Metal contamination in fish and shellfish of the Derwent estuary

A summary of results to December 2020





The Derwent Estuary Program (DEP) is a regional partnership between local governments, the Tasmanian State Government, businesses, scientists, and community-based groups to share science for the benefit of our estuary. The DEP was established in 1999 and has been nationally recognised for excellence in coordinating initiatives to reduce water pollution, conserve habitats and species, monitor river health and promote greater use and enjoyment of the foreshore.

Our major sponsors include Brighton, Clarence, Derwent Valley, Glenorchy, Hobart and Kingborough councils, the Tasmanian State Government, TasWater, Tasmanian Ports Corporation, Norske Skog Boyer, Nyrstar Hobart Smelter and Hydro Tasmania.











Executive summary

One of the legacies of poor environmental management of the Derwent estuary is the accumulation of metals in fish, which poses a significant risk to environmental (DEP, 2015; Macleod and Coughanowr, 2019) and human health (Thrower and Eustace, 1973; Ratkowsky *et al.*, 1975; Dineen and Noller, 1995; DEP, 2015). Metal concentrations in Derwent seafood have been studied for decades (Green and Coughanowr, 2004; DEP, 2010, 2015). This report provides a summary of results from 2006 to 2020.

Principal management actions regarding metal release to the environment and the results of environmental and biota monitoring programs include:

- **Management:** Nyrstar Hobart has continued its onsite remediation with support from state and federal governments. Actions included:
 - Infrastructure construction to intercept stormwater and remove metals prior to its release to the Derwent
 - Construction of groundwater interception walls to slow the connectivity between metal-contaminated groundwater and the Derwent estuary
 - Drilling groundwater extraction bores, extracting and removing metals from contaminated groundwater
 - Sealing the floor of the electrolysis basin, formerly a significant source of ongoing metal contamination to groundwater
- Ambient water quality: Total zinc in ambient waters declined at 17 of 22 ambient water quality sampling sites between January 2007 and December 2019. Lower metal concentration in ambient waters is likely to be a result of a combination of factors, including management intervention listed above but with variability caused by river discharge and continual burial of the most heavily contaminated sediments beneath cleaner sediment, reducing the mobilization of metals from sediment into water.
- Mercury in wild flathead: 72% of legal sized flathead collected from the Derwent in 2018 exceeded the maximum level for mercury, however, the rolling 5-yearly mean mercury concentration in wild flathead declined consistently between the 2010-2014 period to the current rolling 5-year period. This sustained decline suggests declining ambient metal availability but may be related to differences in fish biometrics so until a more robust biometrics dataset is available, results should be considered cautiously.
- Wild fish other than oysters, mussels and flathead:
 - All recreationally targeted fish species sampled from the Derwent in the general wild fish survey of 2019 exceeded the relevant maximum level or generally expected level for at least one metal. Arsenic and zinc were the two metals detected in particularly high concentrations in most fish species, however thresholds for copper and mercury were also exceeded in some species.
 - Different finfish species accumulate different metals. Australian salmon are amongst the species with the highest concentrations of selenium, lead, cadmium and chromium, while mercury is highest in trout, bream and eel. Lead is high in whiting and urchins, crayfish are highest in arsenic and copper and abalone are highest in copper as well as zinc and chromium.
 - Generally, there does not appear to be a difference in metal accumulated by fish collected from mid versus lower-Derwent sites, so health advice applies throughout the Derwent estuary as far as Tinderbox and the Iron Pot, including Ralphs Bay.
 - The concentration of lead, selenium and cadmium appear to have increased in trout and bream since 2007 and it is unclear whether differences between surveys represent different environmental metal availability or other factors.

- Metals in wild oysters and mussels:
 - Cadmium, copper, lead and zinc all exceeded relevant maximum levels or generally expected levels for either wild mussels or wild oysters from sites throughout the Derwent, including the lower western shore.
 - Shellfish harvested from sites closer to the zinc smelter site consistently had higher metal body burdens.
- Metals in deployed oysters:
 - Oysters deployed for six weeks each summer between 2005 and 2019 consistently accumulated metal concentrations such that maximum levels or generally expected levels were exceeded.
 - Deployed oysters accumulated progressively more zinc with increasing proximity to the zinc smelter.
 - Results were variable, although zinc, mercury and lead appear to have declined in oysters deployed to surface waters of Elwick Bay, which may be related to declining ambient zinc availability as detected in ambient water quality monitoring.

Whilst there are some promising signs of reducing metal accumulation, metals remain in the flesh of all wild seafood species collected from throughout the Derwent such that the public are advised by the Director of Public Health as follows:

- Do not consume any shellfish or bream from the Derwent, including Ralphs Bay
- Other fish from the Derwent should not be eaten more than twice a week and the following should further limit their consumption to once a week:
 - Pregnant and breastfeeding women
 - Women who are planning to become pregnant
 - Children aged six years and younger
- When eating fish from the Derwent, it is best to avoid eating fish from other sources in the same week.

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1 Introduction

Industrial activities such as zinc smelting at Lutana, gathers metal-rich rock for processing and this activity poses a variable risk to adjacent receiving environments depending on the quality of environmental management. Once metals enter the environment, they pose persistent toxic health risks throughout the ecosystem (Rainbow *et al.*, 2011; de Souza Machado *et al.*, 2016), one symptom of which is the accumulation of metals in fish and shellfish tissues. Metal accumulation can have sublethal impacts on the organisms themselves (Edge *et al.*, 2012) and pose a health risk to others in the food web, including humans (FSANZ, 2016).

