



Heavy metal concentrations in razorfish (*Pinna bicolor*) and sediments across the northern Spencer Gulf

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Spencer Gulf**

August 2004

*Environment Protection Authority
Adelaide, South Australia*

Heavy metal concentrations in razorfish (*Pinna bicolor*) and sediments across northern Spencer Gulf

Authors: Tracy Corbin and Sam Wade

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For further information please contact:
Environment Protection Authority
GPO Box 2607
ADELAIDE SA 5001

Web site : www.epa.sa.gov.au
E-mail : epainfo@epa.sa.gov.au

Telephone: 08 8204 2004
Fax: 08 8204 9393
Freecall: 1800 623 445

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Contents

1	Introduction	1
1.1	Aims of this survey	3
2	Current emissions of heavy metals in the northern Spencer Gulf region.....	6
3	Impacts of heavy metals in marine systems.....	10
4	Historical information of heavy metal contamination in the northern Spencer Gulf ...	15
5	Assessing heavy metal contamination in the northern spencer gulf	18
6	Survey methods.....	20
6.1	Razorfish	20
6.2	Sediments.....	24
7	Data analysis	25
7.1	Descriptive statistics	25
7.2	Classification of data.....	25
8	Metal concentrations in razorfish	29
8.1	Distribution of heavy metals in razorfish across the northern Spencer Gulf	29
8.2	Comparison of metal concentrations in razorfish with food standards	40
8.3	Summary of heavy metal concentrations in razorfish	45
9	Metal concentrations in sediments	46
9.1	Distribution of heavy metals in sediment samples across the northern Spencer Gulf..	46
9.2	Comparison of metal concentrations in sediments with ANZECC guidelines for the protection of marine ecosystems	54
10	Conclusions	61
	Appendix 1: Relationships between razorfish length and metal concentrations	63
	Appendix 2: Laboratory reporting limits	73
	Glossary	74
	References	76

List of Figures

Figure 1	The northern Spencer Gulf.....	4
Figure 2	Razorfish in their natural environment, with obvious epiphyte growth.....	5
Figure 3	Open shell of a razorfish showing the posterior adductor muscle, the edible portion of the razorfish.....	5
Figure 4	Razorfish collection sites.....	22
Figure 5	Sediment collection sites.....	23
Figure 6	Total arsenic concentrations (dry weight) present in razorfish adductor muscle collected from the northern Spencer Gulf.....	31
Figure 7	Cadmium concentrations (dry weight) present in razorfish adductor muscle collected from the northern Spencer Gulf.....	32
Figure 8	Copper concentrations (dry weight) present in razorfish adductor muscle collected from the northern Spencer Gulf.....	33
Figure 9	Lead concentrations (dry weight) present in razorfish adductor muscle collected from the northern Spencer Gulf.....	34
Figure 10	Mercury concentrations (dry weight) present in razorfish adductor muscle collected from the northern Spencer Gulf.....	35
Figure 11	Selenium concentrations (dry weight) present in razorfish adductor muscle collected from the northern Spencer Gulf.....	36
Figure 12	Zinc concentrations (dry weight) present in razorfish adductor muscle collected from the northern Spencer Gulf.....	37
Figure 13	Relationship of distance from the Pasmenco smelter and metal concentration for zinc, selenium and lead.....	38
Figure 14	Relationship of distance from source and metal concentrations for copper, arsenic, cadmium and mercury.....	39
Figure 15	Classifications of razorfish adductor muscle lead concentrations in the northern Spencer Gulf against food standards.....	42
Figure 16	Cadmium concentrations present in marine sediments in the northern Spencer Gulf.....	48
Figure 17	Chromium concentrations present in marine sediments in the northern Spencer Gulf.....	49
Figure 18	Copper concentrations present in marine sediments in the northern Spencer Gulf..	50
Figure 19	Lead concentrations present in marine sediments in the northern Spencer Gulf.....	51
Figure 20	Nickel concentrations present in marine sediments in the northern Spencer Gulf...	52
Figure 21	Zinc concentrations present in marine sediments in the northern Spencer Gulf.....	53
Figure 22	Classifications of marine sediment cadmium concentrations in the northern Spencer Gulf against aquatic ecosystem guidelines.....	55
Figure 23	Classifications of marine sediment lead concentrations in the northern Spencer Gulf against aquatic ecosystem guidelines.....	56

Figure 24	Classifications of marine sediment copper, chromium and nickel concentrations in the northern Spencer Gulf against aquatic ecosystem guidelines	57
Figure 25	Classifications of marine sediment zinc concentrations in the northern Spencer Gulf against aquatic ecosystem guidelines	58
Figure 26	Classifications of marine sediment for all heavy metal concentrations tested in the northern Spencer Gulf against aquatic ecosystem guidelines	59
Figure 27	Relationship of distance from source and metal concentration for all metals analysed in sediment.....	60

List of Tables

Table 1	Estimated annual metal emissions in kilograms by major industry and diffuse sources in the northern Spencer Gulf region between July 2001 and June 2002.....	8
Table 2	Maximum levels of cadmium, mercury, lead and inorganic arsenic in molluscs as listed in the Australia New Zealand Food Standards Code expressed as mg/kg wet weight.....	26
Table 3	Generally expected levels (GELs) for copper, selenium and zinc in molluscs and crustaceans as listed in the Australia New Zealand Food Standards Code expressed as mg/kg wet weight.....	27
Table 4	ANZECC guidelines for metal concentrations in sediments expressed as mg/kg dry weight	28
Table 5	Dry weight metal concentrations of 105 composite razorfish adductor muscle samples from the northern Spencer Gulf	29
Table 6	Summary of metal concentrations (wet weight) of 105 composite razorfish adductor muscle samples from the northern Spencer Gulf.....	40
Table 7	Classification of cadmium, mercury and lead concentrations of razorfish adductor muscle tissue with food standard maximum levels for 105 samples across 35 sites in the northern Spencer Gulf.....	41
Table 8	Classification of cadmium, mercury and lead concentrations in individual razorfish adductor muscle tissue from the northern Spencer Gulf.....	43
Table 9	Summary of copper, selenium and zinc concentrations in razorfish adductor muscle tissue in comparison with the generally expected levels (GELs) for 105 samples from 35 sites in the northern Spencer Gulf.....	43
Table 10	Summary of copper, selenium and zinc concentrations in razorfish adductor muscle tissue in comparison with the generally expected levels (GELs) in individual razorfish samples collected from four sites in the northern Spencer Gulf	44
Table 11	Dry weight metal concentrations of 59 sediment samples from the northern Spencer Gulf.....	46
Table 12	Classification of sediment metal concentrations of samples collected during 1976–81 at 59 sites across the northern Spencer Gulf.....	54

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Summary

The northern Spencer Gulf is an important marine region that provides environmental, social and economic benefits for South Australians. Vast areas of seagrass meadows, mangrove forests, mudflats and saltmarshes support a diverse range of marine and coastal creatures and plants. The region is a significant nursery and feeding area for numerous fish, mollusc and crustacean species including many commercially and recreationally important species. Marine ecotourism is becoming increasingly widespread in the region, with a significant focus on the spawning of the Australian giant cuttlefish near Whyalla.

