Mercury and arsenic in Victorian waters: a legacy of historical gold mining

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Report

Contents

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Executive summary

This report presents the results of a study carried out by Environment Protection Authority Victoria (EPA) to assess the levels of mercury and arsenic in sediments and fauna. This investigation is part of EPA's River Monitoring and Assessment Program (RiverMAP)

The objective of this study was to evaluate mercury and arsenic contamination in aquatic ecosystems that have been historically exposed to gold mining activities. The study focused on priority waterways valued for recreational fishing to identify where human health risk assessment may be warranted. The following rivers and streams were monitored as part of RiverMAP's water quality 'hotspot' investigation:

- Avoca River
- Big River
- Buckland River
- Coliban River
- Livingstone Creek
- Loddon River
- Ovens River
- Sailors Creek
- Thougla Creek

The results of the study show evidence of mercury and arsenic contamination in rivers and streams in historical gold mining regions. EPA's monitoring revealed that many of the rivers and streams in the study contain concentrations of mercury and arsenic in the sediment that are above environmental guideline values.

Sediments from nearly half of all sites monitored exceeded the Interim Sediment Quality Guideline (ISQG) 'low trigger' value for mercury (0.15 mg/kg) that is set above expected natural background concentrations (0.01–0.1 mg/kg). Arsenic concentrations were above the ISQG low trigger value (20 mg/kg) at nearly 75% of sites monitored.

At three reaches where ISQG guidelines were exceeded (Big River, Sailors Creek and Loddon River), EPA conducted biological testing to assess whether elevated levels of sediment-bound mercury and arsenic were reflected in fish and yabbies. The results from biological testing on tissue samples were compared with the maximum levels (MLs) prescribed in the *Australia New Zealand Food Standards Code.* These levels provided EPA with a useful benchmark to assess whether further investigation and human health risk assessment was needed.

Overall, arsenic concentrations in fish and yabbies were generally low at all three waterways. At Sailors Creek and Big River, mercury concentrations in fish and yabbies were also below the maximum level (ML). However, at Loddon River, the concentration of mercury in predatory redfin perch and samples of common carp exceeded the ML. EPA found that young redfin perch (1–3 years) contained concentrations of mercury above the ML, whereas mercury concentrations in common carp were found to increase steadily with age, and only fish more than 10 years old exceeded the ML.

It is important to note that an exceedance of the ML in one or more fish does not suggest that recreationally caught fish pose a significant risk to consumers. Rather, an exceedance of the ML is considered a trigger for further investigation and human health risk assessment. As a result, the findings from this study were referred to the Department of Health and Human Services (DHHS) to assess potential human-health impacts. EPA conducted further testing on two additional fish species living in the Loddon River (Murray cod and golden perch), which led to DHHS providing public advice about the consumption of fish living in the Loddon River between Laanecoorie Reservoir and Bridgewater.

1. Introduction

For over twenty years the Department of Environment, Land, Water and Planning (DELWP) and its predecessors have funded Environment Protection Authority Victoria (EPA) to monitor the condition of rivers across Victoria. Historically, monitoring has focused on aquatic macroinvertebrates as indicators of water quality and ecological health. In 2012, a revision of the program resulted in a reduction in broad-scale macroinvertebrate monitoring and the implementation of the current River Monitoring and Assessment Program (RiverMAP). The aim of RiverMAP is to identify water quality issues and guide management actions by State Government to help improve the condition of waterways across Victoria. This is being delivered through three streams of work:

- Development of an ecological model to explore the relationship between catchment land use, vegetation, and biotic indices. This model will help to guide and predict the outcomes of revegetation works on river health and aquatic macroinvertebrate communities.
- Water quality 'hotspot' investigations that focus on specific sources of contamination and pollution in high priority rivers and streams.
- Monitoring macro-invertebrates at 66 long-term sites that are representative of a range of Victorian freshwater habitats.

This report presents the results of a study carried out to assess the levels of mercury and arsenic in sediments and fauna among priority waterways valued for recreational fishing. During the planning of hotspot investigations, EPA, DELWP and catchment management authority (CMA) staff nominated pollution sources that threaten priority waterways: three CMAs (Goulburn Broken, North Central and North East) and EPA Victoria nominated metal pollution from historic gold mining sites as a potential threat to priority waterways across the state.

1.1 Mercury, arsenic, and gold mining

Mercury is found in various forms on earth and is released into the biosphere through a range of natural and anthropogenic processes. Natural sources of mercury include weathering of mercury-containing rock, volcanic eruptions, and bush fires. Human activities such as the combustion of fossil fuels, metal production and artisanal gold mining have also significantly increased the amount of mercury in the environment (Nelson *et al.* 2009). Mercury is a potentially harmful environmental contaminant, especially in aquatic environments where bioavailable forms of mercury can become increasingly concentrated up the food chain (Boening, 2000). In Victorian streams, trace amounts of mercury are sourced from the erosion of mercury-containing geological formations including the Great Dividing Range (Hart, 1982). Historical mining practices involving the use of mercury have also caused significant levels of contamination in Victorian waterways following the discovery of gold during the 1850s. From this time until the 1930s, the use of concentrated mercury was popular among artisanal miners to extract gold from crushed ore (Bycroft *et al.* 1982). The residual mercury that resulted from the gold mining process was poorly managed and either retained in dams temporarily or released directly into nearby waterways (Tiller, 1990). Due to the persistence of mercury in the environment, many waterways in gold mining catchments still contain elevated levels of mercury and studies have demonstrated that historical mines and tailings dumps may remain sources of mercury for many decades after mining has ceased. A number of previous Victorian studies have reported elevated levels of mercury in historic gold mining areas such as Reedy Creek in north east Victoria (Churchill *et al.* 2004); the Lerdederg River (Bycroft *et al.* 1982); Steiglitz (Lake & Sokol, 1986); sections of the Goulburn and Ovens Rivers; and parts of Lake Eildon and Lake Dartmouth (Fabris, 2002).

In the aquatic environment, mercury binds to organic particles and settles out in sediments; only relatively small amounts of mercury dissolve in the water column (Tiller, 1990). Under anoxic conditions, microbiological processes within the sediment can lead to inorganic forms of mercury being converted to methyl-mercury (MeHg). MeHg is a biologically accessible and potentially harmful form of organic mercury. The transformation of inorganic mercury into MeHg is the first step toward bioaccumulation of mercury in aquatic organisms (Hsu-Kim *et al.* 2013). This transformation, together with the persistence of MeHg in tissue, results in biomagnification across the food chain (Ward *et al.* 2010). For this reason, predatory fish; fish with long life-spans; and other fish-eating wildlife can accumulate concentrations of mercury in their tissues that greatly exceed the concentration of mercury in their surrounding environment. Numerous studies have demonstrated that human exposure to MeHg is strongly associated with fish and shellfish consumption (Chien *et al.* 2010; Liu *et al.* 2014; Pirard *et al.* 2014; Schaefer *et al.* 2014). Consumption of highly contaminated fish may result in adverse health effects, particularly in the developing central nervous system. As such, health authorities recommend that young children, pregnant women and women intending to become pregnant limit the consumption of certain fish species known to accumulate elevated levels of mercury.

In addition to mercury, historical gold mining activities have released arsenic from gold-bearing ores. Among the historical goldfields of Victoria, tailings dumps and overburden (unprocessed waste rock) containing high levels of arsenic have

been linked to the contamination of surrounding soils (Pearce et al. 2012) and waterways (Churchill *et al.* 2004; Sultan & Dowling 2006). As with mercury, the effects of arsenic on aquatic life, and the potential health risks posed by contaminated fish, are dependent on arsenic's form and concentration (Madigan et al. 2005; Rahman et al. 2012). In the aquatic environment, arsenic exists in several forms and inorganic forms are generally considered more harmful to human health and aquatic life compared with organic forms of arsenic. Aquatic organisms such as fish and crayfish have been shown to accumulate arsenic in various forms following exposure through the diet, gills or skin (Rosemond et al. 2008; Williams et al. 2009). However, due to fish and crayfish's ability to metabolise arsenic, most of the accumulated arsenic in these organisms is retained in organic form and reports of biomagnification across the food chain are rare (Rahman et al. 2012). Nonetheless, fish and other aquatic food sources living in contaminated streams may contain elevated levels of arsenic and are potential dietary sources of human exposure to arsenic.

2. Objectives

The objective of this study is to evaluate mercury and arsenic contamination in aquatic ecosystems that have been historically exposed to gold mining activities. The specific objectives are:

- Map the location of past and present goldmines in Victoria and identify clusters of mines within the catchments of high-value reaches valued for recreational angling.
- Evaluate total mercury and total arsenic concentrations in sediments from high-value reaches close to the identified clusters of mines.
- Assess total mercury and total arsenic concentrations in selected fish and crustaceans from three reaches showing contaminated sediments as defined by current environmental guidelines (ANZECC/ARMCANZ, 2000).
- Identify reaches that warrant further consideration and risk assessment to determine the potential for human health impacts from consumption of recreationally caught fish and crustaceans.

3. Methods

3.1 Study design

A targeted sampling design was used to select sampling sites. In contrast to a probability-based sampling design that involves random selection of sampling units, the targeted design selected sampling sites based on two a priori defined factors: mines density and aquatic values (sections of stream or 'reaches' that are valued by recreational anglers). The targeted design allowed EPA to understand pollution at specific reaches and meant that resources for sampling and analyses could be efficiently allocated.

3.2 Sample site selection

A spatial analysis was carried out to map gold mine clusters along high-value reaches across Victoria (Section 4.2.1). A total of 35 sites from 10 reaches were identified for sediment sampling. Following sediment sampling, three reaches that contained the highest levels of mercury and arsenic were re-visited to assess contamination in aquatic biota.

3.2.1 Spatial analysis: identifying mining 'hotspots'

The spatial database MINSITE (unique ID ANZVI0803002225) was used to identify gold mines in Victoria. MINSITE is part of DELWP's geoscientific data package and includes information on mine location, mineralisation type, extraction method, and mine size. In total, 16,322 gold mines across Victoria were obtained from the database (Figure 1). All gold mines identified in the database were used for the density analysis (section 4.2.1.1 below). For 9,962 gold mines, additional information such as mineralisation method was available. For the remaining 6,360, details on mineralisation methods were not available.

3.2.1.1 Density analysis of mine data

The Kernel density tool in ArcGIS 10.2 was used to identify dense clusters of mines from the MINSITE database across Victoria. This tool is based on a quadratic kernel function (Silverman 1986) and calculates the density of features (i.e. mines) around each output raster cell and fits a smooth curved surface over each point (ESRI, 2011). Figure 2 shows the output of the Kernel density analysis across the state.

