Tackling Sydney's smog

The word 'smog' has undergone a major change of meaning in recent years. It was coined early this century to describe the choking mixtures of smoke and fog that had long afflicted London and other cities where large amounts of coal were burnt. Today it is used more often to describe something quite different: the 'photochemical' air pollution first recognized in Los Angeles after World War II and now one of the most serious environmental problems in many of the world's cities — including Sydney, the subject of this article.

Much progress has been made in controlling the first type of smog, mainly through the development and use of equipment that drastically reduces emissions of smoke particles from factory chimneys. Photochemical smog, however, is proving very difficult to control.

It is a highly complex phenomenon. Unlike the old London-style smog, the photochemical variety is not just the product of mixing various pollutants into the atmosphere. Instead, it results from chemical reactions between pollutants and atmospheric oxygen. These reactions occur only in sunlight — hence the 'photo' in 'photochemical'.

The pollutants that take part in the reactions, called the smog precursors, are nitrogen oxides and hydrocarbons. One of the main sources of both is motor-car exhaust. The hydrocarbon emissions result from incomplete combustion of petrol, and nitrogen oxides are inevitable by-products of the combustion of fossil fuels in air.

Nitrogen oxides also come from the chimneys of factories and power stations. Evaporation of petroleum from oil refineries and storage depots, and during the filling and emptying of tankers and filling of cars, is an important source of hydrocarbons. So is evaporation of solvents, notably from paints and chemicals used for dry-cleaning and degreasing.

Ozone

The main product of the smog-forming reactions is ozone, and ozone readings provide the usual measure of the degree of photochemical pollution on any day. Other noxious gases, notably peroxyacetyl nitrates (abbreviated to PAN), form in smaller quantities. Some of the reaction products are minute particles, and these are responsible for the grey haze that forms on days when ozone readings are high. (The brown haze often seen over Sydney in the cooler months is a separate

It is common for a day's peak ozone readings to be recorded when the sea breeze returns the polluted air. problem, not caused by these reactions.)

Much has yet to be learnt about the effects on human health of the various constituents of photochemical smog, particularly about possible long-term chronic effects. However, there is no doubt that people can experience eye irritation and difficulties with breathing during severe smog. In March 1976, 13 children taking part in high-school sports in Sydney suffered chest pains and breathing difficulties and were admitted to hospital; photochemical smog appears to have been responsible. Similar incidents have occurred during smogs in Los Angeles and Tokyo.

Photochemical smog can severely damage some plants: tomatoes and petunias are notable examples. Evidence is accumulating that it can also cause significant reductions in crop yields, even where the plants suffer no obvious damage. For example, one study has put the cost of smog-caused yield reductions in cotton crops in California's San Joaquin Valley in 1975 at as much as \$30-40 million. Another effect of the smog is to accelerate natural deterioration of rubber.

The New South Wales State Pollution Control Commission (SPCC) estimates, from measurements elsewhere in Sydney on the day, that the high-school children apparently affected by smog in 1976 were exposed to an ozone concentration of more than 0.2 parts per million. This is four or five times the maximum natural background level. But it is well below the highest 1-hour average concentration so far measured in the Sydney region — 0.38 p.p.m. — recorded at the seaside suburb of Coogee in March last year.

The World Health Organisation (WHO) has adopted 120 micrograms per cubic metre (about 0.06 p.p.m.) as a long-term goal for maximum ozone concentration averaged over 1 hour. The U.S. Environmental Protection Agency has adopted a slightly less strict goal — a 1-hour average of 0.08 p.p.m.

The State Pollution Control Commission's monitoring records show a gradually worsening smog situation in Sydney. The WHO ozone goal was exceeded on 129 days during 1976, compared with 80 days in 1972, and maximum concentrations show a rising trend.

