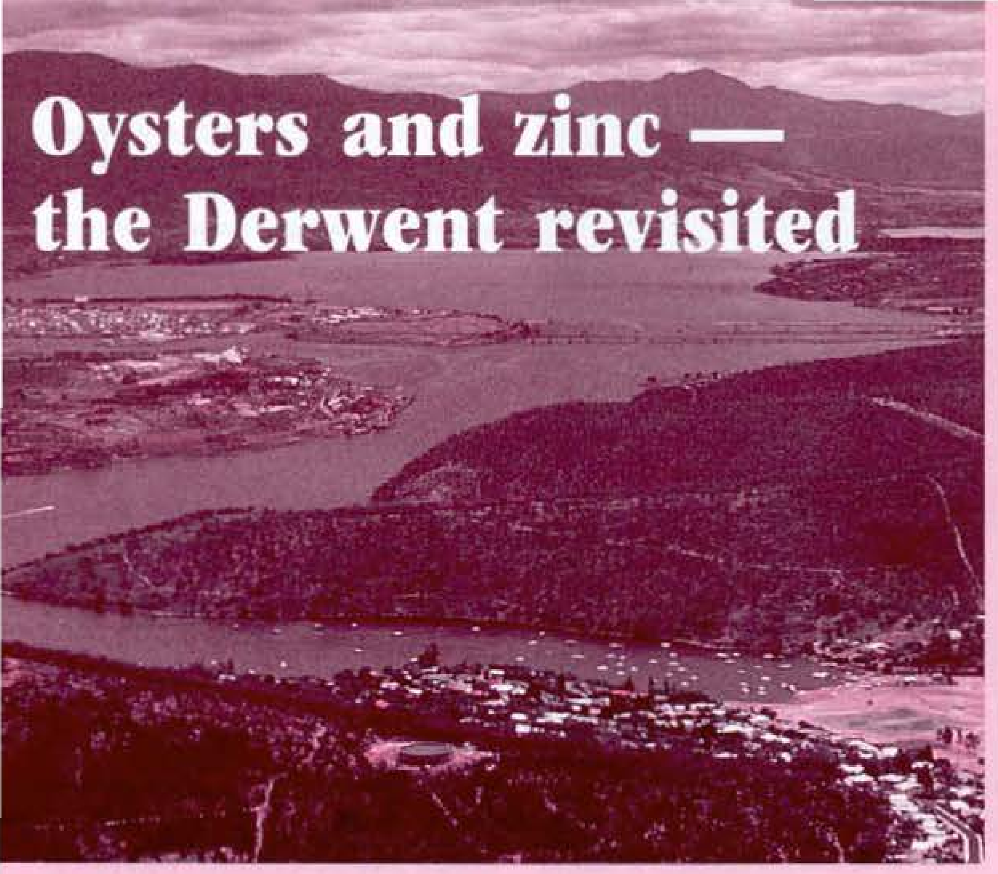
Oysters and zinc — the Derwent revisited



Pollution in the estuary of Tasmania's Derwent river was reported in the first edition of *Ecos* back in 1974. The problem concerned the presence of heavy metals, particularly zinc.

In anything other than very small quantities, heavy metals are toxic to most living things, especially mammals. However, shellfish can tolerate comparatively high levels of most heavy metals, and oysters growing in the Derwent estuary were actually accumulating these metals to such a high level that consumption of as few as six oysters, far from being aphrodisiacal, could cause a gourmet to vomit from zinc overdose.

You're unlikely to vomit if you eat oysters in Hobart now — provided you don't drink too much of the excellent Tasmanian wine — and if you do get ill the cause is not likely to be zinc.

Most would now agree that, although the Derwent is not exactly clean, the pollution by heavy metals has decreased considerably since 1974. The flow of the Derwent estuary is now much better understood — as are the life of its bacteria, the metabolism of oysters, and the effect of heavy metals on mammals — thanks to the large research effort that the pollution problem stimulated.

Oysters analysed in 1972/73 by the CSIRO Division of Food Research's Hobart group (now part of the Division of Fisheries Research), led by Dr June Olley, contained high levels of the heavy metals zinc, copper, and cadmium. Lead was also added to the list after analysis by scientists at the University of Tasmania. Later, fish were found with high levels of mercury, an even more worrying contaminant.

The likely source of the heavy metals was not hard to guess. The Electrolytic Zinc Company operates a refinery for the production of zinc at Risdon, a northern suburb of Hobart, on the Derwent River. The mineral that is the raw material for zinc production, sphalerite, is essentially zinc sulfide, but contains, along with zinc, many other metals as unwanted impurities. In the process of purification some of these were, and to a far lesser extent still are, discharged into the river.

Other potential sources of pollution also exist. Further upstream is Australian Newsprint Mills, and a chocolate factory and an abattoir complete the list of large-scale industries along the shores.

Under the river more potential pollution lurks. On 5 January 1975, an ore-carrying ship, the 'Lake Illawarra', crashed into one of the supporting pillars of the Tasman road bridge across the Derwent, while *en route* to the zinc refinery. The bridge was cut in two, and the ship sank, taking with it thousands of tonnes of heavy-metal-containing ore.

The river is deep at that point, and the vessel and its cargo were not salvaged. The zinc sulfide ore has not been a serious source of pollution. Some scientists think that it never will be, as the ship is now covered with a blanket of silt, and the heavy metals within the cargo are effectively buried; others are not so sure.