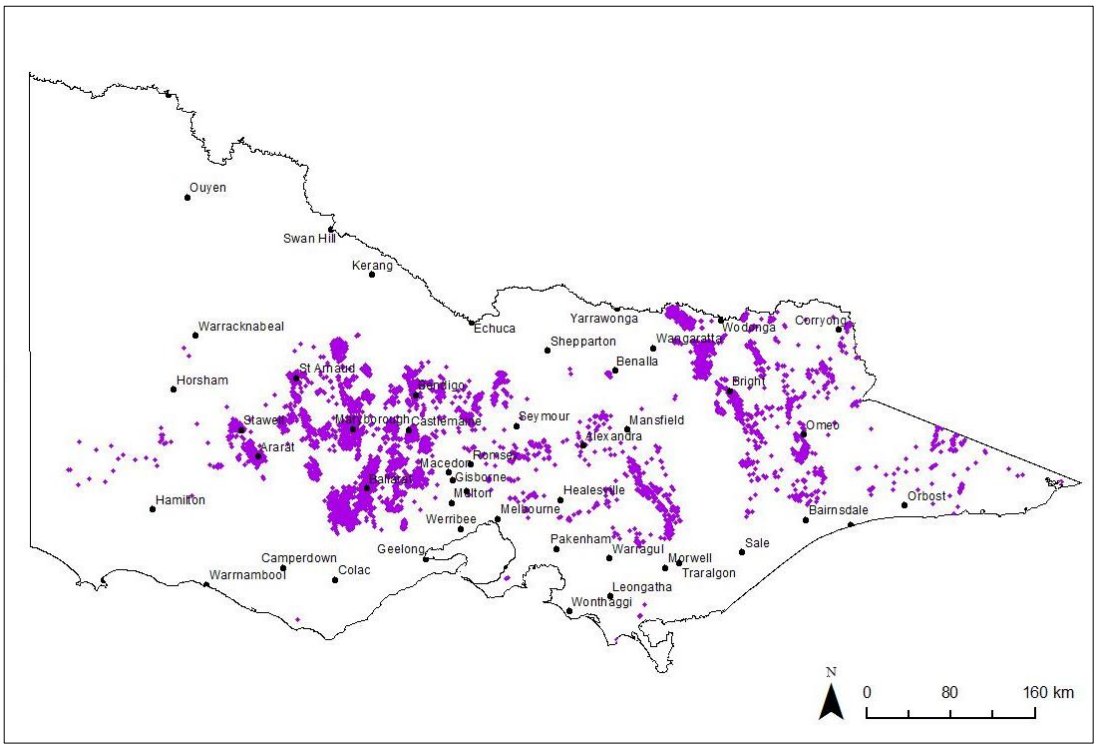

Figure 1 - Spatial distribution of goldmines in Victoria obtained from MINSITE database

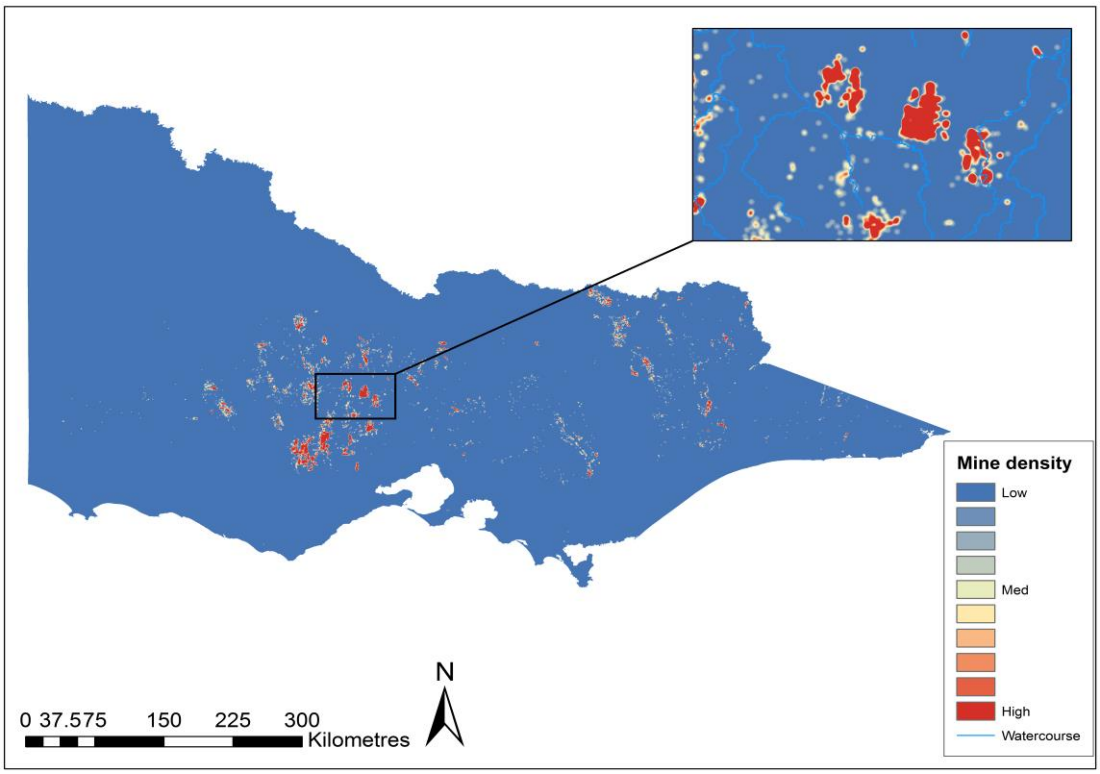

Figure 2 - Spatial distribution of Victorian goldmines displayed using Kernel density analysis

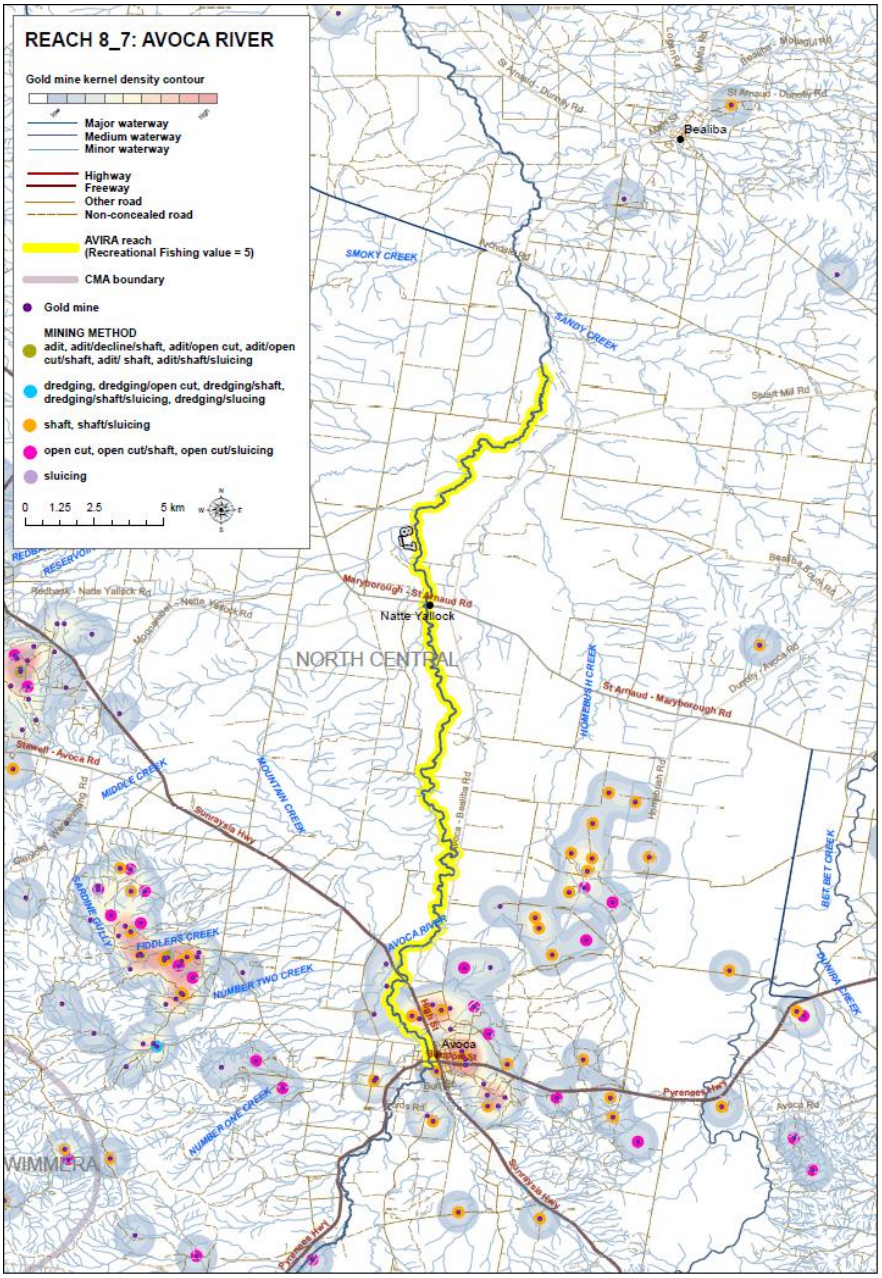

Figure 3 - Kernel density analysis of Victorian goldmines along a high-priority section of the Avoca River

3.2.1.2 Identification of highly valued reaches

An overlay analysis was used to identify reaches highly valued by recreational anglers within the defined mining hotspots. The kernel data was overlaid with data from DELWPs Aquatic Value Identification and Risk Assessment (AVIRA) spatial database, which houses detailed information on key values of Victoria's waterways (Figure 3). Assets in the AVIRA database are described using environmental, social, or economic value types (Table 1). Categories are determined by grouping related values, while a 'measure' describes particular waterway characteristics. Figure 3 displays an example of a detailed map that was produced and used to guide the selection of sediment monitoring sites.

Table 1 – An example of an AVIRA metric for recreational fishing

Value type	Category	Measure	Metric	
			Descriptor	Value score
Social	Activity	Recreational fishing	Listed as a priority/key/popular fishery in a Regional Fishery Management Plan OR rated as a 'best fishing water' in *A Guide to the Inland Angling Waters of Victoria*	5
			Some recreational fishing occurs	3
			Not known to be used for recreational fishing	1
			Not suitable for recreational fishing	0

3.2.1.3 Reach prioritisation

Stream reaches containing high-density gold mine clusters, which also yielded a value score of '5' for recreational fishing in AVIRA were selected for sediment sampling. Figure 4 displays the value score for waterway reaches in the AVIRA database; those highlighted in yellow intersect with high density gold mine clusters and were included in the sediment monitoring.

