Antarctica). However, they are now seeing that chemical processes, previously thought unimportant, are causing the Antarctic ozone hole; a substantial effect on regional ozone concentrations is resulting even from present chlorine levels (previously regarded as 'safe').

Because we are currently putting CFCs into the atmosphere five times faster than natural processes can dispose of them, the amounts of CFCs in the atmosphere will still be increasing even after the envisaged 50% cuts have taken place in 1999. If we wanted the amounts of atmospheric CFCs to grow no bigger, and the Antarctic ozone hole to stop deepening, we would need to cut their emissions by 85%.

As the Protocol stands at the moment, by 2020 stratospheric chlorine levels will be about three times the present level (10 times the amount present before use of CFCs became widespread).

Maybe if the Montreal delegates had known the results of the latest Antarctic probings they would have made the emission limitations more stringent. Fortunately, the Protocol contains provisions for reassessments, and these must be undertaken at least every 4 years.

Chlorine is it

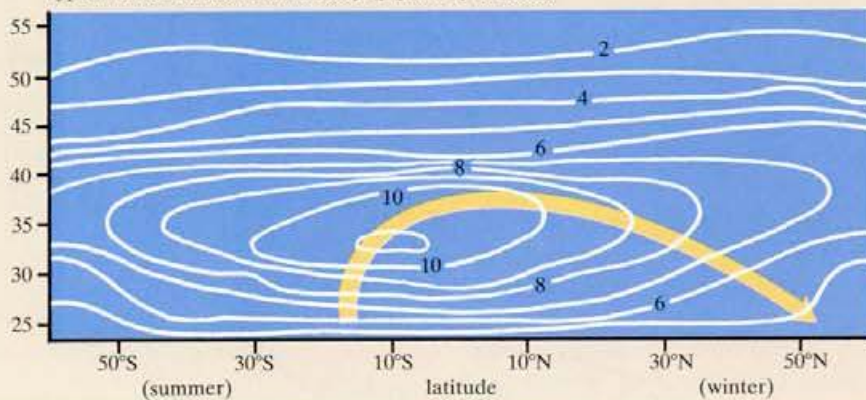
The latest Antarctic probings involved international teams of scientists and technicians operating high-flying aircraft out of southern Chile between 19 August and 30 September last year. Managed by NASA, the Airborne Antarctic Ozone Experiment saw researchers from agencies and universities in the United States, Britain, and several other countries working together to find the cause of the recurring Antarctic hole.

An ER-2 aircraft made 12 sorties from Punta Arenas (Chile's southernmost city) as far south as 72° and at altitudes up to 19.5 km, carrying sensitive instruments to measure the chemical content and meteorological properties of the air. A larger modified DC-8 made 13 flights; this heavily instrumented plane was limited to an altitude of 11.1 km, but it reached the South Pole on several occasions, and finally flew right across Antarctica to New Zealand. The scientists also made use of ground-based and satellite observations.

When the Experiment's initial findings were released on 30 September, it was immediately apparent that chlorine, acting within the unique Antarctic meteorology, was to blame for the ozone depletion. As

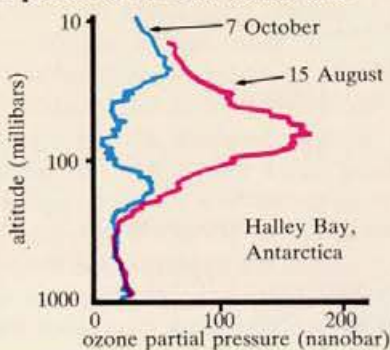
Ozone moves from Equator to Poles

typical levels of ozone in January (p.p.m. by volume)



Ozone is formed by sunlight — mostly above the Equator. Its predominant movement is from the Equator towards the winter Pole. Because the lower atmosphere is denser, most of the ozone can be found below 35 km (the peak in relative abundance).

