# Ozone comes down to earth

through a photochemical amog-North Sydney is blourd, and

Ozone is a form of oxygen with a pungent, refreshing odour, says the *Concise Oxford Dictionary*. Tell that to a citizen of Los Angeles, Sydney, or Melbourne on a day of photochemical smog. 'Acrid and irritating' would be a better description of the smell, and ozone certainly isn't good for you. A concentration of 6 parts per million (p.p.m.) can kill rats in 4 hours.

Concentrations of less than 0.8 p.p.m. have been shown to interfere with the functioning of human lungs. Adverse effects on vision have been detected at levels between 0.2 and 0.5 p.p.m.

The health-giving properties of the gas are mythical. It isn't ozone that smells good at the seaside; there's no more there than at ground level anywhere. However, we'd be lost without the stuff. The stratosphere, the region of the atmosphere about 15-60 km above ground, contains ozone in concentrations ranging up to more than 10 p.p.m. This is the shield that stops most of the sun's skin-cancercausing and sunburning ultraviolet radiation from reaching us. If that shield goes, we fry, which is why people were so concerned a few years ago when it was suggested that exhaust gases from supersonic passenger jets would set off reactions in the stratosphere that could drastically reduce ozone concentrations.

But it's nice to keep ozone at a distance, and that isn't easy when the sun shines over a city of hundreds of thousands of running cars, and climatic conditions and hills limit gas-mixing in the atmosphere. Ozone is the principal ingredient of photochemical smog, which results when ultraviolet rays from the sun encourage nitrogen oxides and hydrocarbons, mainly from car exhausts but also from factory chimneys, to react with atmospheric oxygen.

Concentrations up to 0.99 p.p.m. have been recorded on smoggy days in Los Angeles—well above the minimum level for adverse effects on lungs. Sydney and Melbourne have had readings of more than 0.25 p.p.m.; vision can be slightly affected at this level. Many big cities suffer photochemical smogs. A typical ozone level on a bad day is 0.20p.p.m. The natural ozone concentration near the ground is much lower, reaching a maximum of only about 0.03 p.p.m.

Clearly there are good reasons for scientists to take an interest in ozone in the atmosphere. There were good reasons even before people became aware of its role in city smogs and before supersonic jets were thought of. The CSIRO'S interest began nearly 20 years ago, and has continued and expanded. The ozonemonitoring network set up by the Organization's Division of Atmospheric Physics is the most extensive in the southern hemisphere and one of the most important in the world. Together with similar networks in the northern hemisphere, it can detect changes in the amount and distribution of ozone in the atmosphere. If jet flights or other human activities begin to affect the ozone shield, we should know about it fairly quickly.

#### Balloons

Ozone is oxygen with three atoms grouped together in each molecule rather than the two per molecule in the oxygen we breathe. Its concentration at different altitudes can be estimated by spectrographic methods —seeing how much solar radiation of the wavelengths that characterize ozone is absorbed on its way to the ground. Also, total amounts of ozone in the atmosphere above an area can be worked out this way. Balloon samplings give more precise data on concentrations at particular altitudes.

Ozone measurements can provide information on the movement of air in the stratosphere. This is what the CSIRO people were after initially, and it has remained a major interest. A reasonably detailed picture of the circulation of the southern hemisphere stratosphere has emerged, adding to knowledge of the processes going on in the atmosphere. But, as is so often the case, the new information is raising at least as many questions as it is answering. Things aren't simple up there.

The story starts at Aspendale, near Melbourne, in 1955, when the late Dr Bill Swinbank initiated regular spectrographic ozone measurements at the Division of Atmospheric (then Meteorological) Physics laboratories. The following year measurements began at Brisbane. In 1961

The payload measures ozone in the troposphere and stratosphere.









Dr R. N. Kulkarni took charge of the ozone program; he has since extended the monitoring network to Macquarie Island (about mid-way between Australia and Antarctica), Darwin, Hobart, and Perth. Since 1964, when Dr Barrie Pittock joined the project, weekly balloon flights from Aspendale have provided more-precise ozone measurements at altitudes up to 32 km. All stations except Aspendale are operated by the Bureau of Meteorology. All readings come to the Division.