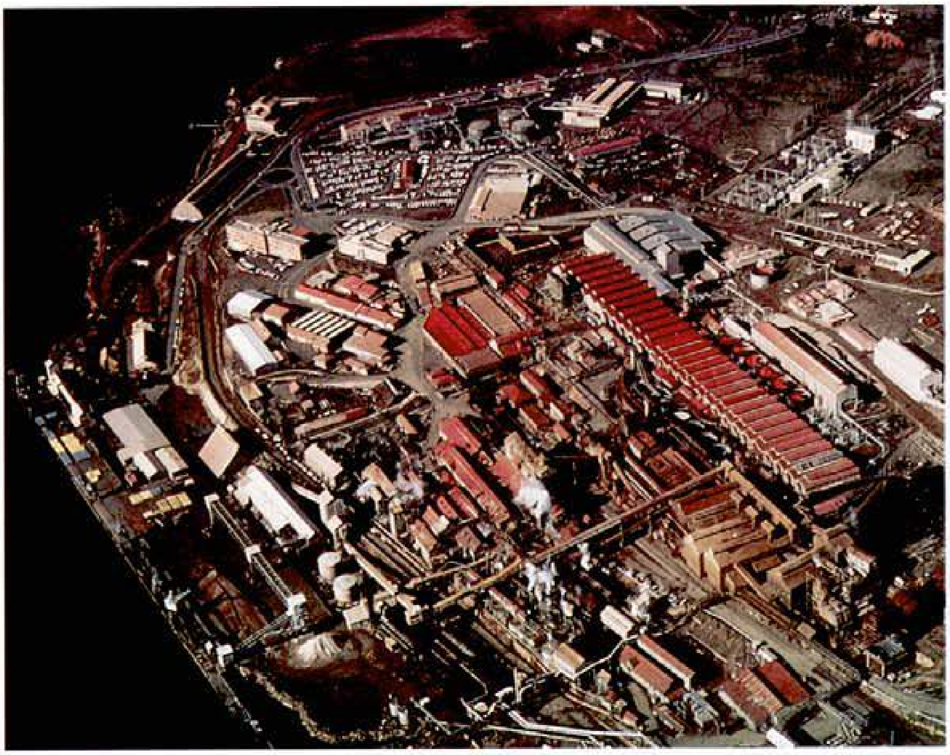
If you are a commercial oyster-grower, and your product is liable to make people sick, you'll probably soon be out of a job. Accordingly, when the zinc pollution problem came to light, oyster-growers approached Electrolytic Zinc for compensation, as this company was the only one on the river to deal in zinc, and so was considered the obvious culprit. A settlement was reached out of court, and all the oysters were removed from Ralph's Bay, an area downstream of Hobart (and about 15 km downstream of the zinc refinery), which was the site of a number of oyster farms.

Onwards from 50

While we were preparing this fiftieth issue of *Ecos* we received some good news. The consultants who have been conducting readership studies of *Ecos* and CSIRO's other quarterly science magazine, *Rural Research*, reported that they had found 'a universal appreciation of the high quality and high standard of publication' of both magazines. They recommended that: 'In view of their readers' extraordinary attraction to *Ecos* and *Rural Research*, their editorial policies and practices should continue unchanged'.

The consultants, Terence W. Beed and Associates, derived their conclusions from extensive interviews with readers and potential readers and from responses to the questionnaire cards distributed with the magazines. They described the return rate for the cards as 'overwhelming' — 'to our knowledge... a record'. They concluded that *Ecos* and *Rural Research* were reaching only a small proportion of their potential readerships, and recommended that a subscription promotion program be initiated. Their detailed recommendations should help us introduce *Ecos* to a wider audience.

Thank you for returning the cards in such numbers and for all the helpful comments. We will be doing our best in the years ahead to continue producing an interesting, useful, and attractive *Ecos*.



An aerial view of the EZ plant at Risdon on the Derwent estuary.

The Tasmanian food regulations then, along with those elsewhere in Australia, allowed a maximum level of 40 parts per million (p.p.m.) of zinc as measured in the wet weight of a foodstuff. Mr Stephen Thrower and Dr Ian Eustace, of CSIRO's Hobart laboratory, found oysters with wet weight levels of zinc of 10 000 p.p.m, and even those with the lowest zinc levels contained eight times more than the limit.

The situation with the other heavy metals was almost as bad. The highest levels found in the oysters were (as wet weights), 35 p.p.m. for cadmium, 148 p.p.m. for copper, and 17 p.p.m. for lead. Analysis of the water where these delectable molluscs were growing revealed the following figures: zinc 200 μg per litre (or 0·2 p.p.m.), cadmium 4·5 μg per litre (0·0045 p.p.m.), copper 7·4 μg per litre (0·0074 p.p.m.), lead 14 μg per litre (0·014 p.p.m.). Notice that the concentrations in the water are far lower than those in the organisms; we shall be returning to this important fact later.

Once the heavy metal 'scare' was on, people naturally thought about other human food in the estuary. Some commercial fishing for squid and fin-fish takes place in the Derwent, and many amateurs may also eat what they can catch there. So CSIRO's Food Research Unit analysed samples of various marine animals, including fish, from many sites along the River.

Mussels, as well as oysters, were discovered to have levels of lead and cadmium unacceptably high for human consumption. Mr Kevin Wilson of the Australian Government Analytical Laboratories measured mercury contents and found several fish species with levels well above the permitted maximum for fish of 0·5 p.p.m. wet weight.

The present

So how has the situation changed? Oysters are no longer grown in Ralph's Bay, and many growers from there moved to Pipeclay Lagoon and Cygnet — two relatively nearby sites that do not form part of the estuary proper, although estuarine water may find its way to Pipeclay Lagoon.

Oysters now generally fall within the health guidelines, for two reasons. Firstly, heavy metal concentrations are lower at the sites away from the estuary, and secondly, some of the guidelines for metals in food have changed. For example, the maximum permitted concentration of zinc has been raised to 150 p.p.m. for all foods apart from oysters, for which it is now 1000 p.p.m. in most States.

Tasmania has gone even further and has set a limit of 1500 p.p.m. for zinc in oysters, and most of its own oysters now fall within the guideline. That they do so is an indication of an important improvement in the lot of oyster-eaters, for a reduction in the concentration of zinc also implies a decrease in that of cadmium — at least, in polluted areas, for the two metals are generally found together in ore.

