

# From soil to stratosphere?

Of all the suggested threats to the earth's protective ozone layer, perhaps the most insidious is the growing use of nitrogen fertilizers and nitrogen-fixing plants. The fear is that worldwide increases in the levels of soil nitrogen will boost the emission rate of nitrous oxide from the ground and that this will reduce ozone concentrations in the upper atmosphere.



**An Atmospheric Physics stratosphere probe is prepared for launching at Mildura.**



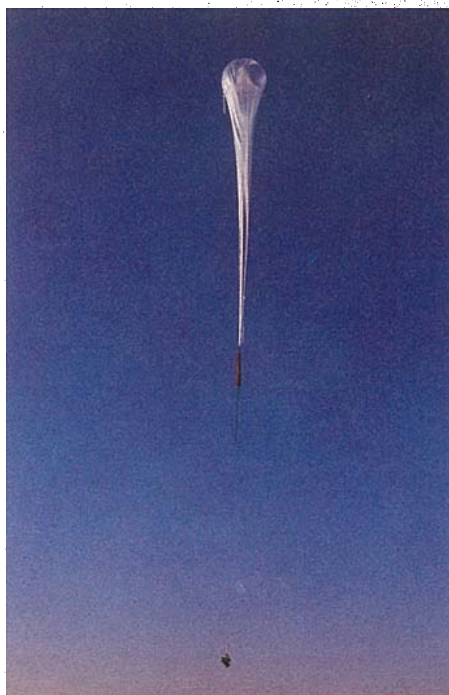
**The instrument package is retrieved from its bush landing site.**

The reason why some people are particularly concerned at this possibility is not that a real threat has been shown to exist; in fact, the hypothesis is riddled with uncertainties. The problem is that, if the threat does prove real, we may have to live with it. While the world could get by without supersonic jets and spray cans with fluorocarbon propellants — the other suggested major sources of man-made ozone-destroying gases — increasing levels of soil nitrogen will probably be essential if food production is to keep pace with the needs of the world's rapidly growing population.

However, changes in the ways the fertilizers are manufactured and applied may make it possible to increase the amounts used without boosting nitrous oxide emissions.

If the ozone content of the stratosphere does decrease, more ultraviolet radiation of the kind that can cause skin cancer and reduce plant growth will reach the ground. Some changes in world climate would also be likely. *Ecos 14* looked at effects that might follow an ozone reduction.

Ozone is continuously created and destroyed in the stratosphere, and the balance between the rates of creation and destruction determines how much is present at any time. The impact of short-wavelength ultraviolet radiation from the sun on ordinary oxygen produces the ozone, and various chemical reactions destroy it. By injecting into the atmosphere chemicals able to take part in these reactions, technological Man



**The balloon begins to expand as it rises.**

can increase the rate of destruction, and hence reduce average concentrations.

Two nitrogen oxides, nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>), appear to be the main natural compounds involved in the ozone-destroying process. They form in the stratosphere from nitrous oxide (N<sub>2</sub>O), which originates in soil and the oceans.

Nitrous oxide production is a step in the biological nitrogen cycle, on which all life depends. In this cycle, nitrogen gas from the air is 'fixed' to form compounds that plants and animals can use. Later, it returns to the atmosphere.

Some returns as nitrogen gas (N<sub>2</sub>), and some as the compounds ammonia (NH<sub>3</sub>), nitric oxide, nitrogen dioxide, and nitrous oxide. All those compounds, except nitrous oxide, are removed rapidly from the lower atmosphere and return their nitrogen to the soil. The only known fate of nitrous oxide in the natural environment, however, is conversion in the stratosphere to ozone-destroying nitric oxide, and to nitrogen dioxide.

Globally, microorganisms that fix nitrogen from the air are the main source of soil nitrogen. The best known and probably most important are bacteria of the genus *Rhizobium*, which operate from the root nodules of clover and other legumes.

Increased use of legumes in agriculture this century has presumably increased the amount of nitrogen in soil throughout the world. So has the spreading of nitrogen fertilizers, which adds nitrogen in fixed form directly to the soil.