## South and north differ

The ozone that shields us from the sun's ultraviolet rays is, paradoxically, produced by ultraviolet radiation from the sun. Production takes place in the stratosphere at altitudes above 30 km. Ultraviolet radiation with wavelengths of less than 240 nanometres (nm)-a nanometre is a thousand-millionth of a metre-breaks ordinary oxygen molecules into atoms. These then combine with other oxygen molecules, forming ozone. The ozone shield prevents all ultraviolet rays with wavelengths less than 290 nm from penetrating to the ground, and greatly reduces the amount of radiation up to 320 nm getting through. It is radiation with wavelengths below 320 nm that causes sunburn and skin cancer.

The CSIRO group's first major discovery was that the distribution of ozone in the southern hemisphere was quite different from that in the northern hemisphere. The CSIRO network data, with other people's data from the northern hemisphere and Antarctica, show that in the northern hemisphere the maximum ozone concentration is usually over the Arctic whereas in the southern hemisphere it is over the latitudes 40°-60° (Macquarie Island is about 54° South). The explanation for the difference is stronger poleward circulation in the northern hemisphere. What is the reason for that? The answer isn't known, but perhaps the much larger land area in the northern hemisphere affects air circulation.

Because equatorial regions receive the greatest intensity of solar radiation, most of the ozone is produced there. The poleward circulation takes it north and south. This circulation is much stronger in winter than summer; the fact that ozone maximums are observed in spring rather than summer or autumn shows this. Production would be greatest in either hemisphere in summer because the sun is more directly above then, but the stratospheric winter wind concentrates it.

The poleward circulation probably results from, among other things, greater ground-level heating in equatorial regions causing the air mass to rise there and spread outwards. Unfortunately some of the other fascinating information that the monitoring is throwing up is much more difficult to explain.

For example, in the late 1950s and early 1960s, spring maximum ozone concentrations in the stratosphere rose one year, fell the next, rose again, and then fell; there was a regular pattern of small but definite oscillations. Mr Geoff Garnham and the late Dr Peter Funk, of the Division of Atmospheric Physics, were the first to report this discovery. The oscillations stopped about 1963 but resumed in 1966 and have continued since then. About 1960 it was noticed that winds about 30 km above ground blow from the east one year and from the west the next; actually on average the wind is easterly for about 13 months and westerly for about

13. However, when the ozone oscillations stopped the wind cycle changed; the westerly blew for about 18 months and the easterly for about 14. Perhaps a link exists between the winds and ozone levels.

### Cycles and sunspots

There may be a link between both these cycles and the activity of the sun—sunspots, geomagnetic storms, and so on. About 1963–64, a trough in solar activity occurred, coinciding with the break in the ozone and wind cycles. The mechanism of the link, if it exists, is not known.

Increased solar activity since 1963, including a rise in ultraviolet radiation output, may also be associated with rises in the amount of atmospheric ozone measured in many parts of the world. Ozone increases of up to 10% between 1960 and 1969 have been reported overseas; the causes aren't known. A rise of 6% was measured at Darwin between 1966 and 1970 and one of 5.7% at Brisbane between 1960 and 1969.

Actually the increases may not be as great as they appear. Dr Kulkarni has examined evidence of change in the character of haze over Brisbane, and estimates that just over half the reported ozone increase there is due to calculation problems brought about by the change.

In the 1960s the number of smaller particles in the haze increased in relation to the number of larger ones. He calculates that the Brisbane ozone increase should come down to about 2.5%, and suggests that increases reported elsewhere should be reassessed in the light of these findings.

However, it appears that increases have definitely occurred since 1960, in spite of the fact that supersonic military jets have been flying in the stratosphere throughout



# Photochemical smog

Think of photochemical pollution and you're likely to think of Los Angeles. It was first noticed there in the early 1940s, and sometimes reaches very unhealthy concentrations.