Local organisms can indicate metal availability and can be monitored to determine human health risks associated with their consumption (Wilson, 1994), as well as potentially providing some indication of whether metal availability is changing in response to management action (USEPA, 2000). Oysters, mussels and flathead were historically selected as the bioindicators in the Derwent to assess human health risks associated with recreational harvest and consumption. As sessile filter feeders, bivalves were considered likely to indicate the sitespecific biological availability of metals in the water column, while flathead were selected as a biomonitoring tool because they are the main recreationally targeted finfish species in Tasmania and were thought to have relatively high site fidelity (Green and Coughanowr, 2004).

This report details the current state of knowledge on metal concentrations in ambient waters and fish bioindicators. The authors are not toxicologists or public health professionals so any interpretation of results beyond comparison to FSANZ guidelines (2016) has been either approved or explicitly provided by the Tasmanian Department of Health.

1.1 Maximum metal levels in food

Food Standards Australia New Zealand (FSANZ) sets guidelines for metals in seafood using a combination of maximum levels for arsenic, cadmium, mercury, and lead, and generally expected levels for copper and zinc (FSANZ, 2016; Table 1-1). Maximum levels have been set only for those foods that provide significant contributions to total dietary exposure for a given contaminant and are based on human health risk calculations. Maximum and generally expected levels set for metal and metalloids refer to total concetrations, except for arsenic which refers to the toxic inorganic forms, arsenate and arsenite (Table 1-1; Sharma and Sohn, 2009). In this report, arsenic is reported as total arsenic, and therefore should be interpreted with caution.

Generally expected levels are not legally enforceable and were developed for those contaminant/commodity combinations with a low level of risk to the consumer and only where adequate data were available.

Table 1-1 National food guidelines for metal levels in seafood (FSANZ, 2016)

		Generally Expected Levels (median/90 percentile) (mg/kg)				
	As (inorganic)	Cd	Hg	Pb	Cu	Zn
	·		0.5 for most fish (1.0 for sharks			
	2	no set	and other			
Fish		limit	specified fish)	0.5	0.5/2	5/15
Molluscs	1	2	0.5*	2	3/30	130/290
		no set				
Crustacea	2	limit	0.5*	no set limit	10/20	25/40

Note: GELs are from the FSANZ Standard 1.4.1 Amendment dated March 2016. Where * represents a mean value from the minimum number of fish required to be sampled. See schedule 19 of Standard 1.4.1.

1.2 Aims

This report aims to present all relevant information enabling the public to understand the degree of metal contamination in the Derwent estuary and to:

- Compare results to relevant maximum levels and inform public health
- Better understand the degree of metal contamination in the Derwent estuary
- Where possible, identify trends

2 Methods

Metal accumulation in fish and human health risk was assessed by monitoring metal concentrations in:

- Ambient waters: monthly from the same sites each event
- Wild flathead (*Platycephalus bassensis*): annual from the same sites each event
- Wild fish other than oysters, mussels and flathead: Intermittent and occasional
- Wild oysters and mussels: Triennial harvest from the same sites each event
- Deployed oysters: annual deployment of oysters into the Derwent for 6 weeks each summer, same sites each event

A brief summary of methods is provided below to enable readers to understand the results provided in this report. More details are available in State of the Derwent reports (Coughanowr, 1997; Green and Coughanowr, 2004; Whitehead *et al.*, 2010 and Coughanowr *et al.*, 2015). All data was collected by Nyrstar, samples analysed by Analytical Services Tasmania and data analysed and reported on by the Derwent Estuary Program.

2.1 Method summary: Ambient water quality

The Derwent Estuary Program coordinates monthly ambient water quality monitoring of 29 sites throughout the Derwent estuary as a cooperative initiative between the Tasmanian Government, Nyrstar Hobart and Norske Skog Boyer (Figure 2-1). Physicochemical parameters are sampled throughout the water column using handheld multiprobes that are calibrated immediately prior to each sampling event.

Additional samples are collected from surface waters (~0.5m below the surface) and the benthic zone (~1m above the seabed) for laboratory analysis of combined ammonia+ammonium (NH4+), combined nitrite+nitrate (NOx), total nitrogen (TN), dissolved reactive phosphorus (DRP), total phosphorus (TP), true colour, total suspended solids (TSS), total organic carbon (TOC) and total zinc. Depth integrated samples were collected using a Lund tube (Talling and Lund, 1957) for laboratory analysis of chlorophyll-a. Samples were placed in an insulated cool-box containing ice before taking them to the laboratory immediately upon completion of the sampling event. All laboratory analyses were conducted by the NATA-accredited laboratory Analytical Services Tasmania.

Historically a suite of metal species, both total and dissolved, were sampled. However the broad suite of analytes was reduced to total zinc because the concentration of most other metals was principally below the laboratory reporting limit. Discussion of metals in ambient waters therefore refers to ambient total zinc. Zinc serves as a good proxy for those metals that are present as residues in zinc ores (e.g. cadmium, mercury, lead, and to a lesser extent copper) but a poor proxy for metals with other sources (e.g. nickel, cobalt, chromium). The Derwent Estuary Program currently makes the tentative assumption that if ambient zinc is changing, then so too are other metals although this assumption cannot be tested under the existing operational budget of the DEP.

Data was analysed using the Correlated Seasonal Mann Kendall method for trend detection within the "trend" package in R (Hirsch and Slack, 1984; R Core Team, 2013; Thorsten, 2018). Missing values were filled with the last observation carried forward and professional judgement was used to interpret the validity of statistical analysis results, particularly when missing data was filled and when laboratory minimum limits of reporting had been adjusted by the laboratory throughout the period 2007 to 2020.



