

Spray cans and the ozone layer

Shortly after World War II, researchers in the United States discovered that two compounds of chlorine, fluorine, and carbon, used since the 1930s as refrigerants, were also very good at dispensing aerosol sprays from conveniently sized cans. These fluorocarbon gases, commonly referred to by the trade name 'freon', made possible the now ubiquitous deodorant and hair-spray aerosol cans, and are also used to eject many other products from their containers. In 1951 another use was found for them — in production of the foam plastics polyurethane and polystyrene.

Sooner or later, the fluorocarbons find their way into the atmosphere. Spray cans now account for about three-quarters of world-wide emissions, while the remaining quarter is divided almost evenly between air-conditioning and refrigeration on the one hand and foam-plastics production on the other.

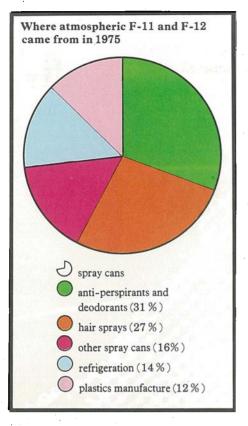
In 1975, something like 3000 million cans ejected more than 500 000 tonnes of the fluorocarbons. Hair sprays, and deodorants and anti-perspirants, accounted for about three-quarters of this output, and cans containing a myriad of other products, including medicines, insecticides, and various coatings, released the rest.

The fluorocarbons perform their functions excellently. Moreover, they are non-flammable, non-toxic except at very high concentrations, and odourless, and they do not leave stains. They are also unusually inert chemically, an important quality that, among other advantages, gives spray cans containing them a long shelf life.

This inertness, however, has one serious disadvantage that was not recognized until 1974. It means that fluorocarbons released into the atmosphere, unlike many other air pollutants, are not quickly broken down and removed. Scientists are now suggesting that rising concentrations in the atmosphere are a threat to us all. The CSIRO Division of Atmospheric Physics, and various organizations in other countries, now include fluorocarbons among the atmospheric constituents regularly monitored.

Causes for concern

The first-recognized and probably most important cause for concern is the possibility that fluorocarbons reaching the stratosphere will reduce concentrations of ozone there, with the result that more ultraviolet radiation from the sun will reach the earth's surface. Possible consequences include an increased incidence of





Spray cans on display.

skin cancer and harm to some animal and plant species, including crop plants.

The other main risk is that increasing fluorocarbon concentrations in the atmosphere will tend to gradually increase temperatures at the earth's surface because of the efficiency of the fluorocarbons, even greater than that of carbon dioxide and water vapour, at trapping outgoing thermal radiation.

The two compounds causing the concern are commonly referred to as F-11 and F-12; their chemical formulae are CCl_3F (F-11) and CCl_2F_2 (F-12). They have different boiling points, vapour pressures, and other properties, and can be mixed, or used singly, in different applications. In an aerosol can, for example, F-12 gives the type of high-pressure spray sometimes wanted with insecticides or paints, while F-11 gives a much more gentle spray and is used with things like hair sprays.

World-wide production and release of these fluorocarbons grew by about 10%per year up to 1974, and then fell in 1975 and 1976 by about 15%. Total output in 1975 was nearly 700 000 tonnes, divided in about a 3:2 ratio between F-12 and F-11. How much of the fall in output was due to concern about the hazards of fluorocarbons and how much to the world economic slump and the economic attractiveness of competing products can only be guessed.

In Australia, production in the financial year 1975-76 totalled about 16 000 tonnes — only 2% of world output and was divided almost equally between F-11 and F-12. Here, too, production fell last year — by something like 10% — after many years of strong growth.

Assessing the risks

Since the first scientific report expressing concern about the possible impacts of these compounds in the stratosphere was published in 1974, considerable effort has been put into assessing the risks.

Most activity has been in the United States, by far the world's largest producer of F-11 and F-12 and the source of nearly half the total output. In January 1975 the Federal Interagency Task Force on Inadvertent Modification of the Stratosphere was set up, and its first job was to conduct an intensive study of the fluorocarbon-ozone question. Late last year the Committee on Impacts of Stratospheric Change of the United States National Research Council completed a detailed study of all environmental effects of release of the chemicals.

