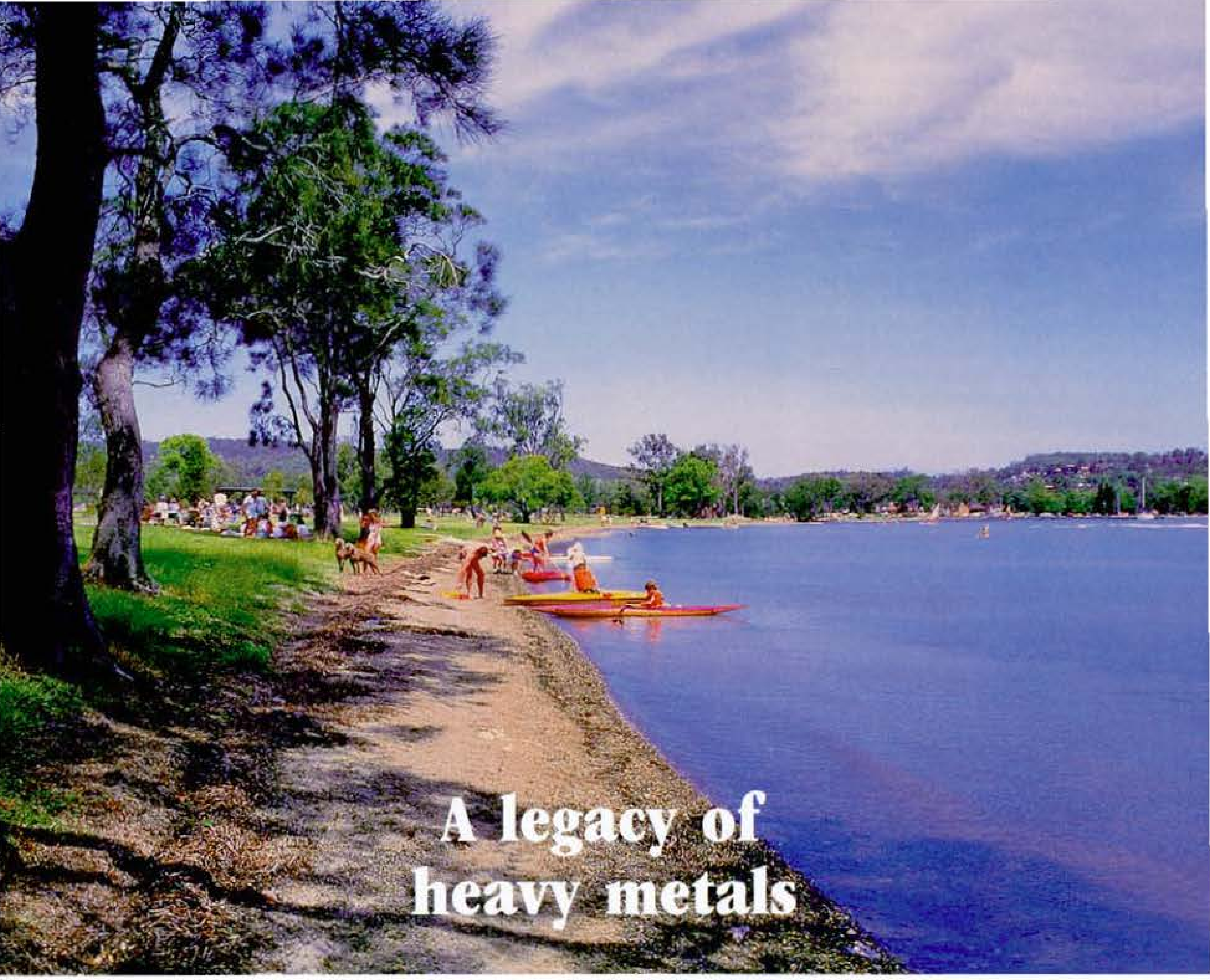


A legacy of heavy metals

Picturesque Lake Macquarie.

For nigh on a century, picturesque Lake Macquarie, a 125-sq.-km estuary on the outskirts of Newcastle, N.S.W., has had the misfortune to be burdened with a variable flow of heavy metals — lead, zinc, cadmium, selenium, and copper — and other pollutants.

Since last century, the lake's shores have seen the the establishment of collieries, a lead and zinc smelter, a fertiliser plant, a steel foundry, and three coal-fired power stations. Recently, the lake has also attracted extensive urban development, creating the need for several sewage-treatment works.

