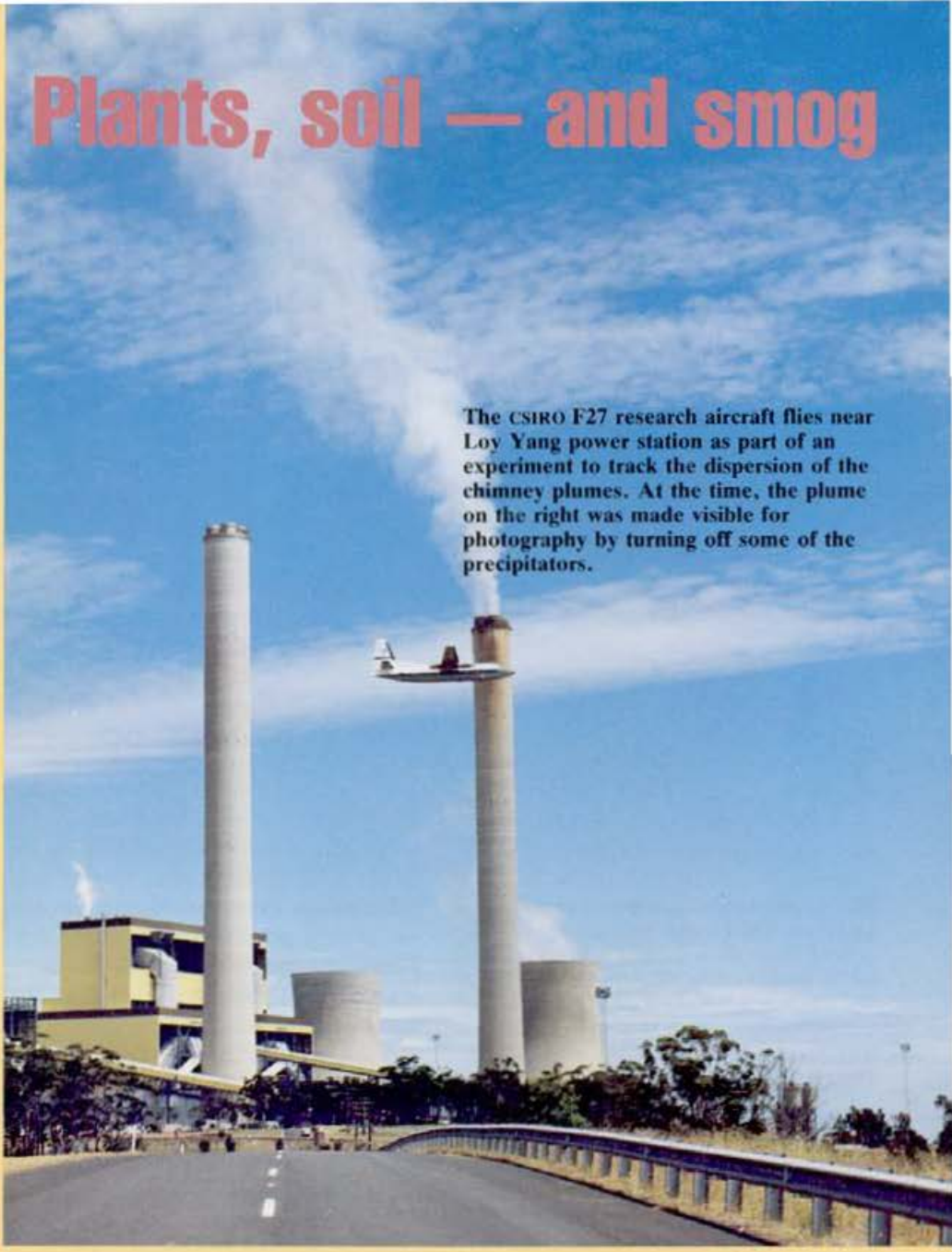
Plants, soil — and smog



The CSIRO F27 research aircraft flies near Loy Yang power station as part of an experiment to track the dispersion of the chimney plumes. At the time, the plume on the right was made visible for photography by turning off some of the precipitators.

