As much as we know about Sydney's smog

Sydney's first full-blown case of photochemical smog appeared in 1971. In the decade or so since, the phenomenon has recurred numerous times.

The many unhappy returns of smog days have had one benefit. They have allowed scientists to gain a fair understanding of the intricacies that presage the smog's unwelcome visitations.

In May 1982, scientists got together to pool their knowledge and compare notes at an invited symposium on Sydney's atmosphere organized by the CSIRO Division of Fossil Fuels. This article reports some of the information and insights that came out of the conference.

However, much mystery remains shrouded in the smog — in particular, the scientists do not understand completely why pollution episodes have occurred much less frequently in recent years than in the middle of last decade.

The National Health and Medical Research Council (NHMRC) has recommended a maximum ozone level of 12 p.p.h.m. (parts per hundred million). The summer of 1976/77 contained 60–70 days in the summer smog season when ozone exceeded that level. In recent years there have only been 9 or 10.

Smoggy Sydney

With 3 million inhabitants, 1·6 million motor vehicles, four oil refineries (at Sil-verwater and around Botany Bay), a number of petrochemical plants and heavy industrial areas, and plenty of warmth and sunshine, it's not surprising that Sydney is affected by photochemical smog. Indeed, Sydney shares with two other Pacific cities, Los Angeles and Tokyo, the dubious distinction of having recorded the highest ozone levels in the world (although Los Angeles has recorded much higher levels and many more episodes than Sydney).

In the last few years all five of the mainland State capitals have recorded ozone levels at least equal to the NHMRC's recommended air-quality limit. However, as the table on page 4 shows, Sydney is clearly Australia's most smog-bound city. (The figures are not precisely comparable, because the larger cities have more recording stations, but they certainly give a good idea of the relative severity of the smog problems.)

Although ozone is the principal constituent of photochemical smog, it is not the only one. Other undesirable chemical compounds are also formed by reactions in the air. The chemical 'soup' becomes visible, as various non-volatile compounds form and condense. This haze

They identified more than 200 hydrocarbon species in Sydney's atmosphere.

is the reason the word 'smog' is applied to this kind of air pollution, although the effect on visibility is the only point of similarity with the smoke-induced foggy air pollution for which the word was originally coined.

Unlike pollutants such as sulfur dioxide or carbon monoxide, the toxic constituents of photochemical smog are not emitted: rather, they form in the atmosphere. Man furnishes two types of ingredients for the smog-forming reactions — hydrocarbons and oxides of nitrogen — while nature provides oxygen and sunlight.

The oxides of nitrogen, mainly nitrogen dioxide (NO_2) and nitric oxide (NO) and known collectively as NO_x, are emitted as a result of combustion. Cars, power stations, and all oil- and gas-fired units inevitably contribute them. Hydrocarbons are emitted in car exhaust gases, evaporate from petrol tanks, fuel lines,

Smog prevention will be easier if emissions of the most reactive hydrocarbons can be preferentially limited.

and service stations, and enter the air from paints and industries using solvents.

Under the influence of sunlight, the ingredients react together. Sunlight is needed, so smog episodes are worst in summer and on clear days. Because the reactions take time to proceed, mid afternoon is most frequently the time of maximum ozone concentration. The delay also means that often the peak is registered in a locality some considerable distance downwind from where the ingredients were released earlier on.

Campbelltown is on the outskirts of Sydney, but the sea breeze blows city air over it on summer afternoons. As a result, the average ozone maximum is higher, and occurs later, at Campbelltown than at Lidcombe, a central suburb.

This much of the picture is fairly well known, and was built up from information gathered during the 'Sydney Oxidant Study' in the summers of 1975/76 and 1976/77 (see the box on page 6).

In May 1978, *Ecos* 16 gave a broad outline of the Sydney smog picture as it was then known, which included an account of the meteorological factors at work. Since then, continued research has filled in many more details.

For instance, the hydrocarbon ingredients of smog and their main sources have now been pinned down. The smog-forming activity of each component has been measured, so attention can now be focused on the most troublesome of the emissions. And yet, inevitably, the other gaps in our knowledge of this most complex phenomenon have become more apparent.

Sources

Identifying the hydrocarbons in Sydney's air and tracking down their sources has been a project of the Atmospheric Science Section of the CSIRO Division of Fossil Fuels since 1975. Under the leadership of Dr Maurice Mulcahy, the Section's work has concentrated on measuring the trace quantities of hydrocarbons in the air and studying the chemistry of each type.

In this work they have been assisted by Dr Frank Whitfield and Mr Kevin Shaw, of the CSIRO Division of Food Research,

