Melbourne smog and the new breed of cars

Australian Design Rule 37 is intended to reduce the smog levels in our major cities to healthier levels. From the beginning of this year, all new cars have had to comply with new emission limits. As a result, new cars have catalytic converters in their exhaust systems, incorporate measures to reduce evaporative losses of petrol, and use unleaded petrol.

The smog chambers, loaded with polluted air and illuminated with lamps that simulate sunlight.

Taken together, these changes should reduce the emission of smog-producing hydrocarbons (non-methane hydrocarbons, or NMHC) of vehicles complying with ADR 37 by about half (compared with pre-1986 vehicles). It will probably take about 10 years before 90% or more of the old cars disappear and are replaced by the new breed.

But how will halving the emissions from individual vehicles affect that major pollution indicator, ozone? This noxious gas, the principal component of photochemical smog, results from raw pollutants — the precursors, principally nitrogen oxides (NO_x) and NMHC — stewing together in the atmosphere for hours under the influence of sunlight. Some of the reaction pathways involved are now understood, but predicting how ozone levels will change in response to a change in emission levels still involves a degree of educated guess-work.

Mathematical models, which incorporate many of the chemical and meteorological variables concerned, are helpful, but they invariably contain a number of simplifications.

For this reason, scientists at the CSIRO Division of Atmospheric Research have conducted experiments using smog chambers, filled with samples of polluted Melbourne air, to find out what ozone levels are likely to be after ADR 37 takes effect. In a smog chamber — a transparent inert container — an air sample is irradiated with light, and the resulting photochemical reactions are studied using sensitive analysis equipment.

Of course, smog chambers have their drawbacks. One of them is that the walls of the chamber can influence the course of the photochemistry inside it. For example, the notionally unreactive FEP Teflon film from which such chambers are usually made evidently provides a minute, but significant, source of the powerful OH radical. Most hydrocarbons in urban air enter the cycle of smog-forming reactions predominantly by interaction with this radical. Yet OH occurs naturally at a concentration of only about 1 in 10^{13}, and without it ozone would fail to appear.

So another aim of the scientists was to assess how well a smog chamber can simulate actual outdoor conditions.

What they did was use an aircraft to follow parcels of Melbourne smog throughout the course of a day of high smog levels and, from samples taken, measure how its chemical make-up, particularly ozone, evolved with time. Later, they put another sample of the same raw ingredients (a bagful of polluted early-morning air from the Central Business District) in their smog chamber and subjected it to conditions of light and temperature equivalent to those it would have experienced on a typical smoggy day. In this way they showed that, for a wide range of smog precursor concentrations as starting points, the ozone levels produced in the smog chamber matched those reached by free-roaming smog parcels.

This satisfying outcome allowed the researchers to go one step further. They placed in their chamber exhaust gases derived from a car running on unleaded petrol and fitted with a catalytic converter. The conclusion from this experiment was that, when all vehicles comply with ADR 37, Melbourne smog levels should not go above the acceptable level of 120 parts per billion (120×10^{-9}) set by the Victorian Environment Protection Authority. (This level is the 1-hour average that is not to be exceeded more than once per year.)

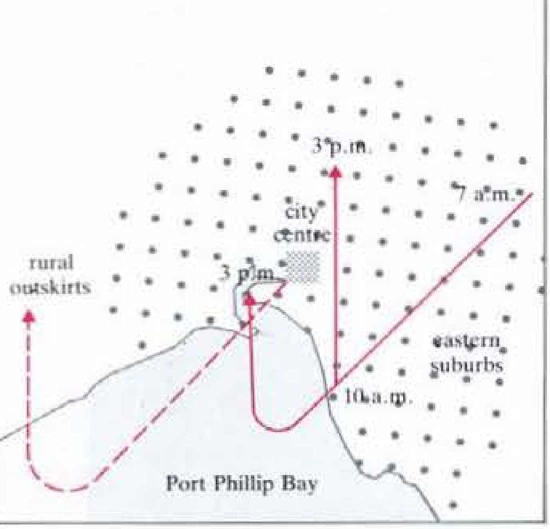
Indeed, even under the severest conditions mimicked in these experiments, levels should not go much above 90 p.p.b. — a welcome change from the 160 p.p.b. or more presently experienced on bad days. In the summer of 1984/85 ozone levels exceeded the acceptable limit on 16 days, and the table on page 12 shows the incidence in other years.

Recipe for smog

The smog-chamber experiments were the final part of a lengthy study on Melbourne smog by a group led by Mr Tony Evans, now retired from CSIRO. Other members of the group were Dr Ian Weeks, Mr Tony Eccleston, and Mr Tom Firestone.