But obviously the raising of the levels in the guidelines, and the determination of a special level for oysters so different from that for all other foods, needs some explanation. Zinc is the only metal in the guidelines for which oysters are singled out. In part, this is due to the findings of research that examined zinc concentrations in oysters growing in uncontaminated areas.

Mr John Thomson of the Tasmanian Department of Sea Fisheries carried out much of this work. He looked for zinc, cadmium, copper, and lead in oysters and mussels from the sea off Port Davey in the remote south-west of the State. The area is completely isolated from urban and industrial centres, with the nearest road being 50 km away.

In the 32 oysters that he sampled on three occasions between 1975 and 1978, he found zinc values ranging from 322 to 4860 p.p.m., with the mean being close to 1000 p.p.m. Ten of the oysters contained more than this quantity, and none was below the old standard of 40 p.p.m. However, in the 39 mussels examined, quantities of zinc were far lower, with 34 mussels falling within the old standard. In other words, mussels, although growing in exactly the same place, contained vastly less zinc than did the oysters.

Mr Thomson concluded that the metals found in the animals came from quite natural sources, and represented the

The oyster *Cassostrea gigas*, commonly cultivated at many sites around Tasmania.

'background level' of heavy metal contamination in an area apparently untouched by significant human activity. It seems that oysters, but not mussels, will accumulate zinc even though it may only be present in low concentrations in the water around them.

A possible reason is that oysters need a lot of zinc because they have a lot of calcium in their tissues. The explanation of that is that in many organisms calcium frequently competes with zinc to attach to various organic molecules. Zinc is necessary for the functioning of many enzymes (see the box on page 6), and to ensure that it attaches to these enzymes a high level of it must be present to dilute the calcium competing with it. This occurs in the oyster; but in the mussel, much of the animal's calcium is used up in the calcareous shell, rather than being distributed around all the tissues, so relatively low levels of zinc are sufficient to ensure that all the zinc-requiring enzymes have their metal atoms attached.

Biomonitors

So if a researcher uses mussels, for example, as possible indicators of pollution of the sea by zinc, the results would probably be more reassuring than they ought to be. Using organisms as yardsticks on pollution is called biomonitoring, and specific organisms must be selected as biomonitors for specific heavy metals. Even so, problems abound.

Dr Nick Elliott, now of CSIRO's Division of Fisheries Research, has been wrestling with some of them. He studied the use of certain marine organisms as biomonitors while at the Zoology Department of the University of Tasmania, in collaboration with Dr David Ritz and Dr Roy Swain. Knowing from previous work by others that barnacles could accumulate copper and zinc, and that the zinc content of barnacle tissues paralleled the concentration of the metal in surrounding waters, he studied the barnacle *Elminius modestus* and its possible use as a biomonitor.

However, what he found should serve to illustrate some of the problems inherent in the use of organisms as monitors, and the caution necessary in interpreting the findings from them.

He discovered that an inverse relation exists between the concentrations of copper and zinc in the tissues of this barnacle. In the presence of high levels of copper in the water, the barnacle accumulates copper and rids itself of its zinc, while the reverse happens in barnacles exposed to high zinc concentrations. As the two metals are likely to occur together in contaminated water, the barnacle seems an unsound monitor.

EZ's final product — zinc — which earns Australia valuable export dollars.

In a subspecies of the common edible mussel Dr Elliott again noticed an interaction between different metals. Unlike the situation with the barnacle, however, in the mussel the presence of zinc increased the uptake of copper, but decreased the uptake of cadmium.

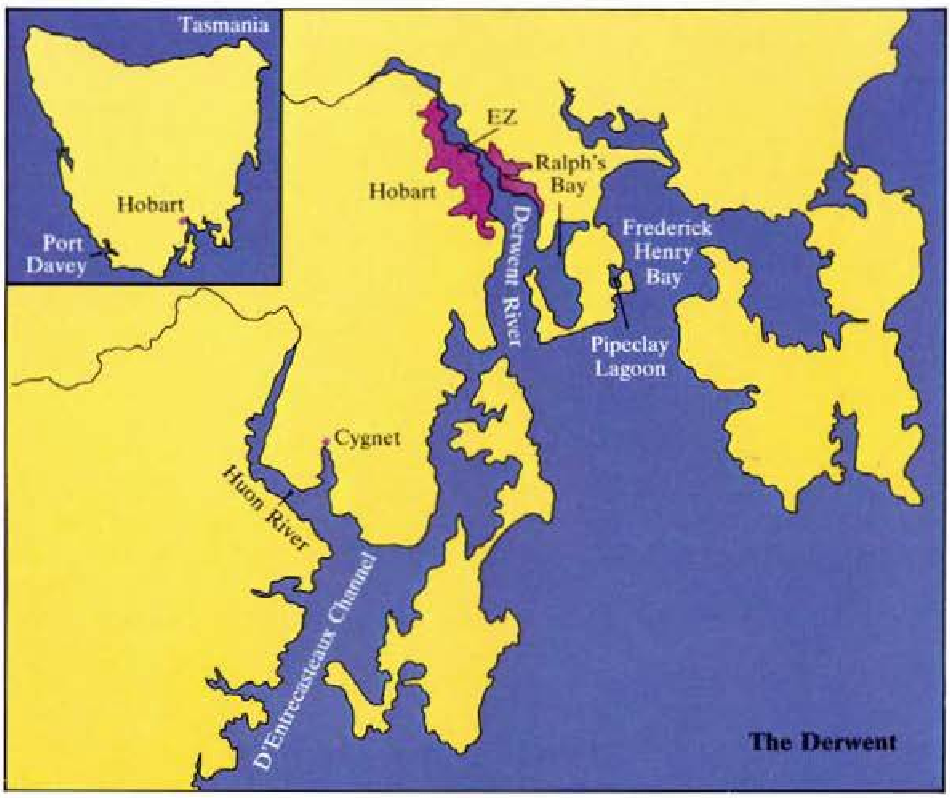
The list of subtleties that he unravelled could go on. Clearly, interactions between heavy metals in living systems represent a worrying source of error in any biomonitoring program.

