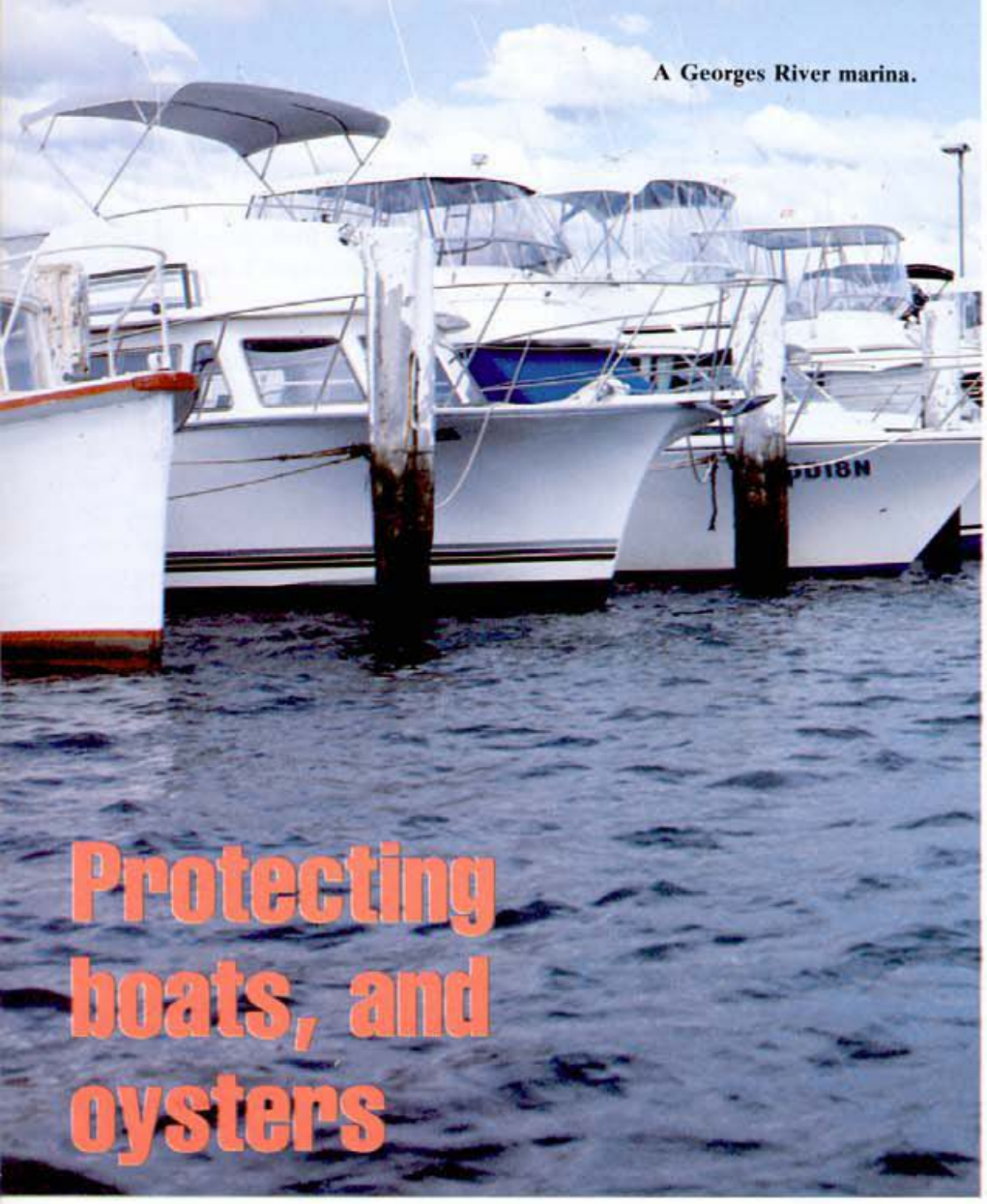


A Georges River marina.

Protecting boats, and oysters

'Boat people' — from the Navy down to the weekend sailors of the suburbs — know that barnacles and other marine creatures like a good boat bottom. Leave your boat in the water and before long creatures looking for a surface on which to set up home will colonise the smooth lines of its hull.

This fouling slows boats down (with large craft it can add considerably to the fuel bill), and if left unchecked may accelerate the rate of corrosion and decay.

So, for years, conscientious boat-owners have regularly applied anti-fouling paints to preserve the sleek smoothness of their crafts' undersides. The paint keeps barnacles and the like at bay because it contains tin, incorporated in an organic compound called tributyltin (TBT), which is toxic.

