Metal Concentrations in Fish and Shellfish of the Avon-Heathcote Estuary/Ihutai and Rivers: 2008

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What are **heavy metals?** How do they get into our **rivers** and **estuaries**?

Heavy metals, such as cadmium and lead, and metaloids like arsenic, are present naturally in relatively low amounts in the earth's crust. They are stable and cannot be degraded or destroyed, so they tend to accumulate in soils, water, and the atmosphere. We absorb trace amounts of some heavy metals from our food, drinking water, and the air. These very low levels generally have no adverse affect, and in some cases can be beneficial, for example trace amounts of selenium, zinc, and copper are essential to maintain the metabolism of the human body. However, human activities from industry (such as mining, smelting) and the run-off from urban and agricultural land-use increase the concentrations of these metals in the environment, potentially to levels which could have adverse effects on humans and animals. Small children and infants are particularly susceptible to ingesting high levels of heavy metals as they consume more food per kilogram of body weight than adults. In addition, the toxic effects of certain heavy metals can be particularly detrimental to children's developing organs, especially the brain.

Many heavy metals enter rivers as run-off from roads, factories, or agricultural land. They are washed through the stormwater system into the rivers where they can accumulate in the sediment. Eventually they may make their way down river to an estuary, which traps the river sediment and thus accumulates metal contaminants. This means that the sediment in rivers and estuaries can have high contamination loads of heavy metals. The metal concentrations are likely to vary by site depending on where contaminated sediment is accumulating.

In general marine and freshwater organisms accumulate contaminants from their environment and have been used extensively to monitor heavy metal pollution. Shellfish feed by filtering particles out of the water and often accumulate contaminants, which can have a direct impact on our health if we eat shellfish that have high heavy metals concentrations (e.g., above the safe limits set by the New Zealand Food Safety Authority; FSANZ). Many signs have been erected around the Avon-Heathcote Estuary warning the public about eating shellfish. Estuary and freshwater fish may also accumulate heavy metals, potentially making them unsafe to eat. Lead, mercury, and cadmium can be present in fish naturally at low levels, or at higher levels as a result of pollution. Mercury also bio-accumulates, meaning that animals further up the food-chain also accumulate the mercury in the smaller animals that they eat. This can have important implications for the type of fish we eat.

Maximum allowable levels of metal contaminants in food (FSANZ, 2008)

Metals (mg/kg)	Crustacea	Fish	Molluscs (shellfish)
Mercury	0.5	0.5	0.5
Cadmium	n/a	n/a	2
Lead	n/a	0.5	2
Arsenic (inorganic)	2	2	1

One of the signs around the estuary warning of the danger of eating shellfish collected there