The northern Spencer Gulf region is also an important industrial area. Major active industries include the Pasminco¹ lead-zinc smelter at Port Pirie, OneSteel steelworks at Whyalla and the Santos liquid hydrocarbon processing facility at Port Bonython. Utilities in the region include the NRG Flinders Northern and Playford coal fired power stations at Port Augusta and SA Water wastewater treatment plants at Port Augusta, Port Pirie and Whyalla.

Industries contribute the majority of heavy metals entering the northern Spencer Gulf region through emissions to air, land and water. Studies conducted over a number of decades have shown elevated levels of metals in the northern section of the gulf, particularly in Germein Bay near Port Pirie. In response to a sampling program conducted by the South Australian Health Commission and the South Australian Research and Development Institute (SARDI), the collection of marine benthic molluscs has been prohibited from the majority of Germein Bay since July 1996 (figure 1).

This study investigates the extent of heavy metal contamination in the northern Spencer Gulf by examining the concentration of metals in both an indicator organism (razorfish) and in marine sediments.

Accumulated heavy metal concentrations in the razorfish, a bivalve that filters its food from the water (figure 2), have been used as an indicator of metal pollution in the gulf. Razorfish samples were collected from 35 sites between Port Augusta and Wallaroo. The posterior adductor muscles (figure 3) in the razorfish were removed and analysed for arsenic, cadmium, copper, lead, mercury, selenium and zinc, and concentrations were compared with the current food standards outlined in the *Australia New Zealand Food Standards Code*.

Examined in conjunction with this is previously unpublished sediment data collected in the late 1970s to early 1980s by the Department of Geology, University of Adelaide. The top 2 cm of 59 sediment core samples were analysed for total concentrations of cadmium, chromium, copper, lead, nickel and zinc.

Lead concentrations in razorfish collected from one site did not comply with food standards, exceeding the maximum level allowed in molluscs. This site was situated approximately 7 km north of the Pasminco smelter at Port Pirie, within the prohibited zone (figure 15). Of the six sites investigated in the prohibited zone, this was the only site to have elevated concentrations of lead. Cadmium and mercury concentrations complied with food standards at all sites. Food standards do not currently exist for copper,

¹ now known as 'Zinifex'

selenium and zinc as safety assessments have indicated these metals do not contribute significantly to dietary exposure and are therefore considered to pose a low level of risk to public health.

Some of the highest concentrations of lead, selenium and zinc were detected in razorfish collected from sites within the prohibited zone near Port Pirie. Elevated concentrations of zinc were also measured in razorfish from False Bay near Whyalla. Concentrations of these three metals were found to be related to the distance from the Pasmenco smelter, indicating a decrease in concentration as distance from the smelter increased. The opposite was seen for mercury concentrations in razorfish, with the highest concentrations recorded at sites located the furthest away from the smelter. It is possible that this mercury is from natural geological sources.

High concentrations of cadmium, lead and zinc were found in sediments throughout the northern area of the gulf. Metal concentrations were classified as good, moderate or poor against the marine sediment guidelines in the *Australian and New Zealand Guidelines for Fresh and Marine Water Quality (2000)*. Three sites were classified as poor, two of which showed elevated concentrations of cadmium, lead and zinc, while the other showed elevated concentrations of cadmium. These three sites included the site closest to Port Pirie, one approximately 34 km north of Port Pirie and the other near Red Cliff Point, approximately 56 km north of Port Pirie (figure 22). The concentration of metals in the sediments did not appear to be related to the distance from the Pasmenco smelter.

Several studies have been conducted on the northern Spencer Gulf over the past few decades. These studies, most of which have concentrated on the areas around Port Pirie and Whyalla, have included investigations of the water and sediment quality as well as biological studies, most of which have concentrated on areas around Port Pirie and Whyalla. Many organisms in the gulf have been found to store large quantities of heavy metals, particularly lead, zinc and cadmium, in their tissues. Studies conducted on the ecosystem of the northern Spencer Gulf have also shown that contamination in this region has affected biodiversity, evident as a reduction in seagrass fauna and epifauna near the pollution sources. The present study investigated a greater area of the gulf than previously but still highlighted elevated concentrations of some metals in both Germein Bay and False Bay.

In recent years Pasmenco has reduced the concentrations of heavy metals being discharged to the marine environment through the introduction of a new treatment system. While these reductions are significant, there is still a substantial load of metals being discharged to both water and air in the northern Spencer Gulf region. Currently, Pasmenco's most important environmental priority is to reduce raw and roast fume emissions from their slag fumer, with the aim of reducing blood lead levels in infants in Port Pirie. OneSteel is currently involved in a \$10 million plan to reduce dust emissions from their plant. While these modifications will help to improve current conditions, the legacy of over 100 years of pollution in this region will continue to have an impact on the marine environment. The Environment Protection Authority will continue to monitor the northern Spencer Gulf.

1 Introduction

The northern Spencer Gulf is an important natural asset that provides social and economic benefits for South Australians, as well as having significant environmental value. The shallow waters of the gulf support the largest coastal wetland system in the state. Vast subtidal seagrass meadows, extensive supratidal saltmarshes, intertidal mangrove forests and mudflats sustain an important and diverse aquatic ecosystem (Edyvane & Boxall 1997).

The region is a significant nursery and feeding area for a number of commercially important fish, mollusc and crustacean species including King George whiting, southern sea garfish, snapper, southern calamari, blue swimmer crabs and king prawns. The aquaculture of yellowtail kingfish is expanding in the northern area of the gulf and ecotourism continues to grow due to the annual spawning of the Australian giant cuttlefish *Sepia apama*, bringing many recreational divers to Whyalla.

The northern Spencer Gulf has been an important industrial area since the Port Pirie smelter began operating in 1889, followed by the Whyalla steelworks in 1941. From an environmental perspective, historical practices were generally far worse than those used today, leaving a significant legacy of historical contamination. Harbour sediments in both towns were polluted, and dredge spoil contaminated with high concentrations of heavy metals was dumped in False Bay near Whyalla and in Germein Bay near Port Pirie; under today's regulations, this practice is no longer allowed.

Currently the major industries in the area include the Pasminco lead-zinc smelter at Port Pirie, the OneSteel steelworks and mills at Whyalla, and the Santos liquid hydrocarbon processing facility at Port Bonython. The area also has a number of significant utilities including the NRG Flinders Northern and Playford coal fired power stations at Port Augusta, and three SA Water wastewater treatment plants, located at Port Augusta, Port Pirie and Whyalla, that discharge sewage effluent to the marine environment. While these industries are of great economic and social value and the utilities are an important part of the infrastructure of our state, it must be recognised that they present significant environmental threats to the gulf.

Industrial pollutants can be released directly into the marine environment in wastewater, or indirectly via atmospheric deposition or stormwater runoff. Polluted stormwater runoff from urban and agricultural areas may also add pollutant loads to the gulf. Protection of the natural environmental values of the gulf from these threats will also safeguard the economic and social benefits that flow from recreational and commercial fishing, aquaculture and ecotourism.

