Fluoride and trees


The open-topped fumigation canopies with their filtered air intake.

Aluminium is a much-used metal in modern life, but unfortunately you can't just dig it out of the ground. Usually it is mined in the form of aluminium hydroxide (alumina). A smelter heats the alumina until it is molten, mixes it with molten cryolite — a fluoride salt — and then performs electrolysis to yield elemental aluminium.

The process produces hydrogen fluoride gas from the cryolite and, although smelter operators use a process called scrubbing to contain as much of it as possible, some escapes into the atmosphere. The quantity of gas involved is small (of the order of 0·5 kg per tonne of aluminium produced). The precise amount depends on the design of the smelter — modern ones contain the fluoride considerably more efficiently than older ones — but the obvious question arises: to what extent does all this affect the environment?

When the International Aluminium Consortium of Western Australia proposed a smelter for Kemerton, W.A., they decided to commission an integrated study to check on the environmental effects, as scientists in eastern Australia (where six smelters operate) and in the United States had reported damaging effects on the plant life around such smelters.

The Consortium therefore asked a number of scientists to compile a report on fluoride pollution — among them Dr Frank Hingston, Mr Jeff Galbraith, and Mr Geoff Dimmock, of CSIRO's Division of Forestry and Forest Products Perth laboratories.

These CSIRO staff collaborated with Dr Goen Ho of the School of Environmental and Life Sciences at Murdoch University in Perth and Mr Bob Horne of the Western Australian Department of Conservation and Environment. As part of the study, Mr Dimmock mapped the soil and vegetation types, and the levels of groundwater in the area. He and Dr Ho, in a series of laboratory and field experiments, then examined the capacity of various soil layers to retain any fluoride that might find its way into the ground from drainage waters.

Some soils retain fluoride far more than others, and hence act to slow the passage of fluoride into the groundwater. More than 90% of the area of the proposed smelter site comprises soils with a very limited capacity to hold on to fluoride and this, coupled with the presence of a high water table in the area in summer, would need to be taken into account.

Dr Hingston's team mainly studied the effects of hydrogen fluoride gas on four

The pitiful state of a young jarrah tree after 361 days of exposure to 0·5 μg of fluoride per cu. m of air.


By contrast, *A. flexuosa* shows little, if any, damage after 254 days' exposure to the same concentration. The control is on top.

Intermediate levels of damage were suffered by tuart (*E. gomphocephala*), shown here after 254 days' exposure (upper leaf) compared with a control (lower leaf).

Also intermediate in its sensitivity is marri (*E. calophylla*), shown here after 151 days of exposure to 0·5 μg per cu. m of air. You can clearly see the yellowing and curling of the leaves.

species of native tree that occur commonly in that area — jarrah (*Eucalyptus marginata*), marri (*E. calophylla*), tuart (*E. gomphocephala)*, and a peppermint (*Agonis flexuosa*) that forms an understorey with jarrah and tuart stands.

But conducting such a study is easier said than done. You have to enclose the plants, deliver the fluoride accurately in minute amounts, regularly check the concentration of the gas, and maintain these conditions for many weeks before measurable symptoms appear in the plants.

At CSIRO's laboratories in Floreat Park, Perth, the scientists built 12 open-topped canopies of PVC film to enclose trees of heights 1·5 to 2 m. Pumps continuously pushed air in from the base, and the humidity and temperature of the air in the canopies remained close to that of the real world outside.

The next step was to add a known amount of the gas, but of course when dealing with such tiny quantities you must be careful: it's possible that a minute concentration of fluoride in the air entering the canopies could upset the desired concentrations within. So all the air was specially filtered before it was pumped in to remove any possible external fluoride.

The scientists divided the trees into three separate groups: one group received no fluoride, another had hydrogen fluoride added to give a concentration of 0·3 μg per cubic metre of air, while the third received 0·5 μg per cu. m. These values represent concentrations typically found at about 1 km and 2 km respectively from a smelter; of course, the actual figures vary with the prevailing winds.

The scientists chemically monitored the fluoride concentration in the canopies. To minimise the possibility of any other factors influencing the outcome, all trees grew on the same soil type and received identical watering.

Experimental subjects

Just as in a trial in medical research — for example, testing a new drug on human volunteers — botanists and foresters measure a variety of responses in their subjects to see how these may change physiologically following exposure to something. Dr Hingston and his assistants took samples of leaves, stems, twigs, and wood, as well as large and small roots, during the course of the 254-day trial. They analysed all of these for their fluoride content.

They also looked for any visible signs of disease; many symptoms of plant ill-health show up in the leaves, so the scientists compiled a photographic record of leaf changes.