So why use biomonitors at all? Why not analyse the water directly, or the sediment at the bottom, where the contaminants may eventually settle out?

What makes the use of biomonitors so important is the fact that it is, after all, living things, taken from the sea or a river, that we use for food. The actual concentration of contaminant in sea water, unless it is exceptional, does not concern us as much.

The important point is that some heavy metals may form chemical complexes that are, biologically speaking, inert, and therefore not important to human health or to

Hobart and surrounding areas. Oysters are no longer grown in Ralph's Bay.



Metals and health

It would be quite wrong to assume that all metals are pernicious substances and bad for human health.

Among the wide variety of metals that we are likely to come into contact with in an industrial society, those of greatest health interest are mercury, cadmium, arsenic, lead, nickel, vanadium, tin, chromium, selenium, iron, zinc, and copper. Some of these, such as the last five and possibly tin, are micronutrients: that is, we need them in the diet in minute amounts (iron in larger amounts). Many are co-factors without which particular enzymes could not function.

But micronutrients can be toxic at higher concentrations — 'too much of a good thing'. Other metals — such as mercury, cadmium, and lead — are not required at all for life, and are extremely toxic even in very small doses.

We now recognise zinc as a very important trace element in human and animal nutrition. It is linked with the function of about a hundred enzymes and, as these include some of those used in the replication of DNA and in protein synthesis, it is necessary for cell division. Zinc also has a role in maintaining the stability of the cell membrane. In higher organisms, like ourselves, zinc deficiency plays havoc with the immune response that protects against infectious disease. Other symptoms of its lack include failure to grow, poor wound healing, skin lesions, and problems with giving birth.

The human body, which contains between 1 and 2 g of zinc, cannot effectively mobilise and make use of its small stores of the element in times of need, so we require it continuously in small amounts in our diet. But, as with other metals, we do not absorb all that we eat. In the case of zinc, we may absorb between 25 and 40%. Fish, meat, and nuts are good sources of the element, but certain substances in the diet can prevent its absorption.

Zinc deficiency has been reported in many countries, especially among underprivileged people, and is considered to be a possible problem in Australia in some Aboriginal communities (see *Ecos* 40).

What about too much zinc? On the whole, zinc is far less toxic than most other metals, and also it hardly accumulates in us. More than about 500 mg of zinc in solution will cause vomiting, which then partly removes the problem. (Zinc is sometimes used medically to induce vomiting.) Death is reported to have occurred after consumption of a massive 45 g of zinc sulfate. Symptoms of zinc toxicity, apart from vomiting, are nausea, abdominal pain, dizziness, and lack of co-ordination.

Inevitably, many more toxic metals are finding their way into the biosphere in increasing quantities because of human activity. For example, mercury is used in electrical equipment, paint, fungicides, and pharmaceutical preparations, and it also enters the biosphere because it is a contaminant of petrol and coal.

Inorganic mercury compounds and mercury vapour are toxic, but they do not become concentrated in food webs. Chronic poisoning by inorganic mercury has been known for some time. The symptoms include irritability, tremors, and other nervous disorders. The phrase 'mad as a hatter' originated because of symptoms of toxicity due to the mercury used in the processing of felt for hats.

Organic mercury is even more toxic and is subject to 'biological magnification' — that is, it is found in increasing amounts further up the food chain.

Methyl mercury is the worst form of organic mercury. It selectively attacks nerve cells, and symptoms may appear weeks to months after exposure. The most famous incident involving methyl mercury poisoning occurred in Minimata, a small Japanese seaside city dominated by the chemical plants of the Chisso Corporation.

In the early 1950s residents noticed that birds were falling from their perches or flying into buildings, and that cats were running in circles or falling over themselves. This queer behaviour spread to fishermen and their families, who suffered numbness, trembling, loss of co-ordination, mental confusion, violent thrashing, unconsciousness, and eventually, in 40% of cases, death. Apparently normal mothers gave birth to severely affected offspring. Research showed that 'Minimata disease', as it became called, was in fact methyl mercury poisoning, and that effluents from the chemical corporation were to blame. (However, it was not until 1973 that Chisso Corporation admitted liability and paid reasonable compensation.)

What happened at Minimata was a classic case of biological magnification. The mercury, probably discharged in an inorganic form, is methylated by bacteria. These may be eaten, or they may release methyl mercury when they die.

Relatively small amounts of the pollutant in the the water are taken up by microscopic plankton, which are a food source for the next stage of the food chain. Small fish would eat thousands of plankton, and take on board all their mercury. These small fish are then eaten by larger ones, and at each stage the amount of mercury stays about the same, but the amount of biological material in which it resides gets less — and so the concentration increases. But, crucially, there is no efficient way of excreting mercury; eventually the top carnivores — fishermen, fishing birds, and the cats that may feed on those birds — are ingesting large and poisonous quantities, sufficient to kill.

Cadmium, another poisonous metal, is chemically similar to zinc, and the two metals generally occur together in Nature. But whereas zinc is essential to human life, cadmium is not, and even in small doses it can cause kidney damage. If inhaled, cadmium can cause lung fibrosis, and evidence is accumulating to suggest that it may also be carcinogenic.

The main intake of this unpleasant heavy metal comes, for many humans, in cigarette smoke. A '20-a-day' smoker may absorb twice as much from smoking as through his or her diet. How poisonous is cadmium? To give an idea, it suffices to say that 5 p.p.m. of it in air for 8 hours is a lethal dose. In the United States, the maximum permitted concentration in air for work environments is 0·1 p.p.m. Quite possibly, the unmonitored concentration in a smoke-filled bar after work may be more worrying!