In 1967 calculations were made, based on the Los Angeles experience and taking into account car numbers, climate, and so on, which indicated that photochemical pollution would come to Sydney about 1998. These were presented to the Scnate Committee on Air Pollution, along with a more pessimistic prediction that 1992 might be the year, and the Committee concluded in its report in 1969 that Sydney could face a photochemical pollution problem within 30 years. 'Australia is not immune to this kind of pollution,' it warned.

How right the Committee was. In the 5 years since it presented its report, both Sydney and Melbourne have experienced many photochemical smogs.

Photochemical pollution usually occurs in warm, calm, sunny weather. A temperature inversion-an increase in temperature with altitude instead of the normal decrease-stops the pollutants getting away by preventing up-and-down air mixing. Morning traffic and, to a lesser extent, factories emit oxides of nitrogen and various hydrocarbon compounds. These react, with the help of ultraviolet radiation from the sun, to produce the smog-a mixture of ozone, nitrogen oxides, and oxygenated hydrocarbons. When the smog reaches its peak, usually in the early afternoon, the ozone content vastly exceeds that of the other pollutants.

Photochemical smogs can be recognized by their acrid smell and haze. Also they cause eye irritation and dryness of the throat. Scientists have noted increases in attacks among asthma sufferers at ozone levels above 0.25 p.p.m., a sign of adverse effects on the respiratory system. The ozone can also damage some plants and cause rubber to crack.

The first indication of photochemical pollution in Melbourne came in March 1967, when 0.09 p.p.m. of ozone were measured in ground-level air at the Division of Atmospheric Physics laboratories at Aspendale, 30 km from the centre of Melbourne. This is about double the maximum ozone concentration found in unpolluted air.

Daily 1 p.m. readings at Aspendale from June 1968 produced maximums of 0.075 p.p.m. in 1968 and 0.11 p.p.m. in 1969, both indicating mild photochemical pollution. Between 1969 and 1971 the average 1 p.m. ozone reading rose by about half, indicating a marked increase in photochemical ozone production. The maximum ozone concentration measured at Aspendale up to the time this was



written was 0.14 p.p.m. on May 27, 1973.

The Victorian Environment Protection Authority now makes daily ozone measurements in the centre of Melbourne and publishes the results in the newspapers with figures for other air pollutants. The EPA's highest reading up to the same time was 0 26 p.p.m. on December 11, 1973—a day of unpleasant smog.

Sydney shares with Los Angeles some features that encourage the formation of photochemical smogs. It is about the same distance from the equator, bounded by mountains, and subject to similarly frequent, although briefer, temperature inversions overhead.

In 1969 the Air Pollution Control Branch of the New South Wales Department of Health conducted a survey in the city, which suggested that photochemical pollution didn't exist there or was minimal. Another survey in 1971 showed that it had well and truly arrived, with maximum readings of about 0.24 p.p.m. being recorded. Continuous measurements have been made in the city and at some suburban centres since December 1971. In 1972 concentrations greater than 0.08p.p.m. lasting for an hour were measured 137 times, and the maximum was just over 0.25 p.p.m. The highest reading up to the time this was written was 0.28 p.p.m., on March 1, 1973.

Photochemical pollution in Sydney and Melbourne so far has been mild compared with that in Los Angeles, where ozone readings up to 0.5 p.p.m. are not uncommon and the maximum to date, recorded in 1956, was 0.99 p.p.m. However, it has arrived with somewhat startling suddenness.



this period. Distribution has also changed. In the lower stratosphere, between about 10 km and 25 km, ozone concentration has decreased slightly over the last 8 years. Above 25 km it has increased. The changes are probably due to changing circulation strengths at the two levels, but what causes those is a mystery.

Dr Kulkarni believes clues to many of the puzzles about what goes on in the stratosphere may be found in the mesosphere, the atmospheric region next up from the stratosphere. His group has recently begun using spectrographic methods to look at turbulence at a height of about 100 km, and hopes to discover links with events below.

# Going down

The ozone swept poleward in the stratosphere from the equatorial regions also loses height. Eventually it and the air it is travelling with enter the troposphere, the bottom portion of the atmosphere. Researchers have estimated that in a year something like three-quarters of the air in the stratosphere flows down into the troposphere.

