

# AEROSOLS AND OZONE : HOW REAL IS THE THREAT?

## Roy Herbert

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There are fears that the ozone layer, high in the stratosphere, is under threat from man-made chemicals and will no longer shield us against harmful radiation as efficiently as in the past. But there is a lot yet to be learned about the atmosphere, for it is a bewilderingly complex reaction vessel. One thing is clear, that any pronouncements about stratospheric ozone should include plenty of provisos.

The Victorians thought highly of Ozone. They went down to the seaside and inhaled deeply, expanding their lungs as far as they would go. Ozone, according to popular belief at the time, could be smelt in the sea air (it was probably the difference between the clean air of the seaside and the polluted air of the towns) and it was supposed to do you good in some indeterminate fashion. The Victorians were right, but not in the way they thought. Ozone was certainly doing them good and every one else, too. It is doing us good now. It has always done so. So fundamental is ozone to us that life could not have developed on earth without it. But it does not do its job at the seaside or in the air we breathe. Ozone is working for us high above the earth's surface, in the stratosphere.

One of the many characteristics that distinguish man from the rest of creation in his ability to change his environment, for good or ill. In recent years there has been a theory that he was, almost inadvertently, changing it for the worse and moreover, at the level of the stratosphere, where damage would be irreversible. That meant that the ozone on which we depend would be affected, with consequences that would be bad and could

be catastrophic. For, to come to the point of all this, ozone forms a layer at high altitude that protects us from harmful radiation from the Sun. It was in danger because we had begun to use certain chemicals in such quantity that they were getting up into the stratosphere and starting a process there that threatened to destroy the ozone shield.

Most of us have used the chemicals concerned. Squirting our shaving cream or hairspray, aiming insecticide sprays at flies, painting with a can instead of a brush, we were all, according to some authorities, taking part in destroying our own protection. We were doing the same thing in using refrigerators. We were helping the destruction by sitting on foam cushions and using foamed plastics in the other hundred ways that we do. All these products use chemicals called chlorofluorocarbons.

## Villains in Disguise

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CFCs, as they are called for short, were discovered in the USA. There is a range of them, but they all have fluorine, chlorine, hydrogen and carbon

atoms in their molecules. First of all they were used as refrigerants because they are neither poisonous nor flammable, as their predecessors were. During the Second World War they proved their efficiency as propellants in aerosols and more recently, as agents for foam-blowing to make the familiar light, resilient plastics. Two of them, known as F11 and F12, are ideal materials. They are chemically stable and fairly cheap to make. F12 has a low boiling point of  $-30^{\circ}\text{C}$  and F11 has a higher one of  $24^{\circ}\text{C}$ . By juggling the proportions of the two it is possible to produce propellants specially fitted to practically any requirement. These two CFCs are by far the most important of the range and industry the world over had made them in quantity for years. In 1974, annual production had reached about 475,000 tonnes for F12 and nearly 400,000 tonnes for F11. After that there was a sudden drop. It was the year of the dawning suspicion that CFCs might be villains in disguise.

The stratosphere is the layer of the atmosphere above the troposphere, which can loosely be termed the air we breathe. In the stratosphere, the atmosphere is tenuous. It contains nitrogen and oxygen, as does our breathing air, but some of the oxygen instead of being in the usual two-atom form, has molecules of three atoms; that is ozone. The amounts of it are small, around five or ten parts per million of the already thin air. Moreover, the stratosphere is not a definite section, like the layer of a cake. It extends from about 15 to 50 kilometers above the earth's surface and its height varies from the Poles to the Equator. Nevertheless, there is enough ozone in this fluctuating region to protect us from the Sun. In addition to the energy we know as heat and sunshine, the sun pours out radiation at other

frequencies, including ultra-violet. Ultra-violet is harmful to life; there is, for instance, a well-recognised connection between it and cancer. The ozoneosphere, as some like to call it, absorbs the ultra-violet, so it is essential to us and clearly should be inviolate from man himself.

It appeared some years ago, though, that man was about to damage it. The concentration of ozone in the stratosphere depends on the amounts of other trace gases there, including oxides of nitrogen. Exhaust gases from supersonic aircraft contains quantities of them and if fleets of these machines were going to fly in the lower atmosphere, as once predicted, then ozone would be destroyed and far more ultra-violet would get through to the ground. The fleets of supersonic aircraft did not materialise and the threat vanished, but it has alerted everyone to the subtlety and sensitivity of the stratosphere.

## Long Life

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Early on, manufacturers of CFCs had realised that the fate of their products in the atmosphere was important. Their very stability made them obvious subjects for investigation. In 1972 an international panel was set up and work carried out by it suggested that the concentration of the two CFCs in the atmosphere had risen at a rate that could be linked to their manufacture and release. That could mean that they had a long life in the atmosphere.

The stage was set for the revelations of two US researchers, Professor F.S. Rowland and Dr. M.J. Molina of the University of California. They published their theory (which was based partly on information that the manufacturers had provided)

that CFCs were not broken down at all in the atmosphere. Neither was their 'sink' for them there. What happened they said, was that the CFCs rose higher and into the stratosphere. There they were decomposed by radiation from the Sun. Chlorine atoms were liberated by this and started chemical processes that destroyed ozone. There was very little chance of the stratosphere being able to cleanse itself of the chlorine. The only process that would do this was one in which chlorine combined with hydrogen from naturally occurring methane, to form hydrogen chloride that fell lower and was eventually rained out. But it could not remove much.