Figure 2-1 Derwent Estuary Program ambient water quality sampling sites

2.2 Method summary: Wild flathead

Total metal loads in flathead (*Platycephalus bassensis*) were assessed by the current and former owners of the Hobart zinc smelter. Wild flathead were sampled every two years, targeting up to 10 fish above legal size (>320 mm) from seven locations in the Derwent estuary and 20 fish from a reference site at Mickey's Bay, Bruny Island (Figure 2-2). Fish from each site were measured, weighed, gutted, rinsed in deionized water, and submitted to Analytical Services Tasmania. A representative sample of flesh was extracted, dried, ground and analysed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) for total concentrations of arsenic, cadmium, copper, chromium, iron, lead, manganese, nickel, selenium and zinc. Mercury concentrations were analysed by cold vapour atomic fluorescence spectroscopy (CV-AFS). Metal concentrations are expressed in mg/kg wet matter basis (WMB).

The legal-size limit for flathead changed in 2016 from 300 mm to 320 mm, so reference to legal sized fish in this report includes results from fish >319 mm long, even when referring to fish sampled prior to 2016. The monitoring program was reviewed by Jones et al. (2013) and led to some changes aiming to enable better interpretation of trends. Consistent data before and after these changes has been used in this report. Total mercury and total zinc concentrations are discussed in this report because they are consistently detected at above the laboratory limits of reporting while other metals are not. Results were compared to relevant maximum levels or generally expected levels (FSANZ, 2016).



Figure 2-2 Wild flathead sampling sites

2.3 Method summary: Wild fish other than oysters, mussels and flathead

Species other than flathead have been intermittently sampled to assess metal concentrations in their flesh and to understand possible human health risks of consumption. Results from the following studies was used for the interpretation provided in this report:

- Verdouw, 2008; Verdouw *et al.*, 2010
- Derwent Estuary Program (2011)
- Derwent Estuary Program (2020)

Methods by Verdouw (2008) are available in Verdouw (2008) and Derwent Estuary Program methods are provided below.

Samples of the following species were collected by an experienced contractor, Mark Stalker, using either hook and line, gill net or diver collection from various sites throughout the Derwent:

- Abalone (Haliotis rubra)
- Crayfish/ southern rock lobster (Jasus edwardsii)
- Brown trout (Salmo trutta)
- Australian Salmon (Arripis truttaceus)

 Short-finned eel (Anguilla australis)

- Tasmanian whitebait (Lovettia sealli)
- Bream (Acanthopagrus butcheri)
- Yellow-eyed mullet (Aldrichetta forsteri)
- School whiting (Sillago bassensis)

• Cod

(Pseudophycis barbata)

 Short-spined sea urchin (Heliocidaris erythrogramma) Fish were measured, weighed, rinsed in deionized water, and stored on ice in a cool box prior to transport to the NATA accredited laboratory, Analytical Services Tasmania. A representative sample of flesh was extracted, dried, ground and analysed by ICP-AES for total concentrations of arsenic, cadmium, copper, chromium, iron, lead, manganese, nickel, selenium and zinc. Mercury concentrations were analysed by CV-AFS. Sea urchin and whitebait samples from all sites were mixed and analysed as one integrated sample. Metal concentrations are expressed in mg/kg WMB.

All results were compared to relevant maximum levels or generally expected levels (FSANZ, 2016) and visually compared between sampling events. Statistical analysis was not conducted between sampling events because the sampling programs were not designed for this purpose and data are not quantitatively comparable.

2.4 Method summary: Wild oysters and mussels

Nyrstar Hobart and the previous managers of the smelter site sampled wild mussels and oysters every three years from sites throughout the Derwent region (Figure 2-3). The contractor (Mark Stalker) navigated to each site on each event using a vessel-mounted GPS, then anchored onsite and dived using scuba, aiming to collect mussels and oysters of all sizes. Twenty mussels and oysters were collected from each site, shucked, rinsed in deionized water then placed in a labelled sampling bag and frozen prior to submission to the laboratory, Analytical Services Tasmania. Flesh was dried, pulverised and analysed using ICP-AES for cadmium, copper, lead and zinc. Mercury concentrations were analysed by CV-AFS. Metal concentrations are expressed in mg/kg WMB. Mean values were calculated for each of the following regions and plotted against relevant maximum levels or generally expected levels:

- Above the Tasman Bridge
- Below the Tasman Bridge on the eastern shore
- Below the Tasman Bridge on the western shore
- Ralphs Bay
- The D'Entrecasteaux Channel (reference site)



Figure 2-3 Nyrstar Hobart map of triennial shellfish harvest locations

2.5 Method summary: Deployed oysters

In 2004, Nyrstar Hobart commenced annual deployment of cultured oysters of consistent age to various locations throughout the estuary. The goal was to enable better comparison of accumulated metal loads between different sites.

Oysters are sourced as much as possible from a consistent location to minimise variability caused by regional differences in background metal availability, but some changes to the source population have occurred. In 2019, oysters were sourced from Circular Head near Smithton because this site was Pacific Oyster Mortality Syndrome (POMS) free and presented no risk of spreading POMS to farms in the Mickey's Bay area. Oysters have been sourced from this site since 2016. From 2005 – 2016 oysters were sourced from Little Swanport. In 2004 oysters were sourced from Barilla Bay.

Thirty-two oysters were put into oyster baskets and one basket deployed into surface waters at nine sites in the Derwent (Figure 2-4) and one site at Mickey's Bay, Bruny Island. One basket was deployed into mid-water and one just off the seabed at sites Elwick Bay Pavilion (EBP), the Nyrstar Hobart wharf (ZHSW) and Beltana Beacon (BB). Baskets were deployed to Derwent sites on 8 December 2018 then retrieved on 19 January while in Mickey's Bay baskets were deployed on 9 December 2019 then retrieved on 20 January 2019.