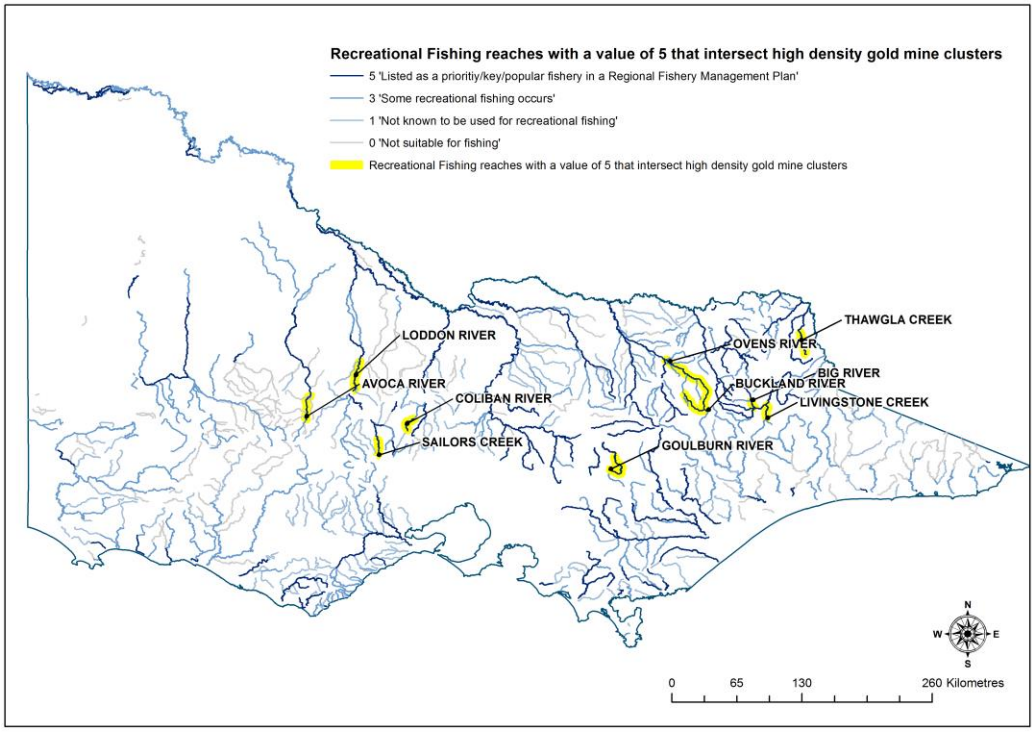

Figure 4 – AVIRA reaches highly valued for recreational angling that intersect with hotspots produced by kernel analysis

3.3 Sediment collection and analysis

Sediments play an important role in aquatic ecosystems by providing food, habitat and refuge to a range of biological communities (Simpson *et al.* 2005). Sediments also act as both a source and a sink for pollutants that can affect water quality and impact the aquatic food web. The majority of sediments are derived from weathering processes such as erosion, but discharges from mining activities can contribute sediment and metal contaminants to aquatic ecosystems (ANZECC, 2000b; Simpson *et al.* 2005). Small-sized sediment particles (e.g. silt and clay, < 63 µm) are of greater concern than large-sized particles (e.g. sand, > 63 µm – 2 mm) as they have a greater surface area and thus higher adsorption capacity. Pollutants retained on fine sediments can then be taken up by plants and animals in aquatic food webs (Simpson *et al.* 2013). For these reasons, small sediment fractions are routinely analysed and have been shown to be a reliable measure of metal pollution due to gold mining activities (Bycroft *et al.* 1982; Tiller, 1990).

Sediments were collected from 35 sites located within 10 reaches between June and October 2014 (Appendix 1). Sediment was collected using a shovel to scrape the top 5 cm of bed material, which was then transferred into a 20 litre polypropylene pail. Each sediment sample was then wet sieved through 500 µm and 63 µm nylon mesh nets. The fine sediment fraction (< 63 µm) was retained and transferred into 500 ml glass jars with Teflon lined lids. Sediment jars were stored in a refrigerator ($\leq 6^0$C) before being delivered to ALS Environmental (Scoresby, Melbourne) for analysis of total mercury and total arsenic concentration (USEPA, 1994). Concentrations of mercury and arsenic in sediment samples were compared against the Interim Sediment Quality Guideline (ISQG) values as outlined in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC/ARMCANZ 2000). The ISQGs specify sediment contaminant concentrations that are likely to impact on water quality and pose a risk to aquatic ecosystems (Table 2). ISQGs are set with low and high trigger values which, if exceeded, indicate that there are possible (low-trigger value) and probable (high-trigger value) ecological risks from metals in the sediment.

Table 2 –ISQG trigger values for mercury and arsenic in sediments

Contaminant	ISQG Low (mg/kg dry wt.)	ISGQ High (mg/kg dry wt.)
Mercury	0.15	1
Arsenic	20	70

3.4 Biological sampling and analysis

Biological sampling was conducted between October and November 2014 at 12 sites along three priority reaches: Loddon River, Big River, and Sailors Creek. Biological sampling is useful for assessing whether metals in sediment are being bioaccumulated by aquatic organisms which can lead to potential risks for human consumers of contaminated fish and crustaceans.

3.4.1 Target organisms

Aquatic organisms, especially piscivorous fish, can accumulate metals following exposure through the diet or surrounding environment. The organisms selected for monitoring in this study were chosen based predominantly on their recreational importance and (in the case for mercury) high trophic status due to the ability of MeHg to biomagnify up the food chain. Target species included brown trout (*Salmo trutta*) and redfin perch (*Perca fluviatilis*) which are top-order predators and highly sought after by recreational anglers. Additionally, flathead gudgeon (*Philypnodon grandiceps*), and the common yabby (*Cherax destructor*) were included in analyses to provide further information about the presence of metals in prey species. While not all species were present at each site, each sampling location contained at least one of the species described below:

Common yabby (*Cherax destructor*)

C. destructor is distributed throughout Victoria and inhabits freshwater creeks, rivers, lakes, farm dams, irrigation channels, and wetlands. It is relatively long-lived (up to two years) and feeds mainly on detritus and opportunistically on small fish, crustaceans, and other invertebrates (e.g. chironomids). *C. destructor* has been shown to accumulate mercury and arsenic in muscle tissue and is a useful indicator of metal contamination in aquatic environments (Lake & Sokol, 1986; Williams *et al*. 2009).

Brown trout (*Salmo trutta*)

S. trutta is an introduced species considered important for recreational angling in Victoria. This species inhabits cool, flowing streams and some lakes and reservoirs across the state. *S. trutta* feeds on freshwater invertebrates, wind-blown terrestrial insects and small fish (Allen *et al.* 2002). Previous studies in Victoria have demonstrated the potential for *S. trutta* living in mercury contaminated environments to accumulate higher than expected levels of mercury (Fabris, 2002).

Redfin perch (*Perca fluviatilis*)

Introduced from Europe, this species inhabits cool, slow flowing or still waters throughout Victoria. A carnivorous fish, *P. fluviatilis* feeds on crustaceans (including yabbies), zooplankton and other small fish. Individuals generally mature within 2-3 years and reach 40–50 cm in length and 1–2 kg in weight (Allen *et al.* 2002). Due to its feeding preferences and trophic status, *P. fluviatilis* is likely to accumulate heavy metals in contaminated environments (Miller *et al.* 2013).

Flathead gudgeon (*Philypnodon grandiceps*)

P. grandiceps is a native species common in moderate flowing streams and lakes in Victoria. Their diet consists of small fish, crustaceans, insects, and tadpoles. In small waterways, this species can be at the top of the food chain. Although flathead gudgeon are not targeted by recreational anglers, this species was tested because it is likely to provide information about the potential for bioaccumulation of heavy metals and because it is consumed by predatory fish including *P. fluviatilis*.

Common carp (*Cyprinus carpio*)

C. carpio is common in the Murray-Darling system and prefers still or slow-flowing waters with abundant aquatic vegetation (Allen *et al.* 2002). It is long-lived and feeds on crustaceans, insects, molluscs, and seeds. Carp are also known to feed on detritus and aquatic plants when food is in short supply. This species may occasionally be eaten by recreational anglers and was tested in this study.

3.4.2 Sampling method: electrofishing

Electrofishing was used to temporarily stun nearby fish for a few seconds, allowing them to be netted. Electrofishing was conducted using a 24-volt portable Smith-Root® LR20B backpack electrofisher. Output, frequency and duty cycle settings were adjusted to suit the electrical conductivity and water depths at each site. Sampling locations were fished in an upstream direction and across a range of available habitats such as pools, backwaters, and among aquatic vegetation. At two sites on the Loddon River (GMM and GMO), an electrofishing boat was used to collect large fish from the open water (Figure 5). Stunned animals were retrieved from the stream with the aid of a dip net. Non-target animals were returned to the water immediately. Three sites on the Loddon River between Bridgewater and Lake Laanecoorie were unsuitable for backpack and boat electrofishing due to water depth and the presence of large snags. At these sites, animals were collected using fyke nets (Section 4.4.3 below).

Figure 5 – Boat-based electrofishing on the Loddon River

3.4.3 Sampling method: bait trapping and netting

At each site five rectangular bait traps and 10 pyramid traps (Figure 6) were baited with ox heart and set in pools and slow-flowing sections to capture small animals including *C. destructor* and *P. grandiceps*. Traps were set late in the evening and retrieved the following morning. At three sites on the Loddon River, between Bridgewater and Lake Laanecoorie, two single and one double-winged (5 m) fyke nets were deployed where electrofishing could not be conducted. Fyke nets were checked regularly throughout deployment in order to maintain the welfare and prevent mortality of air-breathing animals such as platypus, rakali and turtles.

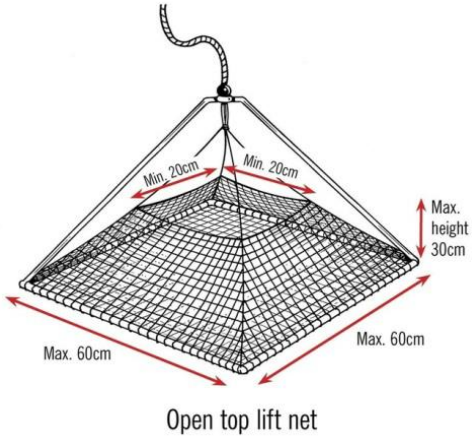

Figure 6 - Pyramid trap used to sample crayfish

3.4.4 Animal handling and sample preparation

Captured animals were held in 20L plastic pails filled with stream water and aerated using a battery air pump. Animals were euthanized by bathing them in a lethal dose of anaesthetic (AQUIS-S® active ingredient isoeugenol) dissolved in water. Anaesthetic baths ranged from 2 to 10 litres in volume and contained the recommended dose of AQUI-S® (175 mg/l for fish and 250 mg/l for crustaceans). Animals were immersed in anaesthetic for a minimum of 20 minutes or until they stopped responding to physical touch.

Yabbies were sexed, weighed to the nearest gram, and measured (occipital carapace length) before a sample of abdominal muscle (approx. 2-5 g of tissue) was removed without the carapace. In the case of fish, total length and weight were recorded before removing a sample of axial muscle (approx.10 g) using a filleting knife. All tissue samples were stored in 50 ml conical polypropylene centrifuge tubes and preserved by freezing at -20°C prior to laboratory processing.

3.4.5 Fish age determination

Fish Ageing Services Pty. Ltd. provided age estimates for samples of *S. trutta*, *P. fluviatilis*, and *C. carpio*. Fish age is determined by analysing growth patterns in the otoliths (ear stones) found behind the brain in bony fishes. The age of a fish is determined by counting the number of opaque zones (annuli) from the primordium to the otolith edge (Figure 7). Figure 7 shows the differences in growth rates shown in an otolith; the transparent zones represent periods of faster growth and the dark bands, periods of slower growth. Age estimates are made for each individual fish by counting the annuli.

Otoliths were extracted, cleaned, dried and embedded in blocks of clear casting resin. They were then sectioned with a modified high speed gem cutting saw using a 250 µm thick diamond impregnated blade. Sections from each otolith were mounted on clear glass microscope slides under glass coverslips using resin. Annual increments were then counted on the ventral side of the section from the primordium to the otolith edge adjacent to the sulcus.