A feature that distinguishes the troposphere from the stratosphere is strong upand-down circulation. One result is that, while the ozone concentration in the stratosphere decreases rapidly as you head towards the ground, in the troposphere thorough mixing means that the concentration is virtually the same throughout. Similarly, exhaust gases from today's passenger jets (which fly in the troposphere) disperse rapidly. In the stratosphere dispersal is much slower; this is one of the causes of concern about what may happen if large numbers of jets are allowed to fly there.

The troposphere is the region of weather, and the scientists have found some interesting links between meteorological events and ozone measurements. For example, ozone concentrations increase behind low pressure systems and decrease behind highs. So far, no way to make use of ozone measurements in weather forecasting has been devised.

Eventually the ozone reaches the ground, and that's the end of the ozone. It is destroyed in a reaction that turns two ozone molecules into three ordinary oxygen molecules. A small proportion is destroyed earlier through contact with particles in the air.

Scientists have been measuring ozone at ground level for more than a century in both hemispheres. The oldest Australian measurements, made at Darwin, date back



Could exhaust from supersonic jets such as the Anglo-French Concorde and the Russian TU-144 set off a chain reaction that may greatly weaken the earth's ozone shield? It's most unlikely, but we ought to keep a close watch on what's going on up there, say the Australian Academy of Science and the Australian Advisory Committee on the Environment.

The possibility was added to the world's worries in 1971, when Professor Harold Johnston of the University of California estimated that 2 years' exhaust from the number of jets expected to be operating in 1985 would cause a reduction, increasing with altitude, of up to half in the amount of ozone in the stratosphere.

His theory is that ozone would react with nitric oxide (NO) from the exhaust to form oxygen molecules and nitrogen dioxide (NO<sub>2</sub>). Then nitrogen dioxide would react with atomic oxygen (O), producing more molecular oxygen and more nitric oxide. The nitric oxide produced by the second reaction would feed the first, which would continue to destroy stratospheric ozone.

The Advisory Committee on the Environment, in a report published in January this year, said the presence of naturally occurring nitrogen oxides in the stratosphere and the nature of the suggested reactions indicated that a reduction in atmospheric ozone should have already occurred if Professor Johnston's projections were correct. However, even though military aircraft had been flying for many years in the stratosphere, a  $10^{\circ}$  increase in ozone appeared to have occurred there. The Committee said the evidence tended to indicate that the Professor's projections were incorrect.

A report published by the Academy of Science in 1972 took a similar view. The Academy said it believed the effect of supersonic aircraft on the ozone layer was not likely to be serious, especially as there appeared to be no possibility of a rapid change occurring. But it said the problem was difficult to assess; unknowns included aspects of the chemistry proposed, the amounts of nitrogen oxides naturally present in the stratosphere, and emission rates from supersonic aircraft.

The Academy recommended that flying in the stratosphere should be kept to altitudes below about 18 km; it said significant destruction of ozone would be less likely there than higher up, where the ozone concentration is greater. It also recommended that the aircraft industry should take all possible steps to minimize nitrogen oxide emissions from engines.

Large fluctuations in ozone concentration in the stratosphere occur naturally; it is the possibility of a persistent reduction that causes concern. As well as producing more skin cancer and sunburn, even a relatively small increase in ultraviolet radiation in the 290–320 nm wavelength range could harm plants and animals and produce climatic changes resulting from a changed heating pattern in the atmosphere.

Scientists in the Department of Theoretical Physics at the University of Sydney have recently calculated the effects that a 10% reduction in ozone would have on amounts of ultraviolet radiation reaching the ground. They found that the increase would be proportionally greater the shorter the wavelength of the radiation and the further from the equator the measurement was made. For example, about mid-way between Melbourne and Hobart, 290 nm radiation would increase by about  $260^{\circ}_{\circ}$  in summer whereas 320 nm radiation would increase by only about 3º o. Farther north, near Townsville, 290 nm radiation would increase by about 180°  $_{0}$  and 320 nm radiation by about 2°  $_{0}$ .

