# Heavy Metals in Christchurch Fish and Shellfish

## 2014 SURVEY

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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 metalloids like arsenic, are found naturally in the environment. They are stable and cannot be degraded or destroyed, so they tend to accumulate in soils, water, and the atmosphere. Humans absorb trace amounts of some heavy metals from our food, drinking water, and the air. Exposure to very low levels (trace amounts) of heavy metals does not adversely affect us, and in some cases can be beneficial — for example trace amounts of selenium, zinc, and copper are essential to maintain our metabolism. However, human activities from industry (such as mining, smelting) and 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 more 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 in run-off from roads, industrial sites, 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 in the Australia New Zealand Food Standards Code (FSANZ, 2015). Many signs have been erected around the Avon-Heathcote Estuary/Ihutai warning the public about eating shellfish due to the potential for contamination from the discharge of treated sewage[1] and stormwater inputs. 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.

1 The discharge of treated wastewater into the Esutary ceased in March 2010 with the creation of the ocean outfall. However, following the 2011 earthquakes raw sewage overflowed into the estuary via the City's rivers for many months due to a damaged sewerage network.



Stormwater entering the Avon River/Ōtākaro

## Hg MERCURY

Mercury occurs naturally in the environment but can also be released into the atmosphere through industrial pollution. It can be transported over large distances and accumulates in the environment when deposited into surface waters and soils. It is present in fish and seafood products mostly as methylmercury (ENHIS, 2007).

Methylmercury accumulates as smaller animals are eaten by bigger animals, so predatory animals 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.

## Cd 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 also be high in cadmium (Gray *et al*., 2005; WHO, 1992). Long-term or high dose exposure to cadmium can cause kidney failure and softening of bones (Vannoort & Thomson, 2006), and high levels of cadmium have been linked to prostate cancer (Gray *et al*., 2005).

## Pb 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).

## As ARSENIC

Arsenic is a naturally occurring element that is common in soils, water, and living organisms. In New Zealand arsenic levels in the environment can increase as a result of mining, geothermal production, treated timber, and erosion caused by intensive land use.

Fish and seafood can accumulate considerable amounts of organic arsenic from their environment, but most foods contain trace levels of organic arsenic and occasional consumption is not a health concern. An acute high level exposure to arsenic can lead to vomiting, diarrhoea, anaemia, liver damage, and death. Long term (chronic) exposure is thought to be linked to skin disease, hypertension, some forms of diabetes, and cancer (Centeno *et al*. 2005). Arsenic is present in our food in different chemical forms, but inorganic arsenic is more toxic than organic arsenic. 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), and most of this leaves the human body within several days. There is no regulatory limit for total arsenic in fish or shellfish. However, it is difficult to reliably measure the forms of arsenic that are present, so many surveys of arsenic content measure total arsenic levels.

**Maximum allowable levels of metal contaminants in food (FSANZ, 2015)**

| | Metals (mg/kg) | Crustacea (e.g., crabs, shrimp, crayfish) | Fish | Shellfish |
|---|---|---|---|---|
| Hg | Mercury | 0.5 | 0.5 | 0.5 |
| Cd | Cadmium | n/a | n/a | 2 |
| Pb | Lead | n/a | 0.5 | 2 |
| As | Arsenic (inorganic)* | 2 | 2 | 1 |

*Inorganic arsenic is estimated to be 10% of total arsenic (USFDA 1993).

# WHERE WE SAMPLED

Estuary fish were collected within the estuary from near the old discharge point of the Christchurch Wastewater Treatment Plant (WTP) (Discharge) and from the western side of the Southshore spit (Southshore). Cockles were collected in these two areas as well as at the southern end of the causeway by Beachville Road (Causeway) which is a popular shellfish gathering site. Due to the small size of pipis collected in previous years, pipis were collected from alongside the shoreline east of the Beachville Road boat ramp (Estuary Mouth) this time around. This site is on the opposite side of the low flow channel to the site sampled in previous years.

Shortfin eels were collected in the Avon River/Ōtākaro downstream of Anzac Drive and Snell Place, and in the Heathcote River/Ōpāwaho just upstream of Opawa Road and Aynsley Terrace. The upstream sites (2.25 km upstream of the original site in the Avon River/Ōtākaro and 1 km upstream of the original site in the Heathcote River/Ōpāwaho) were added to the eel sampling sites from previous years, due to insufficient fish being caught in the original site locations this year.

