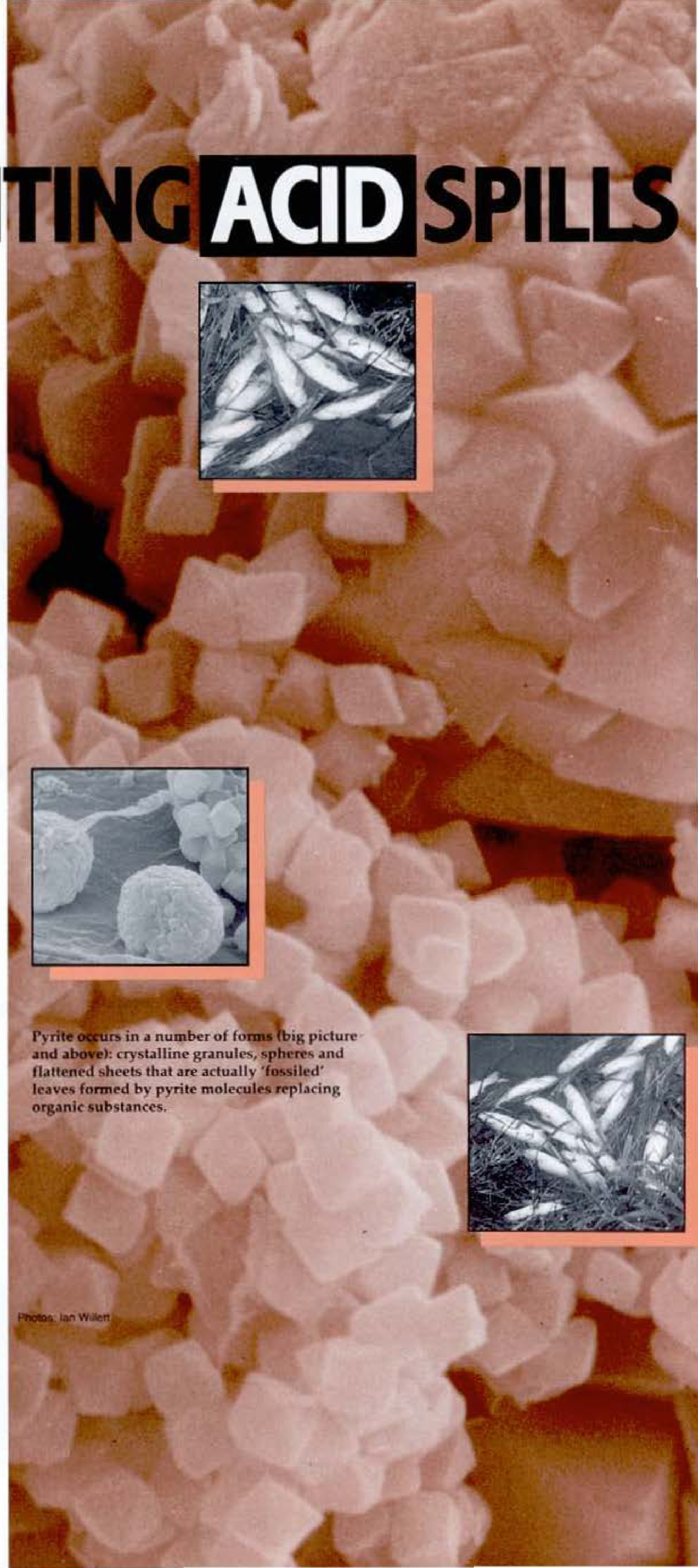
PREVENTING ACID SPILLS

Researchers have devised ways to stop fish kills caused, indirectly, by the ending of the last Ice Age.



Pyrite occurs in a number of forms (big picture and above): crystalline granules, spheres and flattened sheets that are actually 'fossiled' leaves formed by pyrite molecules replacing organic substances.

Photos: Ian Willett

Over recent years a tragic roll-call of disasters, from the Exxon Valdez oil spill to the collapse of the nuclear reactor at Chernobyl, has conditioned us to expect that we ourselves are to blame for the degradation of our environment; so it was understandable that professional fishermen on the lower Tweed River should suspect fellow humans of causing the catastrophic fish kills that occurred on the river in 1987.