However, the amount of radiation

reaching the ground goes up markedly with increasing wavelength between 290 and 320 nm, and even with increases of 180 or  $260^{\circ}$  the intensity of radiation in the 290 nm region would be very low. The effects of such increases are hard to estimate. It is known that rays with wavelengths between 300 and 310 nm are the most effective in causing sunburn. The calculations show that a  $10^{\circ/0}$  ozone reduction would increase 300 nm radiation in summer by about 42°, between Melbourne and Hobart and by about 32% near Townsville. The increases in 310 nm radiation would be about 10° o between Melbourne and Hobart and about 8% near Townsville.

The reports of both the Academy and the Advisory Committee stress the importance of monitoring ozone concentrations. The Academy also says a monitoring program for oxides of nitrogen would be valuable; this would help show whether any significant change in ozone concentrations was due to supersonic aircraft flights. In line with this suggestion, Dr Kulkarni's group is planning to monitor oxides of nitrogen over Aspendale, Brisbane, and Darwin using spectrographic techniques. The equipment will be able to measure nitrogen oxide totals in the atmosphere but not concentrations at different levels.

The Academy report also says it would be desirable to monitor ultraviolet radiation in the skin-cancer-causing and sunburning wavelength range. This was done, in a University of Queensland project, at Goroka, Townsville, Cloncurry, Brisbane, and Aspendale in the 1960s. A new ultraviolet-monitoring program, jointly organized by the CSIRO Division of Atmospheric Physics and the Physics Department of the University of Queensland, should be under way by the end of this year. to the 1860s. Ozone was measured in the Antarctic during the 1901-04 expedition led by Robert Falcon Scott, the British explorer who died in 1912 on his way back to base from the South Pole. Scientists have since greatly improved measuring techniques, and ground measurements are now made regularly in many countries.

Dr Kulkarni initiated a ground-level monitoring program in Australia in 1964, together with research aimed at working out the rates at which ozone is destroyed. This work was taken over by Mr Ian Galbally in 1966, and surface measurements are now made continuously at Aspendale, Darwin, Macquarie Island, and Robertson, N.S.W. The research may help make it possible eventually to piece together an 'ozone budget' for the earth, based on rates of production, lengths of stay in different parts of the atmosphere, and rates of destruction.

## Up by day, down by night

The usual thing is for ozone at the surface to reach a maximum concentration of up to 0.03 p.p.m. during the day and drop back to nearly zero at night. If there is little up-and-down motion in the air, which is usually the case at night, ozone destroyed at the surface is not quickly replaced and the concentration falls. If, on the other hand, strong turbulence exists —and it usually does during the day—the ozone at the surface is constantly replenished and the ground-level concentration rises to about that of the rest of the troposphere.

Mr Galbally measured destruction rates at soil and vegetation surfaces near Edithvale, Vic., and Hay, N.S.W., and at snow surfaces on Mt Buller, Vic. Measurements were also made at Mawson, Antarctica, in a cooperative experiment with the Antarctic Division of the Department of Science. He found that land is about 10 times more efficient as a destroyer than the sea, with snow somewhere in between. A soil-andgrass surface can destroy most of the ozone in the bottom 1 km of the atmosphere in 24 hours.

While snow is not so efficient, it seems to be able to cling to ozone as well as destroy it. Mr Galbally has found that in strong winds, when surface snow is tumbling over lower layers, there is sometimes a large take-up of ozone. Later, the snow surface gives off large amounts. He concludes that blowing snow is able to attach ozone to itself without destroying it.

The sea is a relatively inefficient ozonedestroyer, but it is efficient enough to keep ozone concentrations above it at the same It isn't ozone that smells good at the seaside . . . More probably it's the smell of rotting seaweed or other aquatic organisms.



levels as those above land. The refreshing odour at the seaside that is popularly believed to be ozone isn't caused by a build-up of the gas at the point where the destruction efficiency plummets; no such build-up occurs. More probably it's the smell of rotting seaweed or other aquatic organisms.

# More about the topic

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