According to estimates produced by the United States Council for Agricultural Science and Technology (CAST), worldwide use of fertilizer nitrogen rose from about 3.5 million tonnes in 1950 to nearly 40 million tonnes in 1974. The Council predicts that this figure will grow to between 100 and 200 million tonnes per year by the end of the century. By comparison, CAST estimates that addition of nitrogen to the soil by crops and pasture plants rose only from about 70 million tonnes per year around 1850 to about 89 million tonnes in 1974.

## Glaring gaps

The argument that rapidly growing use of nitrogen fertilizers could pose a threat to the ozone layer rests on the assumption that the increasing addition of nitrogen to the soil will boost nitrous oxide emissions. Increasing use of nitrogen-fixing plants in agriculture could add to the problem. In a report published in 1976, CAST described the potential hazard as serious. The report listed glaring information gaps, and said present data were inadequate to inspire confidence in any of the predictions that have been made about impact on the ozone layer. CAST called for research in many areas.

We don't even know whether concentrations of nitrous oxide in the atmosphere are rising, as they should be if emissions are increasing. Measurements in the United States and West Germany between 1966 and 1968 indicated a rising trend; the West German readings showed nitrous oxide concentrations rising from about 250 to 300 parts per billion (or thousand million). But a few years later, the German scientists were again measuring concentrations of about 250 p.p.b.

Nitrous oxide measurements are few and far between. Dr Colin Roy of the CSIRO Division of Atmospheric Physics took steps to help remedy this situation about 2 years ago, when he began a regular monitoring program.

He measures concentrations of the gas in air collected for the Division's carbon dioxide program (see *Ecos* 7) over Australia and the Tasman Sea, and at the Baseline Air Pollution Station at Cape Grim, Tasmania. Concentrations are also measured daily in

## The hypothesis is riddled with uncertainties.

surface air at the Division's Aspendale, Melbourne, site.

So far, he has detected no trend in concentrations. The data indicate that nitrous oxide is mixed very evenly up to the stratosphere, at a concentration of about 300 p.p.b.

Dr Roy hopes the monitoring will reveal any differences between concentrations in air over land and sea, as these could provide information on the relative sizes of different sources of the gas. They might also point to areas where the gas is destroyed.

A small but statistically significant difference has already shown up; concentrations measured in marine air are about 3–4 p.p.b. lower than those measured in air that has passed over land. The reasons for the difference are being investigated.

Variations in concentration with altitude could provide information on how long the average nitrous oxide molecule takes to rise to the stratosphere — information that could throw light on the possible effects of increased emissions.

## Microbial effects

The natural process producing nitrous oxide about which most is known, and which has been assumed to be the most important, is denitrification. In this process, soil microbes produce nitrogen gas and nitrous oxide from

nitrate ions. Denitrification occurs in water-logged soil and at depth in drier soil — where oxygen is scarce.

Recent research by three CSIRO scientists in Canberra — Dr John Freney and Dr Jeff Simpson, of the Division of Plant Industry, and Dr Tom Denmead of the Division of Environmental Mechanics — suggests that some other microbial process may also be important. Unexpectedly, the scientists detected considerable nitrous oxide emissions from soil exposed to atmospheric oxygen.

In the laboratory, all soils studied, ranging from dry to saturated with water, emitted the gas. The scientists found that, in the field, emissions increased as the temperature of the top soil layer rose. Probably because of this, more nitrous oxide was produced during the day than at night. Adding water produced an immediate marked increase in emissions.

The link with the temperature of near-surface soil and the immediate response to small additions of water indicate that some, at least, of the gas is produced very close to the surface. This would not be expected if denitrification were the only process involved.

Another interesting finding by the Canberra scientists is that soil can simultaneously emit nitrous oxide and increase its nitrate content. As denitrification involves the conversion of nitrate to other compounds including nitrous oxide, some other process must be occurring. The scientists think the nitrous oxide must be coming off during the microbial conversion of ammonia to nitrate, a process that occurs only in aerated soil.

