It rains formic acid in the Top End

Atmospheric scientists have found that rain falling in tropical Australia can contain appreciable amounts of organic acids, principally formic acid (as in ants) and acetic acid (vinegar). Water from individual storms has given pH readings as low as 3·5, an acidity level comparable to the most concentrated seen in the heart of Sydney, where sulfuric acid is the main culprit.

At the start of the 1979/80 wet season, scientists from the Pancontinental Mining environmental laboratory working near Jabiru in the Northern Territory observed that thousands of fish at Ja Ja billabong on the Magela Creek floodplain had died. When analysed, the billabong water showed high levels of acidity and of sulfate ions, together with a toxic concentration of dissolved aluminium.

Presumably, the acid had dissolved aluminium from the local soil and set it free in the water.

But where did the acid come from? The fish deaths were strangely reminiscent of 'acid rain' pollution that kills plant and animal life in lakes and streams of Europe and North America. This event was one of the factors that prompted researchers from the CSIRO Division of Atmospheric Research to collaborate with the Office of the Supervising Scientist in the Northern Territory in studying what was coming down from the sky.

In the three wet seasons beginning 1982/83, Dr Barry Noller of the Office of the Supervising Scientist collected rain-water samples at Jabiru every time it rained.

He first treated the samples with chloroform (to kill bacteria that could alter the water's composition) and analysed them for acidity, ammonia, and dissolved metals. He then sent the samples to the CSIRO laboratory at Aspendale, Melbourne, where Dr Greg Ayers and Mr Robert Gillett used a high-performance liquid chromatograph to identify and measure the types of acids present.

The results of 17 analyses made during 1984/85 are given in the chart. They show that formic and acetic acids contribute most to rain-water acidity. Significantly, the level of sulfuric acid — the type that appeared in the billabongs and is the major contributor to acid rain in industrial regions — was consistently low.

This points to sulfates in the soil surrounding the billabongs as the source of the fish-killing acidity. Dr Noller suggests that the first rains of the wet season raise the water table, dissolving the sulfates and producing sulfuric acid. Subsequently, aluminium dissolves and, depending on its concentration, can kill fish. Since the first observations in 1979/80, several such episodes have been noted.

Later in the wet season, abundant rain dilutes the acid groundwaters to harmless levels. The formic and acetic acids in the rain appear to be quickly consumed by bacteria, and are unlikely to persist for long enough in soil or groundwater to cause acidity problems.

A billabong near Jabiru — fish have been found dead in such billabongs at the start of the wet season.

Yet the presence of these organic acids in the rain raises the interesting question; where do they come from? In the last few years scientists around the world have found that they are a regular feature of tropical regions. Something is going on that doesn't occur in the more closely studied temperate latitudes.

Nobody knows for sure, but it looks very much as if the organic acids waft into the air through the activity of the plant kingdom. We have known for a long time that many plants emit volatile hydrocarbons — as witness, the scents of eucalypts, of a pine forest, of freshly cut grass. However, what we didn't realise until recently was that nearly all plants do so. Most of the hydrocarbons are odourless, at least in the low concentrations encountered in clean air.

A recent estimate has it that each year the world's plants collectively emit nearly a thousand million tonnes of (non-methane) hydrocarbons into the atmosphere. That's about 10 times more than all the world's industry and transport cast off.

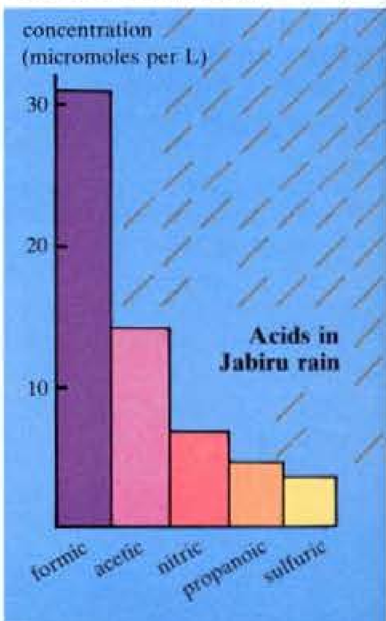
A compound called isoprene probably makes up more than one-third of the plants' outpourings of complex hydrocarbons.

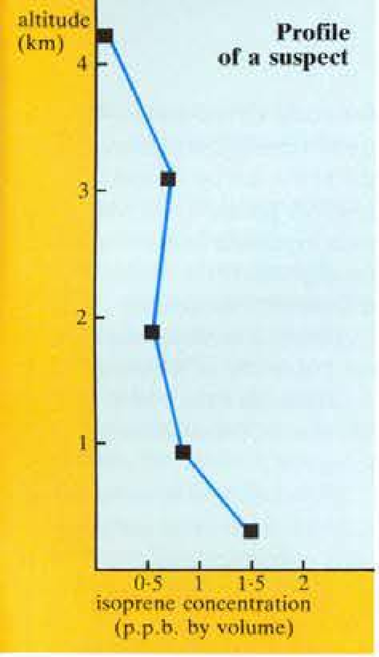
The key to the cause of the tropics' acid rain appears to be that isoprene is particularly volatile at the higher temperatures found near the Equator. Conditions are not hot enough to produce equivalent quantities of the substance at temperate latitudes.