In an organic form, tin dissolves more easily in fats and hence is thought to be able to cross cell membranes more readily. Tributyltin is more toxic than dibutyltin (DBT), which in turn is worse than the monobutyl form. Pure elemental tin is far less toxic than the various organic forms.

More than 70% of the vessels in the world's deep-ocean fleets use anti-fouling paints based on tributyltin, as do many small recreational craft. TBT anti-foulants are widely used in Australia. In the last few years, various countries have reported high concentrations of tributyltin occurring in poorly flushed waters in areas of high boating activity.

Knowing about this, Dr Graeme Batley of the Centre for Advanced Analytical Chemistry, in the CSIRO Division of Fuel Technology, decided to find out whether tin was a significant pollutant in waters around Sydney. In collaboration with the New South Wales State Pollution Control Commission, he started a study in 1987 that produced the first data ever obtained for TBT in Australian waters.

After developing better procedures for measuring TBT in water, Dr Batley and his colleagues took samples from various points in Sydney Harbour, Botany Bay, and the Georges River. It was important to be able to measure the different 'species' of tin-containing compounds, as they differ in their toxicities.

A figure for the total amount of tin in water is not very helpful when considering its damaging effects as a pollutant; what is required is information for all the butyltin compounds, but especially for TBT. After adding a complexing agent, scientists can extract both the organic and inorganic forms of tin using an organic solvent such as hexane.

Using gas chromatography to separate compounds, Dr Batley was able to detect concentrations of TBT down to the level of just one-thousand-millionth of a gram (one nanogram or ng) of tin per litre of sea water. He found the highest concentrations of tin in water samples from around Garden Island and Rushcutters Bay in Sydney Harbour. The Navy's dockyard at Garden Island houses a large part of its fleet, and is where it carries out the anti-fouling of its ships. Rushcutters Bay contains the marinas of the Cruising Yacht Club of Australia.

At other sites, such as Gwawley Bay and Quibray Bay (see the map on page 23), where no obvious point sources of contamination existed, the average concentration was less than 50 ng of tin per litre. In several cases, Dr Batley and his team found differences between the first sampling in July and the second in September. It's quite likely that currents, tides, and flushing, as

A scientist samples sediments at a Georges River oyster lease.

Shell-thickening — one of the effects of TBT — seen here in Sydney rock oysters. The shell on the right is normal.

well as changes in the extent of boating activity, accounted for these.

But the most important factor to take into account when sampling is differences in concentration with depth.

As well as existing in solution, tin will associate with suspended matter, and so ultimately settle to the bottom. However, the highest concentration of TBT occurs in the top few micrometres of water. In this thin surface layer the hydrophobic (or water-shunning) organic tin compounds naturally accumulate. If, as is often the case in marinas, a petrol film is present, then the compounds are likely to go into solution in this.

After sampling the surface microlayer, Dr Batley has found that TBT may be concentrated there to as much as ten thousand times its strength in the water beneath.

Deformed oysters

At about the time that he started his investigations of tin in some of Sydney's waterways, Dr Batley was contacted by Mr Marcus Scammell, a researcher with the Institute for Marine Ecology at the University of Sydney, who had been studying the biological effects of TBT on oysters for an honours degree. Local oyster-farmers had complained of the incidence of shell deformities in their crop, particularly from sites that were poorly flushed or had undergone a relatively recent increase in boating activity.

The earliest reports of these symptoms coincided with the introduction of the tin-based paints in the seventies. Research overseas suggested that TBT could cause abnormal calcification in oysters and a general reduction in their growth rate. It would not be surprising if tin did this — after all, it was chosen as the active ingredient in anti-fouling paints precisely because of its toxic properties.

Problems with oysters cannot be regarded as trivial. In eastern Australia, oyster production has an annual market value greater than $100 million, and much of this is based on the cultivation of the Sydney rock oyster, *Saccostrea commercialis*. No data existed on the levels of tin in these oysters, so Dr Batley and his team went out to sample a number of areas in the Georges River — a major site of production — as well as the Hawkesbury River north of Sydney and, as a possible experimental control to give a baseline value, Wallis Lake on the central coast of New South Wales.

Analysis showed that the highest concentrations of TBT — expressed simply as the weight of tin per gram of oyster flesh — occurred in samples from Sandbrook Inlet (known locally as Brooklyn Bay) on the Hawkesbury River. These unfortunate oysters contained 350 ng of tin in each gram of their flesh compared with a value of only 1·6 ng in those from Wallis Lake, which is probably the natural background level.