Twenty oysters were shucked immediately on receiving the oysters from the source, then rinsed in deionised water, placed in labelled sampling bags then frozen and submitted for analysis to the laboratory Analytical Services Tasmania to determine the baseline metal concentration at the time of deployment. Twenty oysters retrieved from each site were shucked, bagged, labelled, placed on ice in the field and transported directly to a freezer, ready for subsequent delivery in a chilled container to Analytical Services Tasmania for analysis. Upon receipt at the laboratory, the oysters from each basket were combined, digested into a slurry and analysed (as a single sample) by ICP-AES to determine total metal concentration accumulated at each site and deployment depth. Metals are expressed in mg/kg WMB.

The source location of oysters has changed throughout the sampling program due to high background concentrations in the source population and the onset Pacific Oyster Mortality Syndrome in 2016/17. To account for variability in trace metal concentrations already in the control-site oysters, control metal results were subtracted from post-deployment results. Data was not analysed statistically due to the limited number of results from each site, the unbalanced number of samples in each group (reference versus impact) and unequal variances between groups. Conclusions are based on qualitative interpretation only.



Figure 2-4. 2019 Derwent deployed oyster sites

3 Results and discussion

3.1 Ambient water quality

Total zinc in ambient water declined at 17 of 22 (77%) of ambient water quality monitoring sites between January 2007 and December 2019 (Figure 3-1; Figure 3-3; Figure 3-5). Decreases were principally in the mid estuary and bottom waters of the upper estuary. Analysis of trends in waters at the entry points to the estuary help understand whether changes in ambient water quality are due to processes within the estuary or are driven by changes outside the estuary. Surface waters at New Norfolk are the entry point for riverine water from the catchment, while underlying salt water enters the estuary from bottom waters near Tinderbox and moves northerly from sampling sites B1 and B3 (Wild-Allen *et al.*, 2013). Zinc did not change in surface waters at New Norfolk although concentrations at this site are typically very low. There was no change in zinc in bottom waters at B1 or B3.

A further hypothesis is that that zinc concentrations decreased due to increased river discharge and associated dilution. We assessed river discharge trends, and although discharge increased between 2007 and 2010, discharge remained relatively stable thereafter and no significant trend was detected for the full period from 2007 to 2020. While a relationship between ambient water zinc concentration and river discharge is apparent, this is not statistically significant, likely due to the multiple factors influencing estuarine water quality (Figure 3-2, Figure 3-4, Figure 3-6). Although river discharge overall did not significantly increase, summer river discharge did increase between 2018 and 2020 which may have increased flushing or dilution of zinc from ambient waters of the upper Derwent (Figure 3-7). Thus, we suggest that the widespread decreasing zinc concentration in estuarine ambient waters was most likely due to a combination of three factors:

- Proactive site remediation by Nyrstar Hobart including interception and treatment of both stormwater and groundwater and reducing the scale of ongoing metal contamination (Nyrstar Hobart, 2017).
- Variability in summer river discharge leading to differing dilution of contaminated midestuary waters.
- Burial of the most heavily metal contaminated sediments under cleaner overlying sediment due to natural processes (Hughes, 2014; Stevens *et al.*, 2021). This reduces the potential for the most heavily metal-contaminated sediments to be mobilised into ambient waters and estuarine food webs.



Figure 3-1 Zinc (ug/L) in ambient waters of upper estuary site U16/17 with local regression lines and standard error bands



Figure 3-2 Zinc in ambient waters of upper estuary site U16/17 (near the motorboat club) plotted with monthly mean river discharge below Meadowbank Dam



Figure 3-3 Zinc in ambient waters of lower estuary site RBN (northern Ralphs Bay) with local regression lines and standard error bands



Figure 3-4 Zinc in ambient waters of lower estuary site RBN (northern Ralphs Bay) plotted with monthly mean river discharge below Meadowbank Dam



Figure 3-5 Zinc in ambient waters of mid-estuary site U2 (North of the Tasman Bridge) with local regression lines and standard error bands



Figure 3-6 Zinc in ambient waters of upper estuary site U16/17 plotted with monthly mean river discharge below Meadowbank Dam





3.2 Wild flathead

3.2.1 Comparison to maximum levels: limit consumption

Of all the legal sized flathead sampled from the Derwent in 2018 (n=18), 72% had a mercury concentration exceeding maximum level. The current 5-year median mercury concentration from Derwent flathead is 0.58 mg/kg WMB. The current advice from the Director of Public Health is as follows:

- Do not eat fish from the Derwent more than twice a week and the following people should further limit their consumption to once a week:
 - Pregnant and breastfeeding women
 - Women who are planning to become pregnant
 - Children aged six years and younger
- When eating fish from the Derwent, it is best to avoid eating fish from other sources in the same week.

This advice is based on long-term monitoring of flathead and studies on the mercury levels in a variety of legally sized fish caught in the Derwent (Verdouw *et al.*, 2010; Jones, 2013; DEP, 2015).

3.2.2 Temporal comparison: declining but variable

A decline in the rolling 5-yearly mercury concentration was first observed in the 2011-2016 period and has continued until the current rolling 5-year period (Figure 3-8). Whilst the declining mercury concentration indicates a gradual improvement in condition, there is a lot of variability in the data, so we encourage cautious interpretation of these results.