The smog sets in.
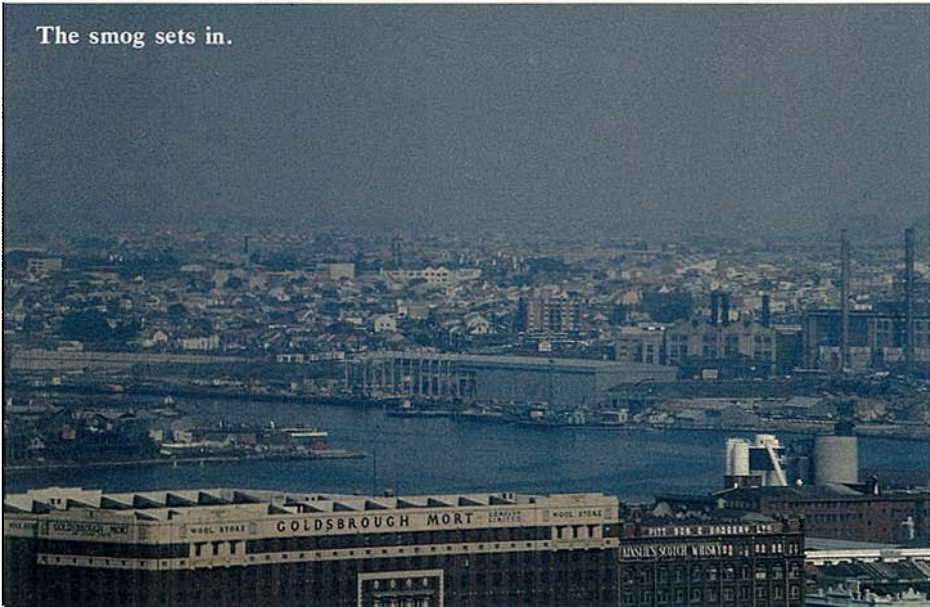
who are experts in the use of a very sensitive analysis system in which the output of a gas chromatograph is fed to a mass spectrometer.

Early in the program, they used this complex technique to identify more than 200 hydrocarbon species in Sydney's atmosphere, ranging in concentration from 50 parts per billion (by volume) to the limit of detection — 0·002 p.p.b. The table on page 5 lists the ten major hydrocarbon constituents of Sydney air and their average concentration. These ten compounds account for about half the weight of all the organic material detected.

In view of their potential for forming photochemical smog, it is interesting to note that the concentration of terpenoids — major constituents of eucalyptus oil — was near the threshold of detection. This indicates that gum trees and other vegetation are unlikely to have any impact on smog formation. However, Ms Suzanne Quigley of the Atmospheric Science

Sydney — Australia's most smog-bound city

ozone level (p.p.h.m.)

	1974	1975	1976	1977	1978	1979	1980	1981
Sydney	20	24	21	29	18	16	19	19
Melbourne		13	25	13	15	15	20	11
Adelaide			9	12	14	11	11	9
Brisbane				12	8	10	11	11
Perth						14	7	—

The table shows the maximum 1-hour average ozone levels recorded in Australian cities. All five mainland State capitals have recorded levels above the NHMRC's recommended limit.

Section is undertaking further studies to make sure.

At first sight, the most straightforward way of attributing sources to these compounds is by producing an inventory of the hydrocarbons that find their way into Sydney's air. The New South Wales State Pollution Control Commission (SPCC)

has made such an inventory and it is shown in the table on the right. It indicates, for example, that 50% of the total emissions come from motor vehicles. As estimates of this kind depend on assumptions about emission rates and vehicle usage, they are inevitably subject to error.

The CSIRO scientists have adopted another method, called 'source reconciliation'. It is based on reconciling the hydrocarbon composition of each source's emissions with the concentrations of the hydrocarbons in air samples. Of course this approach has its drawbacks, too. It assumes that the hydrocarbon species don't react appreciably between release and sampling. Another major problem lies in the variability of most sources; this can be alleviated by the judicious choice of sampling sites and by taking many samples.

Mr Peter Nelson, Ms Quigley, and Dr Martin Smith collected data from hundreds of samples taken on about 50 days. From these they determined the relative contributions from the main hydrocarbon sources that best fit the measured hydrocarbon composition of the air.

The principal sources of atmospheric hydrocarbons (excluding methane, which is essentially non-reactive) turned out to be vehicle exhaust (36%), evaporation of petrol (32%), and evaporation of solvents (23%). Vehicles contributed through petrol evaporation as well as exhaust, with evaporation accounting for about one-third of their hydrocarbon emissions.

Much mystery remains shrouded in the smog.

The top ten hydrocarbons

	average concentration (p.p.b. by volume)
ethylene	12·5
acetylene	10·1
i-pentane	9·0
toluene	8·9
ethane	7·5
propylene	7·4
propane	5·9
n-butane	7·5
n-pentane	5·0
i-butane	4·7

These 10 compounds account for about half the weight of all the hydrocarbons detected.

An inventory of hydrocarbon emissions

source	tonnes per day		percentage of total	
motor vehicles—exhaust	226		33	
—evaporative	89	} 342	13	} 50
—crankcase	27		4	
paints and other surface coatings	96		14	
printing, dry cleaning, etc.	68		10	
storage and transfer of petroleum products	55		8	
process losses from refineries	48		7	
other	75		11	
total	684		100	

This inventory was drawn up by the SPCC for summer weekdays in Sydney during 1979. It indicates that motor vehicles contribute half the hydrocarbons.

To determine the typical hydrocarbon composition of engine exhausts, the scientists took exhaust samples from 67 vehicles selected as being representative of the total vehicle population. A survey of Sydney traffic conducted by the SPCC and the Australian Department of Transport provided the data needed to choose the representative vehicles.

The hydrocarbon mixture contributed to the air by evaporating petrol is of two different types. When petrol evaporates completely, as it does if spilt, or when a car stops and the engine's residual heat dries out the petrol in the carburettor and fuel line, then the hydrocarbon mix in the air is the same as that in the petrol. However, when petrol partially evaporates, as it does from storage tanks, then the air receives only the more volatile hydrocarbons (the headspace vapour) that are in equilibrium with the petrol at the prevailing temperature.