A number of studies have identified heavy metal pollution as a major issue for the region, with significant consequences for the marine environment in the gulf. Heavy metal contamination caused by industry in the region has been detected in animals, plants, sediments, soils, water and air (Edwards et al. 2001; Harbison & Wiltshire 1998; Ross et al. 2003; Tiller et al. 1975; Ward et al. 1982). This contamination has eliminated many marine species and reduced the abundance of others in the vicinity of the Port Pirie smelter (Ward et al. 1982).

Sampling undertaken by the South Australian Health Commission and the South Australian Research and Development Institute (SARDI) led to the prohibition of

collection of benthic molluscs (snails and bivalves such as razorfish) from the majority of Germein Bay (figure 1) in July 1996; the area was closed under section 43 of the *Fisheries Act 1982*. Razorfish samples collected from this area exceeded the food standard guidelines at that time for lead and zinc (Edyvane & Boxall 1997).

Previous studies have generally examined small areas near the Pasminco smelter at Port Pirie and the OneSteel facility at Whyalla. In a comprehensive study of the Port Pirie area, CSIRO suggested that the gulf was contaminated with zinc, and possibly other metals, outside the range of their study area and that a larger scale study would be needed to define the limits of contamination from the smelter at Port Pirie (Ward et al. 1982).

The South Australian Environment Protection Authority (EPA) conducted a survey to examine heavy metal pollution in the northern Spencer Gulf. A total of 158 razorfish samples were collected from 35 sites across an area from Port Augusta in the north to Wallaroo Bay in the south, a distance of approximately 160 kilometres.

Razorfish, *Pinna bicolor*, are large fan-shaped bivalve molluscs that live embedded in one place in the sediment (figure 2). They can be exposed to contaminants present in both the water and the sediment. Razorfish filter water to remove fine organic and inorganic particles as a food source and regularly pass water over their gills to take in oxygen. Metals present either in solution in the water or adsorbed to the inorganic and organic matter can be accumulated in their body tissues. This accumulation makes them a useful indicator of the biologically available metals in the marine environment.

The concentrations of seven metals—arsenic, cadmium, copper, lead, mercury, selenium and zinc—were measured in the posterior adductor muscle of the razorfish, the portion of the razorfish normally consumed (figure 3). These analyses can provide an indication of the metals that are bioavailable to razorfish and possibly other marine organisms in the northern Spencer Gulf.

The results of this razorfish survey are presented in conjunction with previously unpublished data on metal concentrations in gulf sediments collected between 1976 and 1981 by Hails and Gostin from the Department of Geology at the University of Adelaide. In this study 59 sediment samples were collected from an area that extended approximately 80 km from Port Augusta to just south of Port Pirie, and analysed for cadmium, chromium, copper, lead, nickel and zinc. This sediment data was part of a larger survey of seafloor geology, geophysics and geochemistry (Hails & Gostin 1984).

Analysis of sediments can provide information about the long-term deposition of metals in the marine environment. However, some metals in sediments may be biologically inert because they are physically or chemically bound to the sediment particles. Analysis of metal concentrations in living organisms, such as molluscs, complement sediment analysis by indicating which metals might be bioavailable in the environment.

Once in the environment, metals can be cycled through the ecosystem food web, accumulating in organisms either directly from the primary pollution source or by consumption of other organisms with metals stored in their tissues. Organisms can also be exposed to metals through the re-suspension or mobilisation of the sediment.

1.1 Aims of this survey

The key aim of this study was to determine the distribution and concentrations of heavy metals in razorfish and sediments across the northern Spencer Gulf. This information was to be assessed against appropriate guidelines to compare:

- the heavy metal concentrations in the razorfish adductor muscle samples with Food Standards Australia New Zealand (FSANZ) (formerly known as Australian New Zealand Food Authority (ANZFA)) maximum levels (MLs) of contaminants in foods
- the heavy metal concentrations in the sediments with *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* (ANZECC) sediment quality guidelines.

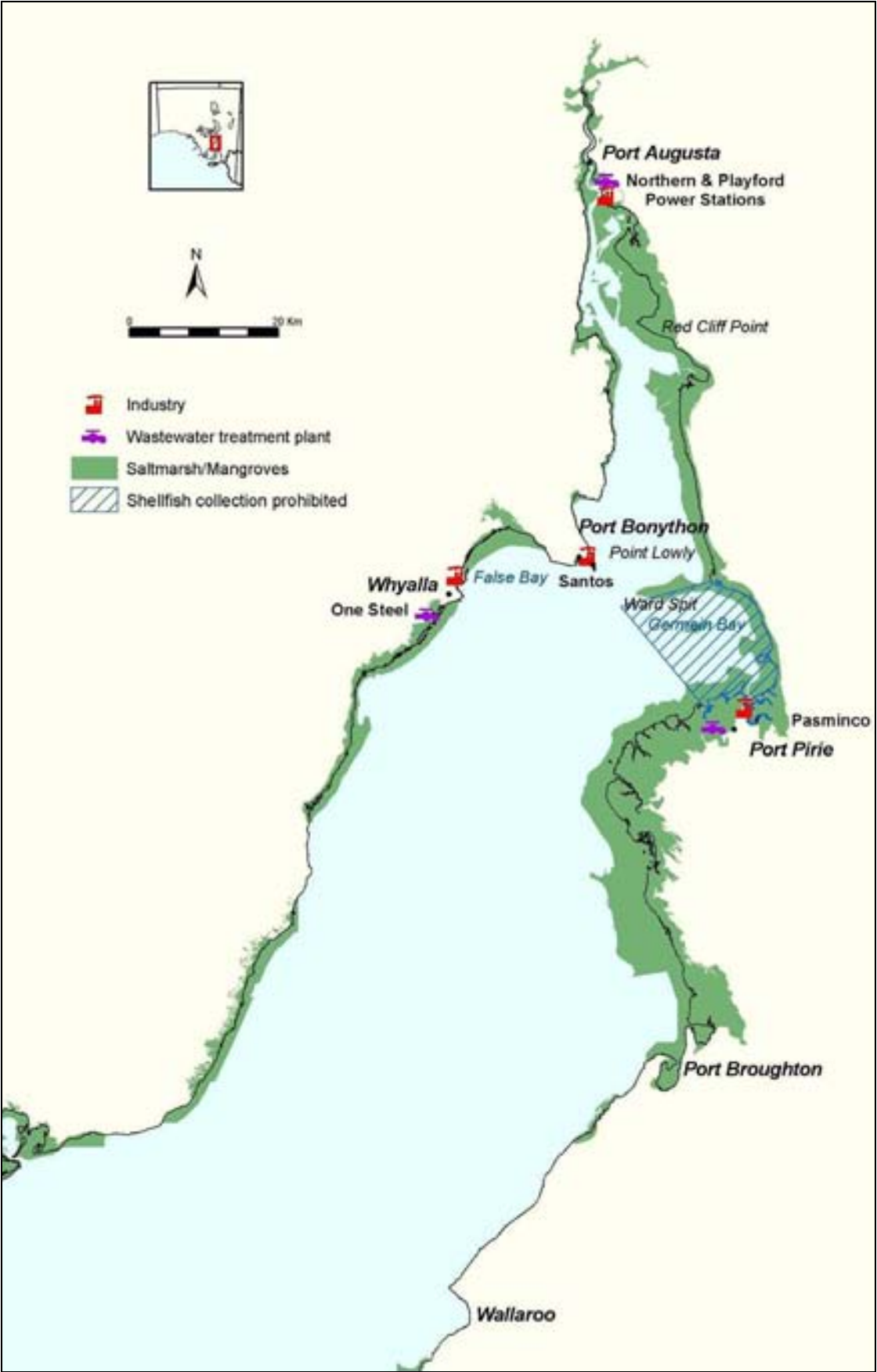


Figure 1 The northern Spencer Gulf



Figure 2 Razorfish in their natural environment, with obvious epiphyte growth
Photo: David Wiltshire, Social and Ecological Assessments