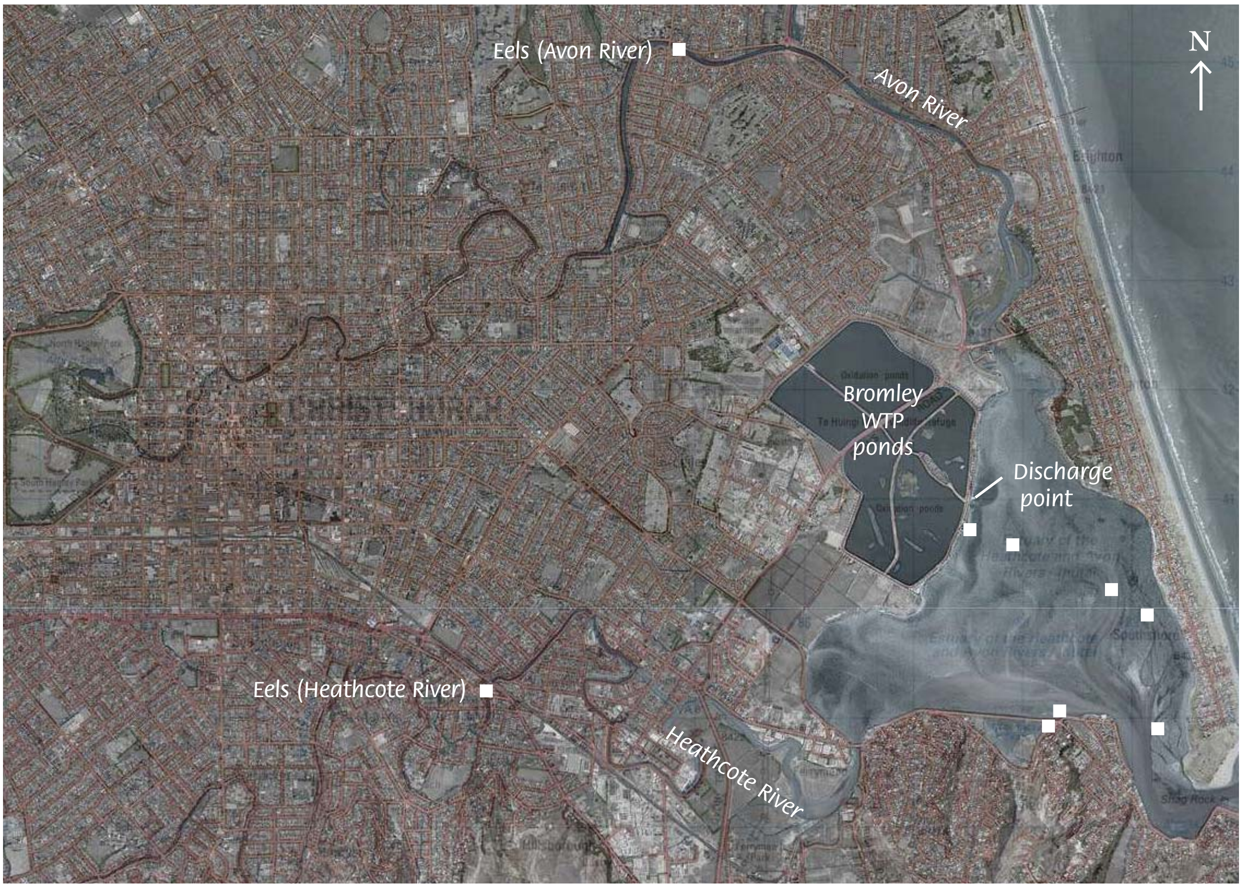
Mercury

Mercury occurs naturally in the environment and it can also be released into the air through industrial pollution. It has a long life in the atmosphere and can be transported over large distances. This mercury is then deposited into surface waters and soils where it accumulates. It is present in fish and seafood products mostly as methylmercury (ENHIS, 2007). Methylmercury accumulates as smaller fish are eaten by bigger fish, so predatory fish tend to have the highest levels. High amounts of mercury can damage our kidneys and central nervous system which can cause memory loss, slurred speech, hearing loss, lack of coordination, loss of sensation in fingers and toes, reproductive problems, coma, and possibly death (Vannoort & Thompson, 2006). The developing brain of a foetus is especially sensitive.

Survey Sites

Where sampling was done

Cockles, sand founder, and yellow-eye mullet were collected within the estuary from near the discharge point of the Bromley Wastewater Treatment Plant (WTP) and from the western side of the Southshore spit. An additional cockle collection site was located at the southern end of the causeway, by Beachville Road, which is a popular shellfish gathering site. Shrimp were collected from the southeastern end of McCormacks Bay, and pipis from near the estuary mouth. Shortfin eels were collected in the Avon River downstream of Anzac drive, and in the Heathcote River just upstream of Opawa Road.



Locations of sampling sites within the Avon-Heathcote Estuary and the Avon and Heathcote Rivers

Cadmium

Cadmium occurs naturally in low levels in the environment and is also used in batteries, pigments, and metal coatings. Volcanic activity, industrial processes such as smelting or electroplating, and the addition of fertilisers can increase the concentration of cadmium in the environment. Shellfish can accumulate cadmium (WHO, 1992). Long-term or high dose exposure to cadmium can cause kidney failure and softening of bones (Vannoort & Thomson, 2006).

Collection

Shellfish

Cockles were collected at low tide using a cockle rake and by hand. The cockle rake is pulled through the sediment and separates out the cockles. The cockles were kept cool with ice packs, their length measured, and then delivered live to Hill Laboratory for analysis. Ten samples per site (of three to five cockles per sample, depending on size) were analysed for mercury, and five samples per site for arsenic, lead, and cadmium.