A profile of the 1987 ozone hole



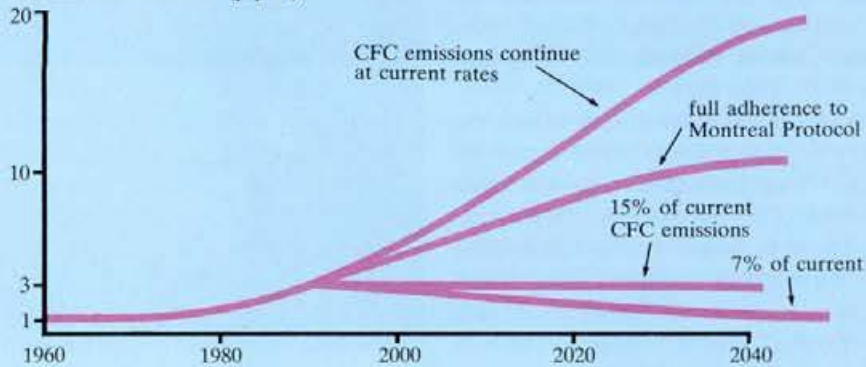
At a height of 16.5 km (70 millibars) the ozone concentration fell by 97% from the level recorded on 15 August 1987, before the 'hole' formed.

the ER-2 flew into the ozone hole, and ozone levels dwindled, the concentration of chlorine monoxide (the smoke from the CFC gun) rose steeply; indeed, small variations in one quantity were matched by opposite deviations in the other.

If we want to see a turnaround in the rising levels of stratospheric chlorine, we will need to cut emissions of CFCs to less than 15% of current rates. However, it should be noted that, although chlorine is the primary cause of ozone depletion, the concentrations of the two can't be directly related. In particular, chlorine is kept out of harm's way when it reacts with methane, and one of the incidental effects of accumulating greenhouse gases is to lower stratospheric temperatures and so favour ozone production.

Trends in stratospheric chlorine

chlorine concentration (p.p.b.)



The 1987 measurements confirm those of 1986, which revealed particularly low levels of NO_x, thus ruling out the solar cycle theory (wherein increased solar activity produces high levels of ozone-destroying nitrogen oxides).

The purely dynamical theories are not looking too good, either. Dr Plumb, an expert in the atmospheric dynamics of ozone transport, once favoured this sort of explanation, but he now believes that observations don't support any such picture.

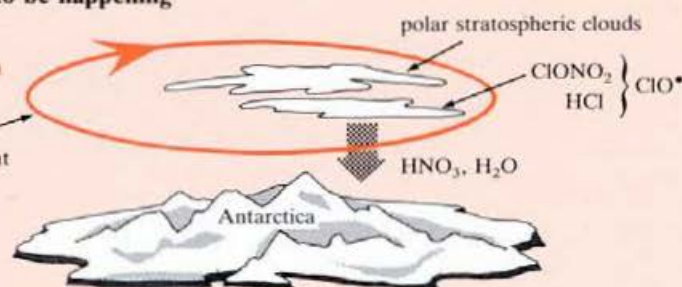
For example, the most popular dynamical theory — that ozone is depleted because the Antarctic sunrise causes upwelling from below — is incompatible with measurements of nitrous oxide (N₂O) and CFCs. These compounds, originating at the surface, should increase in the stratosphere if upwelling is going on. They don't!

And so, the chlorine theory seems to have come up trumps. The big question is

What seems to be happening

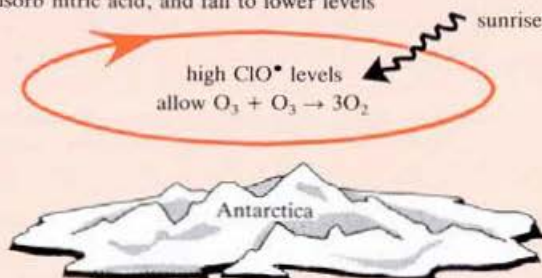
late winter:
precursors form

cold polar
vortex
(‘containment
vessel’)



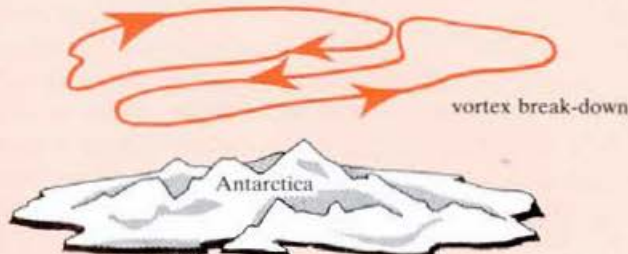
1. polar stratospheric clouds provide surfaces on which ClO^* can form they also adsorb nitric acid, and fall to lower levels

early spring:
formation of
ozone hole



2. with nitrogen absent, ClO^* cannot revert to ClONO_2 sunlight and ClO^* catalyse the reaction of ozone to oxygen

late spring:
break-up of
ozone hole



3. warming breaks up the polar vortex and the ozone hole is filled by air with normal ozone levels

no longer whether CFCs are responsible for ozone depletion, but rather how they do it.