Take some hydrocarbons, add noxious NO_x, stew together in sunlight, and you get a nasty brew containing ozone and other toxic chemicals. We call the result photochemical smog, and it's a bane of major urban populations.

Now scientists have discovered that Mother Nature uses the same recipe. She creates hydrocarbons from living, breathing vegetation and adds nitrogen oxides from the soil; and, under suitable summer conditions (such as those found in Victoria's Latrobe Valley), *voila*! — we see perhaps up to 30 parts per billion (p.p.b.) ozone.

Such a level represents about half the concentration typically reached in the Latrobe Valley on days conducive to smog formation, and the discovery answers the puzzle of why the ozone level there has consistently reached levels above those expected due to anthropogenic (man-made) pollutant emissions.

The answer — provided by scientists involved in the Latrobe Valley Airshed Study — only came after they had access to sufficiently sensitive scientific tools. Without an automatic speciating gas chromatograph that could be left to run at a monitoring site in the Valley, we would be none the wiser. This instrument, developed at the CSIRO Division of Atmospheric Research, can detect and identify hydrocarbons at vanishingly small levels — 0·1 parts per billion carbon (p.p.b.C).

Sources of pollutant emissions

emission (tonnes per year)	percentages of global emissions and sources: natural sources		due to man	
sulfur dioxide (SO_2) $0{\cdot}34 \times 10^9$	42%	decomposition of organisms volcanoes	58%	54% energy 43% industry 2% transport
carbon monoxide (CO) $2{\cdot}8 \times 10^9$	77%	fires methane oxidation oceans	23%	75% transport 15% industry 10% disposal
carbon dioxide (CO_2) 44×10^9	55%	ocean fires plant growth	45%	fossil fuel combustion processes
nitrogen oxides (NO_x) $0{\cdot}13 \times 10^9$ as NO_2	55%	microbes lightning, etc.	45%	55% energy 40% transport
ammonia (NH_4) $0{\cdot}08 \times 10^9$	98%	decomposition	2%	fertilisers
hydrocarbons (non-methane) $0{\cdot}26 \times 10^9$	72%	terpenes from vegetation decomposition	28%	65% transport and refineries 25% industry
dust and aerosols	94%	salts from oceans wind driven, volcanoes	6%	40% energy 60% industry

For the whole globe, annual natural emissions of the major pollutants generally exceed those from human activities. The latter usually cause concern because they are emitted in localised regions at high concentrations, often in populated areas. The figures come from the United States Department of Energy and CSIRO.

Until it came along, scientists essentially had to guess the hydrocarbon content of air — and, as it happened, we now see that their estimates were at least 20 times too high.

Sniffing air caught in flasks filled within native forest on the slopes of Mt Baw Baw, the gas chromatograph picked up (on average) 2 p.p.b.C of isoprene, 2·5 p.p.b.C of 1,8 cineole (eucalyptus oil!), and 4·5 p.p.b.C of assorted terpenes. In addition, it detected, on average, 19 p.p.b.C of distinctively anthropogenic hydrocarbons.

At another sampling site near Traralgon, east of the main industrial area in the Valley, the observed minimum reading with a westerly wind remained at about 15 p.p.b.C of anthropogenic hydrocarbons. These came from within the Valley and from human activities over rural south-eastern Australia.

Scientists in Victoria's Environment Protection Authority have estimated that natural emissions of reactive hydrocarbons within the Valley may be about double the amount emitted as the result of human activities. Moreover, most of the natural hydrocarbons are emitted during the summer months, when temperatures and light intensities support smog production.

On a world-wide scale, recent calculations indicate that 72% of atmospheric hydrocarbons originate from natural sources (see the table above).

NO_x from soil bacteria

The other necessary ingredient for photochemical smog is NO_x — the collective term for nitrogen dioxide and nitric oxide. Both of these compounds are emitted in large quantities by power stations, industry, and motor vehicles in the Valley. In 1984, some 52 000 tonnes of NO_x were emitted by these sources, 87% of it by power stations.

In this context, natural sources appear small. Mr Lee Duffy, Mr Ian Galbally, and Mr Malcolm Elsworth, of the CSIRO Division of Atmospheric Research, calculate that biological sources — principally the soil — emit 9% of the Valley's NO_x during summer. However, there is another factor to consider.