Sydney's smog problem is not nearly as severe as that of Los Angeles, where ozone levels greater than 0.7 p.p.m. have been recorded and smogs occur more frequently and usually last longer. But it is comparable with that in a number of other major cities, including Tokyo and New York. The 1975–76 Annual Report of the SPCC describes photochemical pollution in Sydney as 'one of the growing threats to the urban environment', and says control of air pollution, particularly photochemical smog, is the Commission's greatest single challenge.

Towards control

However, control is most difficult to achieve. The obvious approach is to restrict emissions of the precursors, but there are many complications.

Only two nitrogen oxides, nitric oxide (NO) and nitrogen dioxide (NO_2) , play significant roles in the reactions, but the hydrocarbons involved are many and varied. Some are much more potent smog-formers than others. So the activities of different hydrocarbons, as well as the quantities released, have to be taken into account in devising control measures. Much remains to be learnt about these activities, and about the sources of emission of the different hydrocarbons.

Further complicating matters, studies show that it is not only the actual con-



View from a city building as the smog sets in.



On a typical smoggy day, ozone forms as polluted air is blown seaward in the early morning and then back over the city by the sea breeze.

centrations of nitrogen oxides and hydrocarbons that determine the ozone levels reached on days favouring smog formation, but also their ratio. And the relation between this ratio and the prospects for smog formation is highly complicated and not fully understood. For instance, it seems that in some circumstances increases in nitrogen oxide emissions can reduce ozone levels in the immediate area if hydrocarbon concentrations remain constant, but cause them to increase downwind.

To attempt to unravel the factors responsible for Sydney's photochemical smogs so that the most effective control measures can be formulated, the SPCC initiated in 1974 a wide-ranging research project with the title the Sydney Oxidant Study (or SOS). Scientists from CSIRO, the University of Sydney, and Macquarie University are also taking part.

The SPCC is coordinating the work and does most of the monitoring. It has set up six permanent ozone monitors around the Sydney basin (see the map above), and during the main measurement phase of the study, which ended last year, used a boat to take readings off the coast and in Botany Bay and an aircraft to check pollutant concentrations above the region.

Both the SPCC and the Sydney University team, from the Department of Mechanical Engineering, used instrument-equipped vehicles to follow polluted air downwind and monitor the development of photochemical smog. The Sydney University scientists are using the data gathered to develop models of smog development.



Sydney's Warringah Expressway. Road systems like this are built to keep the growing motor vehicle population moving. Unfortunately, the exhausts that the vehicles emit are major contributors of smog-forming gases.

The Macquarie University team is making meteorological measurements aimed at sorting out the conditions that favour smog development in the Sydney area as a whole and in different parts of it. The role of the CSIRO team, from the Divisions of Process Technology and Food Research, is to measure and test the hydrocarbons in the air with a view to working out the relative importance of different emission sources.

During the main data-gathering phase of the study, the scientists put all available monitoring units to work from dawn on days that weather forecasts indicated would produce high ozone levels. A radio network linked the participants, enabling them to coordinate their activities.

On a typical day, one of the two monitoring vehicles would begin its measurements in the city and the other in industrial suburbs to the west. As the day progressed, each would track parcels of polluted air and monitor the composition of the air as the photochemical reactions proceeded. The SPCC's boat and chartered aircraft would also be in action, as would two Macquarie University meteorological data-gathering units. The data collected by these means supplemented information recorded by the ozone monitors and wind-measuring anemometers located around the city.

Sunny and warm

Photochemical smogs occur only in the warmer half of the year: Sydney's 'oxidant season', as the scientists refer to it, typically begins in October and ends in April.

Conditions favour smog production when a high-pressure cell or ridge is controlling the city's weather, bringing with it clear skies, light winds, and afternoon sea breezes — the perfect summer day. Under these conditions, a temperature inversion normally forms during the night and lasts into the morning, restricting vertical air movement. This inversion joins with Sydney's topography in holding pollutants in the area; the city and suburbs are bounded by 150-m-high plateaux in the north and south and by the Blue Mountains in the west.

In many ways, Sydney's situation is similar to that of Los Angeles. The cities are about the same distance from the equator (latitude 35°) and receive similar amounts of sunshine. Also, both are backed by hills that restrict the outflow of polluted air.