Whitebait and estuary shrimp were not collected as they had been in previous years.

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FIGURE 1: Locations where fish and shellfish were collected in the 2014 survey.

# HOW WE SAMPLED

## SHELLFISH

Cockles (*Austrovenus stutchburyi*) and pipi (*Paphies australis*) were collected at low tide by hand on 28 May 2014. Ten replicate samples per site were collected. For cockles, each sample was made up of 3–4 specimens, while for the pipis five specimens were needed per sample. The shellfish were kept cool with ice packs, their length measured, and then delivered live to Hill Laboratories for heavy metal testing.

Each sample was tested by the laboratory for mercury, and five samples per site for arsenic, lead, and cadmium.

Collecting cockles

Collecting pipi

Measuring cockles in the laboratory

Pipi

## ESTUARY FISH

Yellowbelly flounder (*Rhombosolea leporina*) and yelloweyed mullet (*Aldrichetta forsteri*) were collected from the estuary sites on 22 May 2014. Yellowbelly flounder were collected this year as opposed to sand flounder (*Rhombosolea plebeia*), which were collected in previous years. The change in species is because more yellowbelly than sand flounder were caught at these sites in previous years and therefore they are the more likely species being caught for consumption.

Yellowbelly flounder were caught using a rigid frame weighted drag net (mesh size 25 mm) dragged along behind the boat. Six drags per site were needed to capture the required number of fish. Yelloweyed mullet were caught using rods with six hook herring jigs (Sabiki's) from an anchored boat while releasing a burley trail.

At each site ten fish of each type were placed on ice, anaesthetised and measured in the lab, and delivered to Hill Laboratories for testing. Ten fish of each type were analysed for mercury and five for arsenic and lead. For yellowbelly flounder 2–3 fish were combined for four samples from the Discharge site to make up samples with sufficient flesh for testing, while the remaining samples consisted of one fish only.


Yellowbelly flounder


Fishing for yellowbelly flounder


Yelloweyed mullet


Fishing for yelloweyed mullet

## FRESHWATER FISH

Shortfin eels (*Anguilla australis*) were collected from the Heathcote River/Ōpāwaho and Avon River/Ōtākaro using fyke nets that were baited and set overnight during October and December 2014. On retrieval of the nets 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 or they were large. Mercury levels were tested in ten eels and arsenic and lead in five eels from each site.


Setting a fyke net in the Heathcote River/Ōpāwaho


Eels caught in a fyke net

# OUR FINDINGS

## SHELLFISH

Where possible, we collected shellfish of the size most likely to be collected and eaten. Cockles, however, were smaller at the Southshore and Discharge sites than at the Causeway site (average length of 29-32 mm compared to 41 mm at the Causeway site) (Table 1).

Both pipi and cockles at all sites had levels of cadmium, lead, and mercury below the Food Standards Australia New Zealand (FSANZ, 2011) maximum allowable level set for safe consumption of shellfish (Figure 2). 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. As in 2012, cockles collected from the Discharge site had the lowest levels of cadmium, and mercury, but had the highest levels of lead.

Cadmium concentration was higher in pipi than in cockles. This is different to previous years where cockles at the Causeway site had the highest levels. The cadmium levels in cockles at the Causeway and Southshore sites were lower in this survey than in the 2012 survey (McMurtrie, 2012). This same temporal pattern also occurred with mercury concentrations. In contrast, lead concentrations were higher in cockles from all three sites in this survey compared to the 2012 survey.

Arsenic was lowest in pipi at the Estuary Mouth and cockles at the Discharge site, and highest at Southshore and Causeway sites. This between-site difference is the same as it was in 2012 (McMurtrie, 2012). The 2014 cockle arsenic concentrations are lower than those in 2012 (McMurtrie, 2012). In 2012 an average of 4.9 mg/kg total arsenic occurred in the Southshore cockles.