The problem with cadmium, as with some other heavy metals, is its very long half-life in the body — several hundred days — because it is not easily excreted. Low doses received over a long time can eventually build up to a high body burden.

Zinc. I.E. Dreosti. *Journal of Food and Nutrition*, 1982, **39**, 67–73.

the health of any creatures in an aquatic ecosystem — similar in effect to the argon in air. These unreactive, and essentially irrelevant, complexes would be measured in an analysis of sea water, and could not easily be told apart from heavy metals in other forms, which can interact with living things. So the use of a good biomonitor shows us the quantity of heavy metals finding their way into biological systems, and that is what concerns us.

The zinc link

The years since 1974 have also been busy for the Electrolytic Zinc Company, undoubted supplier of much of the Derwent's zinc. The Company's plant at Risdon was started in 1917 and, although it has been maintained and extended, in many respects it remains old-fashioned compared with similar plants around the world. The design of the original plant, and of some of the later work, took place in the days when contamination of the environment just was not considered important. However, following the oyster 'scare' and the compensation that the Company paid, it was obvious that things had to change.

As well as bad publicity, EZ also had to face legislation in the form of the State's *Environment Protection Act*, which came into force in 1973. This sets limits on the concentration of many contaminants in industrial effluent. (However, the Act allows exemptions to be granted at the Minister's discretion, and EZ, employing more than 1500 people, has received and

Waste water contaminated with heavy metals at EZ. This used to be discharged straight into the river, but now is recycled and used again within the plant.

What makes oysters special

What is it about an oyster that enables it to accumulate zinc and other more toxic metals to levels that may sometimes be as high as 10% of its dry weight, without any apparent ill effect?

Oysters have amoeba-like cells, termed amoebocytes, in their equivalent of a blood-stream, and also in their tissues. These cells are reminiscent of our own white blood cells. Scientists in Aberdeen, Scotland, showed that copper and zinc accumulate inside little membrane-covered bags within the cells.

This fits in with the observation of Mr John Thomson, of the Tasmanian Department of Sea Fisheries, that oysters generally accumulate copper and zinc to a greater degree than other metals. Mr Thomson, with Dr Brian Pirie and Dr Stephen George, of the NERC Institute of Marine Biochemistry in Aberdeen, also found that more than 90% of an oyster's total copper and zinc reside within the amoebocytes.

Now, as the amoebocytes can crawl between cells, they penetrate all other tissues, and so a general analysis of a whole oyster may make it appear that the metals are almost everywhere (with the exception of the mature gonad), leading scientists in the past to wonder how the poor animals were protected. In fact, the hiding-away of the metals mainly within vesicles of the amoebocytes prevents those metals from coming into contact with cells whose functioning may be badly affected by such contact.

Similar protection is afforded to us by our macrophages, also large amoeba-like cells, which scavenge around our lungs for any dirt particles and ingest these, so preventing them from damaging other cells. Unfortunately, the macrophages will eventually die from this behaviour and accumulate, and the often toxic and insoluble particles are therefore not removed from our bodies.

The oyster, however, has a neat solution. According to studies by Dr David Lytton, formerly of the Department of Pathology at the University of Tasmania, and his colleagues, the metal-laden amoebocytes, although they may travel throughout the animal, are found in greatest number in the gills. Using an electron microscope and a technique called X-ray microanalysis for metal identification, Dr Lytton was able to see zinc-containing cells in the central blood spaces of the gill filaments. And, even more importantly, he also saw some of these cells squeezing through the gill tissue to the outer epithelium at the tops of the filaments.

Nobody is quite sure what happens once the metal-bearing cells are outside. Scientists think it likely that they disintegrate, and the membrane-covered metal particles eventually leave the animal. The oyster's gill, therefore, apparently provides a site for the slow removal of the accumulated heavy metals — at least, in animals growing in waters containing high concentrations of the metals.

But we should consider one final point: why do the oysters absorb these compounds in such large amounts from the water in the first place? In part, the oysters' filter-feeding life-style makes it impossible not to; they must filter large volumes of water over their gills to extract small food particles, and inevitably much of what the water contains finds its way into the animals.

But we should also not forget that many of these metals are essential to life. To obtain sufficient amounts of them from water where they would usually occur at very low concentrations, many marine filter-feeding invertebrates deliberately absorb and accumulate certain elements, a policy that has its drawbacks when concentrations become too high — unless, that is, a suitable 'dumping' ability has also evolved.

Metal-containing blood cells of oysters: ultrastructure, histochemistry and X ray microanalysis. B.J.S. Pirie, S.G. George, D.G. Lytton, and J.D. Thomson. *Journal of the Marine Biological Association of the United Kingdom*, 1984, **64**, 115–23.

Cellular metal distribution in the Pacific oyster, *Crassostrea gigas* (Thun.) determined by quantitative X-ray microprobe analysis. J.D. Thomson, B.J.S. Pirie, and S.G. George. *Journal of Experimental Marine Biology and Ecology*, 1985, **85**, 37–45.

Hobart.

continues to receive exemptions from the Act's limits for a number of its operations.)

Furthermore, loss of zinc into the environment means loss of money to the Company; zinc is its product, along with as much of the contaminants in the ore as it can separate out and sell. So it embarked on an expensive series of modifications.

The one with the biggest impact in terms of reducing pollution was probably a contaminated-water recycling plant, which was completed in 1982 at a cost of $2·2 million. In essence, this allows the drainage water from the metallurgical plant to be used again, rather than being discharged in a heavily polluted form into the river. Also, the management installed a plant to recover mercury from the effluent.

These, along with other improvements, have, according to EZ, reduced metal losses from the plant to 5% of the 1973 level, but what this represents in absolute terms EZ will not reveal. The money generated from the recovery of the metals has offset much of the capital expenditure incurred in the building of the new equipment.