Figure 3 Open shell of a razorfish showing the posterior adductor muscle, the edible portion of the razorfish

2 Current emissions of heavy metals in the northern Spencer Gulf region

Industrial pollutants can be released directly into the marine environment in wastewater, or indirectly via atmospheric deposition or stormwater runoff.

The Pasminco smelter at Port Pirie and the OneSteel operation at Whyalla discharge wastewater contaminated with heavy metals into the gulf waters, and both operations discharge metals to air. The power stations at Port Augusta discharge wastewater from ash settling ponds and heated cooling water to the marine environment as well as air emissions from the burning of coal. Three SA Water wastewater treatment plants (WWTPs), one each at Port Augusta, Port Pirie and Whyalla, discharge treated effluent to the gulf waters. These facilities have been discharging waste into the environment for many decades.

Estimated emissions of heavy metals to air and water from major industries, together with diffuse air emissions, in the northern Spencer Gulf region are provided in table 1. These emissions have been calculated using a number of methods including direct monitoring, standard industry emission factors and other modelling methods. Most of the data in this table comes from the National Pollutant Inventory (NPI) program, which requires some industries to estimate and report on their emissions of selected pollutants. In addition to the self reporting of emissions by industry, the NPI program also estimates diffuse emissions to specific airsheds, including Spencer Gulf. This data provides a summary of the types and loads of heavy metals emitted to the northern Spencer Gulf region and the relative importance of diffuse and point sources.

The Pasminco smelter at Port Pirie, which opened in 1889, is one of the largest lead smelters in the world, producing significant volumes of zinc, silver, copper and gold. Historically, heavy metal pollution escaped from the plant as particulate emissions from the smoke stacks, dust blown from the site, spillage of concentrates during loading of ships, and discharging of liquid effluent (Ward et al. 1982). Silt dredged from the Port Pirie harbour area and dumped in Germein Bay has also contributed to metal contamination in the gulf (Edyvane & Boxall 1997). Until 1939 liquid effluent from the plant was released to the Port Pirie River. After this time the effluent was diverted to First Creek, a tidal creek about 4 km northwest of the works (Olsen 1983). Recent figures show that the Pasminco smelter at Port Pirie discharges significant amounts of arsenic, cadmium, lead, mercury, nickel, selenium and zinc to both air and water (table 1). However, concentrations of these metals have reduced considerably in the last decade or so, particularly with the introduction of the process effluent treatment system (PETS). Emissions of arsenic, cadmium, copper, lead and zinc to water have reduced by between 80% and 85% since 1990, while selenium emissions to water have been reduced by 90% (EPA unpublished data).

OneSteel Whyalla steelworks is another important industry in the northern Spencer Gulf region, producing approximately 1.2 million tonnes of raw steel each year. These works were originally owned and built by BHP Steelworks in 1937 but have been operated by OneSteel since October 2000. NPI records for the year 2001-02 show that OneSteel discharges lead and zinc to the water, and significant amounts of both these metals and copper to air.

NRG Flinders operates the Northern and Playford coal fired power stations at Port Augusta, with the Northern station producing the bulk of the electricity NRG sells. The Playford station was first commissioned in 1954 and the Northern station was built and commissioned in 1985. Together these power stations produce approximately 40% of South Australia's electricity. The Northern station discharges chromium, copper, lead and zinc to water and air, while the Playford station discharges only small amounts of some metals to the environment.

Table 1 Estimated annual metal emissions in kilograms by major industry and diffuse sources in the northern Spencer Gulf region between July 2001 and June 2002

Metal	Receiving environment	Pasminco lead smelter	OneSteel Whyalla steelworks	NRG Flinders Northern power station	NRG Flinders Playford power station	Santos Port Bonython	SA Water ^a Port Pirie WWTP	SA Water ^a Port Augusta East WWTP	SA Water ^a Whyalla WWTP	Diffuse emissions to Spencer Gulf ^b airshed
Arsenic	Air	3,200	24	10	0.82	0.094	*	*	*	64.6
	Water	1,100	*	*	*	*	16.0	2.0	8.1	na
Cadmium	Air	3,100	2.8	0.4	0.06	0.52	*	*	*	37.4
	Water	780	*	26	0.8	*	4.8	0.2	0.7	na
Chromium	Air	7,000	380	301	21.2	0.033	*	*	*	183.0
	Water	0.00	*	156	4.7	*	36.2	7.5	21.8	na
Copper	Air	320	170	100	7	0.052	*	*	*	150
	Water	690	*	52	1.6	*	41.3	12.4	36.6	na
Lead	Air	74,000	55	86	6	0.13	*	*	*	1,800
	Water	11,000	160	26	0.8	*	4.7	0.7	1.1	na
Mercury	Air	970	0.61	0.1	0.02	0.12	*	*	*	15.1
	Water	0.00	*	1.6	0.05	*	0.6	0.2	0.66	na
Nickel	Air	4,000	81	70	13	0.99	*	*	*	230
	Water	200	*	10	0.3	*	9.6	1.8	3.7	na
Selenium	Air	3,000	*	1.6	*	*	*	*	*	5.1
	Water	4,200	*	10	*	*	61.6	2.3	11.68	na
Zinc	Air	82,000	240	86	*	*	*	*	*	1,000
	Water	38,000	2,800	260	*	*	355.4	15.3	89.0	na

* no available records, which may indicate low emissions; na = not applicable.

^a data was derived from SA Water monitoring program results (Faulkner 2002a, 2002b, 2002c).

^b from Ciuk (2002).

The Santos liquid petroleum plant at Port Bonython processes and stores crude oil, condensates and liquid petroleum gas. According to NPI figures, between July 2001 and June 2002 the Santos facility did not release any metals directly to water; however, small amounts of arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc were released to air and land.

Each of the major coastal towns in the region—Port Augusta (approximate population 13,800), Port Pirie (16,000) and Whyalla (21,600)—is serviced by an SA Water wastewater treatment plant (WWTP) that discharges sewage effluent to the marine environment.