Power stations put their NO_x into the air through tall stacks — usually more than 100 m high and, in the case of the new Loy Yang stations, up to 260 m high. This means that emissions frequently pass through the inversion layer and do not immediately contaminate the boundary layer underneath where humans, and plants, live.

When we consider pollution at the surface only, we find a much bigger proportion of the summertime NO_x — about 54% — originates from the soil. Dividing the Valley into 10-km grids gives another perspective: for 80% of the grid squares, natural NO_x emissions exceed artificial ones.

Grid squares dominated by grassland or crops emit about 300 kg of NO_x per day in summer, whereas forested squares contribute much less — about 60 kg — per day. The difference relates mostly to the nitrogenous fertilisers that are applied to crops and improved pasture.

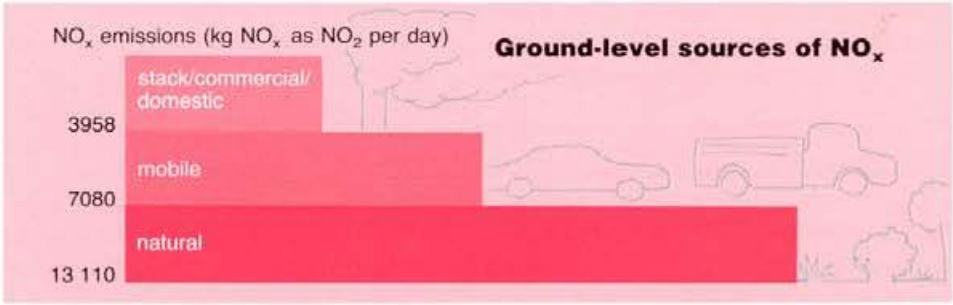
The NO_x comes from the activity of microbes in the top few centimetres of soil. In moist soil, where vegetation grows freely, up to 95% of the NO_x is nitric oxide (NO), whereas in dry soil much of it can be nitrogen dioxide (NO_2). Many other factors control the strength of the bacterial activity, but the most important two are land use (the type of vegetation cover) and temperature.

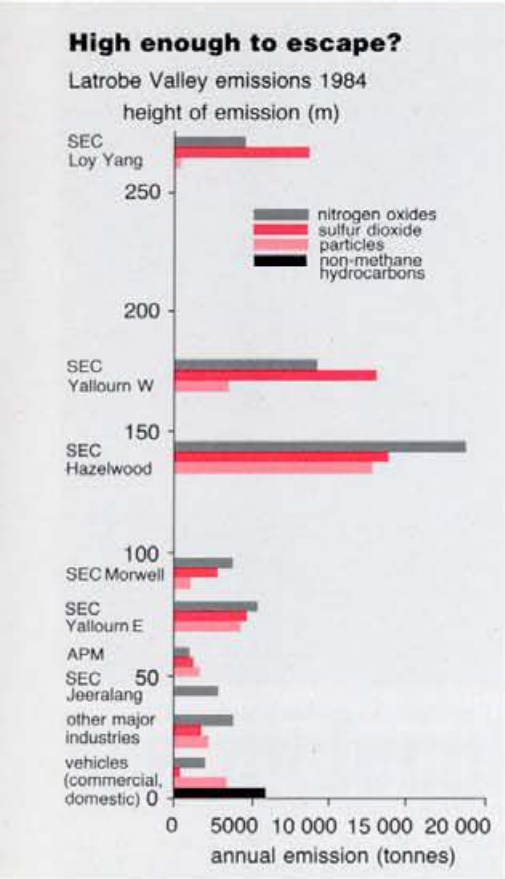
Mr Galbally and his colleagues have measured the NO_x flux from areas in northern Victoria, and have seen how the flux varies directly with temperature. They applied this relationship to the Latrobe Valley case, using figures for vegetation categories (grassland, forest, and cropland) derived from overseas studies.

Figures for soil temperature were derived from measurements made at two sites in the Valley during summer.