By the early 1980s, people had become concerned about an apparent deterioration in the quality of the lake water, and sedimentation of its shallow reaches. (Because of a single narrow outlet to the ocean, tidal flushing of the lake is poor.) In 1983 the New South Wales State Pollution Control Commission (SPCC) carried out an environmental audit there.

The SPCC identified eutrophication as the main environmental problem facing the lake. Increased nutrient levels promote algal growth and turbidity, which inhibits the production of seagrass and the organisms that feed upon it.

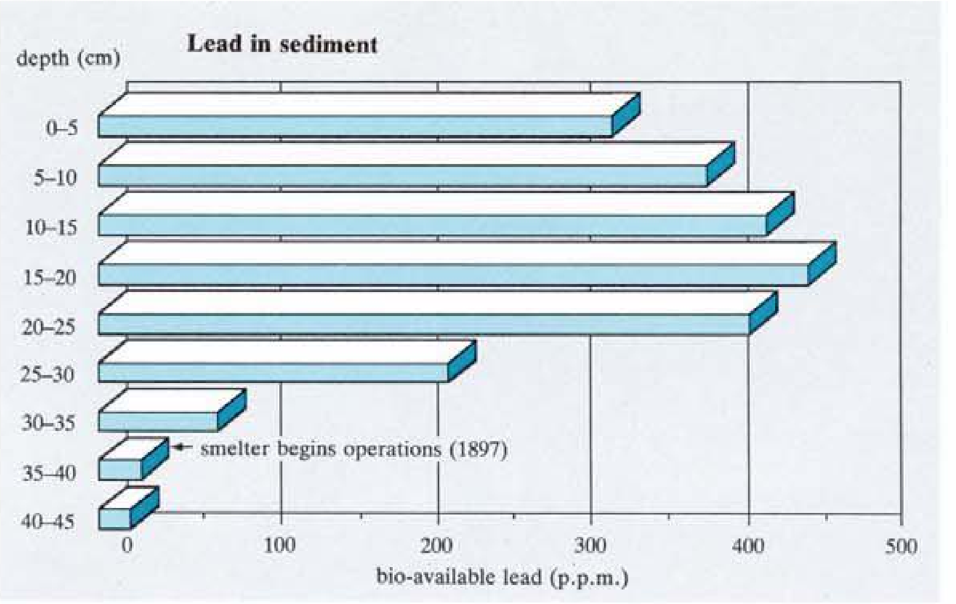
Another important issue was the presence of toxic heavy metals, which had been accumulating since 1897 when the lead and zinc smelter began operating. The SPCC commissioned the CSIRO Division of Fuel Technology to study the rates of mobilisation of heavy metals deposited in lake sediments, and the extent to which aquatic organisms were contaminated. In 1985, CSIRO gave its report to the SPCC, and the findings have recently been published.

In summary, the principal investigator in the CSIRO study, Dr Graeme Batley, sees the lake's heavy-metal problem as largely a legacy of the past. Before people realised what persistent effects heavy metals could have on aquatic ecosystems, Sulphide Corporation's lead and zinc smelter had already discharged, through Cockle Creek, large quantities of heavy metals in its process water.

The heavy metals have settled in the sediments in the northern part of the lake, where, unlike biodegradable organic contaminants, they will persist indefinitely. These elements can accumulate in the food chain, in the process insinuating their way into algae, seaweeds, shell-fish, fish, and — potentially — humans.

For example, Sydney cockles (*Anadara trapezia*) — which give Cockle Creek its name — and hairy mussels (*Trichomya hirsuta*), both from northern reaches, were

This profile of bio-available lead in the sediment about 1 km from the mouth of Cockle Creek shows that 30–35 cm of sediment has been laid down since the smelter began discharging heavy metals in 1897. This means a sedimentation rate of 3–4 mm a year.



found to have accumulated high concentrations of cadmium and zinc. In some cockles, levels of 13 p.p.m. cadmium and 84 p.p.m. zinc (dry weight basis) were sufficiently high to create a possible health risk if people were to collect and eat quantities of these shell-fish. A fuller assessment of shell-fish toxicity is being made by the New South Wales Department of Agriculture.