Mr Clive Easton, an entomologist with Tweed Shire Council, was ideally placed to follow the drama as it unfolded. It began with the prolonged drought of 1985–87, which produced poor angling on the rivers of the New South Wales north coast as higher estuarine salinity led fish to disperse to the rivers' upper reaches. When heavy rains arrived in March 1987, local fishermen looked forward to bumper catches as bream, flathead and whiting returned to the tidal reaches of the Tweed to feast on mosquito larvae washed into the river from low-lying wetlands and flooded sugarcane fields. Following more than half a metre of rain the river was, as usual, loaded with sediment; but instead of clearing over a period of several days, it became crystal clear almost overnight... to reveal a carpet of dead and dying fish scattered across the muddy bottom along the upper two-thirds of the Tweed's tidal reaches.

A week later Mr Easton became aware of the full extent of the catastrophe when he found large numbers of bass, mullet, bream, flathead, luderick, garfish, eels and crabs littering the riverbanks. Ironically, mosquito larvae, instead of providing food for fishes, fed on their rotting carcasses.

Fishermen and other residents contacted the Council and voiced their suspicions that the fish kills must have been caused by run-off from local mines and quarries, by overflow from

FROM FARM LAND

Acid sulfate soils have killed all plant life, creating this 'wet desert' on the north coast of New South Wales.

Ian Willett

When oxygen comes in contact with a granule of pyrite, the resulting sulfuric acid eats away the surrounding matrix of soil.

Murwillumbah sewage treatment works or, more likely, by pesticide run-off from cane-fields. Scientists from the then New South Wales Department of Agriculture and Fisheries examined fish carcasses and found no clues as to the cause of death, although there were signs of asphyxiation. Water samples showed no pesticide contamination, and the presence of large numbers of mosquito larvae confirmed that pesticides were not implicated since insect larvae are far more sensitive to pesticides than are fishes. Significantly, however, the same water samples revealed low pH, indicating a high level of acidity, and low oxygen levels.

When the phenomenon recurred two months later, almost all the remaining fish in the tidal reaches of the Tweed were killed. Similar catastrophic fish kills have been reported from the Richmond, Clarence and Macleay Rivers. Cane pesticides could not have been the cause, since these are not cane-growing areas — but they have been extensively drained for dairy farming since early this century.

The Kempsey and Tweed Shire Councils asked a number of State bodies to investigate the problem, and Dr Ian Willett, a soil chemist from CSIRO's Division of Soils, was called in as a consultant. His initial survey led to the formation of a research team, funded by the Australian Research Council, that included Dr Ian White, a soil physicist from CSIRO's Centre for Environmental Mechanics, and Dr Mike Melville, a senior lecturer at the University of New South Wales' School of Geography.

First, they had to identify the source of the problem. Investigations conducted in the 1960s by CSIRO Division of Soils scientist Dr Pat Walker led to the conclusion that it was neither man-made nor confined to Australia. The same natural phenomenon — albeit one that has been exacerbated by human activities, particularly agri-

Ian Willett

A 1–2% concentration of sulfuric acid may not sound serious, but it's enough to corrode steel: the lowest strand of wire on this fence has been eaten away by acid, which is also corroding metal stiffening-posts and destroying timber fence-posts.

culture — occurs in many areas, including Indonesia, the Mekong Delta, Bangladesh, South America, New Zealand and Holland... and can only be understood by looking at massive global changes that took place thousands of years ago.

During the most recent glacial maximum or ice age, some 20 000 years ago, the sea was about 100 metres below present levels. Global warming subsequently caused sea levels to rise steadily until 6000–7000 years ago, flooding low-lying land on continental margins (destroying land bridges, such as those between Australia and New Guinea, and creating waterways such as the English Channel and Bass Strait).

As the seas rose they mobilised coastal sediments and pushed this material landwards, depositing it on present-day coastlines and in estuaries. Colonisation of these newly formed marine sediments by mangroves and other vegetation in protected tidal flats allowed organic matter to accumulate in generally anaerobic conditions: regular tidal flushing made it possible for bacteria to use the organic matter and to reduce the sulfate in sea water to iron sulfide — commonly known as iron pyrite — at concentrations of more than 1% in the top metre or so of the sediment profile.