To reach their conclusions, the two scientists had to simulate the stratosphere and the troposphere and the way they interacted. They did this in the normal way, by using a mathematical 'model'. They said, forecasting from results they got with the model, that if CFCs were made and used on the scale they had been, the ozone in the stratosphere would have fallen by about one-sixth in twenty or thirty years. That would mean an increase in ultra-violet and an increase in skin cancers at the least. They said also that no important stratospheric process had been left out of their calculations. The right thing to do was to ban all use of F11 and F12 at once unless it was absolutely essential. It had to be done at once because the stratosphere reacted so slowly that any action taken to correct the situation, if delayed, would make no difference.

There was uproar, the US government started to form regulations on the use of CFCs in aerosols. Lobbies sprang up for and against the theory. It was, obviously, not one that could be dismissed out of hand by responsible authorities, but many people in industry and research organisations

thought that a harder look at the complicated region of the stratosphere and what went on there was justified and that there was some weighty criticism that could be made of the hypothesis.

## **Programmes of Research**

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In general, the critics said that there were not enough facts to go on. What we did know about the subject was inconclusive. It was impossible, they said, to be so firm when the mathematical model was too simple to reflect the real conditions, and it was equally impossible when only CFCs had been considered. Naturally, this did not prove that Rowland and Molina were necessarily wrong. The only answer was to find out more. So programmes of research in many countries began, under various bodies, for instance through the European Community and the UN Environment Programme, and in national and industrial laboratories. Still continuing, they involve measurement in the stratosphere by rocket, aircraft and balloon, ground measurements, and laboratory experiments in which the chemistry of the stratosphere is reproduced.

All this work has gone to show that the critics were right in being cautious. A scientific meeting on the subject held at Brighton, in the South of England, in October 1978, was in no doubt that the danger to the ozone layer had been much exaggerated. Before that meeting, which reported research results in many areas and highlighted, too, the risks in relying on instrumental performance to reach conclusions, it had become plain that the stratosphere is a bewilderingly complex reaction vessel.

There is certainly a chlorine cycle there which can destroy ozone, but it has been the chlorine coming from methyl chloride, entirely natural in origin. Though CFCs are reaching the stratosphere, it is far from clear that they have any effect on it. There seems to be fairly strong evidence that, despite Rowland and Molina, there is a sink in the troposphere for CFCs, for they are absorbed on dust particles and broken down by the action of light. That there are knotty problems to unravel is shown by the fact that measurements have revealed the presence of some chemicals, produced in the chlorine breakdown of ozone, in eight times the predicted amount. Yet there is no reduction in the amount of ozone in the stratosphere to correspond. One of the outstanding points discovered is that far from there being a reduction in the amount of stratospheric ozone in the twenty years up to 1977, there has been an increase. It is evident from all this that mathematical models of the churning, reacting stratosphere are a long way from identity with it. They cannot now reflect an accurate picture of what is going on and it follows that they are even less valuable as a basis for predicting what conditions will be like at the end of this century and beyond.

The Brighton meeting emphasised this. One British scientist, Professor Jim Lovelock, called analysis into question, remarking that there were serious difficulties in calibrating the gas chromatographs used. He quoted as evidence the enormously different results obtained when identical samples of air containing F11 and F12 in concentrations found in the atmosphere now were sent to different laboratories. Professor Lovelock, who is concerned with the lower levels of the atmosphere, also drew attention to the fact

that huge amounts of methyl chloride are produced naturally; forest fires, for example, produce as much as ten times the amounts attributed to CFCs.

## Provisos

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There may very well be a process by which the stratosphere renews its own ozone. If it loses ozone in the higher levels, then it may be replaced in the lower, because the very action of ultra-violet reaching there would encourage photochemical reactions that could produce ozone. Whatever else it may have shown; the Brighton meeting made it clear that any pronouncements about ozone in the stratosphere should be made with plenty of provisos and precautions.

That, however, does not absolve manufacturers and users from the duty to see that if it is finally thought desirable, there are alternatives to CFCs and that is a hard goal to aim at. ICI, the largest manufacturer of CFCs in Europe, says that it is rather like being asked to invent another wheel. The properties of CFCs are little short of ideal and to find substitutes that will do the same job, be just as harmless and be proved to have no effect on ozone and be cheap to make is a daunting job for chemists and chemical engineers. But the firm has a large-scale screening programme under way, much of its effort being spent, necessarily, on checking toxicity. It takes years to sort this out, and, though only really promising materials would go through the whole gamut of tests, it is expensive, too, costing more than £ 250,000 sterling for a single compound. Substitutes have been found, about six of them after sixty possibilities were narrowed down. It is unlikely

just the same that any will be found that will take the place of F11 and F12 directly; only one thing is sure —they will be more expensive to produce and to use. They may not, of course, ever be needed, for the present evidence and opinion supports the

view that it would be wrong to ban CFCs. And, fortunately for our peace of mind, that there has been no frightening damage to the ozonosphere and there is not likely to be.

Courtesy: Spectrum