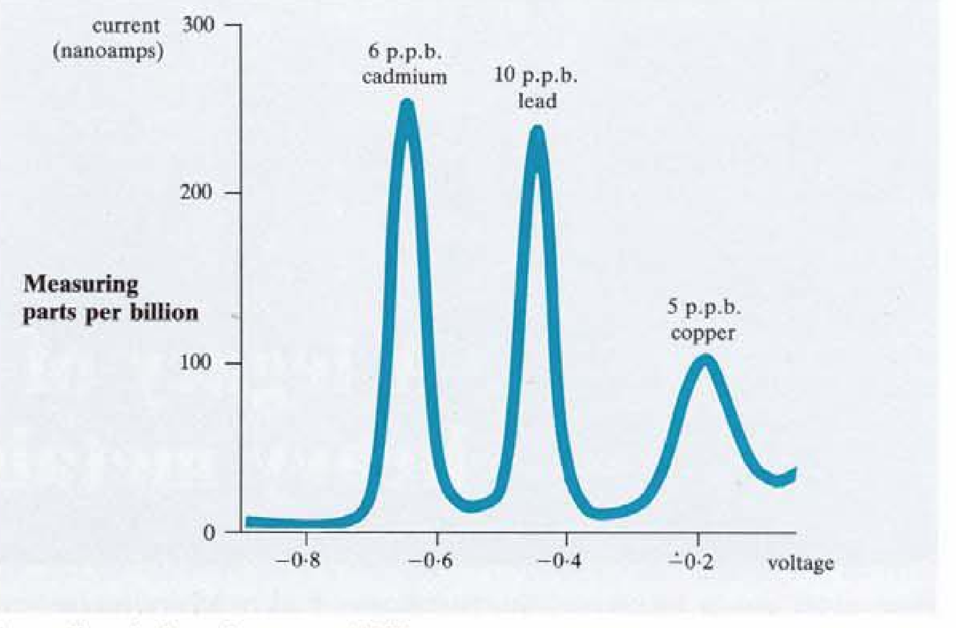
Seagrass (*Zostera capricorni*) was also found to have accumulated metals in both its leaf and root systems. Concentrations as high as 310 p.p.m. zinc and 280 p.p.m. lead were measured. Although seagrasses can absorb heavy metals from both sediment (through their roots) and surrounding water (through their leaves), most of the measured metal is likely to have come from the sediment, where concentrations are generally 100 000 times higher than in the water. Some seagrasses can apparently pump heavy metals from the sediment, through their leaves, to surrounding waters.

Green algae are good indicators of heavy metals in surface waters, and Dr Batley found that northern-dwelling plants were enriched in zinc, lead, and selenium.

In general, Dr Batley found the greatest contamination of bottom sediments, attributable primarily to the old-time smelting operation, extended about 1 km from the mouth of Cockle Creek. Nearly one-fifth of the total heavy-metal burden was deposited in this area.

Zinc, lead, cadmium, and copper were the major contaminants, and these elements were present mostly in forms that could be readily taken up by living organisms. Measured bio-available metal levels of up to 960 p.p.m. zinc and 390 p.p.m. lead are likely to be hazardous to all but the hardiest sediment-dwelling plant or animal. Because of this, and the turbidity of the water, it's difficult to find any shell-fish in the northernmost part of the lake.

Concentrations rapidly diminished away from Cockle Creek: at a distance of 3–4 km from the creek mouth, measurements approached the levels typical of the southern reaches, about 100–200 times less than northern concentrations. Contaminated sediment generally extended down to 20–30 cm, reaching 50 cm close to the mouth of Cockle Creek.



In anodic stripping voltammetry (ASV), the metals in a water sample are plated onto an electrode. Then, reversing the process, they are stripped off using progressively increasing voltages. Each element is carried off at a characteristic voltage, and the size of the current associated with it gives a measure of the metal concentration.

Most of the sediment originates not from the smelter but from urban areas within the catchment. But the smelter's heavy metals have clearly labelled the sediment deposited over the last century. By dividing the above figures by the period the smelter has been discharging doses of heavy metals, Dr Batley calculates that sediment has been building up in northern parts at rates of 1–6 mm per year, figures considerably higher than those derived from previous studies using the less-reliable method of carbon dating.

At this rate, the lake is likely to lose several hectares of its expanse every year (which does seem to be happening) and, without dredging or measures to control silt input, it could theoretically fill up completely over some thousands of years.

Ultra-trace measurement

The good news is that over the past decade the smelter has cleaned up its effluent. Dr Batley calculates that, at current rates of discharge, and on the basis of previous dispersion and sedimentation patterns being maintained, the concentrations of bio-available metals in the newly deposited sediments shouldn't prove harmful.