Figure 7 –Transverse section of an otolith extracted from a 3 year old fish (*P. fluviatilis*). Age estimates are based on the number of annuli as marked

3.4.6 Tissue chemical analysis and quality control

Tissue samples were analysed for total mercury and total arsenic by staff at the Institute for Applied Ecology, University of Canberra. The samples were extracted using the extraction protocol described in Maher et al. (2001) and then analysed using an inductively coupled plasma mass spectrometry (ICP-MS) instrument (Perkin Elmer DRC-e). For quality assurance and quality control purposes during the extraction and analysis of the samples, 2 blanks and 2 certified reference materials (CRM) were used for every 20 samples and the instrument was optimised prior to each analytical run. CRMs used for the analysis were: CRM IAEA 407 (fish homogenate); CRM TORT 2 (lobster hepatopancreas); and CRM DOLT 4 (dogfish liver). Acceptance criteria for all recoveries on SRM's were met. Internal standards Indium, Terbium and Holmium were used as internal standards in addition to the internal standards described in Maher et al. (2001). Re-calibration was performed after 20 samples during the analysis. Metal concentrations in samples of fish and crustacean tissue were reported as milligrams per kilogram (mg/kg) wet weight (ww) of sample.

3.4.7 Comparison of tissue metal concentrations with Australia New Zealand Food Standards Code

The *Australia New Zealand Food Standards Code 1.4.1* sets a maximum level (ML) for metal and non-metal contaminants in specified commercial foods including MLs for mercury and arsenic in fish and seafood products (FSANZ 2015).

MLs are risk-based guideline values that are intended to be applied to lots of commercially sold fish in order to ensure consumer health protection at a population level. Application of MLs for mercury varies depending on the lot size and the species of fish being tested.

For the purpose of this study which is a targeted investigation of certain recreationally caught fish species, MLs prescribed in the Food Standards Code provide a useful screening tool that can be applied to each individual fish to identify where further investigation and human health risk assessment may be warranted. As such, an exceedance of the ML in one or more fish does not indicate that recreationally caught fish pose a risk to consumers. Rather, it would be considered a trigger to identify reaches for further investigation.

The total mercury ML used in the study was 0.5 mg/kg fresh weight. The tissue mercury concentration of each individual fish is compared against this value.

The Food Standards Code prescribes a ML for inorganic arsenic in fish and crustaceans of 2 mg/kg wet weight as this is the component of arsenic considered to pose a potential risk to consumer health. In the absence of a ML for total arsenic, the current study conservatively compares the total arsenic concentration of each individual fish against 2 mg/kg.

4. Results

4.1 Mercury and arsenic in sediments

Mercury was present in sediments collected from all reaches except in samples from Thougla Creek which were below the limits of laboratory detection (<0.05 mg/kg, Table 3). Nearly half of all sites monitored (17 out of 35) reached or exceeded the ISQG low trigger value (0.15 mg/kg) for mercury in sediment (Table 3). Sediments from all sites on the Loddon River, Big River, and Sailors Creek contained mercury in concentrations above the ISQG low trigger value (except for a single site, GMQ, on Sailors Creek). Site GMM on the Loddon River exceeded the high trigger value (1 mg/kg) for mercury in sediments (Table 3, Figure 8).

Arsenic concentrations varied significantly between sites and among the sampled reaches (Table 3). Mean sediment arsenic concentrations ranged from 9.3 and 110.8 mg/kg between reaches and 26 sites exceeded the ISQG low trigger value for arsenic (20 mg/kg) while three sites exceeded the high trigger value (70 mg/kg).

Table 3 – Concentrations (expressed as mg/kg dry wt.) of total arsenic (As) and total mercury (Hg) in sediment samples. Mean and standard error for all sites sampled within a reach are shown in bold. Standard errors are shown in parentheses. N = number of samples collected. * = value above ISQG low trigger value; ** = value above ISQG high trigger value

Reach/Site	As (mg/kg)	Hg (mg/kg)	N
Avoca River	**9.3 (1.5)**	**0.055 (0.01)**	**3**
AVOCA RIVER AT END OF POUND LANE (HIE)	9.0	0.05	1
AVOCA RIVER D/S CHERRY TREE ROAD (HHJ)	12.0	<0.05	1
AVOCA RIVER D/S MILLS LANE (HHV)	7.0	0.06	1

Reach/Site	As (mg/kg)	Hg (mg/kg)	N
Big River	**110.8 (41.9)****	**0.19 (0.08)***	**5**
BIG RIVER AT OMEO HIGHWAY (AAD)	195.0**	0.23*	2
BIG RIVER D/S BUNDARA RIVER (ABT)	55.0*	0.16*	1
BIG RIVER DS MIDDLE CREEK (AHS)	43.0*	0.15*	1
BIG RIVER OFF OMEO HIGHWAY, ANGLERS REST (AHR)	66.0*	0.16*	1
Buckland River	**15.3 (1.9)**	**0.05 (0)**	**3**
BUCKLAND RIVER DS OF ROCKY POINT CREEK (CIA)	14.0	0.05	1
BUCKLAND RIVER US OF BUCKLAND ROAD BRIDGE (CIB)	19.0	<0.05	1
BUCKLAND RIVER US OF CLEAR CREEK TRACK (CHZ)	13.0	<0.05	1
Coliban River	**36.7 (13.7)***	**0.11 (0.04)**	**3**
COLIBAN RIVER AT MALMSBURY PUMPING STATION (FJT)	23.0*	0.09	1
COLIBAN RIVER AT SWING BRIDGE ROAD (TARADALE) (FGP)	23.0*	0.08	1
COLIBAN RIVER AT THE CASCADES (FJV)	64.0*	0.15*	1
Livingstone Creek	**37.0 (8.5)***	**0.08 (0)**	**3**
LIVINGSTONE CREEK AT PARISH LANE (AGD)	40.0*	<0.05	1
LIVINGSTONE CREEK OFF OLD OMEO HIGHWAY (AHV)	50.0*	0.08	1
LIVINGSTONE CREEK OFF OMEO VALLEY ROAD (AHU)	21.0*	<0.05	1
Loddon River	**30.8 (4.5)***	**0.61 (0.46)***	**8**
LODDON RIVER AT ARNOLD (GMP)	25.0*	0.34*	1
LODDON RIVER AT BRIDGEWATER CAMPSITE (GMM)	34.5*	1.3**	2
LODDON RIVER AT ELMSFORD ROAD, POSEIDON (GMN)	25.0*	0.32*	1
LODDON RIVER DS LAANECOORIE RESERVOIR (GMO)	44.0*	0.59*	1
LODDON RIVER DS WIMMERA HWY BRIDGE AT NEWBRIDGE (GMK)	30.5*	0.40*	2
LODDON RIVER US OF END OF BROWNS ROAD (GML)	22.0*	0.21*	1
Mitta Mitta	**33 (0)***	**0.13 (0)**	**1**
MITTA MITTA RIVER AT HINNOMUNJIE BRIDGE (AHN)	33.0*	0.13	1
Ovens River	**53.5 (6.2)***	**0.16 (0.08)***	**4**
OVENS RIVER AT ASHWOOD AVENUE, BRIGHT (CIF)	61.0*	0.16*	1
OVENS RIVER AT MORGANS CREEK LANE (CIG)	59.0*	0.14	1
OVENS RIVER AT PINCH GUT LANE, HARRIETVILLE (CII)	59.0*	0.19*	1
OVENS RIVER BETWEEN MERRIANG & MYRTLEFORD(CIJ)	35.0*	0.13	1
Sailors Creek	**67.7 (11.7)***	**0.44 (0.2)***	**7**
SAILORS CREEK AT BRYCE'S FLAT (GHK)	79.5**	0.46*	2
SAILORS CREEK AT CARROLS LANE (GMS)	58.0*	0.33*	1
SAILORS CREEK AT TWIN BRIDGES PICNIC AREA (GMR)	39.0*	0.42*	1
SAILORS CREEK AT WALLABY WALKING TRACK (GMQ)	20.0*	0.08	1
SAILORS CREEK DS OF HEPBURN-NEWSTEAD RD, SHEPARDS FLAT (GMH)	99.0**	0.67*	2
Thougla Creek	**14.7 (0.3)**	**<0.05**	**3**
THOUGLA CREEK AT MURRAY VALLEY HIGHWAY (AAZ)	15.0	<0.05	1
THOUGLA CREEK AT UPPER THOUGLA BRIDGE (AHO)	15.0	<0.05	1
THOUGLA CREEK U/S GRAYS TRACK (ABP)	14.0	<0.05	1

4.2 Mercury and arsenic in tissue

Biological sampling was conducted along three priority reaches (Loddon River, Sailors Creek and Big River) that contained sediments exceeding ISQG trigger values for mercury (Table 3). The following section provides a detailed description of biological sample results collected from each priority reach.

4.2.1 Loddon River

A total of 33 yabbies (*C. destructor),* eight carp (*C. carpio*), 10 redfin (*P. fluviatilis*), and 34 flathead gudgeon (*P. grandiceps*) were captured from five sites located along the Loddon River between the outlet of Lake Laanecoorie and the town of Bridgewater (Figure 8).

Cherax destructor

C. destructor was collected from all study sites on the Loddon River except site GMO (Figure 8). Body size (OCL) for all individuals ranged between 12 and 36 mm ($\bar{x}$ = 22 mm). Total mercury concentrations in samples of the abdominal muscle ranged between 0.05 and 0.2 mg/kg ww and were below the ML ($\bar{x}$ = 0.09 mg/kg ww, Figure 9). Total arsenic concentrations ranged between 0.09 mg/kg ww and 0.4 mg/kg ww and were well below the ML ($\bar{x}$ = 0.23 mg/kg ww, Figure 10).

