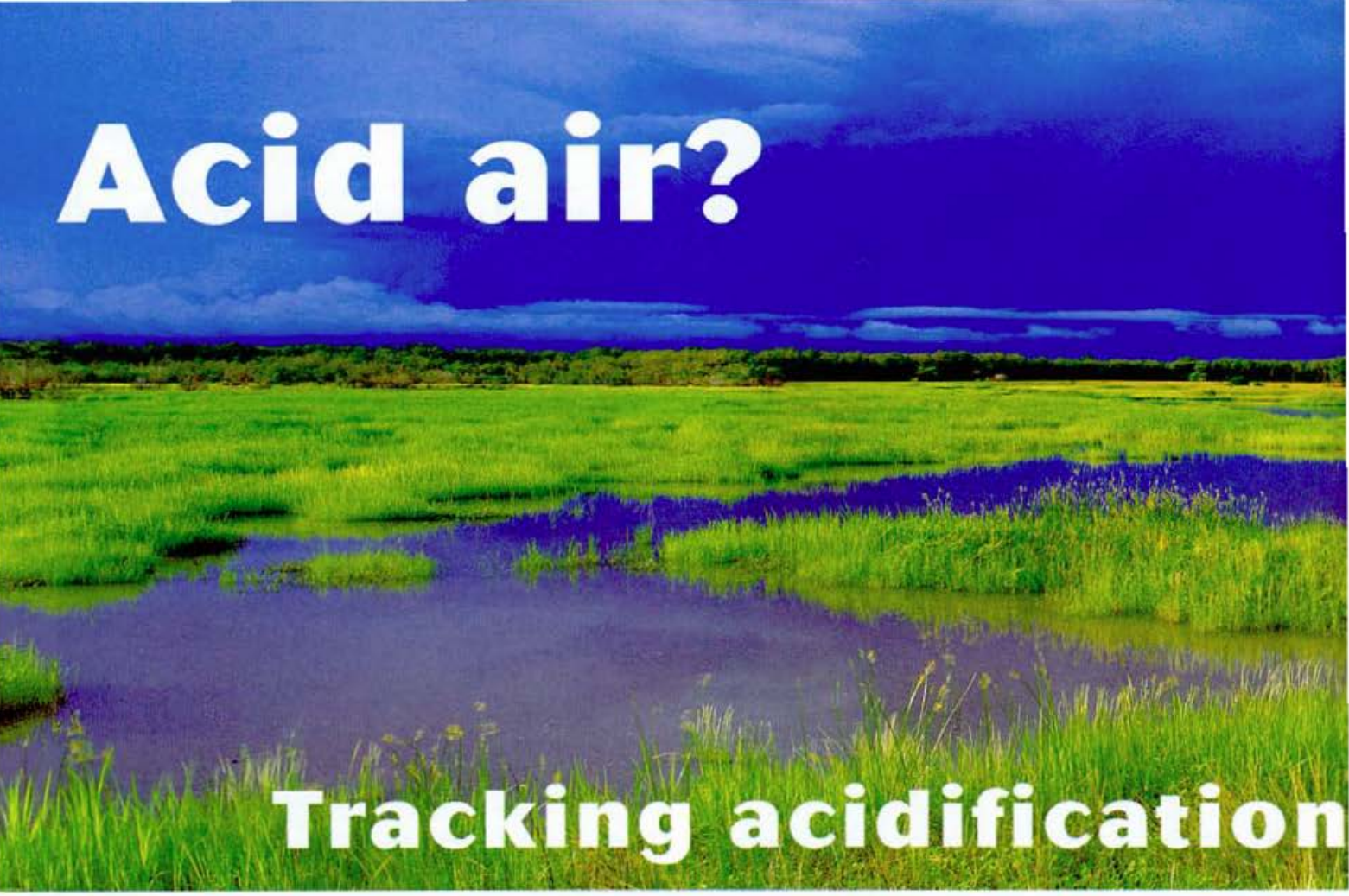
Acid air?



Tracking acidification

Acid rain is a well-known environmental problem in heavily industrialised parts of the Northern Hemisphere. **Paul Holper** outlines what we know about the situation in Australia.