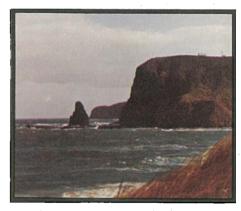
The biggest monitoring program, which has been operating for nearly 4 years, is run by that country's National Oceanic and Atmospheric Administration. Under it, air is collected regularly in Alaska, Hawaii, and American Samoa, and sent for analysis. Fluorocarbon measurements are also made regularly at other monitoring stations around the world, and occasionally from ships and aircraft.

In April last year, the CSIRO Division of Atmospheric Physics began a program

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Members of the CSIRO team prepare instrument packages for a balloon of the type they plan to use to obtain stratospheric air samples for fluorocarbon measurements.



Isolated Cape Grim, Tasmania. The Baseline Air Pollution Station is on the headland.

to measure concentrations in the atmosphere over Australia. Dr Paul Fraser uses a gas chromatograph at the Division's Aspendale, Melbourne, headquarters to measure F-11 levels in air samples collected as part of the carbon-dioxidemonitoring program run by Dr Graeme Pearman.

The CSIRO scientists hope to be able, from both their data and results from other monitoring programs, to work out world-wide average F-11 concentration figures. By comparing these with estimates derived from emission data, they hope to find out how much F-11 is removed naturally from the troposphere — the portion of the atmosphere between the ground and the stratosphere. Experiments to date indicate that very little is removed: the oceans appear to absorb 2-4% of annual emissions, and photochemical reactions to destroy another 1-2%.

By analysing air collected at different altitudes, the scientists also hope to learn more about the way F-11 moves upwards towards the stratosphere.

Last November, the CSIRO team took the opportunity to check their measurements against those made on board an aircraft used by the United States National Aeronautics and Space Administration (NASA) in a survey of minor atmospheric constituents. The NASA team measured concentrations of fluorocarbons, and many other things, at altitudes up to about 12 000 metres, virtually from the North Pole to the South. They were based in Melbourne for 3 days, and during this time the CSIRO team stepped up their monitoring effort. The two sets of readings agreed well.

In October last year, direct measurements of F-11 began at the Baseline Air Pollution Station, recently set up at Cape Grim on the north-western tip of Tasmania (see *Ecos* 13).

A rapid rise

The picture emerging from all the monitoring is of atmospheric concentrations that are rising rather rapidly. The data on F-11 show annual increases ranging from 13 to 28%. The CSIRO measurements show a 19% increase in the region above Australia between the beginning of April 1976 and the end of March 1977.

The monitoring results show that the fluorocarbons spread rapidly throughout the troposphere. As a result, concentrations are only 5-10% lower in the

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Southern Hemisphere than north of the equator, despite the fact that about 95% of releases occur in the Northern Hemisphere. Southern Hemisphere concentrations late last year were about 120 parts per million million (usually referred to as parts per trillion, or p.p.t.) by volume for F-11 and 200 p.p.t. for F-12.

In the stratosphere, where the bulk of the atmosphere's ozone is concentrated, many more measurements will be needed before the distribution of the fluorocarbons is known accurately. However, concentrations there are certainly well below those in the lower atmosphere. Measurements of F-11 in air collected from a high-flying U2 aircraft in October and November last year showed falling concentrations between sampling heights of 15.2 and 21.3 km.

Two factors account for the lower concentrations in the stratosphere. One is the slow rate of movement of air from the troposphere into the stratosphere. The other is the fact that, in the stratosphere, the fluorocarbons are finally broken down by ultraviolet radiation.