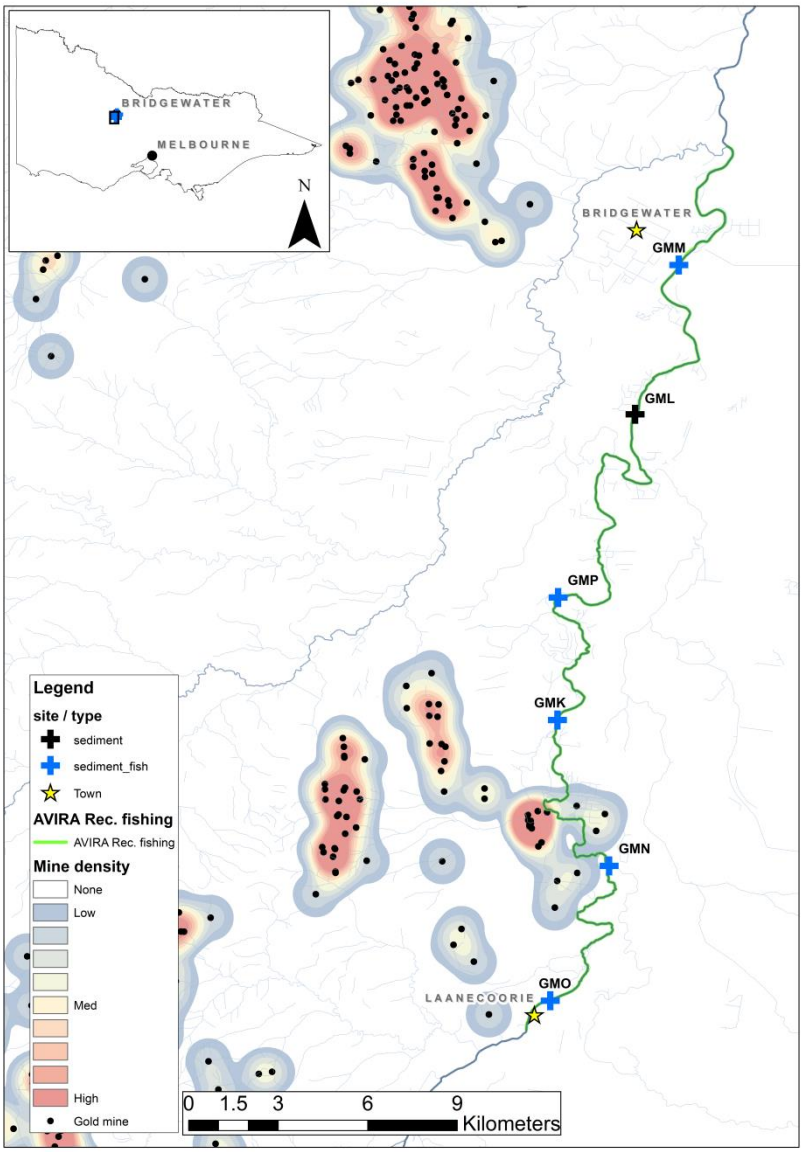

Figure 8 – Gold mine locations, mine density, and monitoring sites along the Loddon River

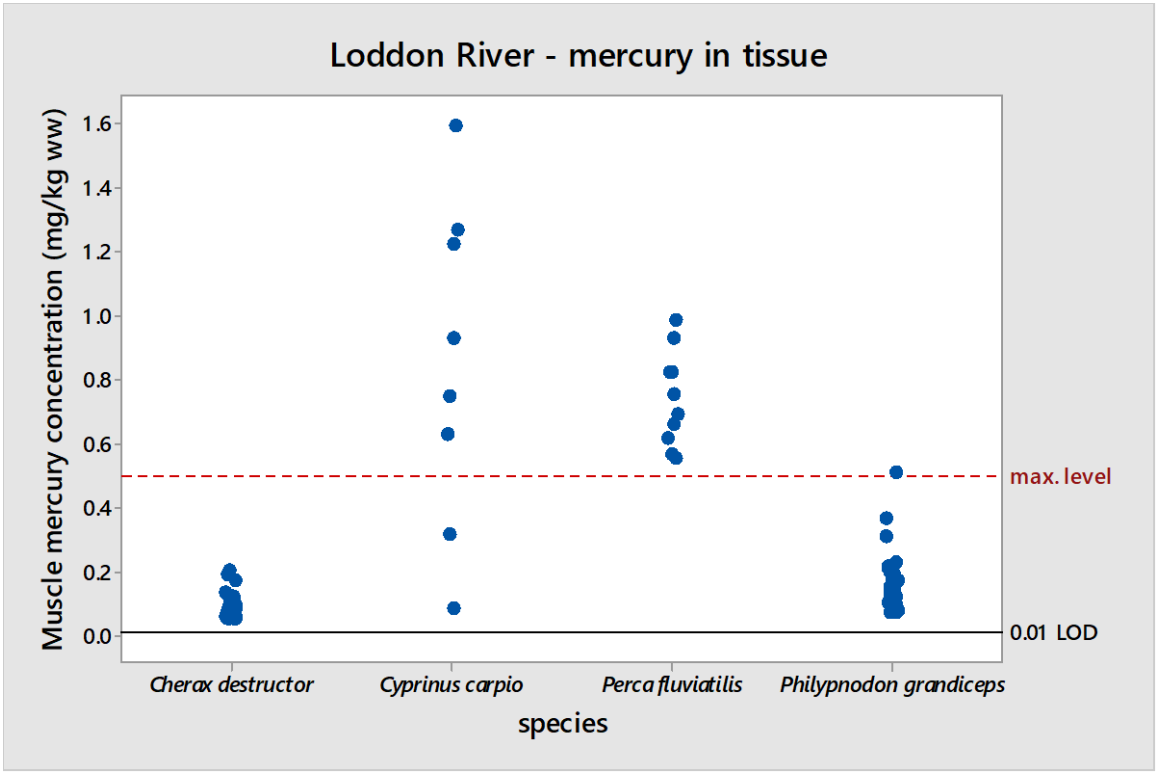

Figure 9 – Mercury in tissue samples from fish and crayfish obtained from the Loddon River. LOD refers to limit of laboratory detection

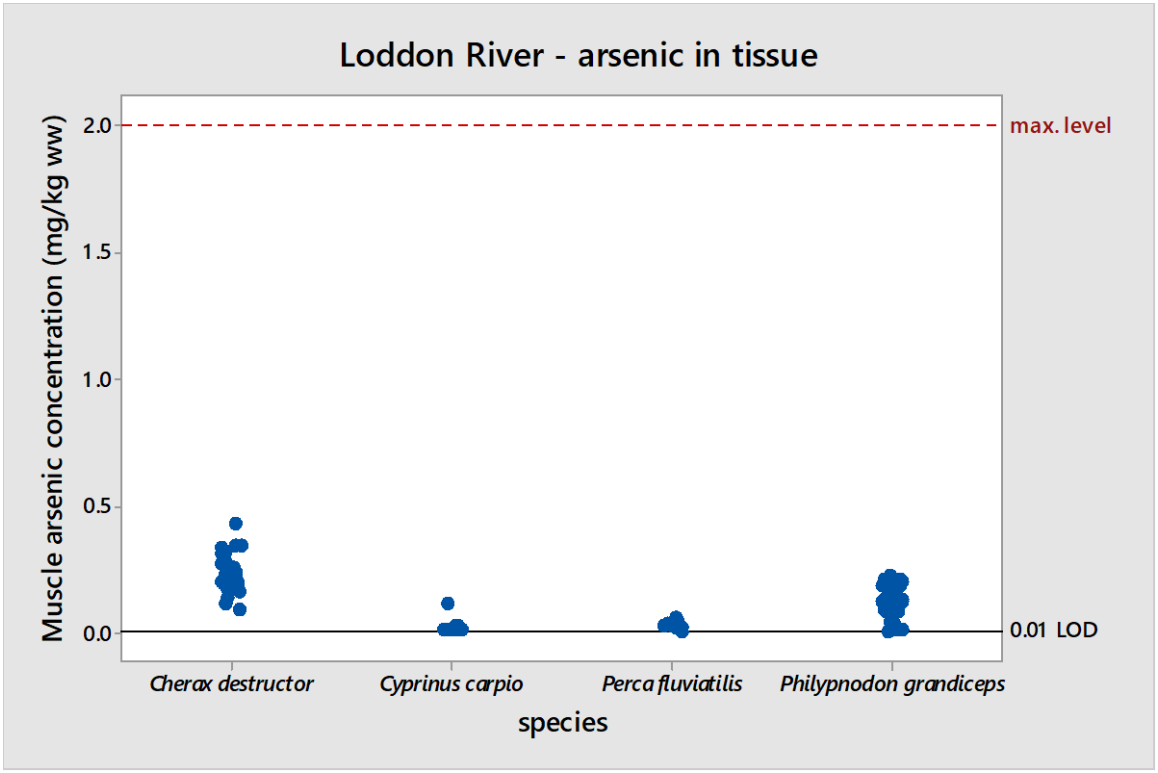

Figure 10 – Arsenic in tissue samples from fish and crayfish obtained from the Loddon River. LOD refers to limit of laboratory detection

Cyprinus carpio

A total of 8 samples of *C. carpio* were collected from sites GMM and GMO (Figure 8). Total length of individuals ranged from 290 mm to 730 mm and age between 2 and 23 years. Arsenic concentrations in carp tissue were low and ranged between <0.01 mg/kg ww and 0.11 mg/kg ww ($\bar{x}$ = 0.03 mg/kg ww, Figure 10). There was greater variability in total mercury concentration which ranged between 0.09 mg/kg ww and 1.59 mg/kg ww. The mean mercury concentration for all samples was 0.85 mg/kg ww, which exceeded the ML (Figure 9). A regression analysis was used to explore the relationship between mercury concentrations in tissue and fish age. This analysis revealed a significant positive relationship between age and mercury concentration in tissue of *C. carpio* (p=0.002, r^2= 0.80, Figure 11) and suggests that carp aged over 8 years are more likely to contain mercury above the ML compared with younger fish.

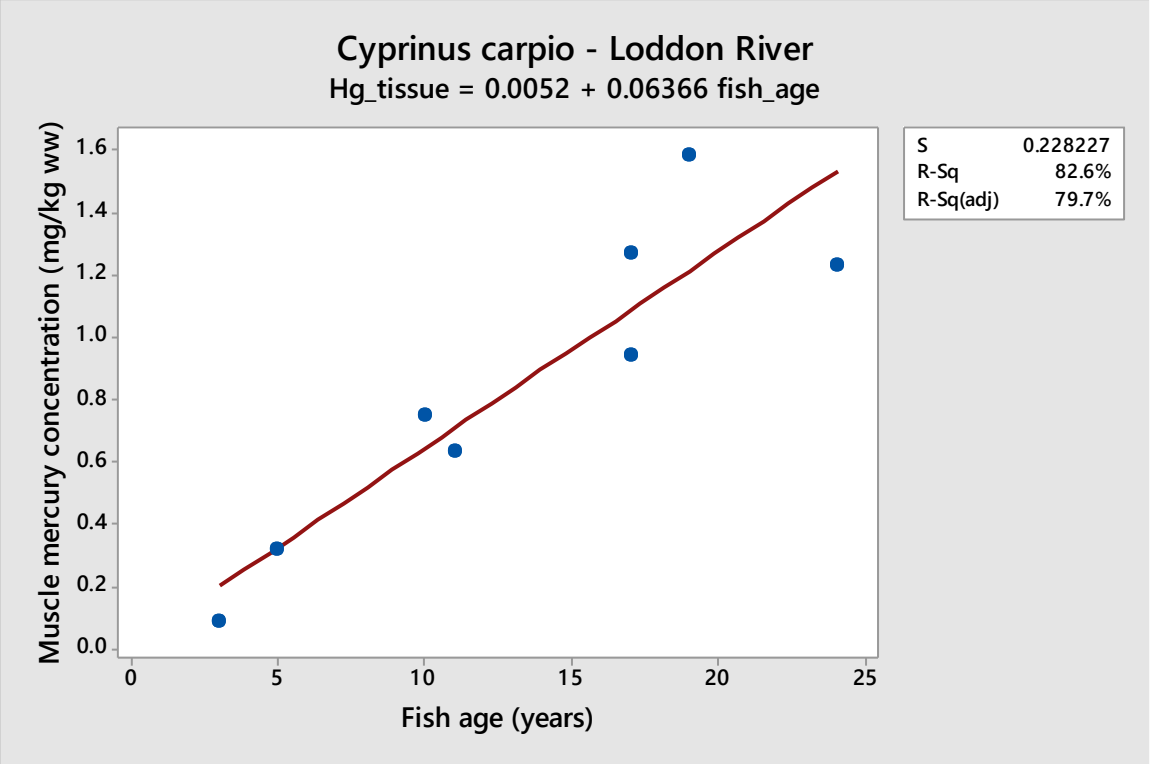

Figure 11 – Relationship between age (years) and mercury concentration (mg/kg ww) in axial muscle from common carp (*Cyprinus carpio*) obtained from the Loddon River

Perca fluviatilis

All samples of *P. fluviatilis* (n = 10) were collected from a single site (GMM) in the town of Bridgewater (Figure 8). Total lengths ranged from 150 to 295 mm and age from 1 to 3 years. Total arsenic concentrations were below the ML and ranged from <0.01 mg/kg ww to 0.06 mg/kg ww ($\bar{x}$ = 0.03 mg/kg, Figure 10).Total mercury concentrations in muscle tissue ranged between 0.56 mg/kg ww and 0.99 mg/kg ww ($\bar{x}$ = 0.74 mg/kg, (Figure 9) which was above the ML. A regression analysis showed no significant relationship between age or total length and mercury concentration in muscle tissue (p= 0.19, r^2= 0.11 for age, p = 0.10, r^2= 0.21 for length).

