Taking the air

Professor Stuart Penkett checks a radiometer on the Cape Grim Station roof.

Paul Holper gets among the action as the pristine winds of north-west Tasmania are summoned to help scientists push the boundaries of atmospheric photochemistry.

Have you ever wondered what happens to air pollutants after a smoggy day? Where do the hazardous chemicals go? Does the wind waft them away to contaminate some other place? Do the pollutants fall out of the sky or transform themselves into innocuous, invisible gases?

Thanks to a chance conversation 10 years ago, we now know far more about the processes that create, and ultimately destroy, photochemical smog.

The conversation took place during a coffee break at a World Meteorological Organisation conference in Sofia, Bulgaria. Professor Stuart Penkett, from the University of East Anglia in the United Kingdom, asked CSIRO's Dr Greg Ayers whether the university could send a peroxide sampler to the Cape Grim Baseline Air Pollution Station in Australia.

Penkett was keen to measure levels of atmospheric hydrogen peroxide, a chemical that arises from the decomposition of ozone. Ozone in the lower atmosphere is a greenhouse gas, and a pollutant that attacks the throat and lungs and irritates the eyes. Ozone is a prime component of photochemical smog.

Cape Grim, in the Tasmania's remote north-west, lies in the path of the often gale-force winds of the roaring forties. For much of the year, air collected at the station comes straight off the Southern Ocean, not having passed over land for weeks.

Under these conditions, air at Cape Grim is as pure as anywhere on the planet. It was this pristine environment that sparked Penkett's scientific interest.

Beam me up

Dr Beverley Allan spent much of January and February in a leaking wooden hut, 20 000 kilometres from her East Anglia home in the UK. She was one of about 50 scientists taking part in the Southern Hemisphere's largest ever investigation of atmospheric photochemistry.

As the word suggests, 'photochemistry' describes the myriad reactions in the air powered by sunlight. These reactions are crucial to just about every environmental problem involving the atmosphere, including smog, the greenhouse effect, ozone layer depletion and acid rain.

No major experiment is complete without an acronym. This one was the Southern Ocean Atmospheric Chemistry Experiment, SOAPEX. The 'soap' in the acronym is apt; the gases of interest cleanse the air of ozone and other pollutants.

It was Penkett's visit to Tasmania in the early 1990s with his peroxide sampler that ultimately culminated in SOAPEX. Filling his lungs with the famed Cape Grim air, he explains the goals of the experiment.

'We're here to study what happens when light shines on the atmosphere boundary layer above the ocean in as natural an environment as we can get,' he says.

The boundary layer is the lowest few kilometres of the atmosphere, in which gases – both natural and pollutants – are thoroughly mixed.

'The Southern Hemisphere is a particularly challenging environment for atmospheric scientists,' Penkett says. 'Here we must measure gases that exist at a fraction of their concentrations in more polluted regions.'

Beverley Allan's hut was perched on the Cape Grim roof. From there, she operated a differential optical absorption spectroscope, an ingenious instrument that fires an intense, ultraviolet light beam. The beam's target was Trefoil Island, 6 km north of Cape Grim. Before SOAPEX began, one of the researchers had flown in a light plane to the island. With a little trial and error, he had aligned a reflector on the ground to bounce the spectroscope beam back to the hut. There, a telescope collected the light, after its 12 km round trip.

The beam was tuned to the specific wavelengths of light absorbed by oxides of nitrogen and nitrate radicals. An electronic

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system connected to the telescope measured concentrations of these gases from the amount of light they absorbed.

The spectroscope also measured levels of compounds of chlorine, bromine and iodine. These too are part of the intricate photochemical cycle, which ultimately determines how much ozone is present in our atmosphere.

Leaping laboratories

During the six-weeks of SOAPEX, Cape Grim was a hive of activity. Every available benchtop supported instruments sustained by a maze of tubing connected to the station's air inlets.

New officer-in-charge at Cape Grim, Dr Neil Tindale, spent most of his first months in the job organising and planning for the experiment. He and other Bureau of Meteorology staff had to arrange all the logistics to ensure that the station would be able to accommodate the dozens of visitors and all their sophisticated equipment. The three UK universities – East Anglia, Leeds and Leicester – flew in their own laboratories.