In Scandinavia, acid rain is often at its worst when winds blow from the south, laden with emissions from industrialised parts of Europe. Countries in western and eastern Europe also share industrial emissions with their neighbours. Australia's relative isolation, however, means that its acidification problems are likely to be home-grown.

Before the 1980s, little was known about rainwater quality in Australia. The vastness of the landscape presents a challenge to anyone setting out to make measurements. Atmospheric conditions in the tropical north greatly differ from those in cities such as Melbourne and Sydney, and from major power generating regions such as Victoria's Latrobe Valley and the Hunter Valley in New South Wales.

During the past 15 years, CSIRO's Dr Greg Ayers has investigated the impact on rainwater of our sprawling cities and growing industrialisation. Ayers is recognised as Australia's authority on atmospheric acidification and his research and monitoring work are helping government and industry to safeguard the environment. He says understanding the extent of the problem is crucial to preventing environmental damage.

Before we began our interview, Ayers proudly demonstrated his latest software: he had chosen as a backdrop for his computer screen a vivid image of the innards of a computer. Never one to do anything by halves, Ayers has installed the sound feature that accompanies the backdrop. So our talk was regularly punctuated by blip-blip noises that someone in Silicon Valley imagines chips might make as they process data.

When it comes to computers, Ayers can best be described as an initiator: always up with the latest. He has a good excuse though to have a powerful processor at his fingertips.

Studying acid rain is not simply a matter of cleaning out a beaker or two, collecting some rain and measuring pH. Rather, it involves carefully planned fieldwork, sophisticated chemical investigations, complex statistical analyses of massive amounts of data and detailed numerical modelling of atmospheric processes.

Scott's pot

Ayers' interest in acid rain was whetted 15 years ago by a visit to the National Center for Atmospheric Research in the United States. During his stay he visited Columbus, Ohio, 'the armpit of America', to study cloud droplets.

Liz Poon

Barbara McKaige

Industries are not the only contributors to atmospheric acidity. In the early 1980s, high acidity levels were found in rainwater at Kakadu National Park, Northern Territory. Subsequent research found that organic acids are common in tropical air. They come from hydrocarbons emitted by plants, a natural process perhaps exacerbated by bushfires and grass fires. At times, the process generates rainwater as acidic as anywhere in Australia.

in Australia and Asia

Robert Dickens

'Pollution was clearly making the water acidic. Some of the droplets had pH values as low as two,' Ayers says.

The Ohio cloud droplets were more acidic than lemon juice and vinegar.

At that time scientists were becoming increasingly alarmed about high acid levels of rain in northern America and in Europe. Forests were being damaged and many ponds, rivers and lakes denuded of life. One typical study reported that in 1900 fishermen netted 30 tonnes of salmon in seven major rivers of southern Norway. Since 1970, however, not a single salmon had been caught.

When Ayers returned home to the CSIRO Division of Cloud Physics in Sydney, where he was working at the time, he decided to find out what Australia's rainfall was like.

'Bill Scott, a colleague, decided that a baby's potty would be an ideal container for collecting rain. So he headed off to the local department store and bought one,' Ayers recalls.

'We shared an upstairs laboratory. Every time it looked like rain, Bill would attach his potty to an old broom handle and stick it out of the window.'

Staff were soon referring to the makeshift scientific equipment as 'Scott's pot'.

Contrary to popular opinion, unpolluted rainwater is not neutral. It is slightly acidic, with a pH between five and six. (On the pH scale, seven is neutral, anything less is considered acidic.) The atmosphere is full of acidic particles released from natural processes. These acids dissolve in the tiny cloud droplets that ultimately fall to earth as rain.

During the summer of 1981, Ayers and fellow chemist Rob Gillett monitored rainwater at 12 sites in Sydney. The water they collected upwind of the city generally had a pH above five.

In metropolitan areas, however, pH averaged 4.4, with the lowest measurement being 3.6. Sulfate and nitrate levels, while low by international standards, were up to three times higher than in less polluted parts of the city.

'Industry and motor vehicles were clearly making rainwater acidic,' Ayers says.

Shortly afterwards, Ayers and Gillett headed south to make similar measurements in Melbourne. They found little evidence of acidity. 'It didn't surprise us greatly,' Ayers says. 'Melbourne is well ventilated. The strong westerly winds on rainy days clear the air. In Sydney, the pollution often accumulates for longer.'