To ascertain the hydrocarbon composition of Sydney's petrol, the scientists, with the co-operation of the petroleum industry, collected samples from Sydney's refineries every month; they calculated an average composition from the 115 collected and analysed. The composition of typical headspace vapour was calculated for an average petrol mixture, assuming a petrol temperature of 25°C.

The scientists assumed that the contribution made by solvents was due to complete evaporation. So they used an inventory of solvents prepared by the SPCC for calculating this contribution. The SPCC prepared a solvent cocktail reflecting the inventory, and its hydrocarbon composition was analysed.

Leaks from Sydney's gas mains constitute another hydrocarbon source, one consisting mainly of methane, ethane, and propane, and this was found to contribute 4% of the non-methane hydrocarbons in the air. Another minor source was iden-tified as process emissions from petrochemical plants and refineries. These amounted to 5% of emissions.

By selecting data according to the direction of wind at the time, the research team could separate out the hydrocarbon contributions from industrial sites and heavily trafficked areas. One finding was that, relative to the other sources, the central business district contributed 8–10% more non-methane hydrocarbons from exhausts than the rest of the city.

Prediction still difficult

Many factors combine to determine whether photochemical smog will occur and how severe it will be: the composition and concentration of precursors — the hydrocarbons and NO_x — are major ones, and environmental conditions of temperature, strength of sunlight and wind, and other meteorological factors are also very important.
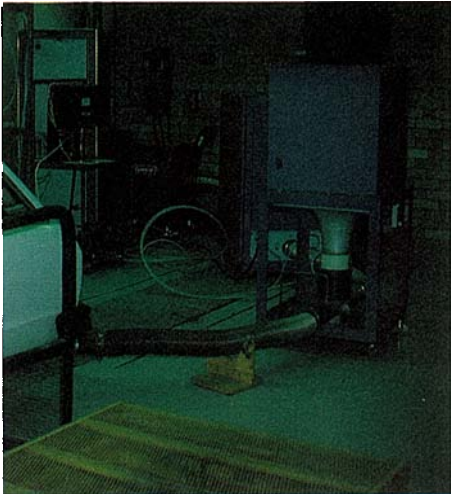
Vehicle exhausts, here being sampled at the SPCC laboratory, are major contributors of smog-forming gases.

The Sydney Oxidant Study

Much of the information on Sydney's photochemical smog was gained over the summers of 1975/76 and 1976/77 during a million-dollar exercise called the 'Sydney Oxidant Study'. The State Pollution Control Commission of New South Wales funded and co-ordinated the study, and the information acquired allowed the Commission to formulate smog-control regulations that are now in force.

As well as the SPCC, participants in the study included Macquarie University (School of Earth Sciences), CSIRO (Division of Fossil Fuels), and Sydney University (School of Mechanical Engineering). Their roles were:

▶ SPCC — to co-ordinate the study; also to supplement the Commission's permanent monitoring network with mobile laboratories on land, at sea, and in the air on days when heavy smog was expected

▶ Macquarie University — to investigate the role of meteorology in the formation of smog

▶ CSIRO — to investigate smog hydrocarbons (their type, properties, local variations, and sources) and to undertake experiments with the smog chambers

▶ Sydney University — to operate a mobile laboratory on days when smog was forecast, and to investigate the relation between the levels of precursors and ozone

'Sydney Oxidant Study: Data Report.' (SPCC: Sydney 1979.)

The reactions that lead to the production of ozone are complex, and still incompletely understood. The various chemical processes involved interact with one another, making the outcome hard to predict.

For example, nitric oxide is an essential ingredient in producing smog. Yet, if the initial concentration of nitric oxide in the atmosphere is increased, it by no means follows that ozone levels will rise too. Indeed, they may decrease because nitric oxide and ozone react strongly with each other.

Dr Keith Post of the Department of Mechanical Engineering at Sydney University has examined data from many smog episodes and proposed a fairly simple formula to relate ozone levels and the concentration of non-methane hydrocarbons (see the box below).

However, the real-life situation is undoubtedly too complex to encompass fully in a single formula. Indeed, the complexities involved — such as those of weather

The sources of atmospheric hydrocarbons

| source	contribution by weight to non-methane hydrocarbons (%)
vehicle exhaust	36
petrol	16
petrol vapour	16
solvents	23
gas	4
petrochemical plants and refineries	5

These figures were obtained by reconciling the composition of hydrocarbons in samples of Sydney air with the composition of the hydrocarbon sources. Despite some differences, there is broad agreement with figures given by inventories.

and non-uniform, or 'lumped', emissions (discussed later) — have led to confusion about the possible outcomes of various smog-control strategies.

Smog-chamber studies

Studies by Mr Graham Johnson and his CSIRO colleagues have sought to unravel what is going on. Their primary tool has been a pair of smog chambers that allow the photochemical smog process to be observed under conditions very similar to those existing in Sydney's air.

The chambers, each of 20 cubic metres, are made of transparent FEP Teflon film, allowing both visible and ultraviolet sunlight to penetrate easily. They can be moved on rails between darkness and full sunshine. Sometimes Sydney air was admitted directly, sometimes purified air, but more often the chambers were doped with particular chemical ingredients — petrol, solvents, blends of hydrocarbons, oxides of nitrogen, or other substances of interest.

A simple formula for ozone

Dr Keith Post of the Department of Mechanical Engineering at Sydney University has found that afternoon levels of ozone can be predicted fairly well from measurements of NO_x and non-methane hydrocarbons in the morning.