In this way, the researchers could derive a Valley-wide figure for daily NO_x emission. They derived a corresponding figure

About half the ground-level sources in the Latrobe Valley are natural. In addition, major stacks liberate 121 900 kg of NO_2 a day, but this largely escapes the boundary layer.





Major industrial sources disperse their pollutants through high chimneys; most of their NO_x therefore escapes the boundary layer. We now find that for emissions of NO_x and reactive organic carbons close to the ground, natural emissions are comparable with artificial ones.

for hydrocarbons — 275 g per sq. km per hour — from the measurements they had made on air from Mt Baw Baw forest.

Computer model of smog

With these figures for precursors to hand, a team of scientists at the Environment Protection Authority — Mr Martin Cope, Dr Frank Carnovale, Mr Barry Cook, and Mr Dennis Hearn — and Mr Galbally from CSIRO ran a computer model of smog production. The model took into account 40 chemical species reacting through 83 pathways.

They fed into the model conditions existing during a 3-day smog episode during 1988 (27–29 January). The Valley is prone to such long-lived episodes because of its 'boxed in' nature. Compared with Melbourne, it has three times as many days when the mid-afternoon ventilation rate — the product of wind speed and the depth of the boundary layer — is low. Pollutants are therefore apt to stew together for extended periods.

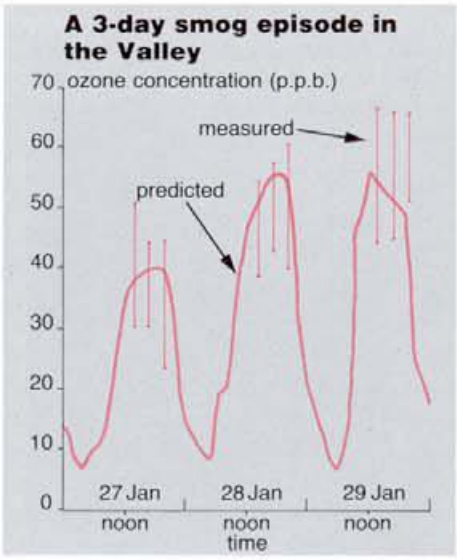
During the episode in question, when the Valley was shut off from outside sources, the observed 1-hour maximum ozone levels at rural sites not influenced by power station emissions were 36 p.p.b., 44 p.p.b., and 50 p.p.b. on the three days. Note that these levels are low relative to recommended standards; the State's Environment Protection Policy (SEPP) considers unacceptable a 1-hour level of 120 p.p.b. of ozone on more than one day per year. On an 8-hour basis, levels of 50 p.p.b. are unacceptable if they occur on more than 3 days a year.

On 29 January the maximum measured ozone concentration in the Valley was 59 p.p.b., but the recording station in question is thought to have been influenced by power station emissions.

How much of the blame for enveloping the Valley's residents with photochemical smog on the days concerned can we place on Nature? The simple answer is — about one-third.

Modelling reflected the actual observed ozone levels fairly accurately, as the graph (below) indicates. Moreover, it showed that the ozone levels were NO_x-limited — that is, the amount of ozone produced was restricted by the availability of NO_x rather than by that of hydrocarbons. In such a situation, if half the surface-emitted NO_x came from natural sources, then ozone levels would be approximately reduced by one-third if these sources were absent. On the other hand, modelling showed that halving (or doubling) the hydrocarbon figure would have very little effect on the ozone levels reached.

Because of the sensitivity to NO_x, any slight addition of such material would tend to increase ozone levels. For example, if 10% of the power stations' emissions were to come back down to earth and become trapped for a day or two, the computer results suggest that ozone concentrations could rise by up to 20%. However, if trapping of the power station plumes rose above 15%, ozone levels should become hydrocarbon-limited and could be expected to decline.



A number of assumptions have been made in the computer model, and Mr Galbally would like to substantiate some of them by actual measurements. In particular, the actual emissions of natural NO_x and hydrocarbons from forested areas are uncertain and may differ from those measured in northern Victoria and overseas. Nevertheless, there seems little doubt that we need to take account of natural sources of ozone in future assessments of pollution levels in the Latrobe Valley.