Deposition, not rain

Ayers is quick to point out that rainwater is just one way in which acidic pollutants reach the ground. Atmospheric scientists believe that just as much acid-causing material is directly deposited from the air. They prefer the term 'acid deposition' to 'acid rain'.

The noticeboard in Ayers' office features a highly simplified periodic table of the elements. It is a table that would gladden the heart of any chemistry student striving to learn the position of more than a hundred elements. The table contains only 'S' for sulfur alternating with 'N' for nitrogen. This is a jocular attempt to draw attention to the two elements central to the intricate chemistry of acid deposition.

One-quarter of the sulfur in the atmosphere is natural. The rest is caused by human activity. Nature releases sulfur through decomposing marine algae and the eruption of volcanoes. Industry releases sulfur dioxide when fossil fuels are burnt and sulfide ores smelted.

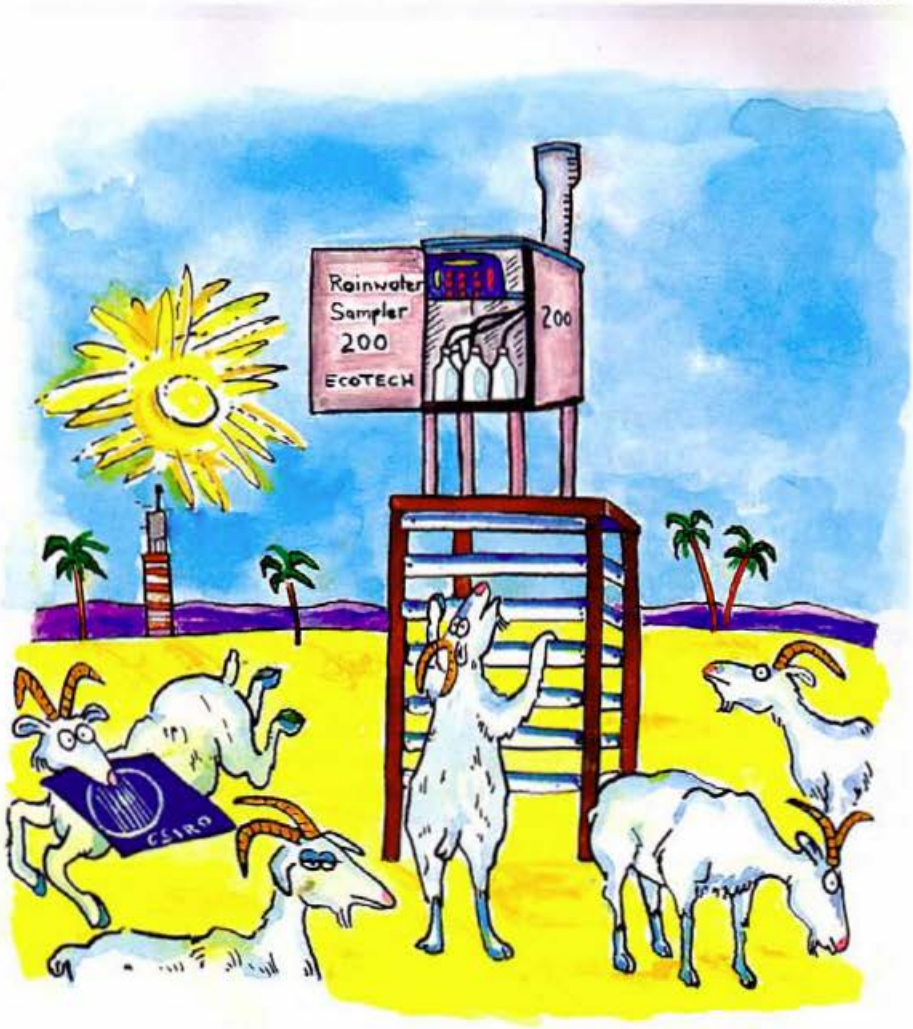
Sulfur dioxide readily forms sulfuric acid in the air, or when it reaches the ground. In the year 1900, global sulfur dioxide emissions were approximately 15 million tonnes. Annual emissions are now close to six times that amount.

Nitrogen oxides are generated by lightning and microbes, and by burning of fossil fuel and biomass. In the atmosphere the oxides are often transformed into nitric acid.