Measurements in 1984/85 showed that the smelter was then discharging only about half a kilogram each of lead and zinc daily, and at this rate it would take at least 500 years for these metals to build up to quantities comparable to those currently found in the top 5 cm of sediment.

The smelter's discharge to Cockle Creek averaged, per L, 40 μg of cadmium, 16 μg

SPCC staff collecting water samples.

of copper, 200 μg of lead, and 500 μg of zinc; after it mixed with creek water, these values would become about three times less.

The discharge water is further diluted once it joins the lake, and Dr Batley's measurements of the dissolved biologically available metal fraction gave averages, for northern sampling sites, of 2 μg of cadmium, 2 μg of copper, 0·8 μg of lead, and 8 μg of zinc per L. At southern sites, levels were 5–10 times less. (As a comparison, some species of algae and fish experience chronic effects — involving physiological damage or reduced reproduction rates — at levels of more than 3 μg of cadmium, 5 μg of copper, and 8 μg of lead per L.)

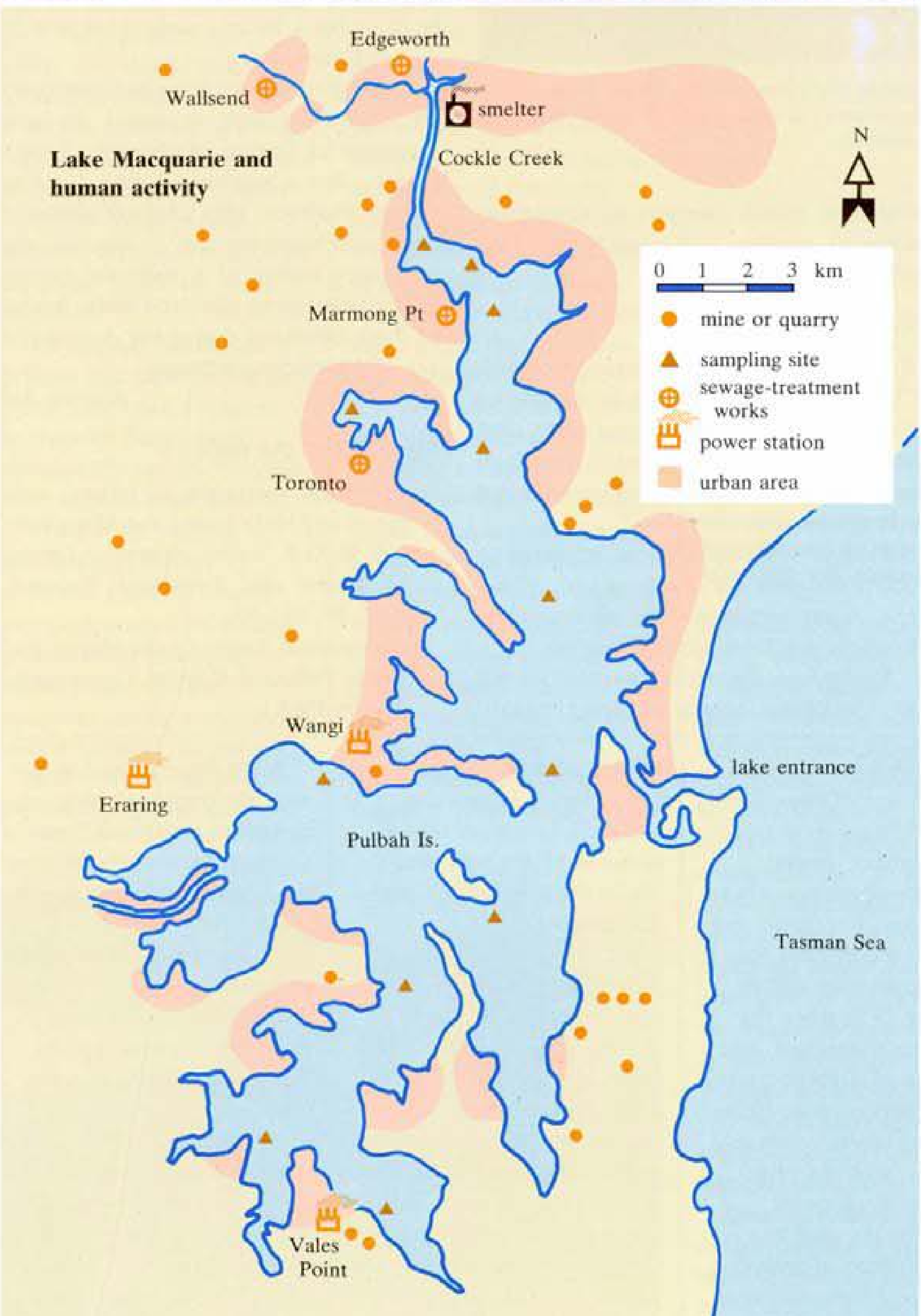
Such levels, involving measurements of parts per billion, are extremely low. One part per billion (equal to 1 μg per L) can be envisaged as a result of dissolving a few grains of sugar (weighing a few milligrams) in a petrol-tanker of solvent. To analyse for such low concentrations is a real challenge to the chemist's art, and is fraught with difficulty. Contamination, or loss, of the target material is all too easy, and few Australian laboratories are suitably equipped.