FSANZ (2015) provides guidelines for levels of inorganic arsenic in shellfish (as well as in fish). However, as this is difficult and expensive to measure accurately, most studies measure total arsenic levels instead. In the USA the Food and Drug Administration (USFDA) had set maximum allowable levels for total arsenic in shellfish at 86 mg/kg (USFDA, 1993). The levels of total arsenic we found in the estuary shellfish were much lower than this (Figure 2). The highest concentration of total arsenic was at least 1/10 that of the safe consumption levels set by the USFDA. The USFDA had also conservatively set the inorganic arsenic component at 10% of total arsenic (USFDA, 1993), Therefore the highest estimated inorganic arsenic levels in the collected samples would be 0.36 mg/kg, which is below the FSANZ guidelines of 1 mg/kg inorganic arsenic.

Collecting cockles

TABLE 1: Average shell length (mm ± 1 std error) of shellfish collected in May 2014.

| | | |
|---|---|---|
| Cockles | Causeway | 41 ± 1 |
| | Discharge | 32 ± 0.4 |
| | Southshore | 29 ± 0.4 |
| Pipi | Estuary Mouth | 56 ± 0.5 |

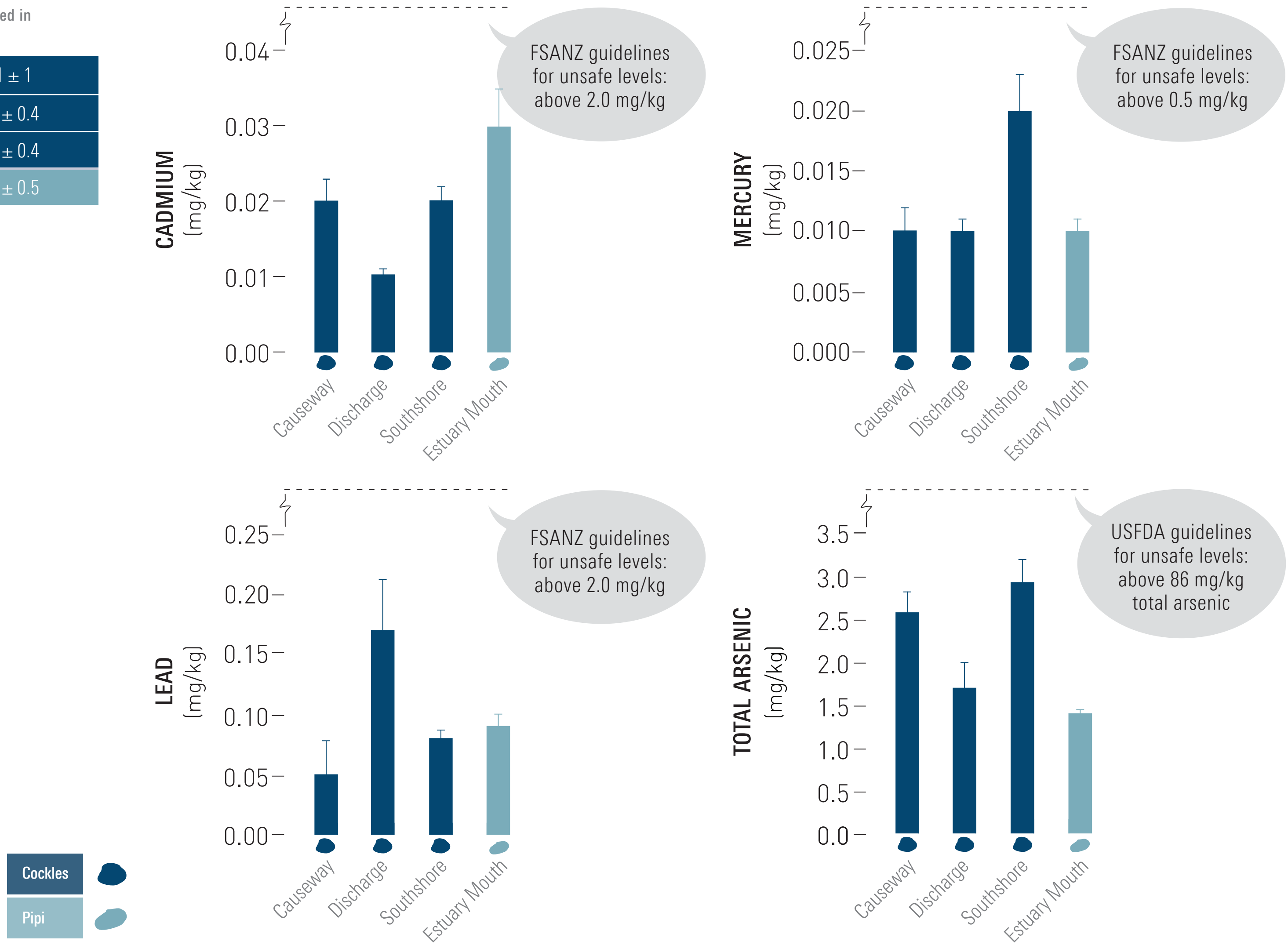



FIGURE 2:

Heavy metal levels (mean ± 1 std error) in shellfish (cockles and pipi) collected from the Avon-Heathcote Estuary/Ihutai in May 2014

## FISH

The size of mullet and flounder collected were compared to the average sizes of these fish in the estuary in 2013 (Woods et al. 2014). The yelloweyed mullet caught in this survey were generally larger than those caught in the wider estuary in 2013 (Table 2). The yellowbelly flounder caught in this survey were generally smaller than those caught in low tide channels but larger than those caught via beach seines in 2013 (Table 2). They were also smaller than the allowable size of 230 mm for recreational fishing.

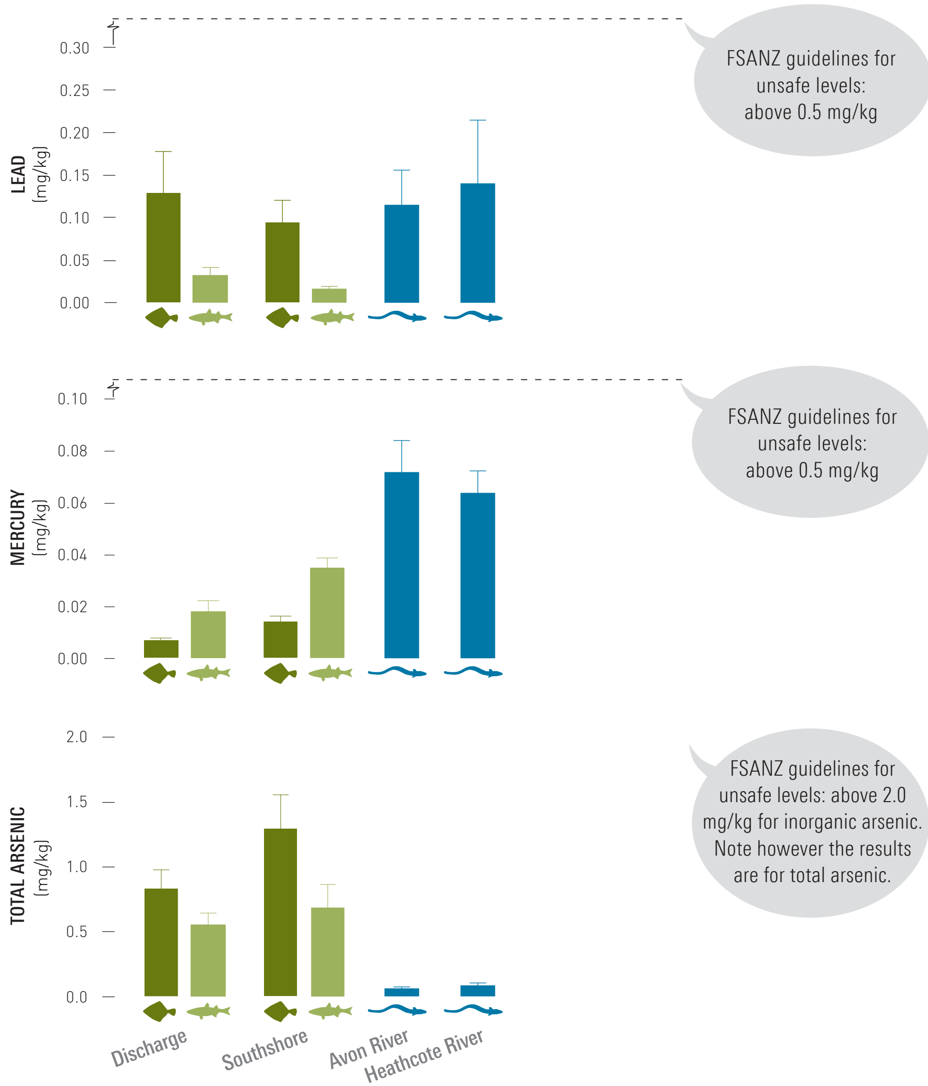
The shortfin eels caught were of similar size between the two rivers (Table 2). We did, however, return the largest eels we caught as they are an important part of the breeding population. There are no size limits on shortfin eels, although the Ministry of Fisheries (MoF) recommends that recreational fishers return shortfin eels longer than 600 mm (Ministry of Fisheries, 2008).