The cockle rake in use at the causeway site

A sample of the cockles (Austrovenus stutchburyi) collected

Collecting cockles at the Southshore site

Collecting cockles near the Bromley Wastewater Treatment Plant discharge. The cockle rake is in the foreground

Pipis were difficult to find and multiple sites were searched near the estuary mouth before a live population was located, in the low-tide channel opposite the Beachville Road corner. Pipis were not especially abundant and were of a small size, despite the presence of a large number of big empty shells.

Pipis were collected by hand, kept cool with ice packs, their length measured, and then delivered live to Hill Laboratory for analysis. As with cockles, ten samples per site (of five pipis per sample) were analysed for mercury, and five samples per site for arsenic, lead, and cadmium.

Locations sampled for pipis at the mouth of the estuary

Some of the pipis (Paphies australis) that were collected, and the shell-bank near where they were found

Lead

Lead is used in batteries, solder, ammunition, and devices to shield x-rays. Most exposure to humans is due to pollution, particularly from lead-based paint and from leaded fuel, both of which are no-longer used in New Zealand.

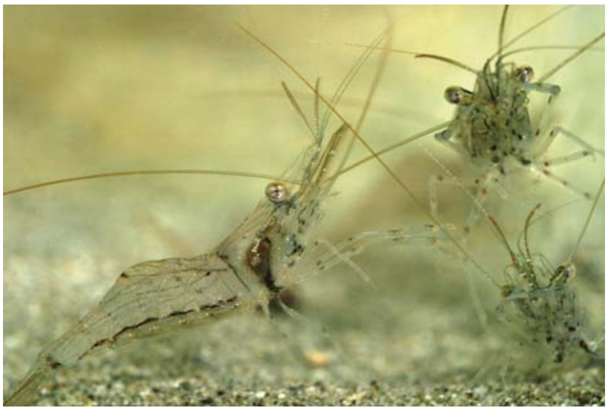
Lead can build up in the body and targets the nervous system, reproductive system, and kidneys. Lead can be stored in bones without harm but if calcium intake increases, the lead will be released from the bone. Children and babies are particularly at risk from damage to their central nervous system, which can cause learning difficulties and behavioural changes. In New Zealand the estimated dietary exposure to lead has been decreasing over time and in general our weekly exposure to lead via our diet is under the guidelines developed by the World Health Organisation (WHO, 2000).

Estuary fish and shrimp

Sand flounder were caught using a weighted drag net (mesh size 1 inch) that was set from the shore. For each deployment, one end was dragged approximately 100 m from the beach and then brought around in an elliptical pattern to meet up with the other end that was held close to shore. The two ends of the net were then dragged onto the beach. At each site ten flounder were placed on ice, measured in the lab, and delivered to Hill Laboratory for testing. Ten of these were analysed for mercury and five for arsenic and lead. At the discharge site a large flounder (300 mm), around the size that is eaten, was also caught and taken for analysis.

A fine mesh (1.5 inch) gill net was used to catch yellow-eye mullet. Using a small boat, the net was set perpendicular to the shoreline at approximately 100 m from the beach for one hour during high tide. Ten mullet were collected from each site, placed on ice, measured in the lab, and delivered to Hill Laboratory for testing. All ten fish were tested for mercury levels and five were tested for arsenic and lead. Note that for the discharge site only eight mullet were able to be caught and tested.

Shrimp were caught using a fine mesh hand net and ten samples weighing 2.5 g each were delivered to Hill Laboratory for testing. All of these samples were tested for mercury and five samples were tested for arsenic and lead.



Shrimp (Palaemon affinis)

photo © S McMurtrie

Arsenic

Arsenic is a naturally occurring element that is common in soils and living organisms. Arsenic levels in the environment can be affected by high levels of soil erosion, the use of pesticides containing arsenic, treated timber, and the presence of smelters or power plants fired by coal.