Tracking of smog by plane comprised the first part of the study, and an article in *Ecos* 29 (August 1981) summarised its main results. This work showed how emissions

Typical smog trajectories



The two typical smog trajectories simulated in the smog chamber. The dashed line shows the path of concentrated emissions from the central city under similar wind conditions.

from Melbourne's eastern suburbs appeared to be most important in leading to high ozone readings over the city. Although the concentration of pollutants in these suburban emissions was only about 60% of that coming from the central city area, meteorological factors conspired to give them more importance in generating smog over the city.

According to Mr Evans, most of Melbourne's smoggy days are brought on by gentle morning winds from the north-east. The wind gathers up pollutants over a long stretch of eastern suburbs, and takes them over Port Phillip Bay. Over water, the mixing height — the thickness of the surface layer in which convection and turbulence keep the air mixed — hardly alters, so the smog reactions proceed undiluted. Then, just at the time in the afternoon when ozone levels have built up to their peak, the regular southerly bay breeze blows the smog parcel back over the city.

As the map shows, the same sequence of winds blows the denser pollutants originating from the central city to the outskirts of Melbourne. In this way, higher ozone levels probably occur outside the city than within it.

Compliance with ADR 37 should substantially reduce the number of smog days, but it will be 10 years before more than 90% of cars comply.

Smog days in Melbourne

	number of days when ozone exceeded 120 p.p.b.
1981/82	12
1982/83	24
1983/84	9
1984/85	16

Motor vehicles contribute most to air pollution in the eastern suburbs, and this made laboratory simulation considerably easier. Exhaust, petrol, and petrol vapour together are responsible for about 90% of airborne hydrocarbons in this area, according to an analysis of Melbourne smog that the scientists carried out. The area doesn't contain any large industrial 'point sources' to affect the chemical make-up of the mixture.

As a result, the smog precursors have a remarkably constant composition. And as they have a widespread source, their concentrations are also largely constant.

The idea of smog-chamber simulation was to collect, first thing in a morning, a bagful of vehicle exhaust, taken by driving through the inner city where emissions are most concentrated.

Scientists then mixed the exhaust with appropriate amounts of petrol and petrol headspace vapour (in a ratio of 75:12:12) to give it the characteristic flavour of eastern suburbs emissions.

The actual simulation involved injecting that mixture into a 200-litre FEP Teflon bag at the appropriate concentration and illuminating it with sun lamps.

A computer ran most stages of the experiment, changing conditions, taking samples, and recording the concentrations of nitric oxide, nitrogen dioxide, and ozone registered by sensitive analysis instruments. Its job was to adjust conditions to mimic a day typical of the dozens of encounters that the aircraft made with a developing smog. Hydrocarbon sampling and analysis were done manually.

Light intensity was adjusted to follow the variation in the sun's rays from sunrise onwards (a clear day in February was assumed). Temperatures were regulated to follow those on the typical day.

Air was injected periodically to dilute the sample in the same way as the expanding mixed layer did on that day. For example, between sunrise and 10 a.m. the mixing height over land rises steadily from 100 m to 300 m on most days, and reaches 600 m by 3 p.m.

Most importantly, pollutants were injected every 15 minutes to simulate the passage of a smog parcel over different parts of Melbourne. A sector-by-sector inventory of Melbourne's emissions of hydrocarbons and nitrogen oxides (NO_x) — compiled by the EPA — allowed the scientists to specify the rate of pollutant injection at any point along a given path.

Two paths, representing what Mr Evans believes give rise to the most troublesome conditions, were chosen for the experiments (see the map).

Both traversed the eastern suburbs in a south-westerly direction at 2 metres per second, and reached Port Phillip Bay at 10 a.m. Here one air parcel stagnated for 2 hours and then turned northwards, again over suburbs, while the other continued on over the water, only to turn northwards later and impinge on the central city. Both simulated pathways ended at 3 p.m., when ozone concentrations are frequently highest.