Scientists began to arrive in mid-January, quickly settling in to hotels, guest houses and private accommodation. Then the air measurements began.

'During SOAPEX, we're learning all about what happens in clean air, as a precursor to a better understanding of what happens in the more polluted Northern Hemisphere,' Tindale says.

'We're also discovering more about the impact of the ocean on the composition of our air, something that's very important to us in the Southern Hemisphere, which is dominated by oceans.'

SOAPEX would be incomplete without ocean measurements. For a week during the experiment, the CSIRO research vessel, *Southern Surveyor*, cruised the Southern Ocean upwind of Cape Grim. On-board, five scientists monitored surface water concentrations of carbon dioxide and oxygen. They also recorded levels of nutrients that sustain the abundant ocean plankton whose photosynthetic cycle influences atmospheric carbon dioxide concentrations.

'Biological processes in the ocean may be having a large impact on the cleansing capacity of the atmosphere,' Tindale says.

SOAPEX participants also had available to them the remarkable aerosonde. This is a small, pilotless aircraft capable of flying continuously for up to 24 hours. Containing two onboard computers and able to respond to changing atmospheric conditions, the aerosonde can literally fly itself.

Melbourne company, Environmental Systems and Services Pty Ltd, supplied the three-metre wingspan, 15-kg aircraft. A 26-cubic-centimetre engine powers the craft, extracting 500 km from every litre of fuel.

Meteorologists have used aerosondes in a number of field experiments during the past few years. Last year, the aerosonde created history when it made the first pilotless flight across the Atlantic Ocean.

Launched from the top of a vehicle speeding along the adjoining Woolnorth Station's air strip, the aerosonde's on-board computer collected data on atmospheric pressure,

Dr Beverley Allan with a spectroscope that fired an intense light beam at a target on an island six kilometres away. Analysing the reflected signal gives concentrations of oxides of nitrogen and nitrate radicals in the air.

A truly radical cleansing agent

THE most important cleansing agent in the air is the hydroxyl radical. 'The atmospheric garbo,' is how one of the SOAPEX scientists describes it.

Chemical bonds comprise paired electrons. A radical, in chemical parlance, is a molecule that contains at least one unpaired electron. These unpaired electrons usually make free radicals so reactive.

The hydroxyl radical is no exception. Its average life expectancy is less than a second. Despite the invaluable role it plays as an atmospheric cleanser, hydroxyl radicals exist in astonishingly small quantities. Generated by sunshine, the greatest concentrations occur in the air at around noon. A cubic kilometre of air will, at most, contain under a one-tenth of a gram of the hydroxyl radicals. At night it will contain none.

Hydroxyl radicals will react with almost any gas emitted into the atmosphere and play a major role in determining the make-up of our atmosphere.

Scientists have theorised for 30 years about the importance of the hydroxyl radical. Until recently, however, accurately measuring the species in the lower atmosphere has been impossible.

Leeds University shipped its hydroxyl-measuring instrument to Tasmania in a huge shipping container. Inside this mobile laboratory, carefully set by crane on a purpose-built slab beside the Cape Grim station, researchers measured the elusive chemical with a laser-based instrument. A high-frequency pulsed laser beam penetrates air drawn via the container roof. The air is cooled to –248°C and reduced to a pressure of just one-thousandth of an atmosphere. The laser beam is set at an ultra violet frequency that will induce hydroxyl radicals to fluoresce slightly. A photo-multiplier measures the fluorescence.

The Leeds team finished the experiment with 20 days and nights of hydroxyl measurements that will be integral to the description from SOAPEX of atmospheric chemistry in the southern hemisphere.

temperature, relative humidity, wind speed and direction. It did this from ground level to a height of 5 km.

Cape Grim's pastoral history

The Cape Grim Air Pollution Station sits on Federal land surrounded by the 22 000-hectare Woolnorth pastoral property.