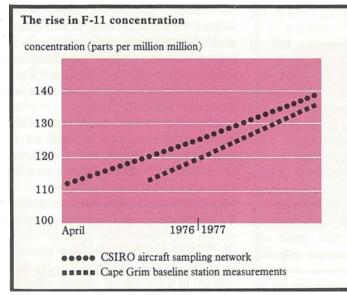
The United States National Research Council's Committee on Impacts of Stratospheric Change estimated that the average F-11 and F-12 molecule takes several decades to reach the heights in the stratosphere, above 25 km, where this breakdown occurs. It is products of the breakdown that take part in ozonedestroying reactions; hence, several decades are likely to pass before fluorocarbons emitted today will have any impact on ozone levels.

The ozone shield

Ozone (O_3) is created continuously in the stratosphere. Ordinary oxygen molecules (O_2) absorb ultraviolet radiation at wavelengths below 240 nm (nanometres, or m⁻⁹), the molecules split into atoms (O), and some of these combine with other oxygen molecules. The result is that, where there was only O_2 , we now have a mixture of O, O_2 , and O_3 .

This ozone prevents all ultraviolet radiation with wavelengths of less than about 290 nm from reaching the ground, which is fortunate because excessive ultraviolet is most dangerous to living things at wavelengths around 265 nm. It also stops most ultraviolet radiation in the 290 nm to 320 nm range; the small amounts that filter through can cause skin cancer and sunburn. Above 320 nm, ultraviolet radiation is harmless, and comes through largely unhindered.

Ozone is also continuously destroyed. Concentrations in the stratosphere fluctuate with natural changes in the rates of production and destruction; in any year, maximum concentrations in spring can be half as high again as autumn minimums, and smaller changes in average concentrations occur from year to year. Nothing Man can do is likely to change production rates, but by adding chemicals such as F-11 and F-12 he can possibly



This graph shows how F-11 concentrations have risen since CSIRO'S monitoring program began in April last year.



The aircraft used in NASA's survey of atmospheric constituents flies out to sea over San Francisco's Golden Gate Bridge.

increase the rate of destruction and, as a consequence, reduce average concentrations.

The main natural destroyers, converting perhaps two-thirds of the ozone produced back to molecular oxygen, are oxides of nitrogen. Others include oxygen atoms, hydrogen atoms, and various combinations of hydrogen and oxygen. Chlorine atoms (Cl) and a combination of chlorine and oxygen (ClO) are minor natural destroyers. They are also the destructive agents contributed by F-11 and F-12.

If the chlorine released from each molecule of the fluorocarbons reaching the stratosphere could destroy only one ozone molecule, its impact would be minimal. The problem arises because that chlorine can destroy thousands of ozone molecules through catalytic reaction cycles such as:

 $Cl + O_3 \rightarrow ClO + O_2$ coupled with $ClO + O \rightarrow Cl + O_2$

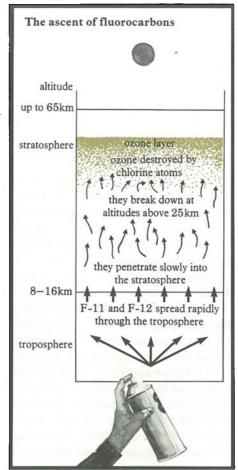
The destruction stops when other reactions occur that incorporate the chlorine in compounds that do not react with ozone.

Uncertainty

The National Research Council committee that examined the environmental effects of F-11 and F-12 releases had no doubt that the fluorocarbons contribute to destruction of ozone. However, its report reveals great uncertainty about the size of the impact. Certainly no ozone reduction attributable to these compounds — or to any other products of Man's technology such as exhausts from supersonic jets, which leave behind nitrogen oxides has been measured yet.

This is not surprising; the NRC report estimates that the fluorocarbons released so far may have reduced ozone concentrations by 0.5%, an amount that would be obscured from detection by the much larger natural fluctuations. Dr Rangnath Kulkarni, who runs the CSIRO Division of Atmospheric Physics ozonemonitoring program, reports one recent natural fluctuation — unexpectedly high ozone readings over Australia in spring last year.

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The chlorine released when F-11 and F-12 break down may increase the rate of ozone destruction. This could lead to reductions in ozone concentrations and a consequent increase in the amount of harmful ultraviolet radiation reaching the earth's surface.