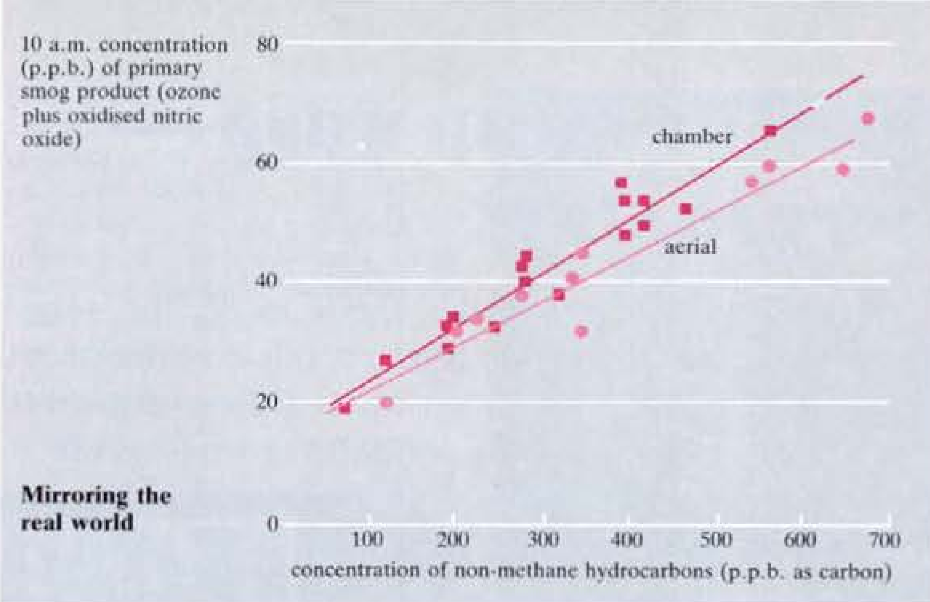
The computer looked after other details: adding small quantities of ozone (about 8% per hour) to make up for that lost to the walls of the bag; and keeping track of the propylene concentration as an indicator of OH concentration.

Actually, the smog chamber was run as a set of four identical chambers, allowing control and duplicate experiments to be run together and thus ensuring that the results obtained were accurate and reproducible.

Hydrocarbons the key

It didn't take many runs to learn that the chamber simulations matched the real world behaviour quite well. Ozone levels at 3 p.m. generally ranged from 100 to 160 p.p.b. for both trajectories — figures that

Samples of polluted air were collected in these bags during an early-morning drive around the inner city.



Mirroring the real world

A bag of polluted air from the inner city was subjected to conditions (of light, temperature, dilution, and extra emissions) similar to those recorded on a typical smog day. As the graph shows, similar ozone levels were produced.

are typical of the readings made by the EPA at its suburban monitoring stations during summer smog days.

However, the ultimate test of the validity of the chamber results was to compare the smog concentrations in it with those measured in the aircraft. Given the same concentration of NMHC to begin with, the chamber had a smog concentration at 10 a.m. only about 10% greater, on average, than that registered in the aircraft. The graph at the top of this column shows this close parallel.

It is the first time that scientists have been able to demonstrate that, after allowing for wall effects, a smog chamber does indeed come close to reflecting the behaviour of outdoor smog.

When the outcome of each Bay-trajectory run was plotted according to the concentration of its starting materials, the other graph on this page resulted. It shows the 3 p.m. concentration of ozone resulting from a morning concentration of NMHC (horizontal axis) and NO_x (vertical axis). From this graph, we can draw two conclusions.

First, we can see that reducing NO_x levels will not always reduce ozone levels; indeed, in some circumstances we could be better off increasing NO_x levels to achieve such an effect. This reflects the complex nature of smog chemistry.

More realistically, we should consider the effect of reducing hydrocarbon concentrations. In this case the effect is dramatic, and even a small reduction in hydrocarbon emissions would have a significant effect. Halving the emissions would, even for a high 10 a.m. NO_x level of 80 p.p.b., reduce the 3 p.m. ozone concentration to well below 90 p.p.b.

Melbourne's atmosphere is particularly sensitive to a reduction in hydrocarbons because the city already has a low $NMHC:NO_x$ ratio (about 7:1).

In the eastern suburbs, particularly, there are no major sources of hydrocarbons apart from motor vehicles. And as a result of Australian Design Rule 27A, which came into effect in 1976, motor vehicles were constrained to emit from their exhaust less than 2·1 grams of hydrocarbons per kilometre travelled. In 1982, Rule 27C limited evaporative emissions during the 2 hours of a special SHED test (Sealed Housing Evaporative Determination) to less than 6 g.

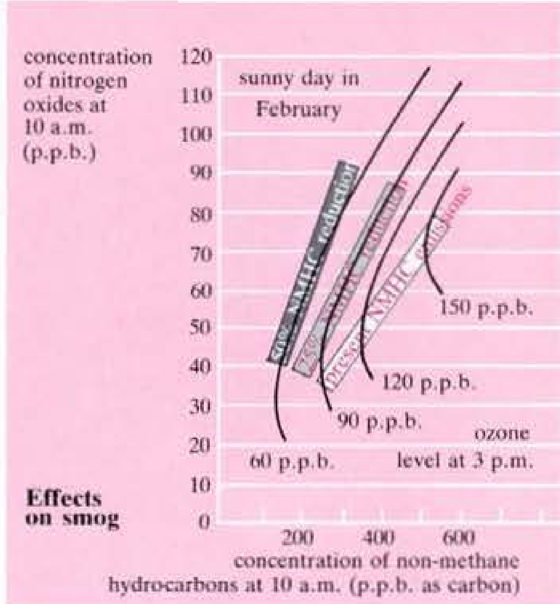
If Melbourne's $NMHC:NO_x$ ratio had been 10:1 or higher, as it often is in Sydney, then a 50% reduction in hydrocarbons would not have had a major effect on ozone levels.