Most foods contain trace levels of organic arsenic and occasional consumption is not a health concern. However, an acute high level exposure to arsenic can lead to vomiting, diarrhoea, anaemia, and liver damage. Arsenic is present in our food in different chemical forms. Inorganic arsenic, which forms when arsenic combines with oxygen, chlorine, or sulphur, is more toxic than organic arsenic and can cause human health risks such as an increased risk of cancer. Most arsenic in our diet is present in the less toxic organic form (for example fish and shellfish mainly accumulate organic arsenic from their environment; WHO, 1981), and most of this form of arsenic leaves the human body within several days. However, it is difficult to reliably measure the forms of arsenic that are present, so most surveys of arsenic content measure total arsenic levels.

For more information see www.FSANZ.govt.nz/consumers/chemicals-toxins-additives/arsenic/

www.otago.ac.nz/geology/features/metals/arsenic.htm

Yellow-eye mullet (Aldrichetta forsteri)

photo © S McMurtrie

Sand flounder (Rhombosolea plebeia)

photo © S McMurtrie

Freshwater fish

Shortfin eels were collected from the Heathcote River and Avon River using Fyke nets. These nets are a series of hoops connected by mesh. Once the fish enter the inverted funnel entrance they can't find the narrow exit and are trapped. These nets were baited and left overnight. The next day the eels were anaesthetised, their length measured, and either taken to Hill Laboratories for analysis or returned to the river if too many were caught. Mercury levels were tested in ten eels and arsenic and lead in five eels.

A fyke net full of eels from the Avon River

Shortfin eel being measured

The longest shortfin eel (Anguilla australis) caught (920 mm) was returned to the river

Results

Shellfish

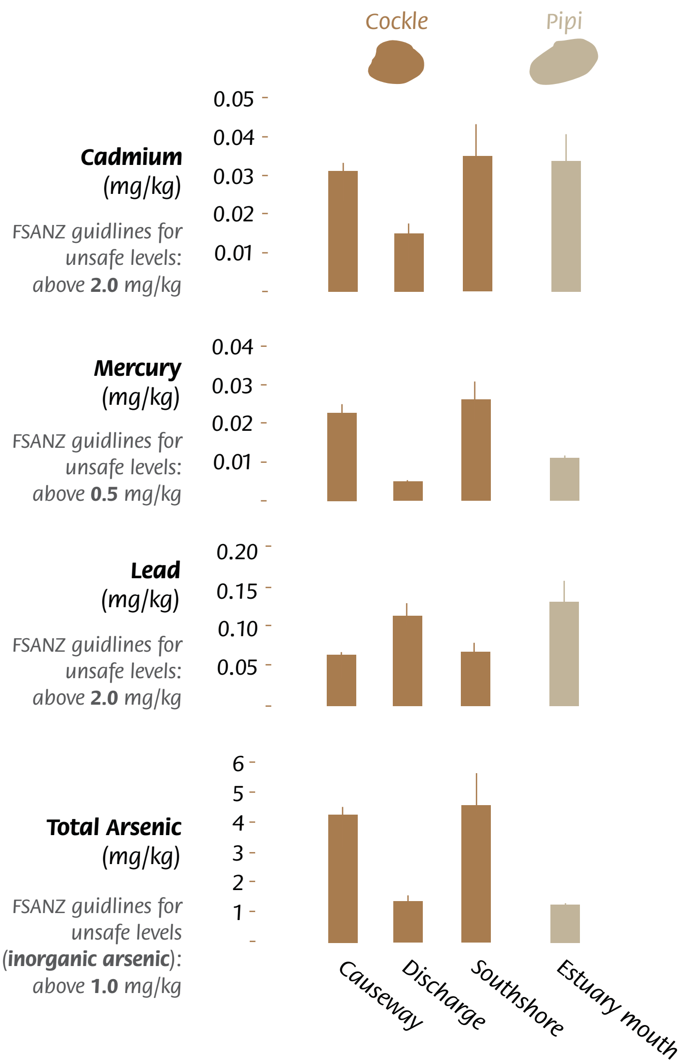
Where possible we collected larger shellfish; the size most likely to be collected and eaten. Cockles, however, were smaller at the discharge site, and no large pipis were found after an hour of searching at the estuary mouth site.

Both pipis and cockles at all sites had levels of cadmium, lead, and mercury that were well below the New Zealand Food Safety Authority guidelines (Food Standards Australia New Zealand (FSANZ), 2008) for shellfish to be consumed. In fact, the average level of all three metals at each site was at least 1/10 that of the FSANZ maximum allowable metal contaminant levels.