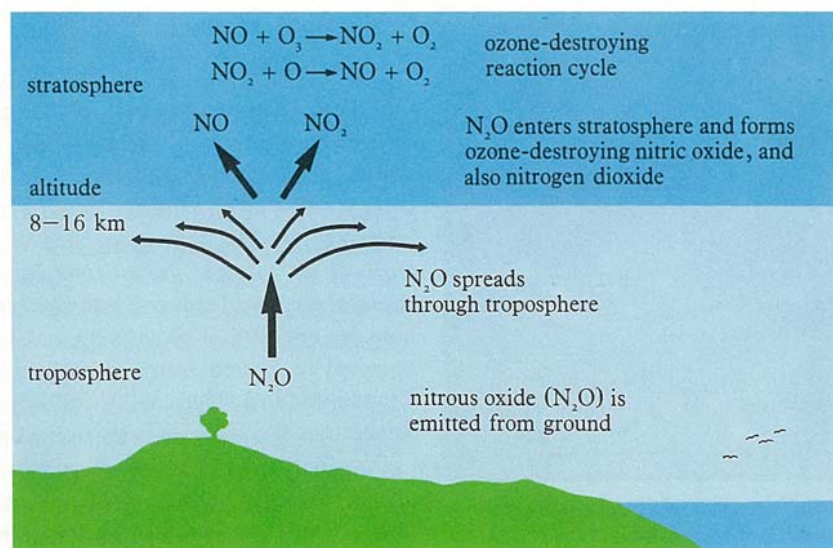
## Data needed

Clearly much remains to be learnt about the processes that produce nitrous oxide in the soil. If world-wide emission rates are to be determined, scientists will need a great deal of information that doesn't exist now on the influence of different soil conditions, and vegetation covers, on emissions.

Lacking this information, people attempting to find out what impact, if any, increasing fertilizer application is having on the ozone layer use indirect means to estimate the earth's nitrous oxide output. One method is to assume that all the nitrogen removed from the atmosphere by fixation eventually returns as either nitrogen gas or nitrous oxide — an assumption that may or may not be valid.

Many problems arise. Not only is an estimate of the world-wide fixation rate required, but also an estimate of the average time it takes for fixed nitrogen to return to the atmosphere. More difficult still, an estimate has to be made of the average ratio of nitrous

## Nitrous oxide and the stratosphere



Nitrous oxide emissions from the ground appear to be the main natural source of ozone-destroying compounds. Use of nitrogen fertilizers may increase these emissions.



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*The data should provide more evidence of how important the nitrogen compounds are as ozone-destroyers.*

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oxide to nitrogen gas in the emissions.

A number of studies have drawn together the limited data that exist on fixation rates. Two of the most recent came from CAST and the Scientific Committee on Problems of the Environment (SCOPE).

Both accepted as reasonable an estimate that, in recent years, crops and pasture plants have fixed about 89 million tonnes annually.

From evidence that it described as 'very patchy', CAST adopted a figure of 50 million tonnes a year for nitrogen fixation in forests. The SCOPE report settled for 40 million tonnes. Both adopted 10 million tonnes a year as the figure for unused land — including desert, tundra, marsh, bog, savannah, and alpine areas. CAST described this estimate as 'very rough'.

Other producers of fixed nitrogen include lightning and the combustion of fossil fuels. CAST suggests figures of 10 million and 20 million tonnes for their respective contributions. SCOPE adopted 19 million tonnes as the figure for combustion.

The estimates put forward with most confidence are those for fixation by the fertilizer and other industries. CAST's total for 1974 is 57 million tonnes of nitrogen, of which 39 million tonnes were used as fertilizer. SCOPE's total, for 1970, is 36 million tonnes.

## All at sea

Now we come to the ocean, an area of great uncertainty. CAST settled on a figure of just 1 million tonnes for the amount of nitrogen fixed by blue-green algae and other ocean organisms, and concluded that rainfall and river flow were bigger contributors of fixed nitrogen to the sea. SCOPE suggested that much more nitrogen is fixed in ocean waters — possibly 30–130 million tonnes a year.

Observations in the North Atlantic show that ocean surface waters there are more than saturated with nitrous oxide, and estimates based on the degree of supersaturation put emissions of nitrogen in nitrous oxide from the world's oceans at perhaps 50–100 million tonnes a year. This seems a large amount, even if the highest estimate of fixation in the seas is correct.