In 2018 the contractors conducting the analysis for Nyrstar Hobart submitted fish samples with skin on, compared to prior when samples were submitted with fish skin off and this is the likely reason for the increased concentrations of zinc in 2018 compared to prior sampling events (Figure 3-8). Nyrstar Hobart is currently having a subset of the samples analysed and data will



be provided to the Derwent Estuary Program in the hope that sufficient sample is available to calculate an adjustment factor that we could apply to the 2018 results.

Figure 3-8 Five-yearly rolling average mercury and zinc concentration from legal-sized flathead sampled from the Derwent estuary.

3.2.3 **Spatial comparison: Mercury high in the Derwent, particularly in Ralphs Bay**

Mercury and zinc concentration in flathead collected from all sites in the Derwent is higher than concentrations in fish collected from the reference site at Mickey's Bay, with the highest

mercury concentrations recorded in fish from Ralphs Bay Spit and Opossum Bay and the highest zinc concentrations recorded in fish from Opossum Bay and Bellerive (Figure 3-9; Figure 3-10). These results are consistent with previous Derwent estuary studies (Verdouw *et al.*, 2010; Jones, 2013).

Spatial variation in metal concentrations in flathead is likely influenced by several factors including fish biometrics, mercury methylation, estuarine hydrodynamics and seasonal fish migration patterns. Fish length, weight and age are known determinants of mercury loading in flathead (Verdouw *et al.*, 2010; Jones *et al.*, 2013). Higher mercury concentrations in fish from Ralphs Bay spit may be partly explained by generally longer and heavier fish caught from this site compared to other Derwent sites (Jones, 2013; Figure 3-11; Figure 3-12). To improve understanding of the influence of fish biometrics on fish metal concentrations and to improve confidence in results, Nyrstar Hobart commenced age and sex determination of fish samples in 2016. There is currently insufficient age and sex data for robust interpretation (Jones, 2013).

Another critical factor influencing the bioaccumulation of mercury in fish is the site-dependent methylation of mercury. Mercury methylation is complex and subject to site specific drivers, fish diet and food chain variability which can affect accumulation. Mercury methylation is thus likely to influence variation in mercury bioaccumulation in flathead amongst sites. A better understanding of this process would require significant funding, robust program design and implementation and should be considered (Jones *et al.*, 2014a).

Higher metal concentrations in fish from Ralphs Bay and Opossum Bay may also be influenced by hydrodynamics (Wild-Allen and Andrewartha, 2016). Fish from Ralphs Bay may experience longer exposure time to metals originating in the mid-estuary compared to other, more well-flushed sampling sites. Finally, comparisons between sites within the Derwent should be interpreted with care given a recent study showing flathead In the Derwent are seasonally mobile (Tracey *et al.*, 2020).



Mercury in legal size flathead

Figure 3-9 Between-site comparison of mercury concentration in legal-sized flathead



Figure 3-10 Between-site comparison of zinc concentration in legal-sized flathead



Length of the sampled legal sized flathead

Figure 3-11 Between-site comparison of the length of sampled legal-sized flathead



Figure 3-12 Between-site comparison of the weight of sampled legal-sized flathead

3.3 Wild fish other than oysters, mussels and flathead

Different finfish species accumulated different metals to differing degrees. Australian salmon were amongst the species with the highest concentrations of selenium, lead, cadmium and chromium, while mercury was highest in trout, bream and eel. Lead was high in Whiting and urchins, crayfish accumulated the highest concentrations of arsenic and copper while abalone were highest in copper as well as zinc and chromium.

3.3.1 Comparison to maximum levels: mostly compliant, some exceedances

The maximum levels or generally expected levels (FSANZ, 2016) for the following metals were exceeded for the fish species listed below:

- Mercury: Bream, trout, eel (Figure 3-17)
- Copper: Abalone, crayfish, Australian salmon (Figure 3-16)
- Arsenic: Abalone, cod, crayfish, whiting (Figure 3-13)
- Zinc: Abalone, Australian salmon, crayfish, eel, urchins, whitebait, whiting (Figure 3-21)

Lead was not detected above the maximum level for any fish species (Figure 3-19).

Arsenic and zinc were commonly detected in particularly high concentrations, although not in bream, cod, or trout.

3.3.2 **Temporal comparison – Variable between and within species**

Differences in metal concentrations between sampling events differs for different species of fish and metal. Different fish ages, sizes and growth rates are likely a factor as are different environmental conditions during each sampling event (Jezierska and Witeska, 2006; Jones *et al.*, 2014b). Collection and analysis of fish age data may have helped explain differences and without this data temporal comparisons should not be considered to reflect differences in environmental availability of metals. Also, different lifespans will be better or worse indicators

for detecting changes over different time scales. Given bream, Australian salmon, trout, abalone and rock lobster can live to >20 years old, these species would be good to target for detecting changes over decadal scales, while the shorter lifespan of other species such as whiting and mullet (~7 years) might make them more suitable for comparison of the body burden of metals between 2007 and 2020 (Atlas of Living Australia, 2020).