Despite the many variations in the development of coastal river floodplains, iron pyrite has generally remained beneath the water table, covered by a protective layer of water and forming an innocuous 'potential acid sulfate soil'. It remains innocuous until it is exposed to air, when it oxidises to form sulfuric acid and creates an actual acid sulfate soil.

While such soils have developed around the world as a result of natural landscape drainage, the process has accelerated in historical times due to human interference. In some situations Nature has its own solution to the problem: the polders (reclaimed fields) of Holland, for example, have accumulations of pyrite below the surface, but thick beds of shells counterbalance this. If the soil is disturbed and sulfuric acid encounters the layer of calcium carbonate, it is neutralised to form gypsum.

Closer to home, much of the estuarine wetland area now contained within Kakadu National Park overlies potentially acid sulfate soils, with particularly high concentrations around the Jabiluka uranium deposit. Jabiluka's uranium could only be exploited if these were neutralised or stabilised, since sulfuric acid released by construction work would rapidly erode the foundations of roads or buildings. According to Dr Willett, development of the mine would pose immense engineering problems.

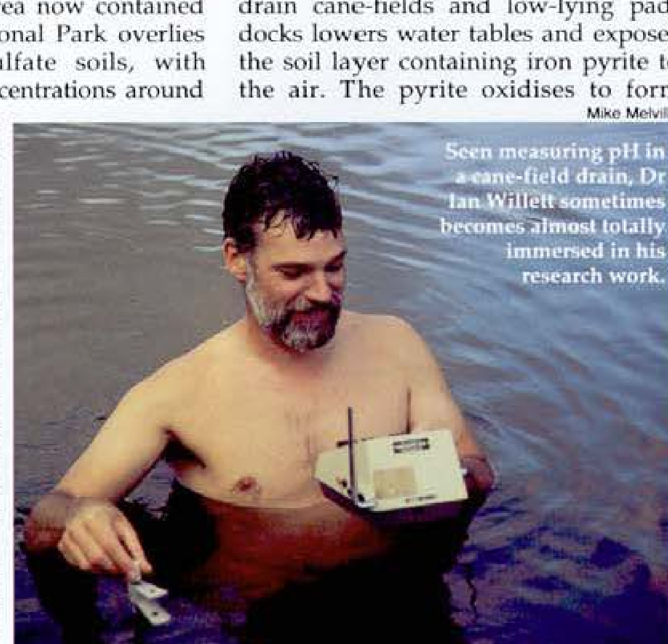
The northern coast of New South Wales provides ample evidence of how human intervention — in the form of draining wetlands for dairy-farming or sugarcane-growing, and mining, residential and tourism development — has mobilised potentially acid sulfate soils with catastrophic results.

In 1989 a working party was convened by Mr Bob Smith of the State's Department of Agriculture and Fisheries to review the impact of acid sulfate soils on the terrestrial and aquatic environments of the lower Macleay River. It found that two main aspects of human intervention have exacerbated the problem.

Draining swamps for cattle pasturage has seen inundation-tolerant native plants such as quillrod (*Phragmites australis*) and water couch (*Paspalum distichum*) replaced by intolerant species such as couch (*Cynodon dactylon*), smartweed (*Polygonum* spp.), pinrush (*Scirpus nodogus*), Nile grass (*Acrocerus macrum*) and clover (*Trifolium* spp.). When low-lying paddocks flood with water after heavy summer rains, these plants die and break down, consuming the oxygen in the stagnant water covering the paddocks: subsequent rain washes this anoxic water into the river, reducing the amount of dissolved oxygen almost to zero and thus killing many gilled organisms.

The combination of prolonged dry periods and the use of floodgates to drain cane-fields and low-lying paddocks lowers water tables and exposes the soil layer containing iron pyrite to the air. The pyrite oxidises to form

Mike Melville



Seen measuring pH in a cane-field drain, Dr Ian Willett sometimes becomes almost totally immersed in his research work.

The result of a Tweed River acid spill.