The FSANZ provides guidelines for levels of inorganic arsenic in shellfish (as well as in fish and shrimp). However, as this is difficult and expensive to measure accurately, most studies measure total arsenic levels instead. In America the US Food and Drug Administration (USFDA) has set maximum levels for total arsenic in shellfish at **86** mg/kg (USFDA ,1993). The levels of total arsenic that we found in shellfish from the estuary were much lower than this, with the highest total arsenic level being 8.3 mg/kg (at Southshore) but with most below 5 mg/kg. Even the highest concentration we measured was at least 1/10 that of the safe consumption levels set by the USFDA. The USFDA has also conservatively set the inorganic arsenic component at 10% of total arsenic (USFDA, 1993). If we apply this rationale to our samples then the highest inorganic arsenic levels that we would estimate to have would be 0.83 mg/kg, still below the FSANZ guidlines of less than **1** mg/kg inorganic arsenic.

Average shellfish shell length *(mm ± 1se)*

Cockles (causeway)	43.4 ± 0.8
Cockles (discharge)	34.6 ± 0.4
Cockles (Southshore)	36.4 ± 0.3
Pipis (estuary mouth)	42.8 ± 1.4



Average heavy metal concentrations in shellfish (± 1se)

The cockle collection site at Southshore

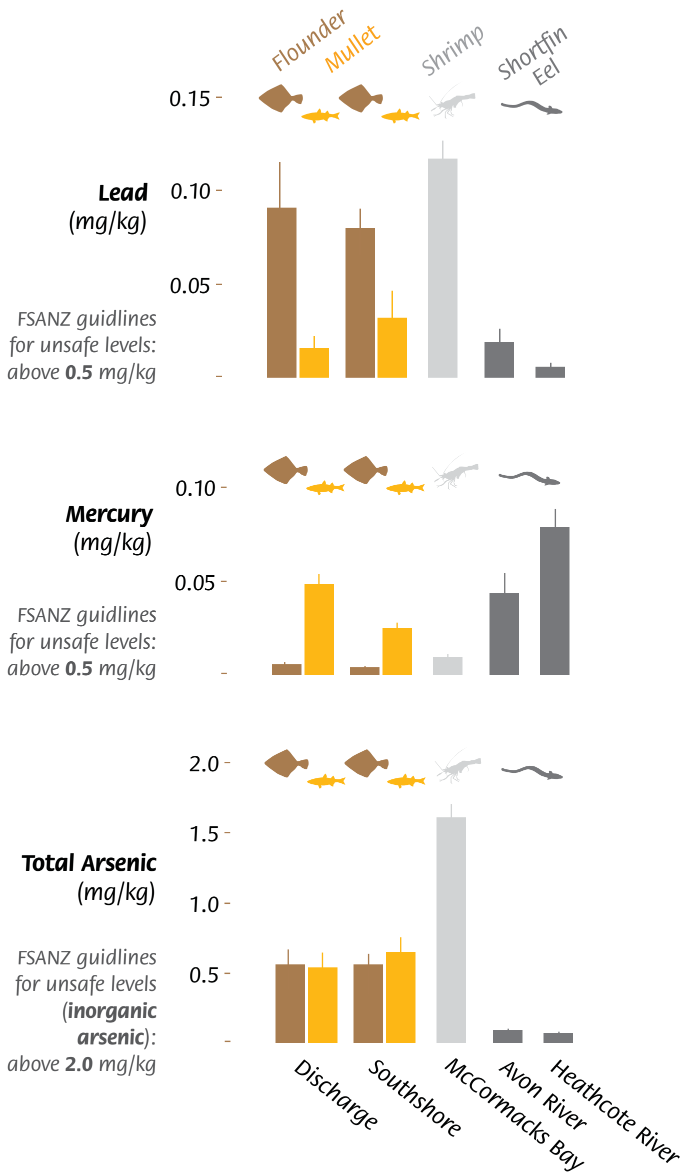
Fish and shrimp

The levels of lead and mercury in shrimp from McCormacks Bay were well below the FSANZ maximum metal contamination levels for food. Following the USFDA (1993) conservative estimate of inorganic arsenic being 10% of total arsenic, the estimated level of inorganic arsenic in shrimp (average of 0.16 mg/kg) is well below the FSANZ **2** mg/kg guideline. The total arsenic levels (average 1.62 mg/kg) were more than two times that of mullet, flounder, and shortfin eels, but were still much lower than for shellfish.