Generalising results for different species caught on different survey events presents the following differences:

- Cadmium, chromium, lead:
 - Concentrations were higher in bream, Australian salmon and trout in 2020 than in 2011 (Figure 3-14; Figure 3-15; Figure 3-19).
- Mercury and zinc:
 - Concentrations in bream and trout were lower in 2020 and 2011 than in 2007 (Figure 3-17; Figure 3-21).
- Manganese:
 - Concentrations were lower in bream in 2011 and 2020 than in 2007 (Figure 3-18)
- Selenium
 - Concentrations were higher in bream and trout in 2020 than in 2007 (Figure 3-20)



Figure 3-13 Arsenic concentrations in various fish species



Figure 3-14 Cadmium concentrations in various fish species



Figure 3-15 Chromium concentrations in various fish species



Figure 3-16 Copper concentrations in various fish species



Figure 3-17 Mercury concentrations in various fish species



Figure 3-18 Manganese concentrations in various fish species



Figure 3-19 Lead concentrations in various fish species



Figure 3-20 Selenium concentrations in various fish species



Figure 3-21 Zinc concentrations in various fish species

3.3.3 Spatial comparison – metal concentrations are not lower in fish from the lower estuary than in fish from the upper or mid-estuary

Generally, there does not appear to be a difference in metals accumulated in fish collected from upper-, mid- or lower-Derwent sites (Figure 3-22) so those targeting seafood from the





Figure 3-22 No difference in metals in bream between upper, mid and lower estuary sites

3.4 Wild oysters and mussels

3.4.1 Comparison to maximum levels: exceedances, particularly for cadmium and lead

Cadmium, copper, lead, and zinc in shellfish all exceeded relevant maximum levels or generally expected levels (Figure 3-23-Figure 3-32). Current public health advice therefore still stands: Do not eat shellfish collected from the Derwent estuary (including Ralphs Bay).

3.4.2 Temporal comparison: highly variable with few consistent trends

Results between sampling events were variable with few consistent trends. The triennial wild shellfish harvest program was designed to determine possible human health risks of exposure to metals if consuming wild harvested shellfish and was not designed with appropriate controls in place to detect trends, so it is overreaching to expect this dataset to detect temporal trends and any future trend detection would be incidental and considered in the context of other monitoring results.

3.4.3 Spatial comparison: higher in the Derwent than outside the Derwent, midestuary sites generally had the highest metal concentrations

Metals were higher in the Derwent than in the D'Entrecasteaux channel and were higher in oysters in the mid-estuary compared to the lower estuary, as expected given the mid-estuary has the highest concentrations of metals in both ambient waters and sediment. Metal concentrations in shellfish from Ralphs Bay were consistently higher than at similar latitudes on the western shore due to the circulation pattern of contaminated mid-estuarine water that moves typically down the eastern shore, into Ralphs Bay then out past Opossum Bay (Figure 3-23-Figure 3-32). There may be a perception amongst the public that the waters of Ralphs Bay

and the lower western shore are cleaner and therefore it is safe to consume shellfish from that region. This is not the case for Ralphs Bay and, while shellfish from the lower western shore had generally lower concentrations of metals than those from other parts of the Derwent, the concentrations of lead in mussels (Figure 3-28) and zinc in oysters (Figure 3-31) from the lower western shore still exceeded the relevant maximum levels or generally expected levels.

Recreational fishers should be advised that shellfish from anywhere in the Derwent estuary, including Ralphs Bay are unsafe for consumption. Furthermore, a standing public health alert warns against collecting and eating wild shellfish anywhere in Tasmania. There is always a risk to human health from eating wild shellfish and therefore, the Department of Health recommends that all shellfish be bought from retail outlets, as there is a quality assurance program covering commercially grown shellfish in Tasmania.



Figure 3-23 Cadmium in wild oysters



Figure 3-24 Cadmium in wild mussels



Figure 3-25 Copper in wild oysters



Figure 3-26 Copper in wild mussels



Figure 3-27 Lead in wild oysters



Figure 3-28 Lead in wild mussels



Figure 3-29 Mercury in wild oysters



Figure 3-30 Mercury in wild mussels



Figure 3-31 Zinc in wild oysters



Figure 3-32 Zinc in wild mussels

3.5 Deployed oysters

3.5.1 **Comparison to maximum levels: exceeded after just 6 weeks in the Derwent**

Although the deployed oyster program was not designed to determine health risks, incidentally, clean oysters translocated into Derwent waters for just six weeks, accumulated sufficient concentrations of metals that they exceeded relevant maximum levels or generally expected levels for lead, cadmium, zinc and copper (Figure 3-37).

3.5.2 Temporal comparison: variable but some decline close to the zinc smelter

Results since 2005 have been variable, but declines seem to have occurred for zinc, mercury and lead in oysters deployed to Elwick bay while zinc seems to have declined in oysters deployed to Cornelian Bay and Bedlam Walls (

Figure 3-33, Figure 3-34), particularly since 2008. Zinc results at all sites in 2019 were higher than in either 2017 or 2018 (

Figure 3-33) and this increase remains unaccounted for.

Variability in the data is likely a result of multiple factors. While there appears to be some relationship between seasonal (December-March) ambient zinc concentration in surface waters from nearby sites (U4, U3, U2 and NTB05) and oyster results, the relationship is weak at best (Figure 3-35, Figure 3-36). Accumulation rates are likely influenced by the complex interactions of various components of water chemistry within the inherently dynamic nature of the estuary, coupled with biological variability such as spawning status and growth rates during deployment (Wright and Mason, 2000). Changes in the source population of oysters over the course of this program, has contributed to variability in the control oyster data (DEP, 2018) exemplified by elevated concentrations of zinc, mercury and copper in control oysters in 2017 and 2018 following the changed source population.



Figure 3-33. Zinc concentrations (mg/kg wet weight) accumulated by surface-deployed oysters at various sites in the Derwent estuary from 2005-2019 inclusive



Figure 3-34. Metal concentrations (mg/kg wet weight) accumulated by surface-deployed oysters at Cornelian Bay from 2005 to 2019 inclusive



Figure 3-35 Zinc concentration from ambient water quality sampling conducted in December to March each year. The year label includes data from the preceding December. Data was collected from sites in the vicinity of deployed oyster sites: U4, U3, U2 and NTB05 and the mean zinc concentration from all sites was used.