Marri trees were the first to show visible signs of damage — after 23 days of exposure to the highest concentration of hydrogen fluoride. Although jarrah showed no signs until 42 days after the start of the experiment, the scientists concluded that it was actually the more sensitive of the two, because analysis showed that, following exposure, the concentrations of elements such as nitrogen and phosphorus in its leaves changed far more than those in other species. Tuart only showed visible effects after 216 days.

The symptoms included the development of yellow patches on the leaves (chlorosis), leaf curling, and, in severe cases, death of the edges of the leaves. (Of course, these symptoms could also arise from other disorders — such as water stress or salt injury — and distinguishing fluoride poisoning in the field may therefore sometimes be a problem.)

Agonis flexuosa was the hardiest of the four, apparently being entirely unaffected by the gas even after 9 months had passed. Interestingly, this species had the lowest density of pores — or stomata — in its leaves, which supports the contention that most of the toxic gas enters the plant through the stomata. (Stomata allow for the exchange of carbon dioxide and oxygen between the air and the leaf cells, so enabling photosynthesis to occur.)

Confirmation comes from the analyses of the levels of fluoride in the various parts of the trees. The sensitive jarrah, after 153 days of exposure, had 84% of its fluoride content in the leaves, with the roots, twigs, and branches accounting for the rest. By contrast, in *A. flexuosa* the fluoride was spread more evenly throughout the plant, with the branches accounting for 30%, the leaves 26%, and the roots, stems, and twigs the remainder. Marri and tuart showed distribution patterns intermediate between these two extremes. The fluoride in roots probably comes from gas absorbed by the soil.

Variety

The scientists also measured the concentrations of the photosynthetic pigment chlorophyll within the leaves of the four species. In the hardy *A. flexuosa*, the level of chloropyll remained exactly the same even after exposure to the higher gas concentration (0·5 μg per cu. m). By contrast, jarrah showed a severe decline in the quantity of its chlorophyll, which paralleled the severe visual symptoms of chlorosis and partial leaf death. (Slightly more chlorophyll was apparently present in the leaves exposed to the greater concentration of hydrogen fluoride, but this was probably a statistical fluke.)

In tuart plants exposed to the lower concentration a definite increase in chlorophyll occurred, while in those

Some problems of fluoride

Ask where you could find fluoride, and many people might answer 'in toothpaste'. Certainly fluoride has become well known because, it is fairly widely agreed, at the correct quantity it can help reduce the incidence of dental caries. Authorities in many parts of the world have therefore added it to the drinking water — and toothpaste-manufacturers have added it to their product.

But fluorides are also among the more toxic pollutants that enter the air as a result of industrial activities. As well as aluminium-smelters, power stations, steelworks, fertiliser factories, and brick-works may all release fluorides. The compounds are also present in a number of commonly used substances such as glass-cleaners, wood-preservatives, herbicides and pesticides, and aerosol propellants.

Fluorides are any compounds that contain the element fluorine, which is a gas (F_2) and, in that form, vanishingly rare on earth. The major industrially produced fluoride is hydrogen fluoride (HF) — also released by volcanoes — but various fluorides are naturally present in small amounts in soil, sea- and fresh-water, and living organisms.

Obviously, as well as native vegetation, other plants will be affected by fluorides, and, through feeding on them, so too will animals. Vines are known to be sensitive, and their fruit as well as leaves can suffer damage. In animals, large doses of fluoride can cause acute poisoning, but this would be extremely rare.

A more realistic cause for concern is long-term exposure to low levels, because most organisms will accumulate some fluoride in their tissues. Animals — including us — may acquire fluoride from plants grown on soils with high fluoride levels, from foods contaminated by air-borne industrially emitted fluorides, and from water.

Adult humans can tolerate up to about 20 mg of fluoride per day, most of which the kidneys can excrete. A diet containing more than this, and consumed for prolonged periods, can lead to a variety of symptoms. Ironically, one of the earliest signs (which may become apparent at lower doses than 20 mg) is harmless mottling of the teeth; other complaints are skin disorders, bone lesions, and calcification of ligaments.

(Most fluoridated water contains fluoride at a concentration of 1 mg per litre; in toothpastes the range is from about 250 μg to 1 mg per gram. Thus water and toothpaste present no known hazard.)

With chronic fluoride damage — fluorosis — obvious symptoms may not appear for some time. Livestock grazing pasture near a source of air-borne fluoride may be at risk, while appearing initially in good health. Diagnosis of the problem in animals is made difficult because we cannot take regular large samples, such as we can do with plant leaves. A urine analysis is currently the best aid.

encountering the higher concentration of the gas the amount of chlorophyll remained about the same as before exposure.