Effluent from Port Augusta East WWTP is discharged to the northern Spencer Gulf via a tidal creek. This plant services a population of around 8000 people with an average outflow of 1.5 ML per day (Faulkner 2002b). Treated effluent from the Port Pirie WWTP is discharged into Second Creek (3 km west of the town centre) which then flows in the northern Spencer Gulf. This plant treats on average 3.6 ML per day (Faulkner 2002a). The plant at Whyalla treats an average of 4.4 ML of effluent per day, with treated effluent being discharged via a tidal creek into the Spencer Gulf (Faulkner 2002c). Monitoring during the 2001–02 period shows all three WWTPs discharge small amounts of metals to the gulf (Faulkner 2002a, 2002b and 2000c).

As part of the NPI program, the South Australian EPA has estimated the aggregate emissions to the Spencer Gulf airshed from sources that do not report to the NPI, such as smaller industries, motor vehicles, aeroplanes, solid fuel burning and other activities (Ciuk 2002). Emissions to the airshed may be deposited on the ground and washed into the gulf, or be deposited directly into the marine environment. However, due to the low rainfall and surface runoff in the region, much may end up stored on land. In the 1999–2000 reporting year it is estimated that small amounts of many heavy metals, including arsenic, cadmium, chromium, lead, nickel and zinc, were released to air through these processes. However, these amounts are minor when compared to the major industrial emissions to both land and water.

3 Impacts of heavy metals in marine systems

Metals occur in mineral deposits and can enter the environment naturally through weathering of rocks and ores. Human activities such as refining of ores and many industrial processes also release metals into the environment, often at a rate far higher than natural processes. Metal contamination can be directly linked to both industrial sources and urban runoff. The wearing of vehicle parts such as tyres, brake pads and brake linings is a major source of metal contamination. Other sources include vehicle and aircraft exhaust, leaking lubricating oil, smelters, power stations, port facilities, WWTPs, chemical producers and manufacturing plants. In the northern Spencer Gulf region the main sources of heavy metals are from the surrounding industries; however, other sources include aeroplanes, paved roads and motor vehicles, commercial shipping and, to a lesser extent, recreational boating, railways and fuel combustion (Ciuk 2002).

Metals such as copper and zinc have biological functions and are essential elements for many organisms, although they can be toxic at higher concentrations. Some other metals, including cadmium, lead and mercury, have no known biological functions and even at low concentrations can be toxic to some forms of life.

The fate and consequences of metals in the aquatic environment depend largely on the physical and chemical conditions of the water. For example, metals are generally more toxic at lower salinities, and a reduction in pH can increase the concentration of soluble heavy metals in water.

In general, dissolved forms of metals are more readily available to exert physiological effects within an organism and for this reason are considered to be more toxic to organisms than their particulate forms. Metals in water can adsorb onto particles such as clay and organic matter, reducing the bioavailability of the metals and the likelihood that they will exert toxic effects on aquatic organisms. Waters that have higher amounts of particulate matter may have higher metal concentrations but, as some of these metals are bound to the particulates, they may not be as bioavailable to organisms.

Heavy metals can have impacts on organisms in a number of ways. Their effect can be acute (or immediate), or more long-term or chronic. Metals can vary in their mode of action within organisms, with variations in the rate of uptake, metabolism and excretion resulting in variations of toxic effects exhibited by the metals. When a number of metals are present at one time, the total toxicity of the metals may be greater than would be expected from the sum of the individual toxicities of each metal. This synergistic effect is not taken into account in current water quality or sediment guidelines (ANZECC 2000).

Heavy metals can also be bioaccumulated in some organisms. Bioaccumulation occurs when the metal is taken up at a faster rate than it is excreted or broken down. In polluted areas bioaccumulation can make some animals unsafe for human consumption.

Arsenic

Sources

Arsenic can be released into the environment naturally by weathering of rocks. It is present in wood preservers (including the commonly used copper chrome arsenate (CCA)), herbicides and pesticides, paints, drugs and dyes (FSANZ 2002). Mining and smelting can also contribute to the release of arsenic into the environment—for example, the use of arsenic to extract iron from iron ore. According to the NPI, in the period

between July 2001 and June 2002 the Pasminco lead smelter in Port Pirie was responsible for the majority of the arsenic contributed to the environment of the northern Spencer Gulf region, discharging 3200 kg of the total 3300 kg to air and approximately 98% of the total 1100 kg to water.

Impacts

Arsenic can be present in the environment as either inorganic or organic compounds, with the inorganic form generally being the more toxic of the two (ANZECC 2000). The most common form in seafood is organic arsenic, usually present as arsenobetaine (ANZECC 2000). In humans, chronic exposure to arsenic can result in skin pigmentations, cancers, high blood pressure, diabetes and reproductive disorders (WHO 2001a). It is believed that arsenic bioaccumulates within the tissues of organisms but does not biomagnify in the food chain.

Cadmium

Sources

Cadmium is produced commercially as a by-product of zinc and lead smelting. It is used in the electroplating process, batteries, dyes, plastics, solders, television tubes and as an anticorrosive agent in metal alloys. It can also be found as an impurity in superphosphate fertilisers (Australian Environment Council 1982a). Cadmium can enter the environment through discharge of wastewater from industries and WWTPs as well as through air emissions. According to the NPI an estimated 4000 kg of cadmium was released to the air and water in the northern Spencer Gulf region in 2001-02. More than 95% of this was discharged from the Pasminco smelter at Port Pirie.

Impacts

Cadmium is a highly toxic metal that readily bioaccumulates in organisms, particularly bivalves (ANZECC 2000). Plants can take up cadmium from the soil and animals concentrate it in the liver and kidneys. In humans, exposure to cadmium can result in nausea, diarrhoea, and liver or kidney damage. It stays in the body a very long time, having a half-life of 10-40 years, and can build up through exposure to low levels over many years (Australian Environment Council 1982a).

Chromium

Sources

Chromium is a naturally occurring element found in animals, plants, rocks, soils and volcanic dust. There are two common forms of chromium: chromium III (an essential nutrient) and chromium VI (a man-made element) (ANZECC 2000). Chromium compounds are used in ferrochrome production, electroplating, leather tanning, wood preserving and pigment production (WHO 1988). It can enter the environment through the burning of fossil fuels and waste incineration (WHO 1988).

Impacts

Chromium III is an essential element which helps the body metabolise sugars; it is relatively non-toxic to humans (WHO 1988). Chromium VI is a known human carcinogen (WHO 1988). It can also be accumulated in the body tissue of aquatic organisms by passive diffusion and can increase the risk of infection in fish (WHO 1988).

Copper

Sources

Stormwater and wastewater are two major sources of copper to aquatic environments, through corrosion of domestic copper piping or from fungicides and insecticides (pH Environment 1995). Vehicle brake pad dust has been identified as another major source of copper. According to the NPI, an estimated 75% of copper emissions in the northern Spencer Gulf region in the 2001–02 year was discharged from Pasmaenco.

Impacts

Copper is an essential element for both plants and animals. It is a key component of some enzymes and an essential part of haemocyanin, a respiratory pigment in the blood of many invertebrates. It is, however, only required in small amounts and is toxic in higher concentrations. Copper is readily bioaccumulated in plants and animals (ANZECC 2000).