Rainfall riddle at Kakadu

In the early 1980s, scientists in the Northern Territory became curious about high levels of acidity found in rainwater at Kakadu National Park. There was no nearby industry to blame, so what was the source of the acid?

Robert Dickens



The Office of the Supervising Scientist in the Northern Territory began to collect rainwater at Jabiru.

After preliminary analysis revealed pH values as low as 3.5, the samples were sent to the CSIRO Division of Atmospheric Research in Melbourne, where Ayers and Gillett were then based, for further tests. The rainwater contained very little sulfuric acid, a gauge of atmospheric acidity caused by industry.

'The low pH was due mainly to formic and acetic acids,' Ayers says. These organic acids have since been found to be a common component of tropical air. They come from hydrocarbons emitted by plants, a natural process perhaps exacerbated by bushfires and grass fires.

Hydrocarbons are responsible for the sweet smell of newly cut grass, the heady aroma of eucalypts and the sharp scent of pine forests. A compound called isoprene makes up more than one-third of complex hydrocarbons released by plants. In the sunny tropics it is quickly oxidised to formic and acetic acids. At times this natural process generates rainwater as acidic as anywhere in Australia.

Probing Australia's power plants

Throughout the late 1980s and the early '90s, Ayers and his team completed studies in three of Australia's largest power generating regions: Victoria's Latrobe Valley, and the Hunter Valley and Western Coalfields of New South Wales.

The Latrobe Valley investigation followed a comprehensive 10-year examination of air quality in the region.

'Large quantities of sulfur dioxide and oxides of nitrogen are emitted in the Latrobe Valley. Some people have forecast emissions quadrupling by the year 2005,' Ayers says. 'The State Electricity Commission of Victoria had the foresight to initiate an acid deposition study.'

The study was limited to rainfall analysis at four sites in the Valley.

Ayers' team needed some way of reliably monitoring and collecting daily rainfall at each site. After some thought, they came up with an automatic sampler containing eight polyethylene bottles mounted on a carousel. At 9 am each day the carousel automatically rotated to position the next bottle beneath the funnel. The sampler logged rainfall to within 0.2 millimetres as well as measuring the rate of rainfall in each shower. A little more sophisticated, as Ayers points out, than the prototype 'Scott's pot'.

So successful were the samplers that

Dr Greg Ayers has been studying acid rain in Australia since the early 1980s. In 1995 he was awarded the Australian Meteorological and Oceanographic Society's highest honor, the Priestley Medal. The award was made in recognition of his contributions to the science of precipitation chemistry and acid deposition, with significant applications to Australia's atmospheric environment.

they are now being manufactured and sold internationally under licence by Ecotech Ltd, a Melbourne-based environmental equipment company.

During some of the Australian studies, great care had to be taken to find inaccessible locations for the samplers, preferably on private land. This had little to do with the quality of rainwater collected. Rather, the big blue circular CSIRO logo often proved irresistible to local shooters.

Each week during the Latrobe Valley study a technician travelled from Melbourne to collect the bottles from the samplers and to download rainfall data to a laptop computer.

It wasn't just pH that was measured back at CSIRO's laboratories. Atomic absorption spectroscopy, indicator colour changes and the latest ion chromatography pinpointed concentrations of a dozen different chemicals to the nearest ten-thousandth of a gram per litre.

'To track down the impact of human activity you've got to measure everything' Ayers says. 'And you've got to do it accurately using the right methods.

'For example, ammonia can neutralise atmospheric acidity. However, once in the soil, ammonia can add to acidity. So simply measuring pH of rainwater doesn't give enough information.'

'They have acid deposition problems in The Netherlands partly because their farms generate so much ammonia.'

And the verdict on the Latrobe Valley?

'According to our measurements, the power stations there are not significantly adding to acidification,' Ayers says. 'Dry deposition of nitrogen dioxide and sulfur dioxide is likely to add more acid to the Valley than wet deposition, but even so, levels are low.'

Soils ain't soils

Environmental response to pollutants depends on many factors. Some regions cope with acidification better than others, having larger 'critical loads'. Critical load refers to the greatest assault that an ecological system can withstand before showing measurable degradation.

Scientists determine critical load by examining rock and soil type, land use and rainfall.