In the Georges River, the values ranged from 15 ng per gram in oysters from Quibray Bay to 107–128 ng per gram in those from Scylla bay. The flesh of the 2½-year-old oysters from Sandbrook Inlet weighed, on average, 1 gram. Many of their shells were also curled. By contrast, most of those sampled from elsewhere (aged about 3 years) averaged 3 grams of flesh and had larger shells.

In Woolooware Bay, also in the Georges River, oysters grown nearest the marina had a TBT concentration twice that of those furthest away. Shell curl was present at TBT concentrations in the range of 80–230 ng of tin per gram. From the evidence of a number of samplings, Dr Batley concluded that shell curl only occurred in waters that carried more than 30 ng of tin per litre. Furthermore, the scientists also showed that analysis of water samples *per se* will not always reflect the true state of the TBT problem, given the daily changes to the water by tides and variation in boating activity.

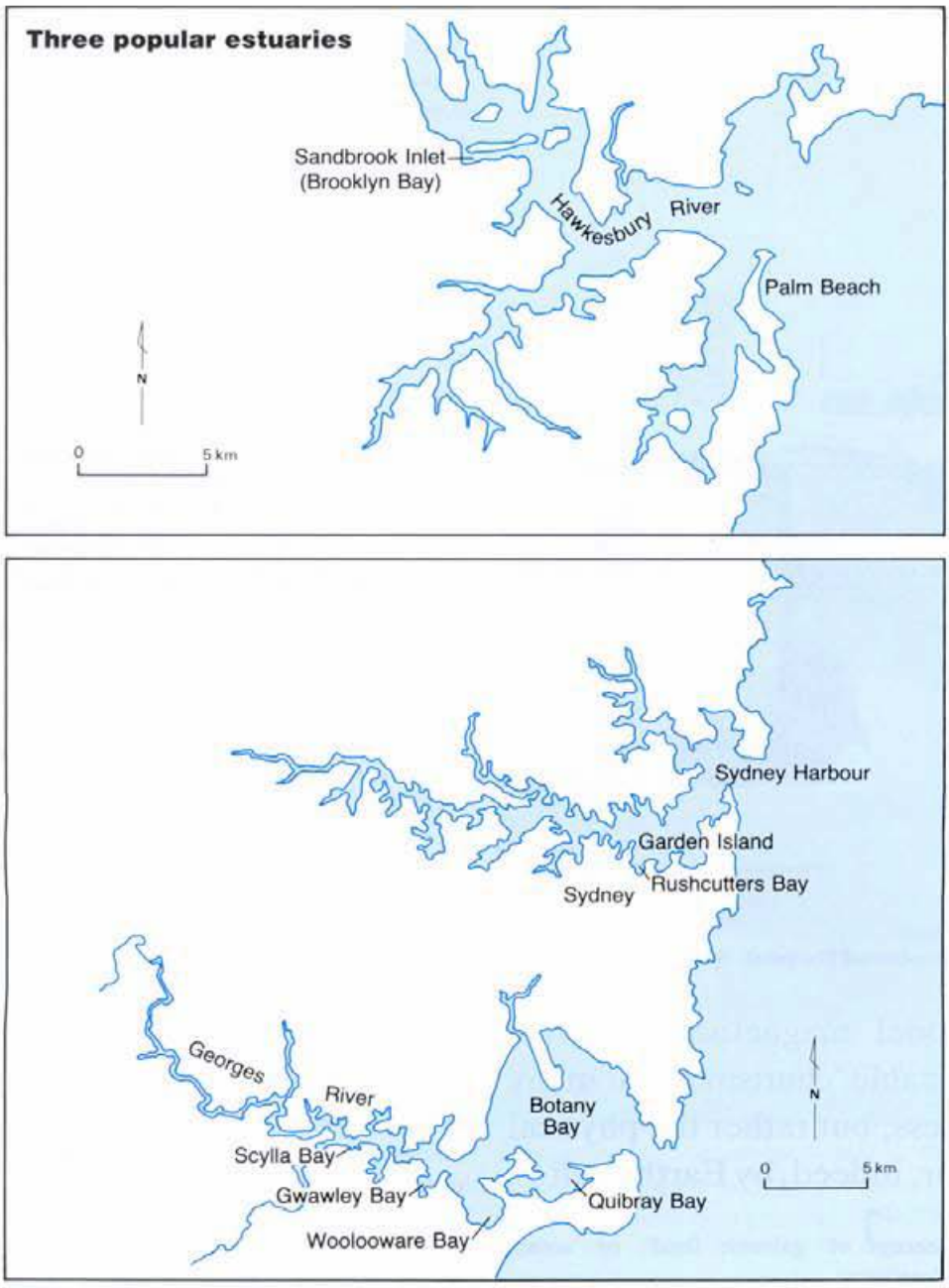
It seems clear, then, that high concentrations of TBT and shell deformities are connected. That is not the same as saying that TBT causes the problem, but evidence that it does so has come from overseas, where banning of TBT paints has led to a recovery in the health of oysters grown near marinas.