An important difference, however, is that Los Angeles experiences semi-permanent temperature inversions in summer while Sydney's are intermittent. This, together with other meteorological factors, results in Los Angeles sometimes experiencing high ozone readings every day for 2-3 weeks. About five consecutive days of smog is Sydney's limit, and the usual pattern is for high ozone readings to occur on only one or two days at a time.

Studies by Dr Robert Hyde, Mr George Hawke, and Mr Adrian Heggie, of the Macquarie University team, show that smoggy days typically begin virtually without wind — just a gentle westerly drift caused by cold air draining from the Blue Mountains towards the coast. This tends to follow the valleys of the Parramatta, Cook's, and George's Rivers, picking up smog-forming emissions from the heavy concentrations of industry bet-

ween Parramatta and the city and from the congested morning traffic.

The temperature inversion prevents these precursors from rising more than a few hundred metres, and they react to form ozone and the other ingredients of photochemical smog as they move slowly eastwards over the city and out to sea. Then, later in the morning or in the early afternoon, the sea breeze comes up and blows the smog back over the city. It is common for a day's peak ozone readings to be recorded when the sea breeze returns the polluted air.

The reactions continue

Ozone continues to be produced as the sea breeze carries the pollution to the western and south-western parts of the Sydney basin. The SPCC's monitoring records for the summer of 1976-77 show that in December, January, and February ozone concentrations reached at least 0.1 p.p.m. more often at Campbell-town, 43 km inland, than at any of the other monitoring sites, all of which are closer to the coast. The sea breeze reached Campbelltown on one day in three during these months, and on 80% of those occasions contained ozone at concentrations of 0.1 p.p.m. or above.

In March, however, the ozone level did not reach 0.1 p.p.m. at Campbell-town, although it exceeded this many times at monitoring sites nearer the coast. The weakening of the sea breeze at the end of summer probably explains the difference: the polluted air is no longer blown back so far inland.

However, Campbelltown — a rapidly developing industrial and residential area on Sydney's fringe — does not experience high ozone levels only after the onset of the sea breeze; like most aspects of the photochemical smog problem, the relation between meteorology and smog incidence is complex. Nearly half the recordings of ozone levels as high as 0.1p.p.m. in December 1976 and January and February 1977 were made in the morning and early afternoon — before the sea breeze arrived.

The State Pollution Control Commission's monitoring records show a gradually worsening smog situation in Sydney.

How smog incidence varies with distance inland

number of hours with average ozone level at least 0.1 p.p.m.



During most of the 1976–77 smog season, the monitor at Campbelltown, 43 km inland, recorded high ozone levels more often than monitors nearer the coast. The January figures illustrate this pattern. In March, by contrast, high levels were recorded most often at Coogee, on the coast.

The Macquarie University team believes that pollutants from the heavily industrialized Silverwater area — brought in by light north to north-easterly winds that often blow in the late morning and early afternoon in summer — account for some of these recordings. The remainder, they suggest, can be explained by recirculation of polluted air brought in by the previous day's sea breeze.

Ten out of the 12 mornings during which high ozone readings were recorded that summer followed afternoons that had experienced high readings with the sea breeze. The scientists suggest that the polluted air becomes isolated from the ground when the nocturnal radiation inversion forms and, overnight, is carried back towards the city by the drainage flow. Then, the following morning, heating by the sun erodes away the inversion and the pollutants mix into the air down to ground level. Light north to northeasterly winds carry the polluted air back to Campbelltown — producing a rapid rise in ozone levels.

In contrast to the situation at Campbelltown, the SPCC's ozone monitor on the coast, at Coogee, recorded concentrations higher than 0.1 p.p.m. only rarely during the summer months, but much more frequently during March. As mentioned earlier, the highest 1-hour average concentration yet recorded in the Sydney region, 0.38 p.p.m., was measured at Coogee on March 31, 1977.