During the Sydney Oxidant Study, he and his colleague Professor Robert Bilger noted that contour lines of afternoon downwind ozone concentration, $[O_3]_{max}$, fell uniformly on a graph of $[NO_x]$ and $[NMHC]$, the upwind morning concentrations of these precursors.

Most occasions of Sydney smog fall
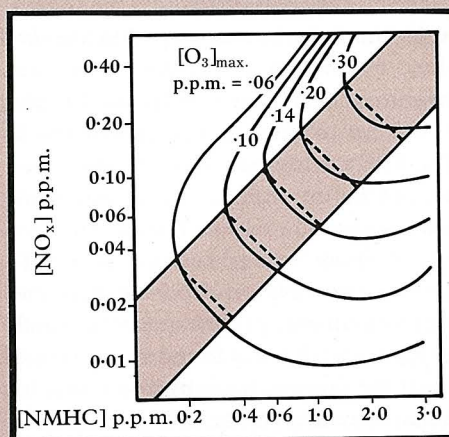
within the shaded area of the graph, representing $[NMHC]:[NO_x]$ ratios between 5 and 20. Within this region, the ozone concentration is related pretty closely to the precursor levels by:

$$[O_3]_{max.} = 0.39 ([NO_x] \times [NMHC])^{0.36}$$

This approximation is shown as the dotted lines on the graph. For some unknown reason the formula did not work so well with data collected by the SPCC during 1980/81. However, CSIRO is developing what is expected to be a more accurate procedure for predicting ozone levels.
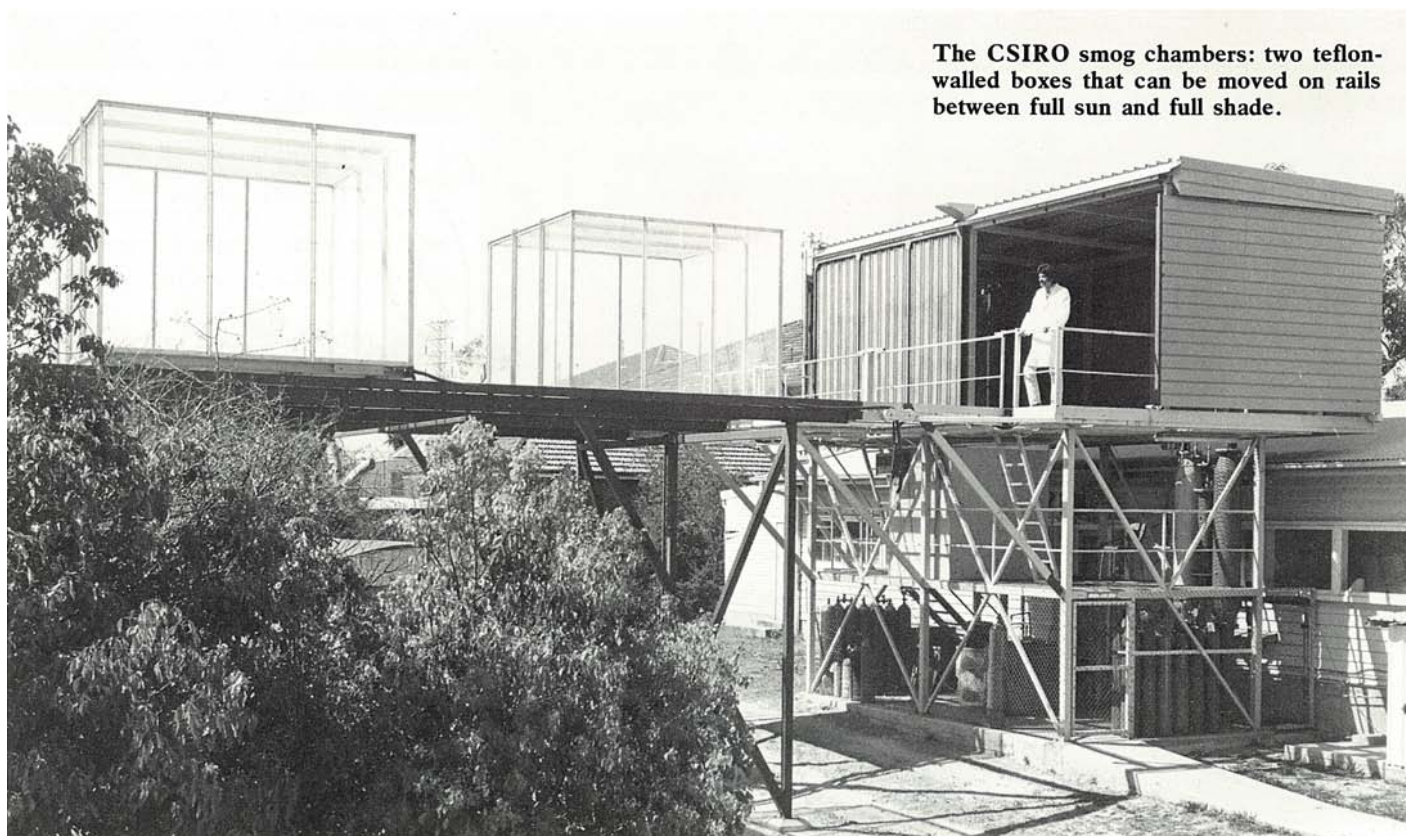
The CSIRO smog chambers: two teflon-walled boxes that can be moved on rails between full sun and full shade.