Lead

Sources

Lead can enter the environment through stormwater runoff, fallout of lead dust, and WWTP and industrial wastewater discharges. Lead is used in solders, plumbing, batteries, ammunition and some insecticides. Historically, it was used extensively in paints, although this is no longer the case in Australia (NHMRC 1994). Other sources of lead include leaded fuel and particles released from brake pads. According to the NPI, the major contributor of lead in the northern Spencer Gulf region for the 2001–02 year was the Pasmaenco smelter, contributing 49% of the total lead emissions to air and 97% to water.

Impacts

Lead can be extremely toxic to marine organisms such as fish, algae and invertebrates, and can be accumulated in the tissues of animals and plants (ANZECC 2000). It is toxic to humans and can cause behavioural, neurological and physiological problems, particularly in children (NHMRC 1994).

Mercury

Sources

Mercury compounds are used in batteries, explosive detonators, dental amalgam, pigments, thermometers and some pesticides, and as catalysts in industrial processes (Australian Environment Council 1982b). Coal fired power stations can be sources of methylmercury as mercury can be a contaminant in coal. Waste incineration and wastewaters can also release mercury to the environment. According to the NPI, in the 2001–02 year an estimated 390 kg of mercury was released to the northern Spencer Gulf region through emissions to air and water, with Pasmaenco contributing 61% of the mercury entering the environment, and 37.5% coming from paved roads.

Impacts

Both elemental mercury and organic mercury compounds can be highly toxic. Mercury appears to be toxic to most types of organisms, with synergistic effects occurring in the presence of copper and antagonistic effects in the presence of selenium (Australian Environment Council 1982b). Many marine animals have high selenium levels, which enable them to tolerate higher mercury concentrations. Mercury is often adsorbed onto particulate matter and can accumulate in sediments. Once there, some aquatic microorganisms convert various forms of mercury into highly toxic methylmercury

compounds, especially under anoxic conditions (Australian Environment Council 1982b). Methylmercury is easily absorbed into tissues of plants and animals but is only slowly eliminated. Because of this slow elimination, methylmercury can bioaccumulate easily, resulting in high levels in the tissue of predators (Australian Environment Council 1982b). Mercury is toxic to humans.

Nickel

Sources

Nickel is used in the nickel plating process, in pigments and batteries, and when making stainless steel and coins (WHO 1991). It is naturally found in soils and air but can be released into the environment through the combustion of coal and oil for power generation, or through the incineration of waste and sewage sludge (WHO 1991). According to the NPI, 4400 kg of nickel was released to the environment in the northern Spencer Gulf region through air emissions during the 2001-02 period, and 210 kg was released directly to the water. The main contributor was the Pasminco Port Pirie smelter.

Impacts

Small amounts of nickel are essential to human health; however, it can be toxic at higher concentrations (ANZECC 2000). In the aquatic environment more than 90% of nickel is associated with particulate matter, although it can be remobilised from sediments. There is no evidence to suggest that nickel bioaccumulates or magnifies up the food chain (ANZECC 2000).

Selenium

Sources

The major natural source of selenium is from weathering of rocks and soils. Emissions from the burning of fossil fuels can also contribute to the presence of selenium in the environment (ANZECC 2000). It is used in the electronics and glass industry, as a component of pigments in plastics, paints, enamels, inks and rubber, in pesticide and fungicide formulations, in anti-dandruff shampoos and in stainless steel production. Radioactive selenium can be used in diagnostic medicine (Nagpal 2001). Selenium can be present in the air from discharges from coal-burning power stations, and in the water from industrial or agricultural discharges. The Pasminco lead smelter contributed almost all of the estimated 7200 kg of selenium discharged to both air and water in the northern Spencer Gulf region in the 2001-02 year.

Impacts

Selenium is an essential trace element for some organisms, being a functional component of some enzymes (WHO 1986). Although essential in small amounts, it can be toxic when present in high concentrations. Too much selenium in humans can result in gastrointestinal disorders, discolouration of skin and diseased nails (WHO 1986). Selenium can be present in solution or attached to sediment particles and has the potential to bioaccumulate in some organisms (ANZECC 2000).

Zinc

Sources

Zinc is widely used in modern society, most commonly to coat or galvanise iron to prevent corrosion. It is also mixed with other metals to form alloys such as brass. Particles released from vehicle tyres and brake linings are a major source of zinc in the

environment. The NPI estimates that 83,000 kg of zinc was released to air, and about 41,000 kg to water in the northern Spencer Gulf region during the 2001–02 year. The top two sources were Pasminco and OneSteel.

Impacts

Zinc is an essential element for both plants and animals and an important component of many enzymes. However, like other metals, it can be toxic in high concentrations (ANZECC 2000). Zinc is known to bioaccumulate in some aquatic organisms (WHO 2001b). In humans, zinc poisoning can result in gastrointestinal distress, leading to nausea and diarrhoea (WHO 2001b).

4 Historical information of heavy metal contamination in the northern Spencer Gulf

A number of surveys have investigated heavy metal contamination in the northern Spencer Gulf region. Most have focused on the region near Port Pirie, particularly Germein Bay, although monitoring and sampling have also occurred in False Bay, near Whyalla. Assessments have been made of metal concentrations on land, in marine sediments and surface waters, in seagrass and in marine animals such as razorfish.

Metal contamination on land

A 1975 study estimated that lead emissions from the Port Pirie smelter had spread over at least 3400 km² of land east of Spencer Gulf, and that the background lead concentrations in soils in this area were about 10 ppm (Tiller et al. 1975). The authors concluded that 2800 km² of this land had one to five times the background level, 330 km² had five to ten times, and 270 km² had greater than ten times the background level of lead. Small areas within 2 km of the smelter were found to have lead concentrations exceeding the background level by a factor of 100 or more. It was conservatively estimated that there had been at least 40,000 tonnes of lead fallout onto land in this region between 1889 and 1975. It is likely that much of this occurred before 1930, at which time significant reductions in lead emissions were achieved at the smelter.

Metal contamination in marine sediments

Research conducted by Tiller (1975) suggests that significant lead deposition had occurred in Germein Bay between the smelter and Port Germein (due north of Port Pirie). In 1973 the South Australian Department of Fisheries conducted a preliminary survey of metals in sediments and aquatic plants in the vicinity of First Creek at Port Pirie (Olsen 1983). They found high concentrations of lead, mercury, copper, zinc and cadmium in sediments, seagrass and algae, the concentrations declining with increasing distance from the mouth of the creek.

Beginning in 1977, the CSIRO conducted a four-year study into the effects of metals on the marine environment in the Port Pirie area (Tiller et al. 1989; Ward et al. 1982, 1986). The CSIRO estimated that, from the beginning of smelting at Port Pirie in 1889 until the time of the study, over 25,000 tonnes each of lead and zinc and 500 tonnes each of cadmium and arsenic had entered the marine environment at Germein Bay. They discovered that approximately 300 km² of marine sediments were contaminated with lead, zinc and cadmium, while smaller areas were contaminated with arsenic, copper, manganese and antimony. About 100 km² of this area had over ten times the background levels of lead, zinc and cadmium, while in an area of 25 km² near the mouth of First Creek, lead and zinc were 200–300 times the background levels and cadmium was 1000 times the background level.