The Macquarie University scientists believe that high ozone readings near the coast late in the oxidant season can be explained by the fact that the westerly drainage flow tends to be stronger and the sea breeze weaker at that time of the year. The polluted air swept out to sea in the morning would move back slowly with the sea breeze, allowing high concentrations of ozone to build up and persist near the coast.

Sources and reactions

The precursors that the sun and wind work with to produce Sydney's photochemical smogs, their sources, and the reactions they undergo are being studied by the other participants in the SOS. Much attention is being given to the hydrocarbons, partly because restricting their emission seems likely to have a bigger impact in reducing smog formation than restricting emissions of nitrogen oxides. Also, a great deal remains to be learnt about the hydrocarbons.

In one of the first projects in the study, scientists from the SPCC worked out the approximate proportions of non-methane hydrocarbon emissions coming from different categories of source. Methane, the hydrocarbon present in greatest quantity in the atmosphere, was excluded

Information gained from the smog-chamber experiments should provide pointers to smog control measures likely to prove effective. because it does not take part in the smogforming reactions.

According to their figures, motorvehicle exhausts are the main emitters (55% of the total), followed by evaporation of petroleum (25%) and solvents (20%). The contribution of vehicle exhausts was derived from figures for emissions from typical vehicles, average distances travelled, and the number of vehicles operating. The SPCC is at present compiling a more comprehensive inventory of hydrocarbon sources, and expects that there will be some changes in the proportions of total emissions attributed to the different sources.

It has identified four areas that emit hydrocarbons in particularly large quantities — the Silverwater industrial region (which includes one of Sydney's two oil refineries), the central business district, the industrialized Matraville—Botany area, and Kurnell (where the second oil refinery is located). These are concentrated sources, but of course hydrocarbons and nitrogen oxides are emitted, mainly by motor vehicles, throughout the Sydney basin.

As part of Sydney University's contribution to the study, Dr Keith Post and Professor Bob Bilger have produced estimates of hydrocarbon and nitrogen oxide emission rates from the Silverwater area and the central business district. They derived their estimates from measurements made while tracking polluted air in their monitoring vehicle. To a rough approximation, they put the hourly daytime output of all hydrocarbons except methane at 56 kg per km² in the central business district and 180 kg per km² in the Silverwater area. Their equivalent figures for nitrogen oxides are 25 kg per km² in the central business district and 18 kg per km² at Silverwater.

Their estimates for the central business district agree reasonably well with those derived from emission inventories, but the figure for hydrocarbon output from the Silverwater area exceeds the inventory estimates by more than 50%. The scientists say this region appears to be a much larger source of non-methane hydrocarbons than expected.

In their monitoring vehicle, the Sydney University team has tracked samples of polluted air from areas where the precursors are emitted to points downwind where time and sun have produced maximum ozone concentrations. This has enabled them to work out relations between initial precursor concentrations and the ozone levels that these can produce. The relations they have derived agree well with those derived by other scientists from American, Japanese, and European data, and confirm that both the ratio of hydrocarbon to nitrogen oxide concentrations and the individual concentrations influence the amount of oxone produced.

Hundreds of hydrocarbons

The CSIRO team, led by Dr Maurice Mulcahy of the Division of Process Technology, is investigating the roles of particular hydrocarbons in smog production. City air contains many hundreds of hydrocarbons. Some are present in much higher concentrations than others, and some play a much more active role than others in the smog-forming reactions. The scientists' aims are to identify the hydrocarbons in Sydney's air, measure their concentrations at a variety of times and places, determine their relative smog-forming activity under local conditions, and work out which are the most important emission sources.

The first step — identification — is not easy, partly because the hydrocarbons are generally present only at concentrations in parts per thousand million. However, using techniques that Dr Keith Murray developed for isolating the components of foods that give them their



London smog-bound in 1956. Control measures introduced since have greatly reduced that city's smog problem. Sydney's smog, the photochemical variety, is quite different and will probably be more difficult to control.