It is important to remember, however, that even if production of F-11 and F-12 stopped today it would be many years, possibly a decade, before fluorocarboninduced ozone destruction reached its peak and began to decline — because air moves so slowly into, and upwards in, the stratosphere.

The NRC report estimates that, if world-wide F-11 and F-12 production continues indefinitely at the 1973 rate, there is a 95% chance that the amount of ozone in the stratosphere will eventually be reduced by between 2 and 20%. It puts the most likely reduction at 7%. Because things move so slowly in the stratosphere, 40 or 50 years would pass before just half the ultimate ozone reduction occurred. If annual output, instead of remaining at the 1973 level, doubles within 10 years and then levels off, the expected eventual ozone reduction doubles.

The biggest area of uncertainty in the calculations is the chemistry of ozone destruction in the stratosphere. One of the

most important questions is how quickly, on average, destructive Cl and ClO form compounds that do not threaten ozone. Last year it was found that the compound ClONO₂ is much more important than previously expected as a reservoir of chlorine in the stratosphere, and this led the NRC committee to lower its predictions of ozone reduction by nearly half. The other main area of uncertainty is in how much of the released F-11 and F-12 finds its way to levels in the stratosphere where it can participate in ozone destruction and how long its rise takes.

Effects of ozone reduction

As well as monitoring ozone levels, the Division of Atmospheric Physics, in conjunction with the University of Queensland Physics Department, uses a network of automatic measuring devices between Port Moresby and Hobart to monitor ultraviolet input. Dr Ian Barton of CSIRO and Dr Don Robertson of Queensland University run the project. Their data, read with Dr Kulkarni's ozone measurements, show that each 1% reduction in ozone increases the amount of harmful ultraviolet radiation penetrating to the ground by about 1.7%, when ozone reductions are relatively small. Bigger reductions produce a proportionately larger ultraviolet increase.

It therefore seems likely that, if fluorocarbon emissions reduced the amount of ozone in the stratosphere by 7%, harmful ultraviolet radiation would increase by an average of something like 12%. The consequences of such an increase are hard to assess, partly because ultraviolet input varies greatly from place to place, decreasing with distance from the equator. Goroka in Papua New Guinea, for example, receives four times as much harmful ultraviolet radiation in a year as Galway, Ireland, according to figures compiled by Dr Robertson. Cloncurry, Qld, receives more than twice as much in a year as Melbourne.

Ultraviolet input varies less with latitude in the summer months, when people are most likely to bare themselves to the sun, than in the rest of the year; in

The biggest area of uncertainty in the calculations is the chemistry of ozone destruction in the stratosphere. F-11 and F-12 are, of course, not the only man-made pollutants of the stratosphere that destroy ozone. Since 1971, when Professor Harold Johnston of the University of California suggested that nitrogen oxides in exhausts from supersonic passenger jets would threaten the ozone layer, a variety of other culprits have been identified.

The risk from jet exhausts is now regarded as much smaller than that from the fluorocarbons. This is partly because the prospects of high-flying supersonic jets taking a big part of the air transport market away from the subsonics is receding, but also because of downward revisions in predicted ozone reductions. Recent estimates suggest that the operation of 100 supersonic aircraft like the Anglo-French Concorde and Russian TU-144 in the Northern Hemisphere would reduce ozone concentrations there by less than 0.5%.

Nitrous oxide $(N_2 0)$ — given off when soil bacteria break down nitrogen fertilizers — possibly gives greater cause for concern. Emissions of this gas as a normal part of the nitrogen cycle in plant life are the main source of ozone-destroying nitrogen oxides in the stratosphere, and hence play a major role in determining the natural abundance of stratospheric ozone. Present fertilizer use is believed to add no more than a few per cent. to these natural emissions, but greater use in the

summer, Melbourne's exposure to harmful ultraviolet radiation nearly comes up to that of Cloncurry. However, somebody moving from Melbourne to Cloncurry and spending the same amount of time in the sun in both places will probably be exposed over a year to a much greater increase in harmful ultraviolet radiation than a stay-put Melbournian living through a 7% ozone decrease.