We don't have any clear understanding of how isoprene turns into organic acids, but we know that the molecule is very reactive, particularly under the action of sunlight.

Some scientists have suggested that, in addition, bushfires and grass fires may contribute appreciable amounts of compounds that turn into organic acids. Certainly, large amounts of biomass are burnt in the Australian tropics — Dr Ayers estimates that about 300 million tonnes of carbon go up in smoke each year from burning vegetation. However, most of the burning occurs

The 17 rain-water samples taken and analysed during 1984/85 showed an average pH of 4·3. Most of the acidity came from formic acid.





A typical profile of isoprene concentration, obtained near Jabiru in November 1985 by the CSIRO research aircraft. Isoprene, released at ground level from foliage, is suspected of causing acid compounds as it rapidly breaks down. This profile fits the description.

before the wet season, so this process is unlikely to be the principal cause of acid rain.

In order to look more closely at the likely role of isoprene as the major source of organic acids, Dr Ayers and Mr Gillett took a series of air samples, on the ground and from the CSIRO research aircraft, near Jabiru during November 1985.

At ground level, they detected isoprene concentrations of from one to several parts per billion (10^9) by volume. But, as would be expected for a reactive gas originating near the surface, concentrations decreased with altitude and were consistently less than 1 p.p.b. at a height of 2 km — the graph shows a typical concentration profile. Under the intense midday sun, the lifetime of isoprene in the atmosphere at Jabiru is probably less than an hour.

Carbon monoxide is one of the break-down products of isoprene, and the researchers found greater than normal concentrations of this gas at all altitudes.

Relevant here are recent findings of American and Brazilian scientists. They traced the origin of two high clouds of carbon monoxide, observed from the space shuttle Columbia over parts of South America, to the vast Amazon rainforest. They also found appreciable levels of acid in the rain there.

The CSIRO aircraft provided a way of sampling the water suspended in cloud as droplets. Dozens of samples were taken from within non-raining clouds (the researchers would have liked to take samples from raining clouds too, but such clouds were observed to contain lightning and dangerous turbulence).

Analysis of the cloud-water droplets gave an average pH of 3·8 — more acidic than the typical pH (4–5) for the rain samples collected on the ground. The difference could be due to dilution of the acid as the water droplets in clouds grow to raindrop size.

The scientists found much the same proportions of various acids in cloud droplets as in rain-water. About 60% of the total acidity is accounted for by formic adic, with 20% by acetic and a little by propanoic acid. Small amounts of other unidentified organic acids are also present (probably citric, glycolic, and lactic), and the remaining acidity is due to nitrate and sulfate.

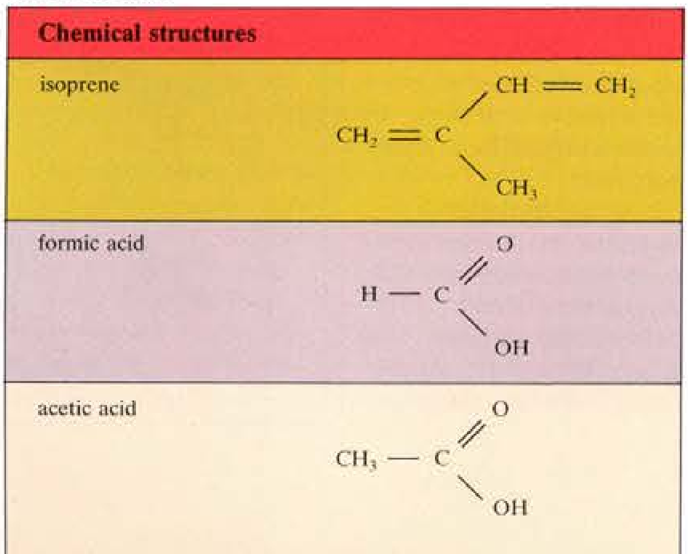
Ground-level measurements of aerosol and gas compositions fitted in with this picture. Taken together, they lead Dr Ayers to suppose that most of the chemicals found in the Top End's air come from natural sources. Only in the case of sulfate, which contributes only a few percentage points to rain-water acidity, is it possible to see man-made sources providing an appreciable proportion of the total amount throughout tropical Australia. Dr Ayers estimates natural sources (bushfires and soils) contribute 74 000 tonnes of sulfur annually, compared with about 250 000 tonnes that the smelter at Mt Isa puts out a year.

Rain samples are analysed with this equipment at the Division of Atmospheric Research.

In the tropics, therefore, acid rain is a natural and harmless phenomenon. With northern Australia's small population and minor industrialisation, it is likely to stay that way.

Andrew Bell

In the tropical atmosphere it is supposed that isoprene reacts quickly with the hydroxyl radical (OH) to produce formic acid and acetic acid.



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