Human health

If oysters are so affected by tributyltin, then what about us? Swimming in or drinking water around marinas would not be harmful due to the tin — although it may not be recommended for other reasons! The concentration of TBT, being in the parts per trillion range, is far too low to have any effect on us.

Oysters, however, along with certain other creatures, are filter-feeders, processing great volumes of water in order to extract nutrients. Furthermore, they tend to filter water more rapidly as the tide goes out and the water level falls. The surface layer of the water carries the highest concentration of TBT, and the oyster will filter most frantically as this layer passes over it. In the process, presumably, it absorbs a far larger load of the pollutant than would otherwise be the case.

What if we eat contaminated oysters? Even in the worst-affected oysters that Dr Batley found, the concentration of TBT in the flesh was extremely low — despite the fact that it could be several thousand times greater than the concentration in the surrounding sea water. As each oyster weighs only a few grams, achieving a similar concentration in our own flesh would require the consumption of truly



The map shows sampling sites referred to in the article.

enormous quantities of oysters, far beyond the capacity of any gourmet.

As far as we know, human health is at no risk from the low levels of TBT that enter water from anti-fouling paints. But the health of the valuable oyster-farming industry is clearly another matter. Following the research of Dr Batley and his collaborators, and pressure from concerned oyster-farmers, the governments of New South Wales, Victoria, and Tasmania have banned the use of TBT-based anti-fouling paints in boats less than 25 metres in length. (Large boats are exempt.) Western Australia is currently considering the matter.

Copper too

Dr Batley's research has also shown high levels of copper in some oysters, a few measurements even exceeding the levels set by the New South Wales Department of Health. Copper is present naturally at higher concentrations than tin, but the increased concentrations found in oysters from parts of the Georges River led to a hunt for a possible source.

The stormwater washed into rivers and harbours after heavy rain is a well-known source of heavy metals. Along with lead from petrol and zinc from rubber tyres, Dr Batley found that copper from vehicle brake-linings can also be present in stormwater.

But first impressions can be misleading, as further research revealed that the levels of copper in river water and oysters did not fluctuate in the same way as did those for lead and zinc, increasing after a discharge of stormwater. Rather, the distribution of high copper levels correlated far more closely with that of TBT.

Dr Batley and his team then went back to the paints, and analysis showed that many of these contained copper along with TBT. Before TBT was added to anti-fouling paints in the 1970s, copper was the active toxic ingredient. Tin, although a general biocide like copper, was considered to be more effective against seaweeds. Many companies kept copper in their paints to achieve a cocktail that would be more effective against a wider range of organisms.

It may seem that, ironically, banning TBT-based paints will only lead to an increase in the use of copper-only paints, which have a higher copper concentration than do the mixtures. But Dr Batley and Mr Scammell discovered an interesting paradox.

In experiments with oysters grown near sticks coated with TBT-based or copper-only anti-fouling paints, they discovered that the presence of TBT increased the levels of copper in the oysters' tissues. (Interestingly this synergism, or acting together, between TBT and copper appeared to work both ways: not only did it ensure the enhancement of copper absorption by the organic tin, but also TBT uptake was increased in the presence of copper.) With TBT banned, it is possible that the uptake of copper by the oysters will be reduced, provided there is no increase in the use of copper paints.

For the foreseeable future, it looks as though some sort of toxin will have to be used in anti-fouling paints. However, new non-toxic varieties, which work because they are slippery and allow for easier removal of attached organisms, are now being released onto the market, so things may change. If you are a boat-owner, you can help the problem by avoiding TBT-based paints, if you live in a State where they have not been banned, and by not painting your vessel too frequently. It is the fresh paint (2 weeks old or less) that leaches into the water the most. A good scrubbing may be as effective as a new coat of paint.

Roger Beckmann

More about the topic

Tributyltin in Sydney Harbour and Georges River waters. G.E. Batley, K.J. Mann, C.I. Brockbank, and A. Maltz. *Australian Journal of Marine and Freshwater Research*, 1989, **40**, 39–48.

Accumulation of tributyltin by the Sydney rock oyster, *Saccostrea commercialis*. G.E. Batley, Chen Fuhua, C.I. Brockbank, and K.J. Flegg. *Australian Journal of Marine and Freshwater Research*, 1989, **40**, 49–54.