In 1825, King George IV granted the Van Diemen's Land Company a vast area in the north-west of the colony that was to become Tasmania. The company's 11 founders had dreams of building at Woolnorth a highly lucrative flock of 250,000 merino and saxony sheep. Although this target was never reached, the property still thrives today.

In 1976, CSIRO scientists chose the 94-metre high treeless cliff top at Cape Grim as the site for a laboratory to track the changing make up of unpolluted air in the Southern Hemisphere.

Today the station is one of the most sophisticated in a global network. Since its establishment, it has constantly monitored the composition of the atmosphere, making more than three billion measurements. Provision of the air strip for launching the aerosonde was one of the many contributions that Woolnorth management and staff made to the success of SOAPEX.

Light, action

As soon as he arrived at Cape Grim, Dr Paul Monks set up his spectrometer next to the rooftop hut. Every two seconds the instrument recorded solar radiation.

'We are mainly interested in the blue and ultraviolet part,' explains Monks, who is from the University of Leicester.

'It is this part of the spectrum that has the energy to initiate photochemical reactions and produce hydroxyl radicals,' Monks says.

Officer-in-charge at Cape Grim, Dr Neil Tindale, at the entrance to the historic Woolnorth pastoral property that surrounds the scientific station.

Rebecca Webb, from the University of Tasmania, adjusts the aerosol sampler flow rate on the roof of the Cape Grim station.

Ozone concentrations peak at around midnight. At dawn, the sun's rays begin to tear these O_3 molecules apart, forming oxygen molecules (O_2) and oxygen atoms. The oxygen atoms react rapidly with water vapour, generating hydroxyl radicals. The hydroxyl radicals soon attack ozone, destroying even more of it.

The fact that hydroxyl radicals are spawned by sunlight explains why SOAPEX took place during summer, when solar radiation is most intense. Hydroxyl radical concentrations are far higher in summer than in winter.

Ozone chemistry becomes much more complicated if there are pollutants in the air such as oxides of nitrogen. These oxides initiate reactions that both produce ozone and destroy hydroxyl radicals, lowering the atmosphere's self-cleansing capacity.

'Pollution levels are low at Cape Grim so we are eliminating as many variables as possible. We will apply what we learn here about radical chemistry to developing strategies for controlling air pollution back home,' Monks says.

An ill wind

Researchers came to Tasmania for measurements in 'baseline' conditions. That is, they wanted the pristine westerly winds, blowing from the Southern Ocean. As luck would have it, they got just a couple of days of these conditions. Most of the time, easterlies prevailed, setting a record for non-baseline conditions for Cape Grim!

Despite this, Penkett rates the experiment a great success. 'We have monitored a number of gaseous radicals, some for the first time in the Southern Hemisphere,' he says. 'SOAPEX has yielded the most complete catalogue of chemicals involved in photochemical reactions in unpolluted air.'

This catalogue includes measurements of dozens of different gases in the atmosphere, linked to meteorological conditions and time of day over six-weeks.

Modellers are now taking this information and using it to check and fine-tune their understanding of atmospheric photochemistry. Environment protection agencies rely on models of atmospheric chemistry to determine which pollutant emissions need to be controlled if air quality is to be maintained or improved.

SOAPEX, says Penkett, will lead to significant advances in the understanding of key atmospheric processes. 'Ultimately, what we have learnt will be essential to future management of our atmosphere and will underpin control strategies for air pollution and climate change.'

Paul Holper is communication manager at CSIRO Atmospheric Research.

Abstract: Earlier this year some 50 scientists converged on the Cape Grim Baseline Air Pollution Station in north-west Tasmania to take part in SOAPEX, the southern hemisphere's largest investigation of atmospheric photochemistry. During the six-week experiment, air measurements were taken from land, sea and air. The aim was to study what happens when light shines on the atmosphere boundary layer above the ocean, the area in which gases are mixed. The study yielded a catalogue of chemicals involved in photochemical reactions in unpolluted air and will lead to significant advances in the understanding of key atmospheric processes.

Keywords: atmospheric phytochemicals, atmospheric gases, air pollutants, Cape Grim, Tas., hydroxyl radicals, Southern Ocean Atmospheric Chemistry Experiment (SOAPEX), spectroscopy.