Microscopic and chemical analysis of sediments suggested that the metal contamination of sediments had originated from a number of sources at the smelter: particles emitted from the smoke stacks; spillage of ore concentrates during handling and shipping; fugitive dust from the smelter; and soluble and suspended metals discharged in smelter wastewater to First Creek. It appears that emissions from the stack are the largest contributor to contamination in the gulf, followed by wastewater discharge (Ward et al. 1982).

Ross et al. (2003) measured concentrations of lead, zinc, cadmium, copper and manganese in seston² samples from Germein Bay. They found that the highest concentrations of metals occurred at a site close to First Creek near Port Pirie; however, they failed to find a relationship between metal concentration in seston and distance from the discharge point.

Metal contamination in seagrasses

A study conducted by Olsen (1983) into metal concentrations in seagrasses showed that the distribution of seagrass did not appear to be substantially changed by metal pollution. They did, however, find elevated concentrations of cadmium, manganese, lead and zinc in the seagrass, and metal contamination was also found in the algae and other epiphytes that grow on the seagrass leaves. Surveys showed that in a 2.25 km² area the standing crop of seagrass leaves contained 73 tonnes of cadmium, 51 tonnes of lead and 571 tonnes of zinc, indicating that a significant amount of metal contamination is being stored in marine organisms (Ward et al. 1982).

The distribution and abundance of animals living in seagrass were adversely affected by metal contamination. Investigations showed that sediment metal concentrations above 0.7 µg/g cadmium and 92 µg/g zinc (about five times the background concentration) caused detectable impacts upon seagrass fauna. The growth of epifauna on razorfish shells was also affected by metals. Razorfish shells are the most common hard substrate on the soft bottom of the northern Spencer Gulf, and each adult shell provides approximately 200 cm² of surface area for other organisms to colonise. Ward et al. (1982) found that in contaminated areas the razorfish shells supported only a limited fauna and the species richness of this shell fauna increased as metal contamination decreased.

Metal contamination in marine animals

In the Port Pirie River and along the Port Pirie shipping channel, Olsen (1983) collected garfish with high concentrations of lead and cadmium, bivalve molluscs high in zinc and lead, and barnacles (a type of crustacean) with high lead and zinc concentrations.

Investigations conducted by Ward et al. (1982) of the distribution of metals in the marine environment around the smelter showed that many organisms, especially filter-feeding ones, are contaminated with heavy metals. The majority of metals present in sediments were found in particles in the 0.01–1.0 mm size range. Particles of this size are easily resuspended into the water column by water movement and may then be taken up by filter-feeders such as razorfish. Additionally, the seston—the main food source for filter-feeders—contained significant amounts of metals. In some areas, especially close to First Creek, the concentrations of dissolved metals were quite high, but this reduced with distance from the outfall, presumably due to dilution and interaction between the dissolved metals, sediments and organic matter.

Ward et al. (1982) found that almost all animals and plants living in the contaminated area had elevated concentrations of lead, cadmium and zinc. Analysis of whole animals showed that some smaller species of crustaceans, bivalve molluscs and fish had elevated concentrations of metals in their body tissues. The edible tissues of razorfish, blue swimmer crabs (*Portunus pelagicus*), king prawns (*Penaeus latisulcatus*) and garfish (*Hemiramphus melanochir*) exceeded the health guidelines of the time.

² particles that are suspended in sea water and may include living organic matter such as plankton, dead organic matter, or inorganic matter such as silt.

Ward et al. (1982) also found a general trend, over a distance of about 20 km, of metal concentrations in water, sediments, fauna and flora decreasing with increasing distance from the smelter. Zinc contamination at this distance was still higher than their determined background concentration, so it was concluded that zinc contamination spread further than their study area.

In July 1996 the taking of marine benthic molluscs was prohibited from the majority of Germein Bay and this prohibition is still in place. This was in response to a sampling program conducted by the South Australian Health Commission which showed that metal concentrations in razorfish in the area exceeded the applicable food standard guidelines at the time. SARDI conducted sampling and analysis of metal concentrations in razorfish, blue swimmer crabs and eight species of fish from the Germein Bay area, particularly around two dredge spoil dumps, disposal areas for sediments from dredging of the Port Pirie River. They found that metal concentrations in razorfish exceeded the standards of the time for zinc and lead but not for cadmium, and metal concentrations in crabs and fish did not exceed guidelines (Edyvane & Boxall 1997). The applicable standards at the time of their study are not substantially different from the current guidelines.

Harbison and Wiltshire (1998) found elevated concentrations of some metals in razorfish collected from False Bay near Whyalla, although these concentrations did not always correlate with the sources of metals. Results suggest that seasonal patterns in currents and variability in turbidity may determine metal concentrations in False Bay, and have more influence on concentrations in filter-feeding molluscs than the distance from point sources (Harbison & Wiltshire 1998).

Edwards et al. (2001) investigated metal concentrations in the flesh of two fish: the yellow-eye mullet and the yellow-fin whiting collected from an estuary near Port Pirie. They found seasonal variations, with concentrations of lead, copper and cadmium in fish collected in winter differing from those collected in spring. They also measured metal concentrations in seston samples and found a strong positive correlation between the seston and concentrations in the fish. They also reported finding that mean lead concentrations in fish exceeded the maximum permitted levels for human consumption, although levels of cadmium and copper did not.

5 Assessing heavy metal contamination in the northern Spencer Gulf

Biology of razorfish

Razorfish (*Pinna bicolor*) are large fan-shaped marine bivalves with a long tip that remains embedded in the sediment. They are widely distributed across the subtropical parts of the Indian Ocean and the western Pacific, and are common, but patchily distributed, in South Australia.

Razorfish are constantly in contact with the water, not only because they are submerged below the water surface but because they are filter-feeders. They draw water into their bodies to filter out small organic and inorganic particles, including microscopic organisms, as a food source. Their shells protect their soft bodies from physical harm; however, due to their regular intake of water, these animals can be exposed to any contaminant that might be present in the water. More importantly, they concentrate soluble metals within their bodies and accumulate metals that are either adsorbed to the particles they ingest or present in the microscopic organisms they feed on.

Razorfish are found in soft sediments and grow in both intertidal and subtidal areas. Once razorfish larvae settle, they stay embedded in the one place for the duration of their adult life. A study in Gulf St Vincent (Butler 1987) has shown that they can live for well over ten years. Subtidal animals grow to over 40 cm in length, although the maximum size and growth rate of animals living in the intertidal zone is less than those that live subtidally. Subtidal animals become reproductively mature at about 15 cm, which takes just over one year. They reach 25 cm in two years, and are about 32 cm long after four years of growth.

Their distribution is often patchy, living in groups rather than individually. Where they do occur, densities of almost 20 per square metre can be reached; however, an average of three to five individuals per square metre is more common.