There is no doubt that sunburn is directly correlated with exposure to ultraviolet radiation, with radiation of the shorter wavelengths having the most effect. According to the NRC report, it is also 'relatively well established' that increased exposure to radiation in the 290nm to 320-nm wavelength range is directly linked, in fair-skinned people, with increased incidence of the most common types of skin cancer. These future could lead to significantly increased ozone destruction. A number of studies of the possible future impact of nitrogen fertilizers on stratospheric ozone are under way in the United States.

The most important man-made contributor of ozone-destroying chlorine to the stratosphere, apart from F-11 and F-12, is almost certainly carbon tetrachloride (CCl₄). Its concentration is being monitored, along with that of F-11, at the Cape Grim baseline station. The measurements there show an average concentration at the end of last year of about 160 p.p.t. (compared with 120 p.p.t. for F-11).

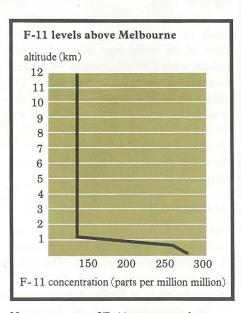
Some of the carbon tetrachloride in the atmosphere seems to have a natural origin, but emissions from its uses as a dry-cleaning solvent, fumigant, fire extinguisher, and metal-degreasing solvent add to natural concentrations.

Mr Ian Galbally, of the CSIRO Division of Atmospheric Physics, recently gathered together information on rates of emission and processes removing the gas from the atmosphere. He then calculated that, if Man's emissions were the only source of carbon tetrachloride, the average atmospheric concentration should be between about 40 and 120 p.p.t. As production figures for the U.S.S.R. and China were not available and he did not include estimates for these countries in his calculations, Mr Galbally concludes that his emission figures and concentration predictions are probably underestimates.

The figures for carbon tetrachloride suggest that this compound is probably comparable now to F-11 and F-12 as a source of stratospheric chlorine. However, in recent years it has been increasingly replaced in its various uses by other compounds, and emissions are not likely to grow rapidly — and indeed may decline — in the future. Emissions totalled about 90 000 tonnes in 1973, compared with a total of about 800 000 tonnes for F-11 and F-12.

Various other compounds, including methyl bromide used in agricultural fumigation and F-22, another fluorocarbon used for refrigeration, could contribute to ozone destruction in the stratosphere. However, present releases are too small for the effects to be significant.

A possible future source of stratospheric chlorine is the Space Shuttle, being developed in the United States as a re-usable replacement for presentgeneration manned rockets, which can only be used once. The Shuttle, as now planned, will emit hydrogen chloride gas as its solid propellant burns. But the quantities are small; it is estimated that 50 Shuttle flights a year would have no more than 1% of the impact of continued release of F-11 and F-12 at 1973 rates.



Measurements of F-11 concentrations show the influence of emissions from the city on low-altitude concentrations.

types, the non-melanomas, are rarely fatal, but can cause severe disfigurement. A correlation between ultraviolet radiation increase and incidence of the far more serious melanoma skin cancers is likely, but not firmly proved, according to the report. Only about two-thirds of new melanoma patients survive for 5 years after diagnosis.

Clearly, many assumptions have to be made in any attempt to quantify the health effects of an increase in average ultraviolet input. This century has seen the growth of sunbathing as a popular pastime, and larger and larger areas of skin are being bared. A trend in the opposite direction could partly offset the effects of an increase in ultraviolet radiation. However, there is no doubt that, from a health viewpoint, any increase in the amount of 290-nm to 320-nm radiation reaching the earth is undesirable.

Effects of an increased ultraviolet input on plants and animals are even harder to assess. Natural fluctuations as large as 10% in average ozone concentrations over spans of a decade or so have not had any impact that has been detected. However, experiments have shown that excessive radiation with wavelengths around 300 nm reduces plant growth and photosynthetic activity. The possible impact on plants and animals of a general ultraviolet increase is only beginning to be explored.

A climate change?