These monitoring records for January 22, 1977, show sharp rises in ozone levels as the sea breeze moved inland.

flavour, Dr Frank Whitfield of the Division of Food Research has been able to identify more than 250 hydrocarbons from air samples collected around Sydney. The scientists think that perhaps 30 of these may play significant roles in smog formation.

Members of the team, including Dr Martin Smith and Mr Peter Nelson, of the Division of Process Technology, have determined the concentrations of some of the most significant hydrocarbons in air collected regularly at five sampling sites. These sites are: Hyde Park in the city centre; Hen and Chicken Bay at Concord, an industrial area; Homebush Bay, also an industrial area; Centennial Park, close to the city in a mainly residential area; and the CSIRO site at North Ryde, which is surrounded by light industry, housing, and park lands. The samples were taken from points at least 50 m from roads, to avoid the effects of exhaust emissions from individual vehicles.

At Hyde Park, the scientists found that concentrations rose to a peak at about 8 a.m., fell to a minimum near midday, and rose again in the afternoon, although seldom to levels as high as those recorded in the mornings. This pattern, which resembles that recorded in Los Angeles and a number of other cities, presumably reflects changes in traffic density during the day. Dispersal by the afternoon sea breeze probably explains why peaks were lower in the afternoon than in the morning.

Hydrocarbon concentrations at all sites varied greatly during the day and between days — sometimes by a factor of a thousand or more. However, despite this variation, the different hydrocarbons were usually present in much the same proportions.

The scientists measured the concentrations of some hydrocarbons in air from Bawley Point, on the New South Wales south coast, to see how readings at a location remote from industry and motor traffic would compare with the city measurements. The concentrations turned out to be very much lower, but the proportions again were generally similiar.

Origins

These proportions can point to the origins of hydrocarbons in the atmosphere, if the hydrocarbon make-up of emissions from different sources is known. The CSIRO researchers have analysed air taken from the Cahill Expressway tunnel in Sydney to find out the relative concentrations of hydrocarbons in traffic exhaust. They



Sydney's setting is the envy of other cities, but it is something of a smog trap.

have also analysed petrol from Sydney's two refineries and the natural gas supplied to the city, and plan to find out the makeup of all solvents used in large quantities.

Using a statistical technique, they have found that a mixture of 68% vehicle exhausts and 32% evaporated petrol would give relative hydrocarbon concentrations very like those found in a number of air samples taken in the metropolitan area.

This does not mean that vehicle exhausts produce nearly 70% of the smogcausing hydrocarbons in the air, because other important sources, notably solvents, were not included in the calculations. But it does illustrate the important role played by emissions from vehicles, particularly cars. The SPCC estimates that Dieselpowered vehicles account for less than 1% of hydrocarbons emitted from exhausts.

As the CSIRO scientists acquire more information about the make-up of hydrocarbon emissions, they plan to use statistical methods to work out more precisely the relative contributions of different sources.

SPCC scientists have estimated the



The smog chamber. The two teflon-walled boxes on the platform have been moved from their covered storage area to face the sun.

contribution of vehicle exhausts to the atmospheric content of some hydrocarbons (members of the aliphatic class, which includes paraffins, olefins, and acetylenes) at various places and times of day. Their technique makes use of the fact that these exhausts are the only significant source of one of those hydrocarbons, acetylene.

Early one particularly smoggy day, the Commission's calculations put the vehicle-exhaust contribution in industrial areas west of the city at 20-33%. In air that had passed over the central business district, the calculated exhaust contribution was 47%. In air returning late in the morning with the sea breeze, it was 49%.

The significance of these figures in assessing the relative importance of motor vehicles as a source of smog-forming hydrocarbons is unclear. The CSIRO team has found that hydrocarbons of the aromatic class (which includes benzene and toluene) are present in much the same proportions in vehicle exhausts as in the original petrol, but that this is not the case with the aliphatic hydrocarbons. It seems that aromatic hydrocarbons are generally more resistant to combustion than the aliphatics.