Elwick Bay Pavilion zinc in oysters and ambient waters



Figure 3-36 Regression between zinc in oysters deployed to surface waters near the Elwick Bay Pavilion and zinc in ambient waters from the nearest ambient monitoring site, U5.

3.5.3 Spatial comparison: Zinc highest in oysters deployed closer to the zinc smelter site

The deployed oyster experiments effectively show that the highest loads are accumulated from sites nearest to the zinc smelter and that oysters deployed into the Derwent accumulated markedly higher concentrations of all metals than those deployed to the reference site outside the Derwent (Mickey's Bay) (Figure 3-37). Oysters deployed at the Nyrstar Hobart wharf (ZHSW) in 2019 again accumulated higher concentrations of trace metals than other sites (Figure 3-37), followed by other sites close to the zinc smelter, Bedlam Walls and Dowsing Point. These results are consistent with those formerly reported (DEP, 2016, 2018).



Figure 3-37 Comparison of metal concentrations (mg/kg wet weight) in surface-deployed oysters between sites in 2019

4 Conclusions

4.1 Health advice

Based on available information, the public are advised by the Director of Public Health as follows:

- Do not consume any shellfish or bream from the Derwent, including Ralphs Bay
- Other fish from the Derwent should not be eaten more than twice a week and the following should further limit their consumption to once a week:
 - Pregnant and breastfeeding women
 - o Women who are planning to become pregnant
 - Children aged six years and younger
- When eating fish from the Derwent, it is best to avoid eating fish from other sources in the same week.

4.2 Temporal comparison

Declining zinc in ambient waters was supported by declines in mercury in wild flathead between 2011 and 2020 and some declines in oysters deployed into sites closest to the zinc smelter site. No consistent trend was detected for other bioindicators, although this is not surprising given none of the biota sampling programs were originally designed for trend detection. The wild flathead sampling program was reviewed in 2013 and amended in 2015 to increase chances of trend detection, but there have only been two events since this program was adapted which is insufficient for statistical confirmation of the apparent trends detected here.

Where declines are evident, it is likely that these are due to a combination of factors:

- Higher river discharge each summer since 2016-17
- Proactive remediation and improved environmental management of the Nyrstar Hobart zinc smelter
- Natural processes leading to burial of the most heavily metal-contaminated sediments, reducing their remobilization into ambient waters

4.3 Spatial comparison

All indicators of metal availability, including ambient water quality sampling and all sessile bioindicators show higher metal concentrations within the Derwent compared to elsewhere. Sessile bioindicators show a positive relationship between zinc concentrations and proximity to the Nyrstar Hobart zinc smelter. The relationship with proximity to the smelter is less clear for finfish, likely in part to less site affinity confounding results. Revision of the sampling design might consider a comparison of finfish metal concentrations within the Derwent compared to outside the Derwent, with less focus on within-Derwent spatial variability.

Higher metal concentrations with proximity to the zinc smelter is likely due to:

- The ongoing source of metal contaminated groundwater entering the estuary from the zinc smelter site
- Ongoing metal contamination from current zinc smelter operations
- The legacy of contaminated sediments and their remobilisation, with sites closer to the zinc smelter being most heavily metal-contaminated (DEP, 2015; Stevens *et al.*, 2021).

There have been major improvements in the operation of the zinc smelter and major efforts to remediate contaminated groundwater on site in recent years (DEP, 2015). Improved environmental management continues and includes expansion of interception and treatment of groundwater, stormwater harvesting and treatment and reduction in ongoing groundwater contaminant sources (Nyrstar, 2021).

Higher metal results in wild flathead and wild shellfish from Ralphs Bay may be due to water quality differences (Jezierska and Witeska, 2006) and hydrodynamics, whereby longer exposure times in this sheltered embayment to metal contamination from the mid-estuary, compared to shorter exposure times experienced by more well-flushed sites (Wild-Allen and Andrewartha, 2016). There may also be unique biogeochemical processes leading to higher metal mobilisation from sediments (DEP, 2015) and biological processes such as growth rates and feeding behaviour may be factors (Jones *et al.*, 2014b).

5 References

Atlas of Living Australia (2020) Atlas of living Australia. *Atlas Living Aust.* Accessed 10 August 2020, from https://www.ala.org.au/.

Coughanowr C.A. (1997) State of the Derwent Estuary: a review of environmental quality data to 1997. Supervising scientist report 129. Supervising Scientist, Environment Australia (Canberra, Australia).

DEP (2010) State of the Derwent Estuary, 2009. Whitehead, J. Coughanowr, C.A. Agius, J. Chrispijn, J. Taylor, U. Wells, F. Derwent Estuary Program (Hobart, Australia).

DEP (2015) The State of the Derwent estuary 2015. A review of environmental data from 2009 to 2014. Coughanowr, C.A. Whitehead, J Whitehead, S. Einoder, Luke E. Taylor, U. Weeding, B. Derwent Estuary Program (Hobart, Australia).

DEP (2016) Deployed Oysters 2016. Whitehead, S Coughanowr, C. Derwent Estuary Program (Hobart, Australia).

DEP (2018) Metals in Derwent Deployed Oysters 2018. Weller-Wong, A Whitehead, S. Derwent Estuary Program (Hobart, Australia).

Dineen R., Noller B. (1995) Toxic Elements in Fish and Shellfish from the Derwent estuary. Department of Environment and Land Management (Hobart, Tasmania).

Edge K.J., Johnston E.L., Roach A.C., Ringwood A.H. (2012) Indicators of environmental stress: Cellular biomarkers and reproductive responses in the Sydney rock oyster (Saccostrea glomerata). *Ecotoxicology* **21**, 1415–1425.