Both in the ocean and on land, the average ratio of nitrogen gas to nitrous oxide emissions is one of the big unknowns. The few observations that have been made of denitrification in the sea suggest that there is very little nitrous oxide in the gas given off. On land, the ratio appears to vary widely. In a recent experiment, Dr Denmead, Dr Freney, and Dr Simpson came up with a figure of about 1% nitrous oxide for emissions from a flooded rice field near Deniliquin, N.S.W. From all the studies available, CAST concluded tentatively that perhaps 6% of the nitrogen emitted on land is in the form of nitrous oxide. CAST had no data from the field.

If the global average is 6% and the amount of nitrogen emitted as nitrous oxide and nitrogen gas in a year equals the amount fixed, then, on CAST's figures for fixation, annual emissions of nitrogen in nitrous oxide should be about 13 million tonnes. On the evidence, emissions from the ocean could be

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anything from about 1 million to 100 million tonnes per year.

## Where does it go?

What happens to the nitrous oxide? The only place where it is known to be destroyed is the stratosphere, and research by Dr Paul Crutzen of the United States National Center for Atmospheric Research suggests that only 9 million tonnes are destroyed there per year.

If, in fact, more nitrous oxide is emitted from the surface than is destroyed in the stratosphere, some must be destroyed elsewhere, and some scientists suggest that the ocean, or some land areas, may extract large quantities from the air.

A group of English scientists, for example, has attributed a slight fall in concentrations measured near the ground at night to absorption of nitrous oxide by soil. They suggest that the night-time inversion layer prevents nitrous oxide from higher in the atmosphere moving down to replace the absorbed gas. When the inversion breaks up during the day, air mixing causes concentrations near the surface to rise again to average values for the lower atmosphere.

The Canberra scientists also have measured slightly lower concentrations near the ground at night. However, they attribute them to lower emission rates — probably due to lower soil temperatures — rather than to absorption of nitrous oxide.

## Two forecasts

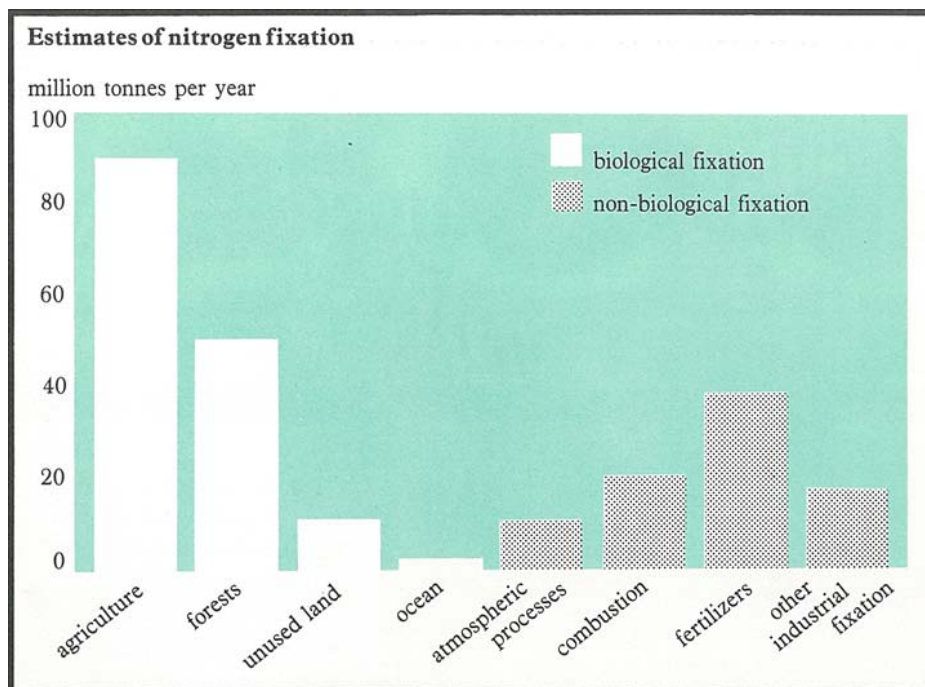
CAST used two approaches in its attempt to forecast the effects of increased nitrogen fertilizer use on ozone concentrations. In both cases it relied on an estimate, derived from laboratory studies, that a doubling of the amount of nitrous oxide entering the stratosphere would reduce ozone concentrations by one-fifth. This estimate has been accepted in United States Department of Transport and National Academy of Sciences studies of threat to the ozone layer.