Most researchers believe that the key lies with chemical reactions that take place on the surface of frozen particles in polar stratospheric clouds. The dark Antarctic stratosphere, isolated in the polar vortex, is intensely cold, reaching -85°C or lower; under these conditions water vapour passes the frost point and ice crystals form.

According to current theory (incomplete though it is), reactions on these crystals provide a reservoir of reactive chlorine that destroys ozone when the sun returns in the spring. Basically, the ice surfaces are required to convert chlorine from inactive forms (such as ClONO_2 and HCl) into active forms like ClO^*

To explain the observed ozone loss, the theory requires ClO^* levels of 1 part per billion — an amount at least 100 times greater than the normal stratospheric concentration. It further predicts that these high levels of ClO^* should be accompanied by low amounts of NO_x and H_2O because the cloud particles fall, taking away both ice and nitrates. With substances like nitric

acid out of the way, chlorine is free to destroy ozone.

Indeed, these predictions have received strong support from the recent Experiment. Levels of ClO^* did reach 1 p.p.b. in a clearly defined region above 18 km and poleward of 68°S ; NO_x and H_2O levels fell abnormally low, and high levels of nitrate were sometimes observed in collected ice particles.

The fast reaction between HCl and ClONO_2 in the presence of ice particles has recently been studied in the laboratory. It appears that chlorine gas (Cl_2) is liberated from ice particles and oxidised to ClO^* , while nitric acid (HNO_3) stays absorbed on them — just as required by the chlorine-blaming ozone-hole theory.

The theory also explains why an ozone hole appears in the Antarctic but not the Arctic: the Arctic stratosphere is perhaps 10° warmer (the polar vortex is not so strong there), and so stratospheric clouds are much less common.

It is becoming clear that meteorology sets up the special conditions required for the unusual chemistry. Scientists are now observing a finely tuned system involving

photochemistry and stratospheric circulation.

They are talking of the polar vortex creating a stratospheric ‘containment vessel’ in which ozone chemistry could proceed without being influenced by mixing with air below or outside. The ER-2 flights showed that the ozone hole remained well inside the vortex.

Why has the ozone hole formed and deepened so quickly, while CFC concentrations have been steadily increasing at only about 5% per year? Perhaps a slight upset in stratospheric circulation precipitated a major change in the chemistry of the containment vessel, some scientists are thinking. Thus, maybe a small reduction in temperature triggered the dramatic deepening of the ozone hole by increasing the amount of polar stratospheric clouds. Alternatively, perhaps the amount of ozone depletion depends very sensitively on the concentration of reactive chlorine (that is, there is a threshold effect).

For the future, two major questions remain outstanding, according to Dr Plumb:

- ▷ How, and to what extent, does the depth of the ozone hole depend on the level of stratospheric chlorine — ultimately, how deep can the hole get?
- ▷ Will loss of Antarctic ozone be followed by loss over the rest of the globe? If the explanation involving ice crystals in the polar vortex is correct, then the area suffering ozone destruction is unlikely to widen. Nevertheless, atmospheric mixing processes could reduce ozone levels outside the vortex simply by dilution.

Clearly, we need to advance rapidly to a full understanding of the processes that control the integrity of the ozone layer. Until we do, we cannot be totally confident that our present policies on CFC emissions won't lead to untoward effects. The Antarctic ozone hole has taught us that our understanding of ozone chemistry is lacking, and we'd best act prudently in preserving an unexpectedly fragile ozone layer.

Andrew Bell

More about the topic

Mystery of the Antarctic ‘ozone hole’. A. Bell. *Ecos* No. 52, 1987, 7–9.

‘Environmental, Health and Economic Implications of the Use of Chlorofluorocarbons as Aerosol Propellants and Possible Substitutes.’ Ed. P.J. Fraser. (Australian Environment Council and National Health and Medical Research Council: Canberra 1988.)