The Company is also slowly removing the large mound of the residue that is formed during the zinc-extraction process. This so-called 'primary residue' contains about 20% zinc and was accumulating in a large pile near the bank of the Derwent. *Ecos* 1 reported that some people had expressed fears that some of this zinc-laden dust could be blown into the river. A compound called jarosite ($Fe_3[SO_4][OH]_6$), containing about 5% zinc by weight, is generated instead of the primary residue. Also the Company can now process that original residue to recover valuable metals and convert the waste iron into jarosite, thereby removing the accumulated mound.

Jarosite inevitably contains zinc, lead, copper, cadmium, and other heavy metals as contaminants. It is dumped at sea, under a licence granted by the Commonwealth government. Monitoring by Mr Mick Haywood and Mr Michael Abramski, of EZ, has failed to detect any significant damage to the marine environment at the dump site. They hypothesise that some of the material, spread over a large area, enters the sediment at the bottom of the ocean, while ocean currents disperse the rest.

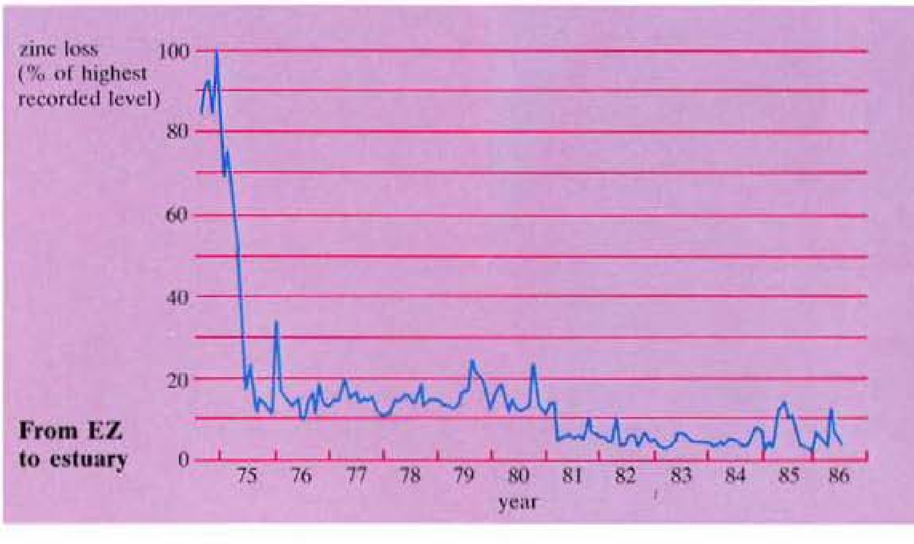
The Company established an environmental services group in 1972, under the direction of Mr Rod Cooper. As well as monitoring the jarosite-dumping process, this group became heavily involved in biomonitoring for heavy metals in the Derwent estuary, starting at the beginning of 1975. Following collaboration with Dr June Olley of CSIRO, some of their results were published in 1982.

Mr Cooper, and Mr David Langlois (formerly of the EZ Company), found that, in the Derwent estuary, zinc and cadmium tended to remain in solution in the water, while copper and lead were mostly in particulate form. They further found that sediment and sand can adsorb the soluble heavy metals when these are at high concentration, only to release them slowly at a later date if concentrations in the water are lower. Oysters living in sediment therefore often have a greater exposure to heavy metals, and were found to have higher tissue concentrations of them, than their fellow oysters living on piles, sticks, or trays.

The EZ scientists also found that hardly any of the heavy metals occurs in the animals' gonads, and the accompanying food stores around them. The size of the gonads varies seasonally, from a very small percentage to up to 50% of the whole body weight. This explained the previously puzzling 'seasonal troughs' of metal concentrations seen in oysters: during the breeding season when the relatively metal-free gonad was at its largest, the whole animal would give a lower value for heavy metal concentration than when the gonad had shrivelled to almost nothing. When the gonad factor was corrected, the scientists found that the tissue concentrations of zinc, copper, and cadmium increased with the size of the oyster.

To determine whether heavy metals in the ecosystem had declined with the increasing efficiency of their plant, the EZ scientists started a test in 1981 using the cultivated oyster, *Crassostrea gigas* (also known as the Pacific oyster). They took young of this species from Pipeclay Lagoon, and transferred them to the old, polluted site of Ralph's Bay. After about 2 months, when the oysters had matured to market size, they collected batches of them, every 3 months, as samples for analysis.

Zinc loss to the estuary from the EZ plant from the time of *Ecos* 1 to the present, as a percentage of the highest recorded level. The information was supplied by EZ.



The Tasman Bridge across the Derwent River was cut in two on 5 January 1975 when a vessel carrying ore to the EZ Company upstream hit the bridge. The vessel sank quickly, and its cargo remains a potential source of pollution in the estuary to this day.

Their results make an interesting comparison with those obtained by Mr Thrower and Dr Eustace back in 1973. The concentrations of heavy metals in oysters aged between 15 and 20 months in Ralph's Bay then averaged 6602 p.p.m. zinc, 90 p.p.m. copper, and 17·7 p.p.m. cadmium.

What the EZ scientists found in oysters of the same age range collected from 1981 to 1983 were the following figures: zinc 1342 p.p.m., copper 16·8 p.p.m., and cadmium 1·3 p.p.m. This shows a vast decrease of 93% in cadmium levels, and about 80% less copper and zinc.

Indeed, of the eleven samples that the scientists took between 1981 and 1983, nine would have met the Tasmanian health requirements for zinc. All the samples would have passed for copper, cadmium, and mercury, but none was within the limit for lead. (They ranged from 2·6 to 6·1 p.p.m., and the limit is 2·5 p.p.m.) Heavy metal levels in oysters grown in Ralph's Bay had plummeted, despite the fact that EZ's production of zinc has increased from 151 000 tonnes in 1974/75 to 195 700 tonnes in 1984/85.