If soil is fertile with a pH greater than 4.5, and rainfall is relatively low, the critical load will be high. The terrain can withstand moderately large additions of acidity without undue suffering.

Conversely, in low pH soils, acidification mobilises toxic aluminium ions. If coniferous forests predominate, or if land is devoted to rough grazing, the result is a low critical load. Even minor acid deposition is undesirable.

Ayers says that in the Hunter Valley the greatest determinant of critical load is land use. The combined effect of farming and industry may be a problem in some areas.

Acidification in Asia

Having surveyed many of the potential acidification hot spots in Australia, Ayers set his sights overseas. He admits today that he had no idea when he began rainwater chemistry measurements back in 1980 that it would lead to such extensive projects here and in Asia.

In 1991, the Australian International Development Assistance Bureau (now AusAID) financed the first ever survey of acid deposition in Indonesia. Data gleaned in the world's fourth most populous country would be a valuable insight into tropical atmospheric chemistry. It would also be a measure of the impact of sulfur dioxide and nitrogen oxide emissions, which had more than doubled since the 1970s.

Rob Gillett and Paul Selleck, a technical officer in Ayers' team, measured rainwater chemistry for a year at four locations on the main island, Java. One of the sites was in the centre of Jakarta, the others to the west near the 1600-megawatt Suralaya coal-fired power station.

'This time it wasn't the shooters that gave us problems, it was goats. We had to mount the samplers on two-metre towers to keep them away,' Gillett recalls.

The local wildlife wasn't the only

A 10-year study of acid deposition in Victoria's Latrobe Valley concluded that power stations were not adding significantly to acidification.

Staff at the Bureau of Meteorology at Jakarta are trained in the use of an automatic rainwater sample in preparation for units to be set up in Sumatra. The levels of acid depostion in Indonesia are comparable with those affecting the worst parts of Europe and North America.

problem faced by the study. Rainfall at each site wasn't monitored independently as planned. Some of the water samples went missing and insufficient thymol was added to collection bottles. The lack of thymol meant that acetic and formic acids were decomposed by microbes prior to analysis.

Despite the difficulties, the study came up with some clear conclusions.

Nitrogen oxide concentrations were up to four times higher in Java than typically found in tropical Australian rainfall; sulfur dioxide levels were up to ten times higher.

'The levels of acid deposition we found in Indonesia are comparable with those occurring in the worst affected parts of Europe and North America,' Ayers says.

Ayers believes that a full assessment of acid deposition is well warranted in Indonesia, combined with an appraisal of critical loads for regional ecosystems.

Since the Indonesian work, the CSIRO team has travelled extensively, initiating studies and providing advice to local authorities. They've worked in Malaysia, New Guinea, Fiji and Brazil. The Melbourne laboratories have seen a steady stream of overseas scientists completing training programs.

Where to from here?

'We're aiming to establish a network of tropical sites for rainwater and atmospheric measurements,' Ayers says. 'We will include five "hot spots" in Indonesia and Malaysia. The baseline station at Charles Point in Darwin will give us relatively unpolluted rainwater and air samples for comparison.'

Ayers is also keen to build up the complete picture of Australian sources and sinks of atmospheric sulfur, showing how the chemical gets into the atmosphere and where it is consumed.

And his view of the significance of acid deposition in Australia?

'Our population is relatively small and we live in a vast continent with widely-dispersed sources of pollution. Nevertheless, there's no doubt that near some industrial regions, acidity is higher than elsewhere.'

More about acid deposition

Bell, Andrew (1987) It rains formic acid in the Top End, *Ecos* 50.

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Networks to monitor the atmosphere

Greg Ayers' idea of a network of tropical sites for monitoring rainwater is based on a global system of air-quality observatories.

Measurements since the 1950s from a scientific station at Mauna Loa in Hawaii had shown that atmospheric carbon dioxide levels were steadily increasing. Scientists were concerned about the effect this increase would have on climate.

In an effort to systematically monitor changes worldwide, the World Meteorological Organization in 1972 established a network of monitoring stations. The stations are located in remote locations, where they sample and monitor background or 'baseline' air unsullied by local sources of pollution.

Today the global air pollution monitoring network includes more than 30 observatories, stretching from the Arctic circle to the South Pole.

Australia's baseline station, operated by the Bureau of Meteorology, is located at Cape Grim, in north-western Tasmania.

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