This is significant, because overseas research indicates that, with the exception of benzene, the aromatics are among the most potent smog producers. The petrol used in Sydney contains about 30% aromatic hydrocarbons; they play an important role in boosting octane ratings. However, some of the aliphatics, notably the olefins or alkenes, can also be very active in smog production.

Manipulating smog

To assist in finding out which hydrocarbons are, in fact, most important in producing Sydney's smog, the CSIRO team has designed and built a large 'smog chamber' at North Ryde. Consisting of two 20-cubic-metre boxes with walls of very thin (0.05-mm) teflon film, it enables the scientists to watch the development of photochemical pollution closely and to manipulate the process by altering the composition of the air in the boxes. There is only one other installation of its type in the world, in the United States.

Teflon was used for the walls because it lets virtually all wavelengths of sunlight through unhindered, including the important ultraviolet part. Also, it is unusually inert chemically, and therefore should not affect the photochemical reactions going on in the two boxes.

Construction of the smog chamber ended in March 1977, and since then Mr . . . the important role played by emissions from vehicles, particularly cars.

Graham Johnson and other members of the team have demonstrated that, as intended, identical air in the two boxes behaves virtually identically when the chamber is exposed to the sun. In experiments now beginning, they are using the chamber to compare photochemical smog formation in air to which particular hydrocarbons have been added (in one box) with the behaviour of untreated air (in the other).

The boxes are filled with air before dawn, when smog-precursor concentrations are low and photochemical reactions could not have begun. Then a quantity of the hydrocarbon being investigated is added to the air in one of the boxes. During the day, instruments measure and record the inputs of visible and ultraviolet radiation and the concentrations of ozone, nitric oxide (NO), and nitrogen dioxide (NO₂) in both boxes.

The scientists are interested in both the amounts of ozone produced and the rates of production. In the atmosphere, if reaction rates are slow there probably will not be time for high ozone levels to build up before the pollution disperses. But in some situations, particuarly where pollutants emitted one day return the next, some hydrocarbons may contribute to high ozone levels despite having slow reaction rates.

Information gained from the smogchamber experiments should provide pointers to smog control measures likely to prove effective. For example, if some solvents prove to have much greater smog-forming activity than others, substitutions may be possible.

Strategy

Some action has already been taken to control photochemical smog — notably the introduction of controls on emissions of hydrocarbons and nitrogen oxides from motor vehicles and measures to reduce emissions of petroleum vapour from oil refineries. The vehicle-emission controls apply to all new passenger cars and vehicles derived from passenger-car designs, such as station wagons and utilities, manufactured since July 1, 1976.

They limit hydrocarbon emissions to $2 \cdot 1$ grams per kilometre and emissions of nitrogen oxides to $1 \cdot 9$ g per km. Introduced nationally after agreement was reached between the Federal and State Ministers for Transport, the limits are enforced in New South Wales under the



This graph shows the build-up of ozone on a sunny day in the CSIRO smog chamber. Nitric oxide is converted to nitrogen dioxide, which takes part with hydrocarbons and oxygen in the ozoneforming reactions.





A car's exhaust is examined in the State Pollution Control Commission's motor vehicle emission control laboratory.

Clean Air Act. The SPCC conducts tests on randomly selected vehicles to check that emissions are within the limits.

The standards are the same as those introduced in the United States in 1973. Since then, however, the limits have been drastically reduced in that country. In California, the limit for hydrocarbons was lowered last year to 0.25 g per km. Australia's Transport Ministers decided early this year to defer introduction of lower limits in this country until January 1981.

The SPCC uses knowledge gained from the Sydney Oxidant Study to advise, with the aim of keeping photochemical smog problems to a minimum, on sites for new urban and industrial developments. Over the next year or so, it plans to develop a coordinated strategy for smog control.

However, overseas experience suggests, and the Commission acknowledges, that the problem will not be solved easily or quickly. Continuing growth in numbers of vehicles and other sources of smog precursors makes the task of reducing the frequency and intensity of smogs increasingly difficult.

More about the topic

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