Philypnodon grandiceps

A total of 34 samples of *P. grandiceps* were collected from all sites except from site GMO (Figure 8). Lengths ranged between 45 and 105 mm. Total mercury and arsenic concentrations in tissue were both low; mercury ranged between 0.07 mg/kg ww and 0.51 mg/kg ww ($\bar{x}$ = 0.16 mg/kg ww, Figure 9) and arsenic ranged from <0.01 mg/kg ww and 0.23 mg/kg ww ($\bar{x}$ = 0.11 mg/kg, Figure 10). Note that, sample means did not exceed the ML's.

4.2.2 Sailors Creek

A total of 50 yabbies (*C. destructor*) and a single brown trout (*S. trutta*) were captured from five sites along Sailors Creek near the town of Daylesford (Figure 12).

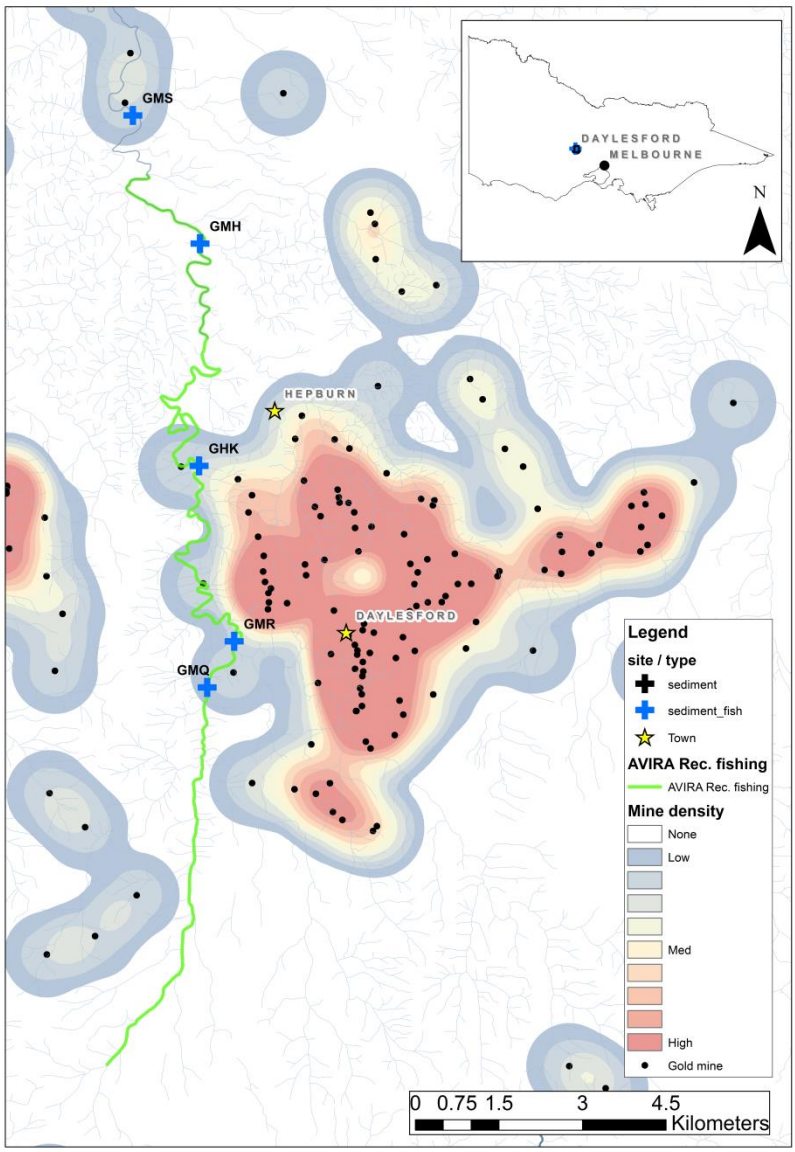

Figure 12 - Gold mine locations and monitoring sites on Sailors Creek

Cherax destructor

Ten samples of *C. destructor* were collected from each of the five sites on Sailors Creek (Figure 12). Body size (OCL) ranged between 17 and 44 mm ($\bar{x}$ = 29.6 mm). Total mercury concentration in the abdominal muscle tissue ranged between 0.06 and 0.44 mg/kg ww ($\bar{x}$ = 0.2 mg/kg ww, Figure 13). Total arsenic ranged between 0.07 and 0.57 mg/kg ww ($\bar{x}$ = 0.29 mg/kg ww). Mean sample concentrations for mercury and arsenic were below the MLs (Figure 14).

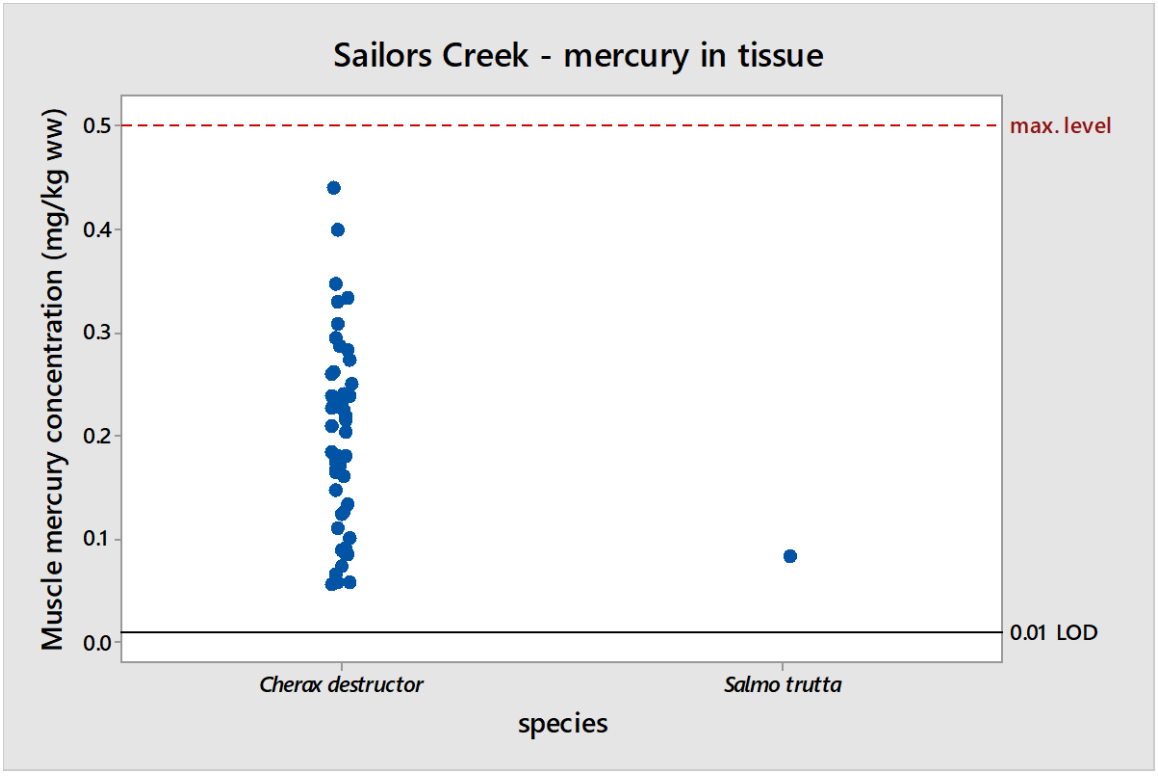

Figure 13 - Mercury in tissue samples from fish and crayfish obtained from Sailors Creek. LOD refers to limit of laboratory detection

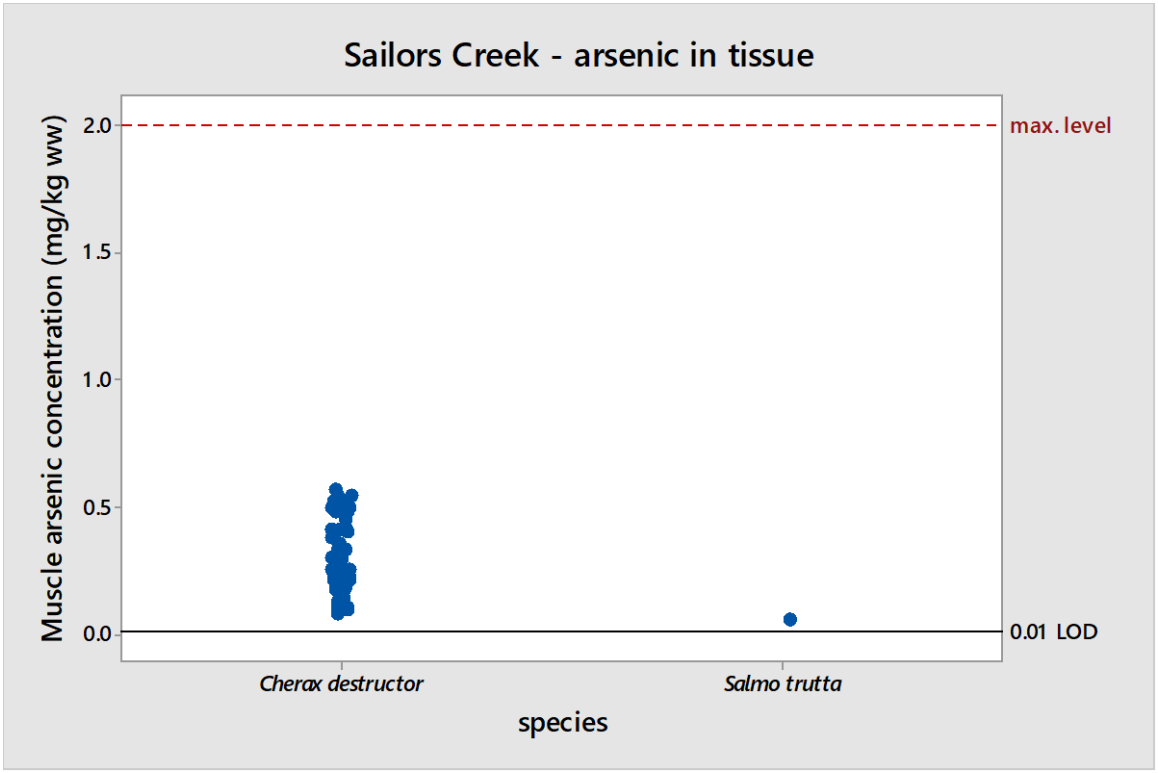

Figure 14 - Arsenic in tissue samples from fish and crayfish obtained from Sailors Creek. LOD refers to limit of laboratory detection

Salmo trutta

A single trout measuring 180 mm and weighing 76 grams was captured at site GHK (Figure 12). The axial muscle contained low concentrations of mercury (0.08 mg/kg ww) and arsenic (0.06 mg/kg ww) which was below the MLs (Figure 14).