Clive Easton

sulfuric acid, which in turn mobilises aluminium in the soil. The acid salts developed by this process become concentrated on the soil surface, killing vegetation.

At sub-lethal levels, the leakage of acid and aluminium into rivers affects aquatic food chains, reducing the populations of fishes, crustaceans and oysters in estuaries and possibly reducing the populations of offshore species (60% of which spend part of their life cycle in estuaries). Fisheries biologists say that loss of habitat, especially as a result of major flood-mitigation schemes, therefore has the potential to reduce fish and prawn catches.

At lethal levels, a sudden influx of acidic anoxic water with high concentrations of aluminium clogs the gills of invertebrate and vertebrate aquatic organisms already stressed by low oxygen levels. A major fish kill in the Tweed River in 1987 was accompanied by a pH of 3·6 and aluminium levels of 2·5 mg per L; during a later fish kill at Cudgen Lake, near Tweed Heads, researchers recorded a pH of 2·6 and aluminium levels of 60 mg per L.

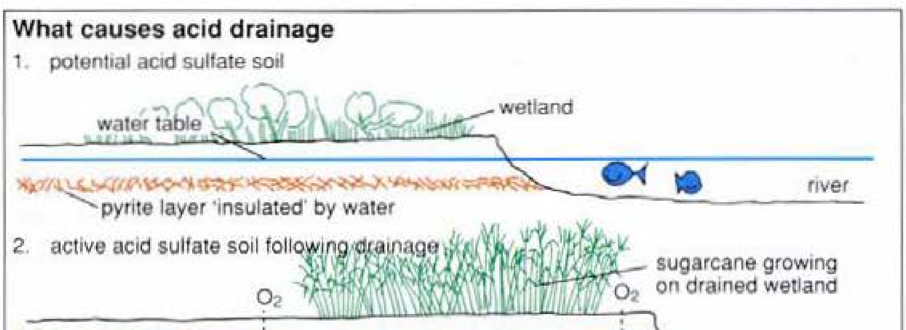
The potential magnitude of the problem is astonishing. Surveys by Dr Willett, Dr White and Dr Melville indicate that the soils of coastal areas in the Tweed Valley alone may contain some 500 000 tonnes of pyrite. About 15 000 ha of floodplain there, used mainly for cane-growing, have a half-metre-deep layer of pyritic soil at concentrations of 1%–10%.

Since iron pyrite oxidises to form sulfuric acid at a ratio of about 1:1 by mass, that means, potentially, half a million tonnes of sulfuric acid lies beneath the region's soils. A spillage from a single 40-tonne tanker-load of sulfuric acid would represent a serious emergency: the amount of sulfide contained in the soil is equivalent to 12 500 such tankers!

Half a million tonnes of sulfuric acid could never be mobilised at one time, of course, but at least twice that amount of lime would be needed to neutralise the soils of the Tweed Valley. The dynamics of the problem were illustrated by the team's preliminary measurements of stream acidity following flooding due to Cyclone Nancy in February 1990. The acidity of McLeod's Creek, a tributary of the Tweed, fell dramatically from a neutral 6 to a sharply acidic 3·5 as floodwaters flowed from drained cane-fields.

Mike Melville

Sediments stirred up in a cane-field drain after rain are beginning to flocculate (revealed by green-blue patches of clarifying water) as sulfuric acid and aluminium are mobilised by the drain's very function — the draining of wetlands by lowering water tables.