Hundreds of experiments allowed the team to build up a fairly detailed picture of the smog-forming mechanisms (see the box on the chemistry of smog on page 8). Study of the chemistry revealed two dominant variables — the concentration of compounds (for which they coined the term 'primary smog product' or PSP) and the amount of sunlight since daybreak. PSP includes the concentration of nitric oxide that has been oxidized to nitrogen dioxide, as well as the concentration of ozone, and gives a better chemical description of the end-product of the smog soup than does concentration of ozone alone. Looked at another way, PSP is a measure of the quantity of molecular oxygen that has been dissociated in the course of smog formation.

The researchers found that a graph of PSP against accumulated sunshine showed a straight line, eventually flattening out near the end of the day. Every case of smog formation they studied fell into this two-stage pattern, a linear phase followed by a plateau. They came to call the first stage the light-limited phase, and the second the NO_x-limited one. Let us see why.

The existence of the plateau shows there is a maximum PSP, or smog density, that a given set of precursors can produce. And the smog-chamber experiments revealed the important finding that this maximum smog level depends only on the initial concentration of nitrogen oxides.

Without the OH at one-millionth of a part per billion, ozone would fail to appear.
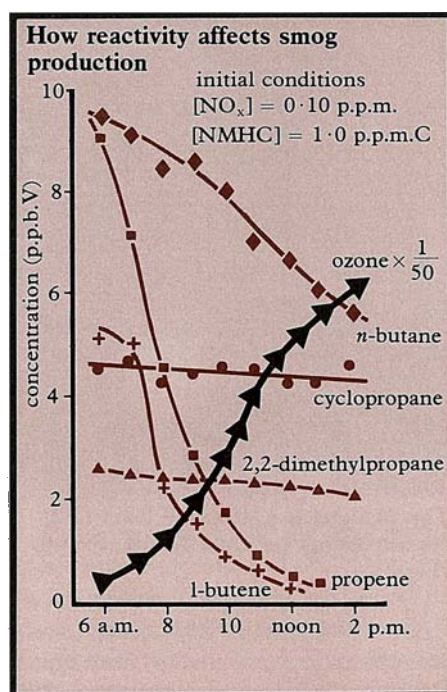
However, before we rush in and start looking for ways to reduce NO_x levels while ignoring the hydrocarbon emissions, that is not quite the full story. It seems that Sydney's meteorology seldom lets the smog-formation process reach the plateau region. The smog is often cleared away by strengthening winds, notably the sea breeze that frequently refreshes the city on hot summer days. Or the smog may be dispersed by the breaking up or deepening of the inversion layer due to convective heating.

And so a more important consideration is the PSP level reached by noon — in other words, we are interested in the rapidity of smog production and hence the steepness of the rising portion of the graph.

The researchers found that, for a given hydrocarbon mixture (we'll talk more about this aspect later), three factors influenced the rate of PSP production:

▶ the initial concentration of hydrocarbons

▶ the strength of sunlight

▶ the temperature

Hydrocarbon concentration is the most important of the three, with PSP (and ozone) levels produced in a given time being directly proportional to this quantity. The seasonal variations of sunlight and temperature have smaller effects.

How reactivity affects smog production

initial conditions
$[NO_x] = 0\cdot10$ p.p.m.
$[NMHC] = 1\cdot0$ p.p.m.C

ozone $\times \frac{1}{50}$

n-butane

cyclopropane

2,2-dimethylpropane

1-butene

propene

The reactivity of a hydrocarbon is just as important as its concentration in contributing to smog formation. In this smog-chamber experiment, 1-butene has given rise to much more ozone than cyclopropane, although both were present at the same concentration initially.
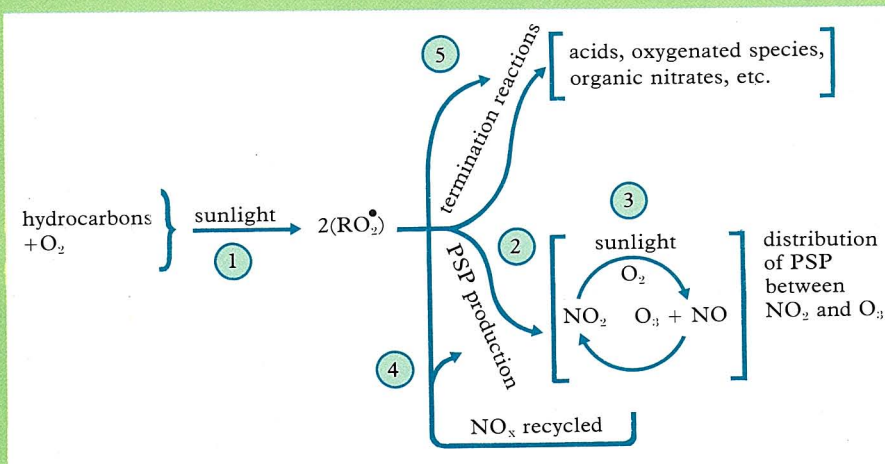
Smog-chamber experiments at the CSIRO Division of Fossil Fuels have allowed the scientists to build up a more detailed picture of the smog-forming process. Many interactions — between a number of competing and consecutive chemical reactions — complicate the chemical processes. Nevertheless, we can identify five basic reactions, as shown in the diagram.