One approach was based on estimates of total world-wide nitrogen fixation. CAST first assumed that fixation increased from 174 million tonnes in 1950 to 237 million tonnes in 1974, and then remained steady until the amount of nitrogen emitted annually as nitrous oxide and nitrogen gas



**Chamber for measuring emissions of nitrous oxide from soil.**

**Measuring nitrogen losses from a flooded rice paddy at Coleambally, N.S.W.**



These estimates, by CAST, are for world fixation in 1974. All except those for fertilizers and other industrial fixation are highly uncertain.

equalled the amount fixed. Using the estimated relation between nitrous oxide increases and ozone levels, the expected eventual ozone reduction came to 7.2%.

If annual nitrogen fixation reached a level 200 million tonnes above the 1950 figure — which could happen by the end of the century if use of nitrogen fertilizer continues to increase rapidly — and remained at that level, the eventual ozone reduction derived by the same method is 23%.

How long these reductions took to occur would depend on the time taken for nitrogen fixation and emissions to reach equilibrium. This could be years or centuries. It would also depend on how long the average nitrous oxide molecule takes to rise from the ground to the ozone layer.

The other method CAST used to calculate possible ozone reductions relies on an estimate — derived from measured variations in ozone concentrations in the lower atmosphere — that the average nitrous oxide molecule is destroyed about 10 years after it is emitted. If this is the case, something like 130 million tonnes of nitrogen in the form of nitrous oxide must be emitted each year to maintain the gas at its concentration of about 300 p.p.b.

As this is a much bigger output than that assumed in the other calculations, any increase produced by nitrogen fertilizers would represent a much smaller proportion of total emissions. As a result, this method gives much smaller predicted ozone reductions — somewhere between 1% and 4% for an increase of 200 million tonnes a year in nitrogen fixation over the 1950 level.

Clearly, if reliable predictions are to be made of the possible effects of increased fertilizer use on the ozone layer, much more information is needed. Uncertainties about the processes in the stratosphere that destroy ozone haven't been mentioned yet, but they are substantial too.

Recent laboratory studies in the United States suggest that nitrogen oxides may be somewhat less important, and derivatives of water vapour somewhat more important, than previously thought as ozone-destroyers. However, the nitrogen oxides still appear to account for perhaps half of total ozone destruction.

#### High-level checks

Dr Ian Galbally and Dr Roy, of the Division of Atmospheric Physics, are using balloons to send instruments into the stratosphere to measure concentrations of nitrogen oxides there. The data that come back should provide more evidence of how important the nitrogen compounds are as ozone-destroyers.

The stratospheric measurements are a joint project with Professor Brian Ridley of York University, Canada, who has made similar measurements over North America. The helium-filled balloons that carry the measuring instruments reach an altitude of about 34 km.

The first launching, from Mildura last December, revealed steadily rising concentrations of nitric oxide — from about 0.2 p.p.b. to 7 p.p.b. — as the balloon gained height in the stratosphere. Temperatures, winds, and ozone concentrations were also

measured, to assist interpretation of the nitric oxide data.

The scientists are planning further launchings, and intend in future to measure nitrous oxide and nitrogen dioxide as well as nitric oxide. They will also measure nitric acid, which is believed to form from nitric oxide and nitrogen dioxide, ending the careers of these gases as ozone-destroyers. The rate of nitric acid formation may be an important factor influencing the rate of ozone destruction.

Launchings are being planned for autumn, when ozone concentrations are lowest, and spring, when they are highest. By making measurements above Alice Springs as well as Mildura, the scientists hope to find out something about the way reactions in the stratosphere differ with distance from the equator.

Projects are under way overseas to measure other chemicals involved in the destruction of ozone in the stratosphere — notably derivatives of chlorine and water vapour. When all the data are put together, a clearer picture should emerge of the natural destruction processes and any impacts that Man's activities could have on them.

#### More about the topic

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