4.2.3 Big River

Twenty three trout (*S. trutta*) were obtained from Big River at sites upstream of Anglers Rest (Figure 15). No other target species were obtained from sampling sites on Big River.

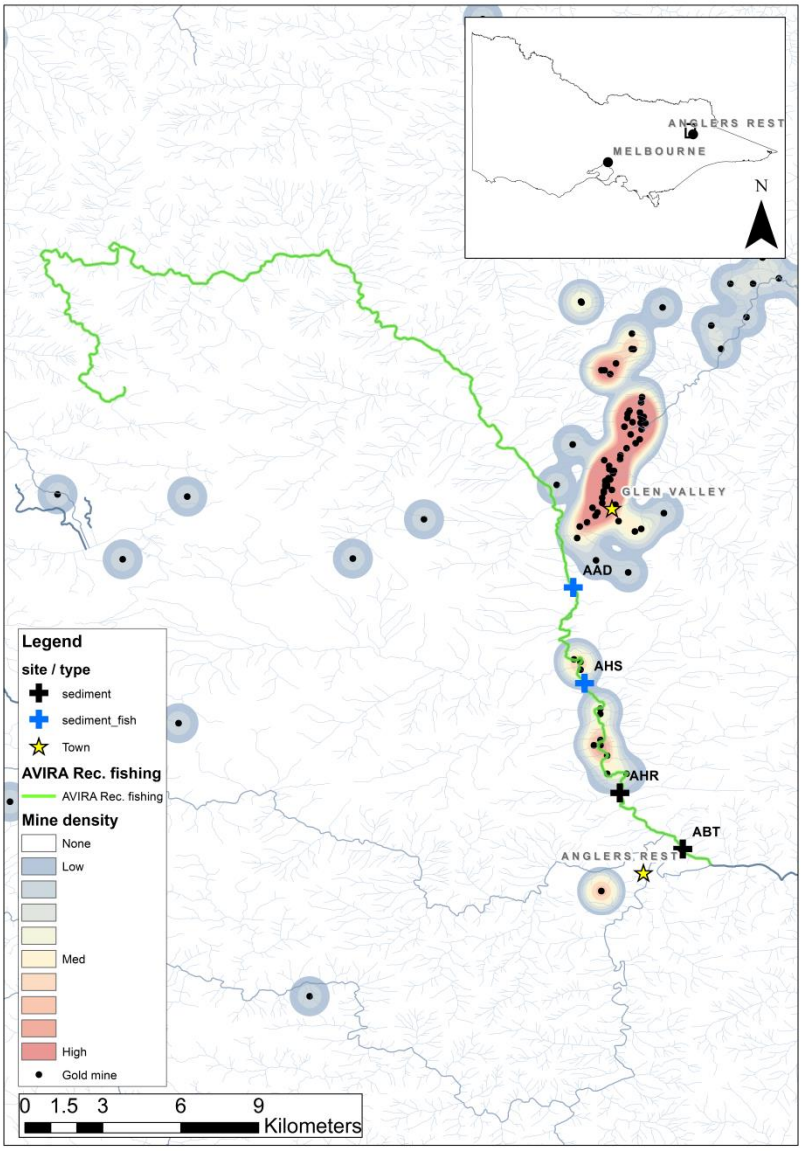

Figure 15 - Gold mine locations and monitoring sites on Big River

Salmo trutta

The total length of individuals ranged from 140 mm to 210 mm and ages from 1 to 2.4 years. Mercury concentration in axial muscle tissue ranged between <0.01 mg/kg ww and 0.32 mg/kg ww ($\bar{x}$ = 0.04 mg/kg ww). Total arsenic concentration ranged between <0.01 and 0.4 mg/kg ww ($\bar{x}$ = 0.07 mg/kg ww). Both mercury (Figure 16) and arsenic (Figure 17) levels were below the MLs.

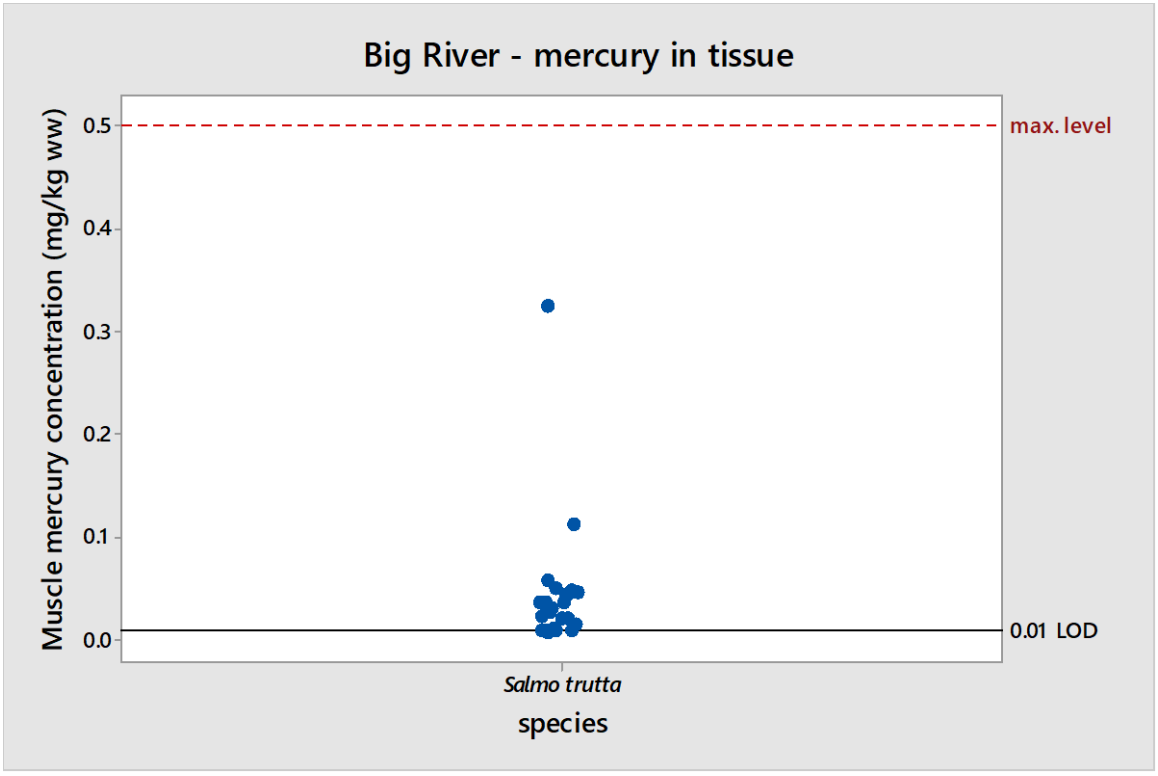

Figure 16 – Mercury in tissue samples from fish obtained at Big River. LOD refers to limit of laboratory detection

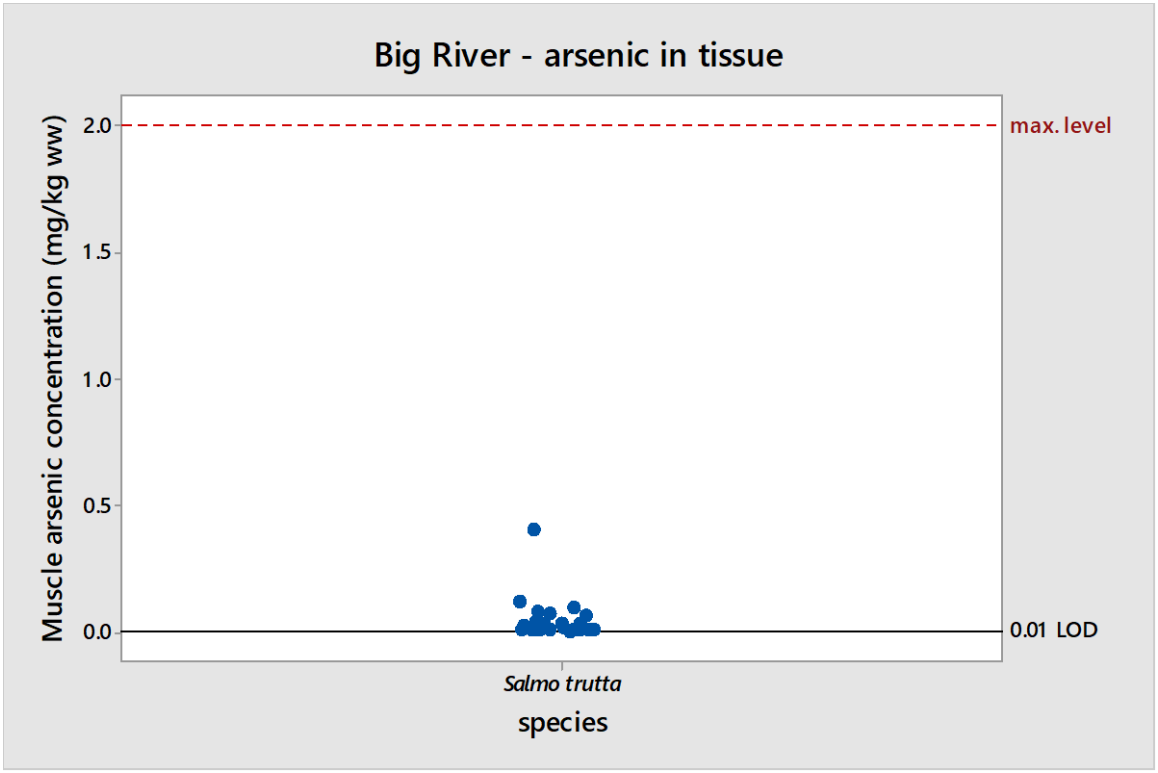

Figure 17 – Arsenic in tissue samples from fish obtained at Big River. LOD refers to limit of laboratory detection

4.3 Mining density as a predictor of contamination

The relationship between gold mine density in the upstream catchment (i.e. no. of mines per Ha) and the level of arsenic and mercury in sediment and tissue was explored using regression. Tissue data from samples of *C. destructor* were used in this analysis as this was the most commonly tested animal in the study. Significant positive linear relationships were observed between gold mine density and mean concentration of both arsenic ($r^2 = 0.846$, $p = < 0.001$) and mercury ($r^2 = 0.591$, $p = 0.003$) in abdominal muscle. Conversely, gold mine density did not correlate well with sediment concentrations of arsenic ($r^2 = 0.037$, $p = 0.116$) or mercury ($r^2 = 0.038$, $p = 0.114$).