FSANZ (2016) Australia and New Zealand Food Standards Code - Standard 1.4.1 - Contaminants and Natural Toxicants. Food Standards Code. Accessed 8 October 2014, from http://www.comlaw.gov.au/Details/F2013C00140.

Green G., Coughanowr C.A. (2004) State of the Derwent Estuary 2003: a review of pollution sources, loads and environmental quality data from 1997 - 2003. Derwent Estuary Program (Hobart, Australia).

Hirsch R.M., Slack J.R. (1984) A Nonparametric Trend Test for Seasonal Data With Serial Dependence. *Water Resources Research* **20**, 727–732.

Hughes S. (2014) Quantifying and Characterising Metal and Metalloid Contamination in the Derwent River Estuary. (Honours thesis) University of Tasmania.

Jezierska B., Witeska M. (2006) 'The metal uptake and accumulation in fish living in polluted waters.' (I Twardowska, HE Allen, MM Häggblom, and S Stefaniak, Eds.). (Springer Netherlands: Dordrecht).

Jones H.J. (2013) Accumulation of mercury in estuarine food webs: biogeochemical and ecological considerations. Thesis, Institute of Marine and Antarctic Studies, University of Tasmania.

Jones H.J., Swadling K.M., Butler E.C.V., Macleod C.K. (2014a) Complex patterns in fish - sediment mercury concentrations in a contaminated estuary: The influence of selenium co-

contamination? *Estuarine, Coastal and Shelf Science* **137**, 14–22.

Jones H.J., Swadling K.M., Butler E.C.V., Macleod C.K. (2014b) Complex patterns in fish – sediment mercury concentrations in a contaminated estuary: The influence of selenium co-contamination? *Estuarine, Coastal and Shelf Science* **137**, 14–22.

Jones H.J., Swadling K.M., Tracey S.R., Macleod C.K. (2013) Long term trends of Hg uptake in resident fish from a polluted estuary. *Marine pollution bulletin* **73**, 263–72.

Macleod C., Coughanowr C. (2019) Heavy metal pollution in the Derwent estuary: History, science and management. *Regional Studies in Marine Science* **32**, 100866.

Nyrstar (2021) Nyrstar Hobart Triennial Public Environment Report 2018-2020. Nyrstar Hobart (Hobart, Tasmania).

Nyrstar Hobart (2017) Triennial public environment report 2015–2017. (Hobart, Tasmania). R Core Team (2013) R: A language and environment for statistical computing.

Rainbow P.S., Kriefman S., Smith B.D., Luoma S.N. (2011) Have the bioavailabilities of trace metals to a suite of biomonitors changed over three decades in SW England estuaries historically affected by mining? *Science of The Total Environment* **409**, 1589–1602.

Ratkowsky D., Dix T., Wilson K. (1975) Mercury in fish in the Derwent Estuary, Tasmania, and its relation to the position of the fish in the food chain. *Marine and Freshwater Research* **26**, 223–231.

Sharma V.K., Sohn M. (2009) Aquatic arsenic: Toxicity, speciation, transformations, and remediation. *Environment International* **35**, 743–759.

de Souza Machado A.A., Spencer K., Kloas W., Toffolon M., Zarfl C. (2016) Metal fate and effects in estuaries: A review and conceptual model for better understanding of toxicity. *Science of The Total Environment* **541**, 268–281.

Stevens H., Chase Z., Zawadzki A., Wong H., Proemse B.C. (2021) Reconstructing the History of Nutrient Loads and Sources in the Derwent Estuary, Tasmania, Australia, using Isotopic Fingerprinting Techniques. *Estuaries and Coasts*.

Thorsten P. (2018) trend: Non-Parametric Trend Tests and Change-Point Detection. R package version 1.1.1.

Thrower S., Eustace I. (1973) Heavy metal contamination in oysters grown in Tasmanian Waters. *Food Technology in Australia* **25**, 546–553.

Tracey S.R., Hartmann K., McAllister J., Lyle J.M. (2020) Home range, site fidelity and synchronous migrations of three co-occurring, morphologically distinct estuarine fish species. *Science of The Total Environment* **713**, 136629.

USEPA (2000) National Guidance: Guidance for Assessing Chemical Contaminant Data for Use In Fish Advisories - Volume 1. *Vol. 1 Fish Sampl. Anal. - Third Ed.* Accessed 9 October 2014, from http://water.epa.gov/scitech/swguidance/fishshellfish/techguidance/risk/.

Verdouw J. (2008) Heavy metal contamination in Derwent estuary fish. University of Tasmania.

Verdouw J.J., Macleod C.K., Nowak B.F., Lyle J.M. (2010) Implications of Age, Size and Region

on Mercury Contamination in Estuarine Fish Species. Water, Air, & Soil Pollution 214, 297–306.

Wild-Allen K., Andrewartha J. (2016) Connectivity between estuaries influences nutrient transport, cycling and water quality. *Marine Chemistry* **185**, 12–26.

Wild-Allen K., Skerratt J., Whitehead J., Rizwi F., Parslow J. (2013) Mechanisms driving estuarine water quality: A 3D biogeochemical model for informed management. *Estuarine, Coastal and Shelf Science* **135**, 33–45.

Wilson J. (1994) The Role of Bioindicators in Estuarine Management. *Estuaries* 17, 94–101.

Wright D., Mason R. (2000) Biological and chemical influences on trace metal toxicology and bioaccumulation in the marine and estuarine environment. *International Journal of Environment and Pollution* **13**, 226–248.