The size of flounder and mullet caught in this survey were generally similar to the average size caught throughout the estuary in 2006 by James (2007). We analysed shortfin eels that were from the most common size range encountered during our trapping, although the largest eels were returned to the rivers as they are an important part of the breeding population of this slow growing species.

The levels of lead and mercury from flounder, mullet, and eels were all well below the maximum acceptable levels for eating fish (FSANZ, 2008). The safe limit for inorganic arsenic in fish is **2** mg/kg, so the estimated level of inorganic arsenic in flounder (est. 0.053 mg/kg), mullet (est. 0.059 mg/kg), and eels (est. 0.008 mg/kg) are all well below this level. For the estuary fish, flounder had higher levels of lead than mullet, mullet had higher levels of mercury, and both had similar levels of arsenic. Shortfin eels generally had lower levels of heavy metals than estuary fish, although mercury levels in eels from the Heathcote River were highest.

As mercury bio-accumulates (i.e., animals higher up the food chain have more mercury contamination as they accumulate the mercury from the small prey they eat), we might expect that larger fish would have higher mercury levels. We measured the mercury levels in a flounder (300 mm long) that was significantly larger than the others tested (average 75 mm long) and large enough to be eaten. This large flounder had higher mercury levels (0.03 mg/kg) compared to the smaller fish (average 0.005 mg/kg). Although this higher mercury level is still not close to the levels the FSANZ recommend as unsafe, it still implies that larger, older fish are likely to have higher mercury levels.



Average heavy metal concentrations in fish and shrimp (± 1se)

Average shortfin eel length (± 1se)

	Avon River	Heathcote River
Length of all shortfin eels caught (mm)*	493.2 ± 26.2	485 ± 20.6
Length of shortfin eels taken for analysis (mm)	409.6 ± 8.42	454 ± 16.3

* 14 extra eels were caught in the Avon River and 5 extra in the Heathcote River

Average sand flounder length (± 1se)

	Discharge Site	Southshore Site
Length of fish analysed in current study (mm)	98.5 ± 12.9*	75 ± 11.1
Length of fish in estuary (James, 2007) (mm)	39 to 110	

* A large flounder (300 mm) was also caught and analysed

Average yellow-eye mullet length (± 1se)

	Discharge Site	Southshore Site
Length of fish analysed in current study (mm)	241.9 ± 14.4	254.5 ± 23.9
Length of fish in estuary (James, 2007) (mm)	73 to 194	194