Step 1: dissociation of molecular oxygen
Sunlight interacts with aldehydes to give hydroxyl radicals. These attack hydrocarbons, and the resulting fragments react with oxygen molecules to give hydro- and alkyl-peroxy radicals ($RO_2^•$).

Step 2: formation of primary smog products (PSP)
The products from Step 1 ($RO_2^•$) react rapidly with NO, to give NO_2.

Diagram:

hydrocarbons $+ O_2$ } $\xrightarrow[\text{①}]{\text{sunlight}}$ $2(RO_2^•)$

② termination reactions → [acids, oxygenated species, organic nitrates, etc.]

② PSP production

③ sunlight O_2 : $NO_2 \rightleftarrows O_3 + NO$ — distribution of PSP between NO_2 and O_3

④ NO_x recycled

Step 3: distribution of PSP between NO_2 and O_3
In sunlight, NO_x cycles continuously between NO_2 and $NO + O_3$.

Step 4: return of regenerated NO

The NO regenerated in Step 3 is returned to Step 2.

Step 5: consumption of radicals
Radicals produced in Step 1 participate in side reactions that remove NO_x.

The Macquarie University team takes measurements on Goat Island, Sydney Harbour.

The reduction in PSP concentration brought about by a change from typical summer to winter temperatures (say 35°C to 20°C) is about the same as that induced by a reduction in light from clear summer day levels to clear winter day ones. Thus, summer days of high temperature as especially susceptible to high ozone levels, whereas smog days are unlikely to occur in winter — as much because of the temperature as the weak sunlight at these times.
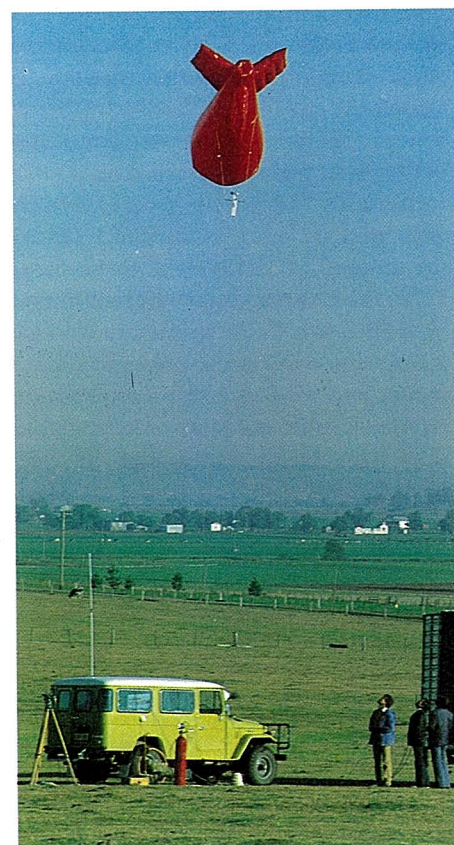
Another factor to keep in mind is that more evaporation of hydrocarbons occurs on the warmer days, accelerating the rates of smog formation. About two-thirds of annual hydrocarbon evaporative emissions happen during the susceptible October–April period.

Reactivity

Although all hydrocarbons will transform into smog given enough sunshine and time, some hydrocarbons are more reactive than others, and will form smog more quickly. In a race against the breaking up of the inversion layer, smog formation will be more advanced in more-reactive hydrocarbon mixtures.

Smog prevention will be easier to achieve if emissions of the most reactive hydrocarbons can be preferentially limited. But which hydrocarbons are most reactive? Mr Johnson and his colleagues have again made use of the smog chamber to put numbers — the rate coefficients — on 41 major components of Sydney's hydrocarbon pollution. The coefficients for 12 of these had not been measured before, and most of the others had not been determined under actual outdoor conditions.

Remarkably, most hydrocarbons in the urban air enter the cycle of smog-forming reactions predominantly by reaction with a single species — the hydroxyl radical. Yet the OH radical occurs naturally at a concentration not much more than one-millionth of a part per billion, about 10^{14} times less than that of oxygen. Without the OH, ozone would fail to appear.

The scientists determined rate coeffi-

An instrument package attached to this 'tethersonde' balloon provided meteorological information for the Macquarie University team.

cients for reaction of hydrocarbons with OH by comparing the rates of disappearance of the species under test with that of a compound (*n*-hexane) whose reaction rate was already well known. Once they had determined the reactivity of the constituent compounds, they could calculate the reactivity of the hydrocarbon mix from particular sources (such as vehicle exhaust).

One important finding was that petrol vapour (from the headspace over petrol) is about 50% more reactive than the petrol from which it originates. This is because volatile and highly reactive olefins are enriched in the vapour. They are 10 to 20 times more reactive than the other hydrocarbons in petrol.