The levels of lead and mercury in yellowbelly flounder, yellloweyed mullet and shortfin eels were well below the maximum acceptable levels (FSANZ, 2015) (Figure 3). Given that total levels of arsenic were all below 2.0mg/kg in all fish, inorganic arsenic levels (which are estimated to be around 10% of total arsenic) would have been well below the maximum acceptable level of 2mg/kg.

There were differences in the mecury, lead and arsenic concentrations between species and in some cases between sites. The most notable differences were the higher levels of lead in flounder and eels, and the markedly greater level of mercury in eels compared to all other fish.


Releasing a large shortfin eel back into the Avon River/Ōtākaro

FIGURE 3:
Heavy metal levels (mean ± 1 std error) in fish collected from Avon Heathcote Estuary/Ihutai (Discharge, Southshore) and Christchurch's main rivers (Avon River/Ōtākaro, Heathcote River/Ōpāwaho in 2014.



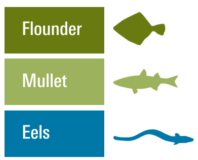




TABLE 2:
Average length of fish (mm ± 1 std error) caught for testing in 2014 compared to fish lengths in the wider area.

| Species | Site | Length of fish taken for analysis (mm) | Length of fish in estuary (Woods *et al*., 2014) (mm) |
|---|---|---|---|
| Yelloweyed mullet | Discharge | 220 ± 10 (caught 10) | Low tide channel trawl: 202 (caught 48) |
| | Southshore | 216 ± 9 (caught 10) | Beach seines: 84 (caught 3,139) |
| **Species** | **Site** | **Length of fish taken for analysis (mm)** | **Length of fish in estuary (Woods *et al*., 2014) (mm)** |
| Yellowbelly flounder | Discharge | 78 ± 5 (caught 17) | Low tide channel trawl: 346 (caught 38) |
| | Southshore | 110 ± 10 (caught 10) | Beach seines: 82 (caught 41) |
| **Species** | **Site** | **Length of fish taken for analysis (mm)** | **Length of all eels caught (mm)** |
| Shortfin eel | Avon River | 504 ± 48 (caught 10) | 494 ± 31 (caught 13) |
| | Heathcote River | 502 ± 56 (caught 10) | 537 ± 32 (caught 12) |

# DISCUSSION

## THE INFLUENCE OF SITE LOCATION

Because shellfish live in the sediment and don't move much they provide a good indication of differences in contaminant concentrations between sites. We found that shellfish from the Causeway and Southshore sites had higher levels of cadmium and arsenic than those from the Discharge or Estuary Mouth sites. The Causeway and Southshore sites are in areas where a number of pipes discharge stormwater directly into the estuary (Figure 4). The results suggest the stormwater may be a source of the cadmium and arsenic.

The results were broadly similar to those found in previous years, with the following exceptions. Cadmium and mercury levels in shellfish from the Causeway site were lower than in 2012. The arsenic levels in cockles from the Discharge site in 2014 were almost double those found in 2012, although they are still below the food safety standards.

For the shortfin eels, the river that they were collected from made little difference to the concentrations of lead, mercury, or arsenic in the flesh.

For the estuarine fish, there were differences in metal concentrations between fish species and small differences between sites. As fish move around so much it is difficult to attribute any differences in heavy metal levels to the location where they were caught. For example yelloweyed mullet regularly move considerable distances up-river (i.e., at least as far as Hagley Park on the Avon River), into freshwater above the tidal zone, where they may remain and feed for some time before returning to the estuary.