Discussion

The influence of site location

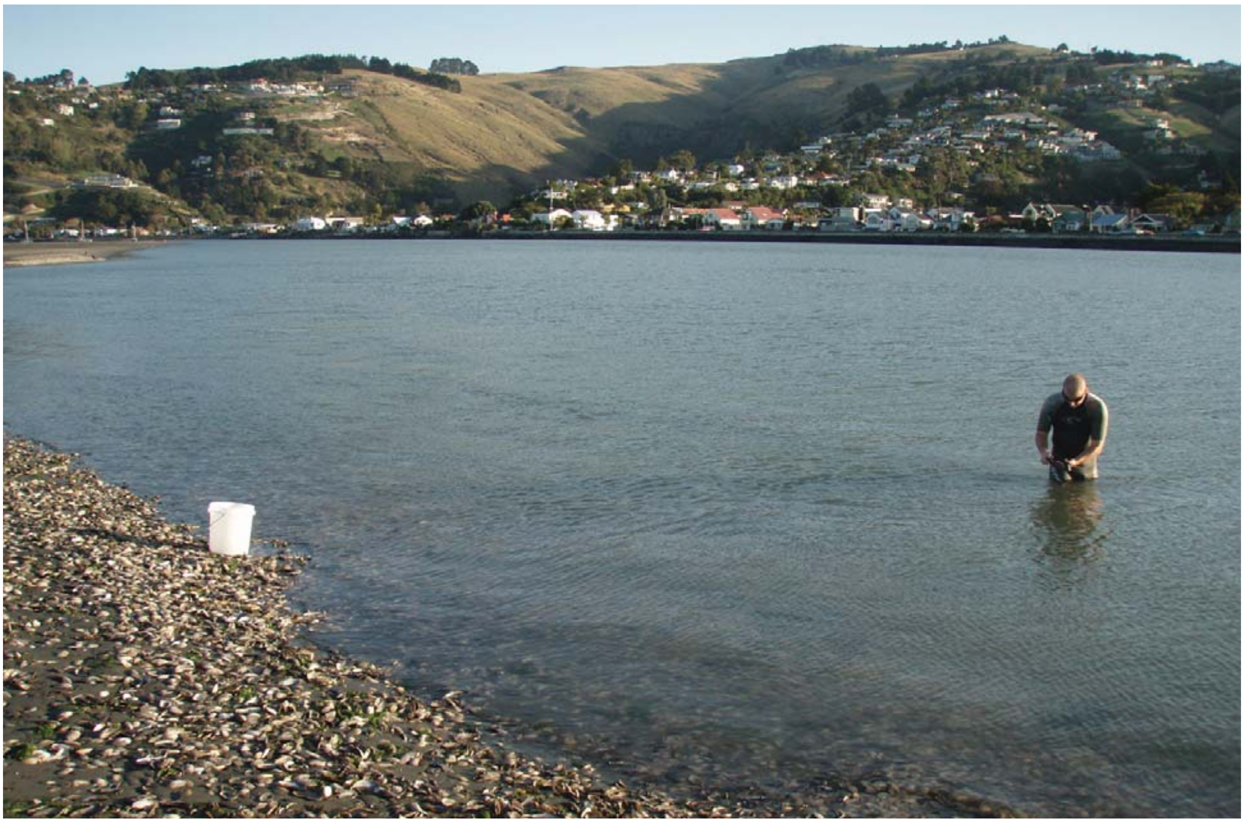
There was no one site that consistently had higher contaminant loadings in fish or shellfish than the other sites. It could have been expected that the animals collected from near the Bromley Wastewater Treatment Plant (WTP) discharge point (lead, cadmium, and arsenic are present in wastewater) would have higher heavy metal contaminant levels than those near the estuary mouth. This was not the case. In fact, cockles collected from the causeway and Southshore sites had higher cadmium, mercury, and arsenic levels than those collected from the Bromley WTP discharge site. This may be a result of flow patterns within the estuary moving river sediment contaminated with heavy metals towards the estuary mouth. However, cockles from the discharge site did have slightly higher lead contamination than the cockles found at the other two sites.

In 1988 the Christchurch Drainage Board (CDB) published a comprehensive report on heavy metal contamination in the Avon-Heathcote Estuary (CDB, 1988). They found that cadmium levels in cockles were relatively evenly spread throughout the estuary, while twenty years later, we found that cadmium levels were slightly lower by the Bromley WTP discharge than at the sites by Southshore or the causeway. Lead distribution results from CDB (1988) were more similar to our results, with higher levels on the western side of the estuary (discharge site) than the more eastern sites (causeway and Southshore). In addition, CDB (1988) found that smaller cockles had higher levels of heavy metals than larger ones. The cockles we collected were slightly larger at the causeway site but this size difference cannot explain the site differences in heavy metal contamination.

For freshwater fish, the river that shortfin eels were collected from made little difference to their heavy metal contamination, with eels collected from both the Avon and Heathcote Rivers having similarly low lead and arsenic levels, while the small difference in mercury levels may be due to age rather than site differences.

For the estuarine fish, there was also no relationship between site and metal contamination. For flounder there was no real difference between sites, while for mullet the discharge site had slightly higher mercury levels. Given the transient nature of both types of fish it is unlikely that any differences would be associated with where they were caught.

The Avon-Heathcote Estuary viewed from Mt Vernon



Collecting pipis near the estuary mouth

The influence of life histories

Some of the differences in heavy metal loadings between the animals collected may be due to differences in life history, habitat preferences, feeding behaviour, and even how metals accumulate.