On the other hand, the solvents used in Sydney have an appreciably lower average reactivity than petrol. Propylene, used in a number of industrial processes, was found to be the most reactive hydrocarbon emission (five times as reactive as vehicle exhaust).
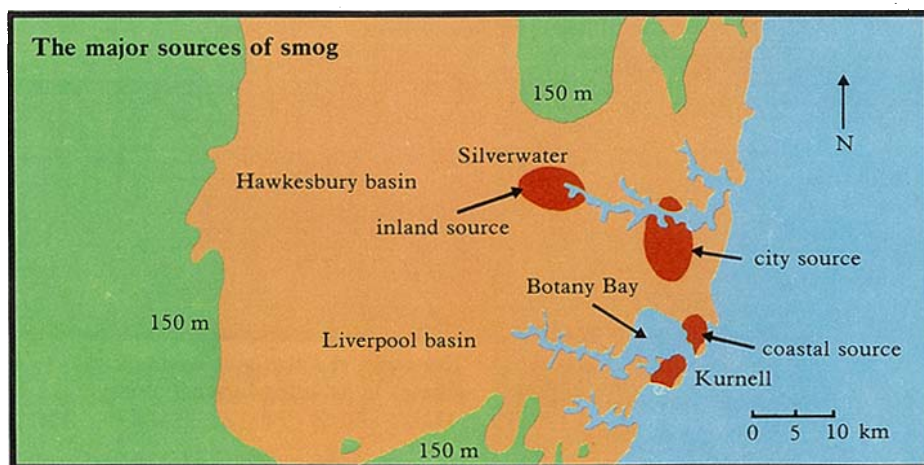
After the scientists determined the reactivity of each hydrocarbon source, they could calculate its percentage contribution to the rate of smog formation. They found that vehicle exhaust, representing 36% of the hydrocarbon emissions, accounted for 33% of smog-forming speed — not greatly differing figures. However, petrol vapour contributes only 16% of hydrocarbons but is responsible for 25% of

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Some scientists think that large point sources of hydrocarbons are to blame for high smog levels.

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the rate of smog production. Balancing matters in the opposite direction, solvents deliver 23% of the hydrocarbons and only 14% of the reactivity. The rest of the results are shown in the table.

The figures show how our use of motor vehicles is the dominant cause of smog. Vehicle exhausts, petrol, and petrol vapour together are responsible for three-quarters of the air's smog-production rate.

Mr Johnson also points out the major role of olefins in creating smog. Despite the fact that these hydrocarbons form only 7% (by weight) of the petrol sold in Sydney, they are the source of up to 44% of the total photochemical reactivity of the air. They are emitted to the air as neat petrol

The major sources of smog

The CSIRO scientists identified three areas as major contributors of smog precursors.

(11% of total reactivity), petrol vapour (22%), and unburnt petrol in vehicle exhaust (a further 11%).

Yet olefins make up the most variable component of Sydney's petrol. Over the course of 31 months, representative monthly samples (made up of 10 smaller samples) of petrol from Sydney's two major refineries were analysed. The month-by-month olefin concentration ranged from 1·8% to 12·8%, averaging 7%. Calculations indicate that a variation of this magnitude in olefin content could cause the rate of smog formation during the morning in Sydney to vary from the average by up to one-third.

Disappearing smog

If at this point it seems that scientists are sorting things out nicely, then be prepared for something they have great difficulty explaining.

We mentioned at the start of the article that, since the middle of the 1970s, smog occurrence has decreased dramatically, as the chart on page 10 shows. From a 1976/77 peak of 66 days when ozone exceeded 12 p.p.h.m., the number of smog days a year has fallen to a handful. What is the explanation?

Inventories drawn up by the SPCC show that emissions have hardly altered. Non-methane hydrocarbons are calculated to have decreased by 9% and oxides of nitrogen to have increased by 7% between 1976 and 1980. These changes are not very significant, and by themselves would have led to virtually no change in the number of smog episodes.

But the observations tell a different story: the highest non-methane hydrocarbon levels have gone down to about one-quarter of their previous values, and peak NO$_x$ levels have increased by about 50%. Current models fail to reconcile these figures with the very large decrease in smog levels. Additional factors seem to be at work.

Of course, one thing we can always blame is the weather. As *Ecos* 16 pointed out, many meteorological factors are involved in ozone production; in particular, the drainage of cool overnight air from the Blue Mountains towards the coast is an important event in ozone production. The strength, depth, and direction of this drainage flow, together with its onset and finishing times, influence ozone levels, and similar considerations apply to sea breezes. The effects of large-scale weather systems, notably anti-cyclones, also have to be reckoned with.

Mr Nelson of CSIRO and collaborators at the SPCC and Macquarie University have found two conditions necessary for high hydrocarbon concentrations. An inversion layer 140–400 m deep, and 3–7°C warmer than the air below it, is needed; and, as the second condition, the wind direction must be such as to allow air to pick up precursors from high-emission areas and take them over the city.

These conditions are usually accompanied by well-developed drainage flow (1–3 m per sec. and 100–200 m deep). However, this last condition is not always necessary. High hydrocarbon concentrations, including the highest recorded during 1979 and 1980, have occurred on days of weak drainage flow.

Other exceptions to the general rule can always be found, and Dr Robert Hyde of Macquarie University has found that no simple meteorological factor can be correlated with ozone levels. Mr Tony Mitchell and his colleagues at the SPCC have found no difference in inversion heights and strengths, temperatures, or dispersion conditions between 1976 and today that could explain the infrequent appearance of the smog.

Yet it may be that, when the complex meteorological interactions are unrav-

Some hydrocarbons are more reactive than others			
source	reactivity (compared with methane)	abundance (% by weight)	contribution to total reactivity of air (%)
vehicle exhaust	248	36 ⎫	33 ⎫
petrol	279	16 ⎬ 68	17 ⎬ 76
petrol vapour	426	16 ⎭	25 ⎭
gas mains leaks	63	4	1
process propylene	1250	1·8	8·4
process propane	80	1·8	0·5
solvents	162	23	14

The more reactive a compound, the greater is its smog-forming ability.

elled, the fickle weather will prove to be responsible. If so, then we may have just been experiencing a temporary respite and, if we don't clean up emission sources, high smog levels will return as unexpectedly as they went.