The findings here cannot, therefore, be applied to Sydney. The smog chambers have been shifted to the CSIRO Division of Fossil Fuels in Sydney, and Mr Graham Johnson and colleagues there plan to use them to expand our understanding of smog photochemistry.

After ADR 37

As the table shows, implementation of ADR 37 should reduce hydrocarbon emissions of each complying car by half compared with 1985 models. The use of unleaded petrol and catalytic converters will reduce NMHC exhaust emissions below 0·93 g per km, and carbon monoxide levels will fall, too. The Rule also limits evaporative emissions during the SHED test to one-third of that required by the earlier standard. Since the NO_x emission standard will not change, the $NMHC:NO_x$ ratio should fall to about 3·5:1.

In order to check that this predicted reduction will indeed have the desired effect, the researchers repeated the smog chamber experiment using exhaust gases obtained from a 1986-model car run on unleaded petrol. They found that the new catalytic converter's performance was better than that called for by the Design Rule, removing about 85% of the hydrocarbons. However, when ADR 37 levels were set, allowance was made for a very gradual decline of the converters' efficiency with age, in line with American experience.



Effects on smog

The smog chamber simulations predict that, if every vehicle were overnight made to comply with ADR 37, and so NMHC emissions decreased by 50%, Melbourne's maximum smog levels would fall to those shown in dark grey. However, it will be 10 years before more than 90% of cars comply, and more cars will be on the roads then. Together with other factors, this means a 25% reduction on present-day values is more realistic, an improvement that should keep ozone levels below 120 p.p.b.

Australian Design Rule 37 implies a theoretical reduction in emissions of reactive (non-methane) hydrocarbons by 50%. Since motor vehicles contribute most to air pollution in the eastern suburbs, total emissions should decrease by about that much if traffic density stays at today's levels. However, as explained in the text, in practice the decrease will probably be less.

Reductions in non-methane hydrocarbons

	present contribution of non-methane hydrocarbons (% carbon)	ideal reduction by ADR 37 (%)	resulting contribution (% original carbon)
motor vehicle exhaust	60	50	30
moving vehicle evaporatives	15	67	5
stationary vehicle evaporatives	15	67	5
industrial solvents and the like	10	0	10
	100		50

Accordingly, 5-year-old cars, with 80 000 km on the clock, should still meet the emission limit.

The test with the new car showed that the converter made little difference to the proportions of different hydrocarbons in the exhaust, except that acetylene was much reduced and benzene enhanced. The concentration of NO_x was unchanged.

Gram for gram, the smog-producing power of the catalyst-modified exhaust differed little from that of the present-day exhaust. The scientists conclude that, if implementation of ADR 37 eventually leads to a 50% reduction in emission concentration, ozone levels will drop to about 60% of their present values.

However, a study by Mr Alex Stewart and colleagues at the New South Wales State Pollution Control Commission suggests a less substantial reduction. The group modelled the effect of ADR 37 on total emissions into the Sydney air basin, and calculated that, in the year 2000, annual hydrocarbon emissions from vehicles will be about 25% less than they are at present. This modelling takes account of increase in traffic density, of trucks and other commercial vehicles that are unaffected by ADR 37, and of a degree of tampering with emission-control devices.

The dark grey panel on the graph indicates the result of a 50% reduction in hydrocarbon levels, and the mid grey the effect of a 25% reduction. We see that in either case ozone levels do not exceed acceptable levels. However, as a qualification, the effect of high concentrations of NMHC, recently detected in the western suburbs by the EPA's expanded monitoring network, needs to be considered. If they persist, they could cause troublesome ozone levels under some wind conditions.

Andrew Bell

More about the topic

A chamber study of photochemical smog in Melbourne, Australia — present and future. L.F. Evans, I.A. Weeks, and A.J. Eccleston. *Atmospheric Environment*, 1986, **20** (in press).

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Motor vehicle emissions into the Sydney air basin. A.C. Stewart, M.R. Pengilley, R. Brain, J.J. Haley, and M.G. Mowle. In 'The Urban Atmosphere — Sydney, a Case Study.' (CSIRO Division of Fossil Fuels: Sydney 1982.)

Tracking Melbourne's smog by plane. *Ecos* No. 29, 1981, 16–19.