Mr Cooper does not dispute that most of the lead he found in the oysters and mussels probably comes from EZ's operations, along with most of the other heavy metals. The Company uses ore that contains 2–3%

Effects of contaminated oysters

When it was realised that the oysters in Ralph's Bay contained potentially toxic levels of heavy metals, Mr Thrower and Dr Olley, of CSIRO's Tasmanian Food Research Unit, fed some of the contaminated oysters to rats to see how this affected the animals. The scientists fed six rats on Ralph's Bay oysters, and four on oysters from uncontaminated areas.

They found that rats whose diet comprised contaminated oysters ate less, and grew less, than their brethren eating the non-contaminated shellfish.

Upon measuring metal levels in various organs of the rats, they found that zinc concentrations were indeed higher in the animals feeding on contaminated oysters. However, cadmium, also in the oysters but at a far lower concentration than zinc (the zinc to cadmium ratio was 1300:1), was present only in negligible amounts.

Rats that were fed on contaminated oysters with a lower zinc to cadmium ratio (from the Tamar River in the north of the State) accumulated more cadmium. The reason, the scientists think, is competition between the two elements, with the zinc pushing the cadmium out of the rats' organs. If the level of cadmium remains constant in the diet but the zinc concentration in that diet increases, then the amount of cadmium deposited in the tissues will decrease. So, if we can extrapolate from rats to humans, the concentration within a foodstuff does not always directly reflect how much ends up in our tissues.

A possible reason for the apparent paradox concerns the chemical similarity between the two elements, which leads to some interactions between them in the rats' bodies. Many animals — including humans — make certain proteins called metallothioneins, especially when heavy metals are eaten in the food. These proteins can attach to a number of heavy metals.

It could be that the zinc metallothionein in the rats also inadvertently does duty for a similar element like cadmium. If the protein is saturated with zinc atoms, it has no more space available for cadmium. The result may be that cadmium does not remain in the animals' organs, or does so at a lower concentration than may be expected.

But how can zinc and cadmium be accumulated together in an oyster, but not in a rat that feeds on it? Research has shown (see the box on page 7) that zinc in oysters is contained within granules inside the cells.

Hidden away like this, it does not compete with cadmium for available space on the oysters' metallothioneins (or equivalent heavy-metal-binding substances), so plenty of cadmium can attach to those proteins, while zinc levels are high within the granules. (Scientists are not entirely convinced that oysters have metallothioneins as such, and if they do, whether these operate in the same way as in mammals.)

In the stomach of the rat or a human eating oysters with a high ratio of zinc to cadmium, the zinc would be released from its intracellular granules, and the cadmium cut off from its metallothionein. Proportions of the metals are then absorbed, and they compete for the metallothioneins of the mammal, where zinc is not sequestered away in granules. Zinc, by virtue of its greater concentration, wins the day, and little of the cadmium remains attached to the metallothionein.

The scientists are not sure that this is necessarily good. They noticed that the rats with the least cadmium deposited in their organs also had the least weight gain, suggesting that they were not benefiting. The fact that cadmium is not attached to metallothioneins may mean that it is more available to move around the body, and wreak more mischief.

With the evidence from the experiment described, and others, Mr Thrower and Dr Olley conclude that a mammal with a high zinc:cadmium ratio in its diet would tend to exclude cadmium from its organs. Complex interactions between metals mean that, when establishing guidelines for maximum concentrations in foodstuffs, we cannot consider a metal in isolation.

Heavy metals in Tasmanian shellfish. 2. The influence of heavy metal ratios on the accumulation and detoxification mechanisms in rats fed contaminated oysters. S.J. Thrower and J. Olley. *Journal of Applied Toxicology*, 1982, **2**, 11–15.

The remote Port Davey area of south-western Tasmania, where Mr Thomson sampled the heavy metal concentrations in presumably 'uncontaminated' oysters in order to establish a background value for zinc.

lead, and sells the lead residue from this, in the form of insoluble lead sulfate, which is loaded onto ships at Risdon.

Loading and unloading at EZ's wharf constitutes a source of pollution that will be hard and expensive to eliminate. But now that the Company has reduced its other sources of pollution so substantially, will it be possible to use the Derwent River once again for the cultivation of shellfish? The answer, at present, is no — and part of the reason is sewage!

Most of Hobart's increasing volume of sewage receives only primary treatment. (Sewage treatment has four possible stages; after the fourth the result is drinkable water.) Primary treatment means that the sewage is merely homogenised into a liquid sludge, screened, and then settled. All of the city's sewage is discharged into the river or estuary. Parts of the river — especially near sewage outfalls — may at certain times contain more bacteria than are desirable.

Oysters, because of their mode of feeding by filtering tiny particles from the water, can easily pick up and retain bacteria in their feeding apparatus. The bacteria do not usually harm the animal, but can be the source of severe gastrointestinal disease in humans who eat the oysters, depending on the number of bacteria present, and whether, and to what degree, they are pathogenic. Similarly, tiny marine algae — dinoflagellates — may sometimes proliferate in the water and if, as in some cases, they contain a toxin, this may be retained in the oysters that feed on them, and eventually may cause unpleasant symptoms in humans.

Sewage also presents another, familiar problem: heavy metals! Because most heavy metals are biologically useless, and in some cases very toxic, many living things, humans included, try not to absorb them. So it is that the bulk of any of these metals that we may eat (and inevitably, small quantities are present in all foods) passes through us into the faeces. (This does not imply that heavy metals are therefore not dangerous; even if we absorb only 5% of the quantity eaten, we can still slowly be poisoned over time because what we have absorbed accumulates in our bodies.)