Melbourne the worst offender

Interesting though that conclusion may be, natural ozone events are never going to produce high photochemical smog concentrations. Yet on some rare days, 1-hour ozone levels do approach 100 p.p.b. How do such extreme events arise? Evidence accumulated by the EPA and CSIRO researchers incriminates Melbourne as the source of this unwanted visitation.

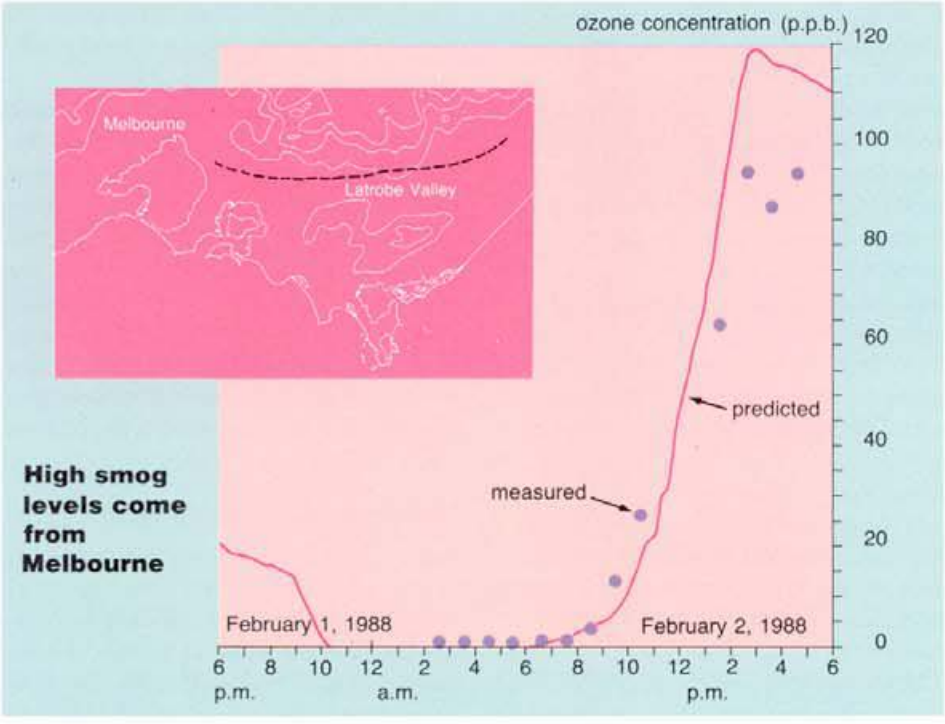
The scientists got hold of the meteorological and air-quality data surrounding a record 100 p.p.b. ozone level measured in the Valley on February 2, 1987. This was the same day on which an ozone level as high as 136 p.p.b. was measured in Melbourne.

By examining the wind patterns on that day, and looking, in reverse, at the sequence of air movements during the day, the EPA team could work out where a certain air parcel — the polluted one over the Latrobe Valley — had originated. Indeed, as the diagram on the next page shows, this approach traced the polluted parcel's path back to the south-east of Melbourne the previous evening.

The researchers initialised their model with contaminant levels typical of Melbourne's background levels at 6 p.m. on such a day (in particular, a surface ozone concentration of 20 p.p.b.), and let the model run. An important factor at work was a strong inversion holding the depth of the parcel to less than 1000 m, and keeping the smog concentrated. Again, as the graph with the trajectory diagram shows, the calculated build-up of ozone in the parcel — to levels near 100 p.p.b. — matched the observed values quite well.

Some substantiation of Melbourne as the pollutant source comes from other mea-

Assuming comparable quantities of natural and artificial precursors (NO_x and reactive organic carbons), modelling of trapped emissions gave predicted levels close to observed ones.



Modelling how stale evening air from Melbourne could stew and form ozone the next day in the Latrobe Valley gave results that matched observations well. On the days concerned, winds would have carried the smog parcel on the path indicated in the inset.

surements, by Melbourne University, EPA, and CSIRO workers, of the halocarbon content of Melbourne and Valley air on ozone-prone days. Mr Hadar Almog and his colleagues detected elevated levels of freon-11 and freon-12 in the Valley on days when they could trace, via the wind trajectories, the source of these distinctive man-made chemicals back to Melbourne. Incidentally, as a measure of the sensitivity of the detecting instrument (a gas chromatograph with an electron capture detector), a high level of freon-12 was regarded as one exceeding 500 parts per million million.