The F-11 and F-12 released into the atmosphere could affect the world's climate in two ways. By reducing stratospheric ozone concentrations, and in the process shifting the distribution of ozone towards lower altitudes, the fluorocarbons could change the temperature distribution in the stratosphere; the effects would flow on to the lower atmosphere.

More likely to be significant is the ability of the fluorocarbons to retard heat losses from the earth and thus raise temperatures on the surface. F-11 and F-12 are much more efficient at this than carbon dioxide. Fortunately, their concentrations in the atmosphere are much lower (about one million times, in fact, at present).

Reduced ozone concentrations in the stratosphere would allow more ultraviolet and visible radiation to reach the ground, tending to warm the lower atmosphere and surface. At the same time, reduced absorption of ultraviolet radiation by ozone in the stratosphere would reduce heating there. The result of this second effect would be surface cooling, because less thermal radiation would be emitted from the stratosphere towards the ground. The changed distribution of ozone in the stratosphere would complicate these effects. The net outcome for the ozone reductions envisaged is unpredictable with present knowledge, but would probably be small.

The direct heat-trapping effect of the fluorocarbons has been assessed, to a

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Taking the sun.

fairly low degree of accuracy. The NRC report gives 0.5 °C as the average surface temperature rise most likely to result eventually (some time next century) from continued release of F-11 and F-12 at the 1973 rate. At that time the concentration of F-11 in the troposphere would be about 700 p.p.t. (compared with about 120 p.p.t. now), and the F-12 concentration would have reached about 1900 p.p.t. (against about 200 p.p.t. now).

The predicted $0.5 \,^{\circ}$ C rise compares with an increase of $2-3 \,^{\circ}$ C expected if the atmosphere's carbon dioxide concentration doubles (from about 300 to 600 parts per million) as a result of continually growing fossil fuel combustion. This is a possibility in the next 50 to 100 years. The latest figures from the CSIRO carbon-dioxide monitoring program show a continuing rising trend. Average concentrations have risen by about 5 p.p.m. to around 332 p.p.m. since the program began in 1972.

Any global temperature rise would be made up of much bigger rises in some parts of the world than others. It would induce other climate changes — notably increased rainfall in some areas. The effects on agriculture would probably depend much more strongly on regional and local changes than on global average changes. Not nearly enough is known to allow the detailed effects of any average temperature rise to be forecast.

Need for data

One thing that stands out clearly is the need for more information on all aspects of the fluorocarbon problem. The NRC committee recommended that high priority be given to further measurements in the atmosphere and to laboratory studies of the chemical processes. It said that with further research it should be



A baseline atmosphere-monitoring station at Barrow, Alaska.



A CSIRO air-sampling pack is installed in an aircraft.

possible within 2 years to reduce the uncertainty in predicted ozone reductions from a tenfold to a four- or fivefold range. The committee recommended that, if ultimate ozone reductions of more than a few per cent. then remained a major possibility, selective regulation of the uses and releases of F-11 and F-12 should begin.

Monitoring fluorocarbon concentrations in the atmosphere is difficult because of their extremely low (parts per million million) concentrations. Not many years ago it would have been impossible. So far the vast majority of measurements have been made on air from the troposphere, because it is much easier to collect than stratospheric air. Most existing readings are for F-11, because the gas chromatographs used in the measurements can handle it much more easily than F-12.

Measurements to date have mostly been on air collected in flasks and sent to a central analysing centre. Contamination in the flasks is a serious problem, and the emphasis is now shifting to direct measurement by gas chromatographs at the monitoring sites. Under an international Joint Global Monitoring Program now on the drawing board, regular measurements of F-11, F-12, and other trace constituents of the atmosphere should be under way by the end of this year at Cape Grim and at isolated sites in South America, Hawaii, and Ireland.

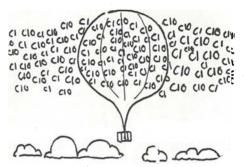
The CSIRO team is planning a series of balloon flights into the stratosphere to monitor F-11 concentrations there. The balloon will carry four flasks, which will each collect air at different altitudes. The first flask will fill at 10-12 km and the last at the maximum altitude of 25 km. These measurements should provide useful information on the rates of movement and breakdown of F-11 in the stratosphere.