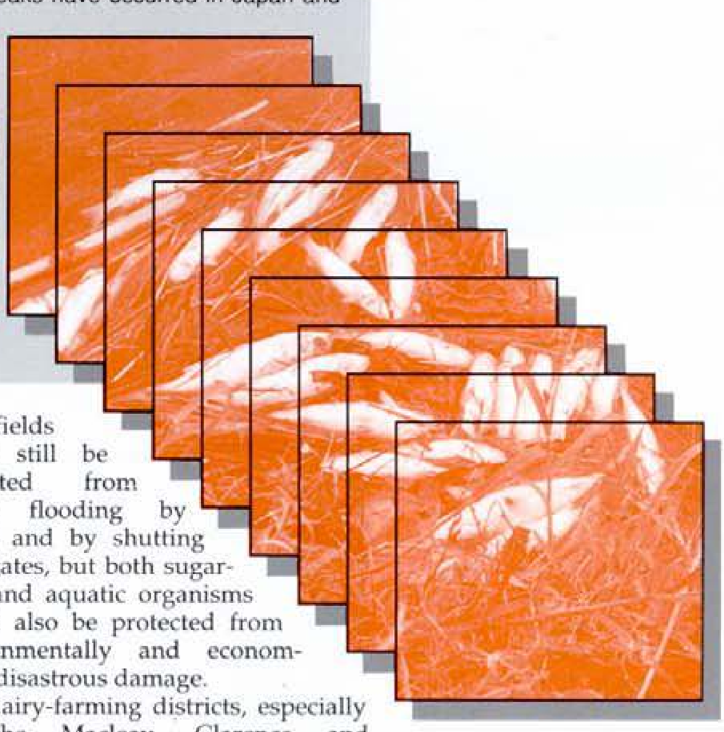
The problem begins when a lowering of the water table exposes 'potential acid sulfate' soil to oxygen.

Red spot disease: the acid connection

Australian fisheries biologists suspect there is a link between run-off from acid sulfate soils and red spot disease or epizootic ulcerative syndrome (EUS), an ulcerative skin disease of estuarine fish that has been reported from much of Australia's eastern and northern coastlines, as well as the south-west of Western Australia.

Studies by Dr R. Callinan and Dr G. Fraser of the New South Wales Departments of Fisheries and Agriculture, have shown that the primary cause of mortality in affected fish is the invasion of skin and underlying muscle by an aquatic fungus, *Aphanomyces*. The sudden appearance of EUS in Australia (the disease was first recorded in Queensland in 1972) and its rapid spread suggest that *Aphanomyces* may be a recent introduction into Australia. Outbreaks have occurred in Japan and the Philippines, where it has dramatically reduced fish stocks in the lakes that supply urban Manila with fish.

Aphanomyces seems incapable of affecting fish under normal environmental conditions, and outbreaks typically follow prolonged periods of heavy rain. It appears that one or more associated changes in estuary water quality (including high acidity, high levels of aluminium and low dissolved oxygen levels) may damage the skin of fish exposed to these changes — perhaps by affecting the skin's protective mucus coating — allowing *Aphanomyces* to invade.



Fortunately, Dr Willett, Dr White and Dr Melville consider the problem can be solved simply and at little or no cost, through a change in cane-farming practices. Cane-growers believe their fields must be drained continually and rapidly by floodgates emptying into adjoining waterways. They suggest that more than 3 days' immersion kills cane roots and reduces productivity, but this belief is based more on tradition than on science; the wild sugarcane that grows along the Sepik River in Papua New Guinea (an important source of new strains for growers in Australia and elsewhere) is more or less permanently inundated, with little effect on productivity or growth.

The research team suspects that productivity losses stem not from inundation *per se* but from inundation following a dry spell or drainage regime that brings oxygen into contact with acid sulfate soils. Flooding generates and releases sulfuric acid and aluminium into the cane plants' water supply, so the roots take up these toxic substances.

Neutralising the soils by adding lime to cane-fields would be unpractical and prohibitively expensive. Instead, the researchers suggest that growers simply adjust the floodgates that drain their fields so water tables can rise to cover — and thus seal — the acid sulfate soil layer. Cane-fields could still be protected from major flooding by levees and by shutting floodgates, but both sugarcane and aquatic organisms would also be protected from environmentally and economically disastrous damage.

In dairy-farming districts, especially on the Macleay, Clarence and Richmond Rivers, Dr Willett suggests winding down drainage schemes so problem areas can return to wetlands. Paddocks affected by rainwater ponding and the subsequent production of anoxic water, and by acid sulfate soils, tend to be unproductive anyway, so primary producers would suffer minimal economic loss.

On the other hand, the gradual return of these paddocks to wetlands would have significant conservation value, not only in the sense of conserving habitats for their intrinsic value but also because the decline of wetlands has resulted in a similar decline in the populations of birds such as ibis, which provide a valuable service to farmers by feeding on insect pests.

Carson Creagh

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