Although typically regarded as marine species, flounder and mullet do not just live in the sea and estuary area, but move up into the lower reaches of rivers to feed. Flounder will move a short distance up-river, although they stay within the tidal zone. Mullet also move up-river to feed, although they will move much further upstream, above the tidal zone where they may remain and feed for several tide cycles before returning to the estuary. In contrast, eels will typically spend most of their life in freshwater, only migrating to the sea to spawn. All three fish species feed on small invertebrates, and in the case of eels, sometimes small fish, which means that their main exposure to heavy metals is likely to be in the food that they eat. Flounder and eels are also bottom-dwelling fish and so may be more exposed to contaminants in the sediment than fish (like mullet) that remain in the water column. Yet because these fish all move around so much, it is not possible to work out where they may have acquired heavy metal contamination.

The age of fish caught would certainly be a factor in the level of mercury found in the flesh, as it bio-accumulates. The higher level of mercury in eels from the Heathcote River may be related to their larger size compared to those caught in the Avon River. Eels grow very slowly and are long-lived, and the eels caught in this study could be between 14 and 22 years old, depending on their sex. The size difference of over 30 mm between rivers could mean the eels caught in the Heathcote River were up to one year older.

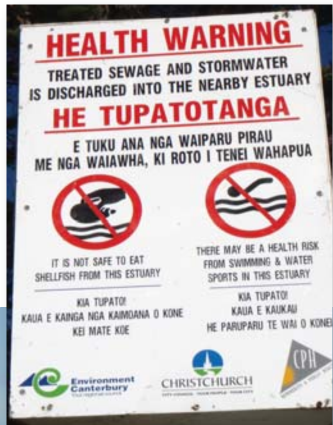
Pipis and cockles are relatively stationary animals that live in the sediment and filter particles out of the water column. Compared to fish, they actively ingest heavy metals bound to particles (organic and inorganic), meaning that they would be more exposed to heavy metals while feeding. Shrimp also feed by stirring the sediment up and collecting very small particles of organic matter, and so they too would be exposed to the heavy metals bound to this food. However, there was no consistent pattern of higher heavy metal contamination in shellfish or shrimp compared to fish. Shellfish and shrimp did have higher arsenic levels than mullet, flounder, and eels. Shellfish and shrimp also had higher levels of lead than mullet and eels, but not flounder. Finally, the highest mercury levels were found in mullet and eels, but because mercury accumulates this may be related to the older age of the mullet and eels compared to the other animals.

So are fish and shellfish **safe to eat**?

Cockles, pipis, shrimp, yellow-eye mullet, sand flounder, and shortfin eels all had metal concentrations (e.g., mercury, cadmium, lead, arsenic) below the FSANZ (2008) limits for safe food consumption. However, this does not necessarily mean that shellfish and fish collected from the estuary and rivers are safe to eat. High levels of the bacteria *E. coli*, which can cause vomiting, diarrhoea, and abdominal pain, are likely to occur in shellfish in the estuary. EOS Ecology is currently conducting monitoring of *E. coli* and enteric viruses in tuatuas along the shoreline monthly, and in cockles within the estuary four times a year. Until the results of this research are known we feel that shellfish from the estuary and rivermouths could be unsafe to eat (especially raw) due to a potential for high *E.coli* bacteria or virus levels.

The flounder, mullet, and shortfin eels are unlikely to have high levels of *E. coli* bacteria or enteric viruses as they do not filter particles out of the water to feed. However, caution always has to be taken when in an urban environment as many other contaminants, such as Polycyclic Aromatic Hydrocarbons (PAHs, formed during the burning of coal, oil, gas, rubbish, and other organic substances) and pesticides, may be present in the tissue of estuary and freshwater animals.

Shellfish, estuary fish, shrimp, and shortfin eels are safe to eat based on heavy metal levels, but in many places they may still be unsafe due to other contaminants. Follow the warning signs, and never eat shellfish raw.



Cockles being collected by the public at the causeway site, by Beachville Road

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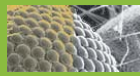
ASSESSMENT AND MONITORING 

RESTORATION DESIGN 

LABORATORY SERVICES 

INFORMATION DESIGN 

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