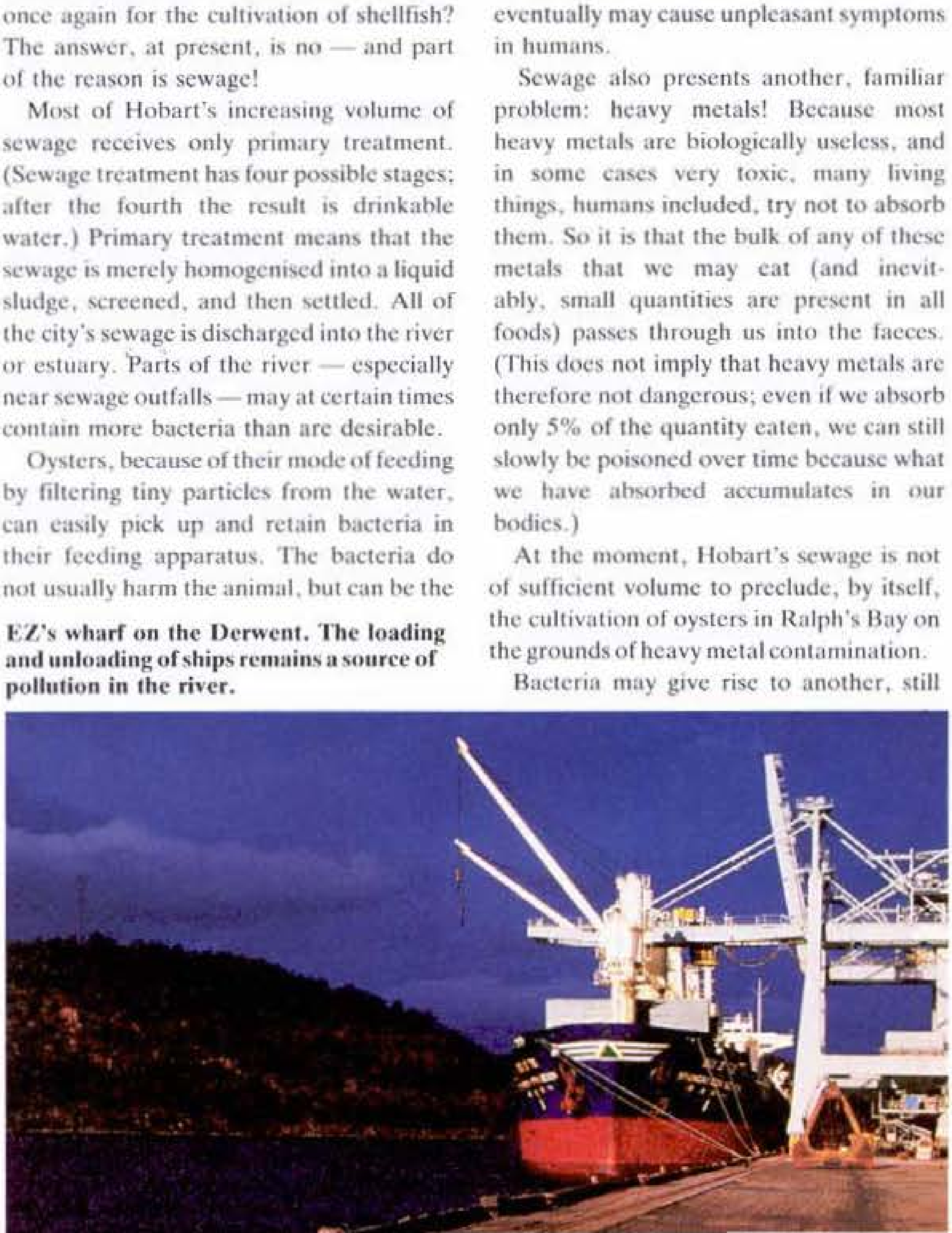
At the moment, Hobart's sewage is not of sufficient volume to preclude, by itself, the cultivation of oysters in Ralph's Bay on the grounds of heavy metal contamination.

Bacteria may give rise to another, still largely unexplored, worry. Scientists now think that some bacteria, probably living in the bottom sediment, convert mercury into the even more toxic form of methyl mercury. Other bacteria can demethylate mercury back to its elemental form, and the balance between the two types may determine the extent of the methylation occurring. The ability to methylate mercury is thought to be genetically linked to antibiotic resistance in some cases, and bacteria carrying antibiotic resistance are probably more likely to be found in association with humans and their animals than living free.

However, whether or not human sewage represents a significant source of methylating bacteria is not proved and much speculation still exists in this area. On the positive side, sewage is known to be able to bind to some heavy metals and so make them, for a time, less available to enter the food chain.

The heavy metal problem may well continue to improve. In the next 5 years, EZ plans to carry out further modifications to contain leakage and improve its effluent treatment. If tertiary sewage treatment (which removes much of the heavy metal load) were introduced, it too would help to reduce pollution levels in the estuary.

Roger Beckmann



EZ's wharf on the Derwent. The loading and unloading of ships remains a source of pollution in the river.

More about the topic

Heavy metal accumulation in oysters grown in Tasmanian waters. S.J. Thrower and I.J. Eustace. *Food Technology in Australia*, 1973,**25**, 546–53.

Heavy metals in Tasmanian shellfish. 1. Monitoring heavy metal contamination in the Derwent estuary: use of oysters and mussels. R.J. Cooper, D. Langlois, and J. Olley. *Journal of Applied Toxicology*, 1982, **2**(2), 99–109.

Heavy metals in the native oyster (*Ostrea angasi*) and mussel (*Mytilus edulis planulatus*) from Port Davey, south-western Tasmania. J.D. Thomson. *Australian Journal of Marine and Freshwater Research*, 1979, **30**, 421–4.

Interaction between copper and zinc accumulation in the barnacle *Elminius modestus* Darwin. N.G. Elliott, D.A. Ritz, and R. Swain. *Marine Environmental Research*, 1985, **17**, 13–17.

'Model Food Legislation.' (Commonwealth Department of Health: Canberra 1985.)