Point sources

Another explanation remains to be considered, and according to Dr Post it can account in large measure for the observed reduction in smog episodes. He and a number of other scientists think that large point sources of hydrocarbons are to blame for high smog levels. The idea is that these sources emit 'parcels' of hydrocarbons that in turn lead to parcels of air containing exceptionally high ozone concentrations.

Dr Post's analysis confirms that no substantial change in the total mass of hydrocarbons emitted has occurred since 1975–77. Morning weather conditions have also stayed much the same.

However, Dr Post has found evidence that parcels of hydrocarbons from large point sources have disappeared in recent years. The evidence comes from looking at the relation between non-methane hydrocarbon (NMHC) concentrations, NO_x levels, and the ratio $NMHC:NO_x$.

Without lump emissions of hydrocarbons, the levels of NMHC and NO_x tend to rise together, whereas large point sources, when emitting hydrocarbons, give rise to air parcels with $NMHC:NO_x$ ratios higher than normal. In other words,

Where have the smoggy days gone?
number of days per year when ozone exceeds 12 p.p.h.m.

based on three monitoring stations

74/75 76/77 78/79 80/81
summer season

Since a peak in the summer of 1976/77, the number of smoggy days has decreased dramatically.

NO_x emissions tend to be fairly uniformly distributed, and air parcels with abnormal $NMHC:NO_x$ ratios indicate point-source emissions of hydrocarbons. And it is just these atypical parcels that have the highest rate of ozone formation.

Hydrocarbon parcels can originate from oil refineries, petrochemical plants, and petroleum storage areas. Although these are not large emitters in the broad scheme of things, a cloud of emissions from them could significantly influence the maximum values of non-methane hydrocarbons (and ozone) measured at nearby monitoring sites. A number of monitors are only a few kilometres from potential point sources.

Better housekeeping now prevails at these hydrocarbon sources. Better engineering practice has allowed some sources identified by the SPCC — a car-manufacturing plant, petroleum loading terminals, and petrochemical plants — to reduce their emissions by 40%. In addition the rapid increase in the price of crude oil since the mid seventies has encouraged measures to reduce evaporation losses of petrol, solvents, and other volatile petroleum products. Solvent recovery and re-use has also become economically attractive.

This therefore may explain why bad ozone episodes have become less common despite the fact that general emission levels have not changed much.

Supporting evidence comes from the SPCC monitoring network. Hydrocarbon measurements at Lidcombe and Rozelle have dropped radically, and examination of the paths of air parcels with high ozone levels indicates that some episodes may have originated at point sources of hydrocarbons.

In 1976, when school children at Sylvania were taken to hospital suffering respiratory distress, photochemical smog was blamed. Evidence has since come to light that a large release of hydrocarbons into the air had occurred from a nearby

point source. The SPCC also has records of a number of other occasions when a high hydrocarbon reading has been followed later by a high ozone reading in the same air parcel.

Perhaps these intermittent lump emissions can be reduced a bit more, or perhaps they can be timed to occur outside the morning precursor-mixing period.

But reductions in hydrocarbon parcel emissions cannot fully account for the observed reduction in smog days. Nobody believes the smog problem can be totally solved by turning the screw a bit more on a few refineries or chemical plants.

Almost certainly, many factors are helping make the air that Sydneysiders breathe less ozone-laden. Even instrument calibrations can be invoked to show that the smog situation is better than it used to be (or appeared to be). More sensitive instruments and better calibration procedures now in use suggest to SPCC scientists that readings back in the mid seventies were perhaps too high. Sydney's record ozone reading — 38 p.p.h.m. at Coogee on March 31, 1977 — has been revised to 34 p.p.h.m.

We now know much more than we did about Sydney's photochemical smog, but there's still more going on that scientists have been unable to identify to date. They cannot explain how one of Sydney's highest ozone episodes — with a recorded 22 p.p.h.m. — occurred on a week-end during a petrol strike . . . and it was overcast as well.

Andrew Bell
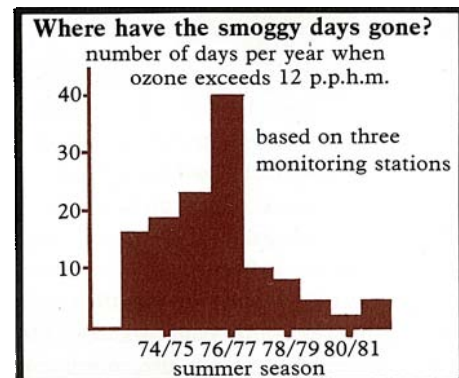
More about the topic

'The Urban Atmosphere — Sydney, a Case Study.' Ed. J.N. Carras and G.M. Johnson. (CSIRO: Melbourne, in press.)
This book seeks to assemble and review all the research undertaken on Sydney's atmosphere in recent years. It contains papers given at an invited conference in May 1982 at Leura, N.S.W., and includes the discussions that followed each paper.

As well as photochemical smog, topics include brown haze, acid rain, and particulate lead. Mr Graham Johnson, one of the conference organizers and editors, says the book 'gives an interesting insight into the current scientific understanding of the processes affecting Sydney's atmosphere'. The editors hope it will serve as a reference work for some time to come.

The book is expected to be available shortly from:
CSIRO Editorial and Publications Service, P.O. Box 89, East Melbourne, Vic. 3002.