A misty day near the Southshore cockle site


Cockle collection site

Stormwater discharge

FIGURE 4:
Small stormwater pipe discharges (locations provided by Environment Canterbury) into the Estuary in relation to the location of the cockle monitoring sites. It is possible the stormwater discharges near to the Causeway and Southshore sites contribute to the higher levels of cadmium, mercury, and arsenic in cockles from these sites compared to the Discharge site.

## THE INFLUENCE OF LIFE HISTORY

Differences in the concentrations of heavy metals in the tested fish are most likely due to differences in life history, habitat preferences, feeding behaviour, and even how metals behave and accumulate in the different species, rather than any site-specific differences.

Yelloweyed mullet are primarily algae eaters (although they will also feed on small invertebrates) compared to flounder that feed on small crabs and other bottom-dwelling invertebrates. The difference in food may explain the differences in lead and arsenic levels between these two fish species.

The age of fish caught could explain the different levels of mercury in the three fish species, as mercury accumulates over an animal's lifetime as well as up the food chain (e.g., predators accumulate the mercury from the prey they eat). The much higher level of mercury in eels than all other animals tested may be related to their greater age and predatory status. Eels are typically regarded as slow growing, averaging around 20-50 mm a year (although growth varies with a range of parameters, including food and water temperature), meaning most of the eels caught would be well over ten years old. Eels were therefore many years older than the other fish caught.

The bioaccumulation of mercury could also explain the higher levels in yelloweyed mullet than in yellowbelly flounder. The caught yelloweyed mullet were estimated to be around three years old (based on regression equations by Curtis & Shima, 2005), and so while not as old as the shortfin eels, would still be older than the caught yellowbelly flounder (which were estimated to be around one year old).

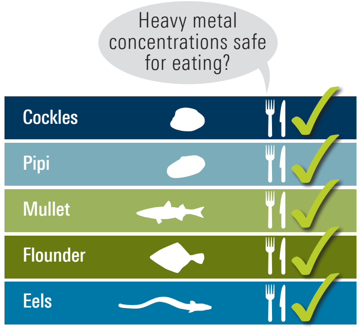
Pipi and cockles are relatively stationary animals that live in the sediment and filter particles out of the water column. Compared to fish, they actively ingest heavy metals bound to particles (organic and inorganic), meaning that they could be more exposed to heavy metals while feeding. Our study and other studies (FSA, 2005) have found that cockles accumulate more arsenic than fish do. This may be partly due to their feeding or habitat preferences.


View of the estuary looking north

## SO ARE FISH AND SHELLFISH SAFE TO EAT?

Cockles, pipi, yelloweyed mullet, yellowbelly flounder, and shortfin eels all had metal concentrations (e.g., mercury, cadmium, lead, arsenic) below the FSANZ (2015) limits. Therefore based on heavy metal levels they are safe for consumption. However, the on-going high arsenic levels in cockles could warrant further investigation, with testing of inorganic arsenic in cockles to properly ascertain the relationship between total arsenic and inorganic arsenic levels.

Despite this clean bill of health, the consumption of shellfish in particular should still be cautioned. Bacteria (*Escherichia coli*, *Salmonella*) and enteric viruses (norovirus)—which can cause vomiting, diarrhoea, and abdominal pain—are still being found in shellfish collected from the estuary as a result of faecal contamination from either human (sewage overflows) or wildlife (birds, dogs) sources. Quarterly monitoring by EOS Ecology for the Christchurch City Council (CCC) over a six year period showed that both *E. coli* and norovirus concentrations at sites near to the Avon and Heathcote River mouth sometimes showed high levels of bacteria and norovirus, related to sewage overflow events (such as following the Christchurch earthquakes and during large rain events), and sometimes during otherwise stable weather (McMurtrie & Hewitt, 2013). While no specific microbiological (either bacteria or viruses) guideline criteria exist for shellfish gathered for personal consumption or non-commercial purposes, the safe *E. coli* limits for commercial food set by the Australian New Zealand Food Authority in 2011 is 700 MPN/100g in bivalves (FSANZ, 2011). Enteric viruses such as norovirus are highly contagious and can survive freezing, meaning that care must be taken when preparing shellfish collected from the estuary. Guidance can be found at http://www.foodsmart.govt.nz/food-safety/foodborne-illnesses/norovirus/, as well as following the warning signs maintained by the CCC around the estuary.





Collecting cockles

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