As the results show, a great variability in sensitivity to hydrogen fluoride exists among four species from the west. Findings such as these are highly relevant to decisions on where to site a smelter, and how to vegetate its immediate surroundings.

The CSIRO scientists were not the first to study native vegetation from this aspect. Dr David Doley, a senior lecturer in botany at the University of Queensland, has exposed many different plant species to hydrogen fluoride — mainly eastern species, but also some Western Australian species including jarrah. He used seedlings and kept them exposed to the gas for 3 months.

His work showed a similar great range in sensitivity to hydrogen fluoride. In general, among the eucalypts, most bloodwoods were fairly sensitive at the concentrations likely to be present near smelters, whereas ironbarks were comparatively resistant.

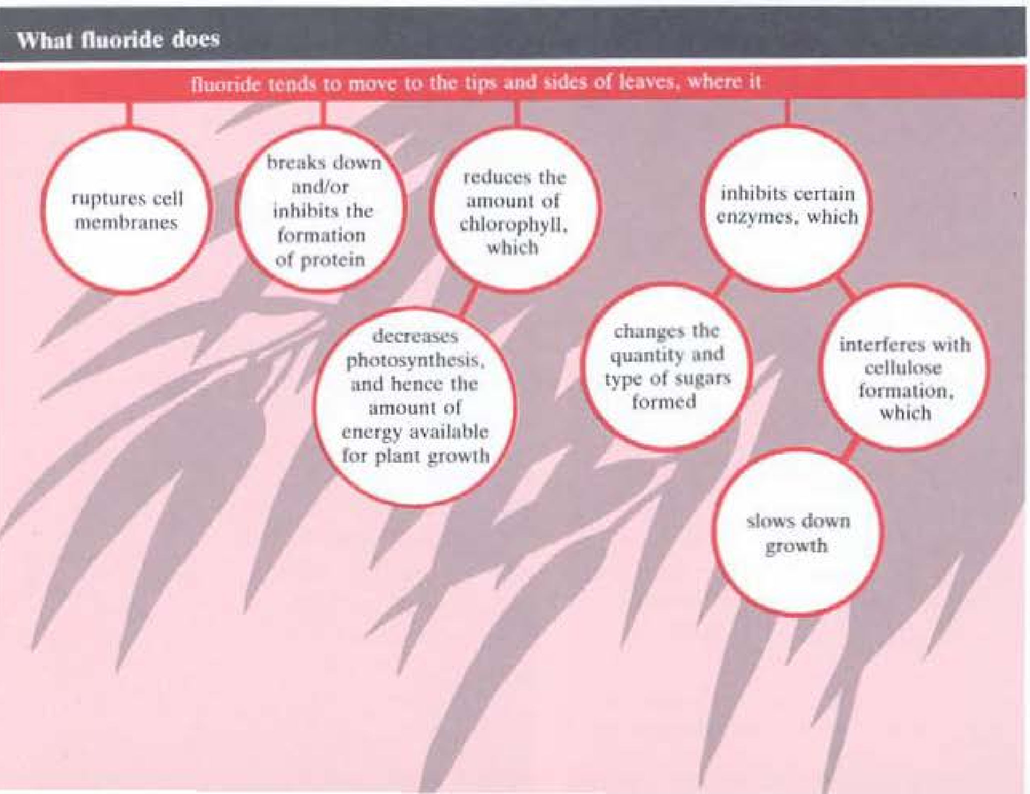
Scientists are not yet sure exactly how hydrogen fluoride damages plants. They know that it can interfere with several enzymes, and seems to upset calcium metabolism. This, in turn, affects the synthesis of chlorophyll and the development of chloroplasts — the organelles of photosynthesis — and hence causes chlorosis. Once photosynthesis becomes inadequate, a plant can no longer feed itself, and other symptoms of energy shortage appear.

Apart from the number of stomata on the leaf, the differences in susceptibility between species is probably due — at the molecular level — to slight variations in the structure of enzymes, these variations affecting the degree to which fluoride molecules can 'jam' or inactivate the enzymes.

It is not just plants that can fall foul of the effects of hydrogen fluoride — see the box — so the more we know about the effects of this gas the more appropriately we will be able to site any future aluminium smelters for Australia.

Roger Beckmann

What fluoride does



More about the topic

Aspects of the effects of fluoride in the environment at Kemerton, Western Australia. F.J. Hingston, G.M. Dimmock, J.H. Galbraith, G.E. Ho, and R.W. Horne. *Department of Conservation and Environment, Technical Series* No. 8, 1986.

'Plant–fluoride Relationships: an Analysis with Particular Reference to Australian Vegetation.' D. Doley. (Inkata Press: Melbourne 1986.)