Thus it seems that people living in the Valley have more to fear from creeping pollution from Melbourne than from the very visible power stations that burn its rich brown-coal resources. Even the greenery that adds so much to the Valley's beauty contributes significantly to photochemical smog.

Outstanding problems

That's hard to swallow when first impressions of the Latrobe Valley are frequently unfavourable — more than 20 towering stacks, sometimes emitting long plumes, commonly hazy air, and, all too often, a pervasive smell.

Well, according to Dr Peter Manins, an atmospheric scientist from CSIRO who has just finished a term as project director of the Latrobe Valley Airshed Study (see *Ecos* 43), the smell comes from a paper mill, the plumes are much more likely to be condensed moisture than smoke particles, and the haze comes from either fog or the burning off of vegetation.

It seems that the number of hazy days — when the 'local visual distance' (LVD) drops below the acceptable level of 20 km — increases remarkably when fire restrictions are lifted. Perhaps the unique meteorology of the Valley and its surrounding mountains amplifies the effect. Nevertheless, the SEPP goal of no more than 3 days per year with unacceptable LVD is breached at many monitoring stations. Some record 10 such days a year, others 20 or even 30.

Dr Greg Ayers and Dr John Gras, of the CSIRO Division of Atmospheric Research, are in the process of analysing small particles collected on filter papers when medium-volume air samplers sucked air through them. It's too early to be definite, but it seems that the chemical make-up of these particles is consistent with burning vegetation as their source.

Can the power stations do no wrong? Yes, occasionally pollution-control equipment fails to function, and a dirty plume results. Also, modelling conducted by scientists at the EPA suggests that 'fumigation', a process that can bring power station plumes to the surface in summer, may sometimes result in increased levels of ozone. Supporting this, the ozone levels observed at one monitoring station on January 29, 1988, in the smog episode described earlier, were associated with small increases in the concentration of sulfur dioxide, a pollutant emitted mainly from power stations in the Valley.

But most of the time, when things are working as they should, the air quality in the Valley is good — much better than Melbourne's and, by most measures, much like that in other rural areas with comparable populations. Sulfur dioxide levels are higher than they would be without the power stations, but they are still well below SEPP goals.

Nevertheless, there are certain areas, until recently overlooked, that do receive a strong impact from power stations. Certainly the majority of the population on the floor of the Valley are protected by the tall stacks that release pollutants 100 m, 200 m, or higher into the air. But what about a farmer who lives on top of the surrounding hills that rise 500–1000 m above the Valley?

Few hillside-dwelling farmers have complained of pollution, but it's certainly true that, occasionally, on calm clear nights, plumes are liable to hit the hills. Monitoring stations set up on Mt Tassie in the Strzelecki Ranges and at Trafalgar South in the Haunted Hills have experienced a few 1-hour concentrations of sulfur dioxide well in excess of 100 p.p.b.

In view of the large increase in sulfur dioxide emissions projected for the year 2005, the Latrobe Valley Airshed Study Steering Committee has recommended that phenomena such as sulfur dioxide chemistry and acid rain, which have received little attention so far, should be the subject of more detailed investigation.

Andrew Bell

More about the topic

Clean Air, number 4, 1988, contains 35 papers presented to a symposium in June 1988 marking the end of the Latrobe Valley Airshed Study. In particular:

Modelling photochemical smog in the Latrobe Valley. M.E. Cope, F. Carnovale, I.E. Galbally, B.J. Cook, and D.R. Hearn.

Biogenic NO_x emissions in the Latrobe Valley. L. Duffy, I. Galbally, and M. Elsworth.

Meteorology and air quality of the Latrobe Valley. P. Manins.

The Latrobe Valley aerosol/visibility study: program aims and some early case study results. G. Ayers, J. Gras, R. Gillett, S. Bentley, M. Edwards, and T. Firestone.

Meteorology and air pollution in the Latrobe Valley. A. Bell. *Ecos* No. 43, 1985, 24–8.