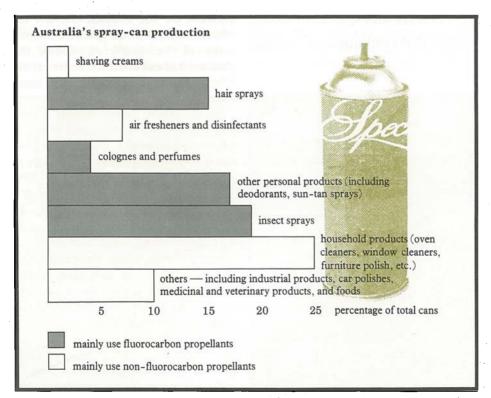
Concentrations in the stratosphere of Cl and ClO, the chemicals that actually destroy the ozone, have not yet been measured, because nobody has been able to do it. Instruments that should make the measurements possible are now being developed in America. These will be vital measurements, confirming or refuting the estimates that have been made on the basis of laboratory experiments of how much ozone the average chlorine atom is able to destroy before it forms a stable compound.

Switch to substitutes

Meanwhile, industry is responding to concern about the effects of F-11 and F-12, and to economic pressures, by reducing its reliance on them, and the first government moves to regulate releases have been made. Most attention is focused on spray cans, by far the biggest source of fluorocarbon emissions.

In America, one State, Oregon, banned the sale of fluorocarbon-propelled aerosols on March 1 this year. Nationally, the Food and Drug Administration and the Environmental Protection Agency announced in April that, from October 26, 1977, all cans using fluorocarbon propellants would have to be labelled to that effect. They also announced that plans would be developed for phasing out nonessential uses of the fluorocarbons in spray cans, to take effect in November,





Australian manufacturers produced about 110 million spray cans in 1975, out of a world total of about 5400 million. Among cans using fluorocarbons, insect sprays account for a much larger proportion in Australia than world-wide.

1978. A phasing out period of about 6 months has been suggested.

Canada is following the United States program. No plans for regulating fluorocarbon emissions have been announced in Europe or Japan, the biggest users after America, or in Australia.

The main alternatives to F-11 and F-12 as propellants in spray cans are various hydrocarbons. These give as good a spray as the fluorocarbons, and are a lot cheaper to produce. However, they have one serious disadvantage — they burn. Aerosol products containing them also have to contain fire-preventing chemicals. One such chemical is water, and spray-can manufacturers use hydrocarbon propellants with many of their waterbased aerosol products.

But deodorants and hair sprays are a problem. Using fluorocarbon propellants, manufacturers have formulated deodorant sprays that leave little or no sensation of wetness or stickiness, and hair sprays that stay fluid on the hair just long enough to coalesce before drying. To achieve the same effects, and equal non-flammability, with hydrocarbon-propelled sprays is proving difficult.

The trend is away from fluorocarbons, however. About half the spray cans sold in Australia now use hydrocarbon propellants, and this proportion may rise, according to one estimate, to 60% next year.

More about the topic

- Atmospheric halocarbons in the Southern Hemisphere. P. J. B Fraser and G. I. Pearman. Atmospheric Environment, 1977, 11 (in press).
- 'Halocarbons: Environmental Effects of Chlorofluoromethane Release.' Committee on Impacts of Stratospheric Change, Assembly of Mathematical and Physical Sciences, National Research Council. (National Academy of Sciences: Washington, D.C. 1976.)
- 'Fluorocarbons and the Environment Report of Federal Task Force on Inadvertent Modification of the Stratosphere (IMOS).' (Council on Environmental Quality, Federal Council for Science and Technology: Washington, D.C. 1975.)
- Man-made carbon tetrachloride in the atmosphere. I. E. Galbally. *Science*, 1976, 193, 573-6.
- Interhemispheric survey of minor upper atmospheric constituents during October-November 1976. NASA Technical Memorandum NASA TM X-73630, 1977 (in press).

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