The CSIRO laboratories at Lucas Heights specialise in 'ultra-trace' analysis. Their clean air is free of all dust particles larger than 1 μm across, lint-free clothing is *de rigueur*, and sticky doormats greet the feet of all who enter.

Dr Batley and his colleague Dr Mark Florence, who have pioneered a number of ultra-trace measurement techniques, principally use anodic stripping voltammetry (ASV) for direct analysis of heavy metals in the parts per billion range.

ASV involves plating the metals in a sample onto an electrode and then, by reversing the process, measuring the minute currents as each metal is sequentially stripped off at its own characteristic voltage. The size of the current corresponds to the concentration of the metal. In addition, the researchers used inductively coupled plasma emission spectroscopy, atomic absorption spectrometry, and neutron activation analysis for the Lake Macquarie task.

The advantage of using ASV when analysing water samples is that the resulting measurements closely approximate the



Tidal flushing of Lake Macquarie is weak because of a narrow outlet to the sea; any pollutant finding its way into the lake from surrounding human activity is apt to stay around.

Inside it's clean — very clean. This CSIRO laboratory is equipped for 'ultra-trace' analysis.

fraction of bio-available metals. This is the fraction that concerns living organisms; the total metal concentration includes chemical forms that are inert, or for other reasons unable to be assimilated.

For analysis of sediments, Dr Batley used five extractants to measure different chemical phases of each metal — the exchangeable cations, surface-adsorbed metals, organically bound metals, bio-available metals (using EDTA as the extractant), and the residual fraction. As it happened, the majority of the metals traceable to the smelter proved to be in bio-available forms.

Dr Batley analysed sediment samples taken by divers who had plunged cylinders 50 cm into the mud at chosen sites throughout Lake Macquarie. Water samples were taken a number of times during the year from these same sites, and at some discharge points. Samples of seagrasses, seaweed, cockles, and mussels were also analysed.

To dredge or not?

Results indicated that, by comparison with Cockle Creek, other inputs to the lake — from the sewerage plants, coal mines, and air- and water-borne fly ash — result in only small increases in sediment metal concentrations.

Treated sewerage effluent appeared to contribute only zinc, the least toxic of the four heavy metals studied, in concentrations ranging from 1 to 2100 μg per L.

Fly ash from the three power stations was an identifiable source of heavy metals; however, its contribution was small, and unlikely to be of major concern.

The only way to get rid of the existing heavy-metal pollution in the north of Lake Macquarie is by dredging up the sediment and dumping it (perhaps in the open ocean). During such a process, the disturbance of the compacted and oxygen-deprived sediment would expose it to oxygenated water. This might liberate a burst of heavy metals, both at the dredging site and at the dump site. Is such an outcome likely?

Dr Batley took sediment samples and mixed them with sea water to see what would happen. Certainly, he observed a rapid increase in dissolved lead and zinc, but the levels were still well below the maximum acceptable short-term concentrations for marine organisms (suggested to be 20 μg per L for lead and copper, and 50 μg per L for zinc).

Backing up this result is a separate study Dr Batley did with an actual dredging operation at Darling Harbour in Sydney (which, like a number of other sites in Sydney Harbour, also contains sediment laden with heavy metals). In this case, the laboratory testing of a sediment sample gave similar (low) dissolved-metal figures to those measured during the dumping at sea of the dredged sediment.

Andrew Bell

More about the topic

Heavy metal speciation in waters, sediments and biota from Lake Macquarie, N.S.W. G.E. Batley. *Australian Journal of Marine and Freshwater Research,* 1987, **38**, 591–606.

'Environmental Audit of Lake Macquarie.' (State Pollution Control Commission: Sydney 1983.)