5. Discussion

The results of this study show evidence of mercury and arsenic contamination in rivers and streams in historical gold mining regions. Monitoring revealed that many reaches contain levels of sediment-bound mercury and arsenic that are above environmental guideline values. Sediments from nearly half of all sites monitored exceeded the ISQG low trigger value for mercury and were above the naturally expected background concentrations (0.01 - 0.1 mg/kg) reported in Hart (1982). Arsenic concentrations were above the ISQG low trigger value at nearly 75% of sites monitored. Examining the occurrence of historic gold mining in the catchments of high-value reaches was therefore successful in identifying sites containing elevated levels of these sediment contaminants. However, the density of mines within the catchment was not a good predictor of sediment-bound mercury or arsenic concentrations. Sediment-bound metal concentrations are likely to vary spatially and across the range of particle sizes present at a site. Therefore, to fully characterise contamination, sediment may need to be collected from multiple locations within a site. An average measure of contaminants over both space and time may be required to explore whether a relationship between mine density and sediment contamination exists. Nonetheless, occurrence of upstream mining can be used successfully to target sampling for sediment contamination.

Environmental guideline values such as the ISQG are designed to trigger further investigation when exceeded. In this case, biological testing was conducted to assess whether elevated levels of sediment-bound mercury and arsenic found in three reaches (Big River, Sailors Creek and Loddon River) was reflected in biota. For total arsenic, concentrations observed in fish and the Common yabby (*C. destructor*) were generally low at all locations. Samples of *C. destructor* showed some tendency to accumulate arsenic which is likely to be sourced from the diet (e.g. chironomids) or through the absorption of soluble arsenic via the gills and digestive tract (Rahman *et al.* 2012; Williams *et al.* 2009). However, the levels of total arsenic observed in *C. destructor* were rarely above 0.5 mg/kg and well below the 2 mg/kg ML (Figures 10, 14, and 17). Levels were similarly low in fish and this finding is consistent with evidence that arsenic does not tend to biomagnify across successive levels in the aquatic food chain (Rahman *et al.* 2012).

For total mercury, biological samples obtained from Big River and Sailors Creek were all below the ML despite sediment-bound mercury being observed above the ISQG low trigger value. Mercury concentrations in tissue samples from *S. trutta* collected from Big River were low, and only a single sample was collected from Sailors Creek which was also below the ML. *C. destructor* was not found at the Big River monitoring sites but was present in Sailors Creek. The levels of mercury in the abdominal tissue of *C. destructor* living in Sailors Creek were below the ML but the presence of mercury in these samples indicates that biological uptake is occurring in this reach. Further study of whether sediment contamination is reflected in fish living in Sailors Creek may be required. However the lack of available fish may negate the potential risks to human consumers at this point in time.

For the Loddon River, concentrations of mercury were generally low in *C. destructor* and *P. grandiceps*, but samples obtained from predatory redfin perch and omnivorous carp exceeded the ML. Elevated levels of mercury were measured in young redfin perch (1-3 years), which is consistent with studies that show consumers at high trophic levels tend to accumulate the greatest amounts of mercury within the aquatic food chain (Mason *et al.* 2000; Chasar *et al.* 2009). *C. carpio* was also found to contain elevated levels of mercury. This is not surprising as carp are omnivorous and bioaccumulate mercury as they feed on animal prey including benthic insects, molluscs, and crustaceans (Tabatabaie *et al.* 2011). Mercury concentrations in *C. carpio* were found to significantly increase with fish age (up to 23 years) which contrasts with the consistently high levels of mercury found in *P. fluviatilis* aged 1-3 years. The Loddon River is also home to golden perch (*Macquaria ambigua*) and Murray cod (*Maccullochella peelii*) which have a similar diet and trophic position to *P. fluviatilis* – this raises concern about the potential for these species to also contain high levels of mercury. The findings of this report should be considered from a human health risk assessment perspective to determine if tailored advice is warranted regarding consumption of *P. fluviatilis* and *C. carpio* sourced from Loddon River. Consideration should also be given to the need for investigation of other fish species present in Loddon River that may also accumulate elevated mercury concentrations.

6. Conclusions and recommendations

This study was successful in using spatial data to identify priority waterways valued for recreational fishing that contained elevated levels of mercury and arsenic within sediments, and in some cases, biota. It is highly likely that historical mines, which can remain significant sources of pollution for many years, are the source of these contaminants. The occurrence of gold mines in the upstream catchment may therefore be used to identify additional streams in Victoria that are likely to be affected by historical mining pollution. However, this method of identifying contaminated sites is limited by the lack of information about the age of mines and mining practices in historical records. Sediment sampling should therefore continue to be used to confirm contamination at locations draining from historical mining regions. Importantly, elevated levels of arsenic and mercury in sediment were not always reflected in samples of tissue obtained from aquatic biota and this reflects the complexity of heavy metal cycling in stream ecosystems (Ward *et al*. 2010; Chasar *et al.* 2009, Mason *et al.* 1999, Rahman *et al.* 2012). Nonetheless, EPA's investigation has identified a section of the Loddon River containing fish (redfin perch and common carp) with levels of mercury above the ML. Following this study, EPA conducted further testing for mercury on two additional species of fish in the Loddon River (Murray cod and golden perch). The results in this report and additional testing data have enabled the Department of Health and Human Services to conduct a human health risk assessment and provide health advice on the consumption of fish from the Loddon River between Laanecoorie reservoir and Bridgewater.

For further information visit:

http://www.epa.vic.gov.au/your-environment/water/recreational-fishing/loddon-river

7. Acknowledgements

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Appendix 1. Site location details and sediment chemistry data from all sites.

Site	Name	Latitude	Longitude	ISC reach	Sample date	Hg (mg/kg)	As (mg/kg)
AAD	Big River at Omeo Highway	-36.8934	147.4636	01_ 29	11/6/2014	0.33	120
AAD	Big River at Omeo Highway	-36.8934	147.4636	01_ 29	30/10/2014	0.13	270
AAZ	Thougla Creek at Murray valley Highway	-36.1740	147.9319	01_ 22	10/6/2014	<0.05	15
ABP	Thougla Creek u/s Grays Track	-36.3335	147.9169	01_ 23	10/6/2014	<0.05	14
ABT	Big River d/s Bundara River	-36.9840	147.5015	01_ 28	11/6/2014	0.16	55
AGD	Livingstone Creek at Parish Lane	-37.0143	147.6000	01_ 30	11/6/2014	<0.05	40
AHN	Mitta Mitta River at Hinnomunjie Bridge	-36.9464	147.6067	01_ 26	31/10/2014	0.13	33
AHO	Thougla Creek at Upper Thougla Bridge	-36.3037	147.9001	01_ 23	10/6/2014	<0.05	15
AHR	Big River off Omeo Highway, Anglers Rest	-36.9646	147.4797	01_ 28	11/6/2014	0.16	66
AHS	Big River d/s Middle Creek	-36.9266	147.4675	01_ 28	30/10/2014	0.15	43
AHU	Livingstone Creek off Omeo Valley Road	-36.9677	147.6052	01_ 30	12/6/2014	<0.05	21
AHV	Livingstone Creek off old Omeo Highway	-37.0898	147.3729	01_ 30	12/6/2014	0.08	50
CHZ	Buckland River upstream of Clear Creek Track	-36.8913	146.8873	03_ 44	13/6/2014	<0.05	13
CIA	Buckland River downstream of Rocky Point Creek	-36.8538	146.8605	03_ 44	13/6/2014	0.05	14
CIB	Buckland River upstream of Buckland Road bridge	-36.7959	146.8493	03_ 44	13/6/2014	<0.05	19
CIF	Ovens River at Ashwood Avenue, Bright	-36.7178	146.9446	03_ 06	12/6/2014	0.16	61
CIG	Ovens River at Morgans Creek Lane	-36.7272	146.9810	03_ 06	12/6/2014	0.14	59
CII	Ovens River at Pinch Gut Lane, Harrietville	-36.8535	147.0802	03_ 07	12/6/2014	0.19	59
CIJ	Ovens River between Merriang and Myrtleford	-36.5528	146.7073	03_ 07	12/6/2014	0.13	35
FGP	Coliban River at Swing Bridge Road Taradale	-37.1278	144.3595	06_ 19	11/6/2014	0.08	23
FJT	Coliban River at Malmsbury pumping station	-37.1914	144.3802	06_ 19	11/6/2014	0.09	23
FJV	Coliban River at the cascades	-37.1017	144.4100	06_ 19	11/6/2014	0.15	64
GHK	Sailors Creek at Bryce's Flat	-37.3177	144.1203	07_ 28 tributary	6/6/2014	0.48	84
GHK	Sailors Creek at Bryce's Flat	-37.3177	144.1203	07_ 28	07/10/2014	0.43	75
GMH	Sailors Creek , Shepards Flat	-37.2818	144.1205	07_ 28	6/6/2014	0.62	88
GMH	Sailors Creek , Shepards Flat	-37.2818	144.1205	07_ 28	07/10/2014	0.71	110
GMJ	Lake Daylesford at south end, Daylesford	-37.3506	144.1401	07_ 28	6/6/2014	0.58	59
GMK	Loddon River at Newbridge	-36.7402	143.9012	07_ 07	10/6/2014	0.48	42
GMK	Loddon River at Newbridge	-36.7403	143.9012	07_ 07	08/10/2014	0.31	19
GML	Loddon River upstream of Browns Road	-36.6482	143.9245	07_ 07	10/6/2014	0.21	22
GMM	Loddon River at Bridgewater campsite boat ramp	-36.6032	143.9377	07_ 07	10/6/2014	1.1	51
GMM	Loddon River at Bridgewater campsite boat ramp	-36.6032	143.9377	07_ 07	09/10/2014	1.5	18
GMN	Loddon River at Elmsford Rd, Poseidon	-36.7843	143.9167	07_ 07	09/10/2014	0.32	25
GMO	Loddon River d/s Laanecoorie Reservoir	-36.8249	143.8990	07_ 07	15/10/2014	0.59	44
GMP	Loddon River at Arnold	-36.7034	143.9014	07_ 07	08/10/2014	0.34	25
GMQ	Sailors Creek at Wallaby Walking Track	-37.3534	144.1216	07_ 28	06/10/2014	0.08	20
GMR	Sailors Creek at Twin Bridges picnic area	-37.3460	144.1260	07_ 28	06/10/2014	0.42	39
GMS	Sailors Creek at Carrols Lane	-37.2611	144.1096	07_ 27	07/10/2014	0.33	58
HHJ	Avoca River d/s Cherry Tree Road	-36.8841	143.5029	08_ 07	5/6/2014	<0.05	12
HHV	Avoca River d/s Mills Lane	-36.9967	143.4694	08_ 07	5/6/2014	0.06	7
HIE	Avoca River at end of Pound Lane	-37.0793	143.4615	08_ 07	5/6/2014	0.05	9