Fishing of razorfish

Razorfish are not collected for commercial purposes but are collected by recreational fishers either for their own consumption or for use as bait. From April 1994 to March 1996 SARDI surveyed the recreational fishing harvest from boats in the state. Over a one-year sampling period they recorded 1293 razorfish collected from the Spencer Gulf region and 3247 from the entire state. This survey only assessed a small proportion of the total fishing effort and the authors did not estimate the total catch of razorfish from this sampling program. However, the result indicates that there is significant collection of razorfish, although the proportion of animals collected for bait versus human consumption was not determined (McGlennon & Kinloch 1997).

Use of razorfish and sediments as indicators of heavy metal pollution

Razorfish readily accumulate heavy metals, remain in the one location after larval settlement, are widespread throughout the gulf and are easy to sample. Boening (1999) states that marine molluscs have a low tendency to bioaccumulate chromium but a high tendency to bioaccumulate such metals as arsenic, cadmium, copper, lead, mercury, silver and zinc. He suggests that they passively accumulate metals far more readily than fish and are therefore a better monitoring tool. Ward et al. (1986) found that a correlation between distance from the Pasminco smelter and concentrations of metals in razorfish

reflected the geographic spread of metals from the smelter. The concentrations of metals in the body tissues of razorfish may therefore be used as an indicator of the bioavailability of metals in the area in which they are living and, more broadly, as an indicator of the distribution of metals within the gulf.

It is important to note that organisms can take up, store and excrete metals to varying degrees, and concentrations found in one organism are not necessarily representative of other organisms. For example, filter-feeders such as razorfish may be exposed to different concentrations and take up metals at different rates than animals that feed in other ways. Similarly, organisms that live in the sediments can be exposed to different concentrations and take up metals at a different rate than organisms that live in the water column.

The razorfish data has been used in conjunction with sediment data collected in the late 1970s to early 1980s. Although this data was collected more than 20 years before the razorfish were sampled, it provides information about the longer-term deposition of substances in the environment. Because metals remain in the environment for decades, they continue to be cycled through the ecosystem. Sediments can serve as 'sinks' for heavy metals from the overlying water, and under certain conditions heavy metals can then be released from the sediment and become available to organisms in the water. Metal-contaminated sediments can also be resuspended in the water column through wave action and then be ingested by marine organisms such as fish and filter-feeding bivalves.

While razorfish do not have a high degree of contact with the sediment, they can consume suspended sediment particles. Measuring concentrations in the tissues of razorfish provides an indication of bioavailable substances in the environment, within the life span of the organism, through ingestion of substances adsorbed to sediment particles and of soluble substances in the water column.

6 Survey methods

6.1 Razorfish

Survey design

The aim of this survey was to determine the variability in metal concentrations in razorfish across the northern Spencer Gulf. To achieve this, a total of 35 locations, most around 10 m deep, were identified along the eastern and western sides of Spencer Gulf. Sites were approximately 10–20 km apart, although the density of sites was higher around the Port Pirie and Whyalla areas to gain a better understanding of the distribution of heavy metals in these areas. The razorfish collection sites are presented in figure 4. Specimens were collected between 26 February and 15 March 2001.

Three composite samples, each consisting of five animals, were collected at each site. This allowed within-site variability to be examined as well as patterns between sites. Additionally, this approach is consistent with the former Australian New Zealand Food Authority (ANZFA) sampling protocol for the assessment of mercury in molluscs (FSANZ 2003); ANZFA was the current authority of food standards at the time of sampling. In all, 105 composite samples were collected, three at each of the 35 sites. At some sites, fewer than five razorfish were collected in each composite sample due to either their sparseness or the collection of dead razorfish; however, each composite sample comprised a minimum of three razorfish. In total, 508 razorfish were collected.

Due to patchy distribution, razorfish could not be found at a number of intending sampling sites in the gulf; instead, alternative sites were chosen in the field. Ultimately, 32 sites were located in the area between Port Augusta, at the tip of the gulf, and Point Jarrold, 22 km south-west of Port Pirie and 44 km south-east of Whyalla. To help determine the extent of metal contamination in the gulf a further three samples were collected further south, one near Port Broughton, approximately 50 km south of Port Pirie, and two in Wallaroo Bay, approximately 100 km south of Port Pirie. The latter three sites were sampled with the assumption that metal concentrations should be at or near background levels at this distance away from industrial sources.

A number of studies have shown that metal concentrations in bivalves can be related to the length or body size of the animal (Cubadda et al. 2001; Ritz et al. 1982; Walker et al. 1982). However, for some bivalves, such as the blacklip abalone and the blue mussel, no such relationship has been found (Walker 1982). It was unknown if a relationship existed between size of razorfish and metal concentrations. To avoid this potential problem, razorfish as close as possible to 30 cm long, preferably within the 25–35 cm range, were collected.

To ascertain the importance of size on heavy metal concentrations, 10–15 additional razorfish were collected from four sites around the gulf that were already being investigated in the main study. These animals were chosen to include as wide a size range as possible. The length of each individual razorfish was measured and this data was then examined to determine if a relationship between razorfish length and metal concentrations existed. The results of this analysis are presented in Appendix 1.

Field methods

Sites were located using a global positioning system (GPS), the boat approaching from and being anchored down-current of the site to minimise the chance of contamination from the exhaust or oil. To prevent any sampling bias, a standardised sampling technique was used. Upon arrival at each location, a 50 m tape was rolled out from the anchor into the current. The tape was marked at 5 m, 25 m and 45 m and scientific divers collected five razorfish at each of these distances. Divers collected the razorfish by hand and each composite sample was placed in a separate plastic bag and stored in an esky.

The razorfish were measured and then dissected on shore at the end of each day. Clean stainless steel tools, used to remove the posterior adductor muscle from each razorfish, were washed with distilled water between samples. Dissection was carried out in the shell to prevent the adductor muscle from coming into contact with any surfaces to minimise the risk of contamination. Care was taken to ensure that only muscle tissue was placed into the sample jars. Samples were then frozen and freighted to the laboratory.

Laboratory analysis

The razorfish muscle samples were analysed by the food products laboratory at Queensland Health Scientific Services using inductively coupled plasma mass spectrophotometry (ICP-MS) after microwave digestion. Moisture content was measured for each sample so dry weight and wet weight could be calculated accurately, rather than using a generic conversion factor. This allowed comparison with both food standards, which are expressed as wet weight, and previous research that reported dry weight, including the studies by Ward et al. (1982, 1986).

Concentrations of arsenic, cadmium, copper, lead, mercury, selenium and zinc were determined in each sample. These metals were chosen because they are currently being discharged from industries into Spencer Gulf, some in high concentrations, and they are also believed to be readily accumulated in marine molluscs (Boening 1999). The laboratory's analytical limits of reporting (LORs) for each element are provided in Appendix 2. These LORs are based on dry weight analysis.

Quality control and assurance was maintained by running analyses of reference materials in association with the razorfish tissues. The recovery of metals from the standard reference materials was satisfactory and within the required range.

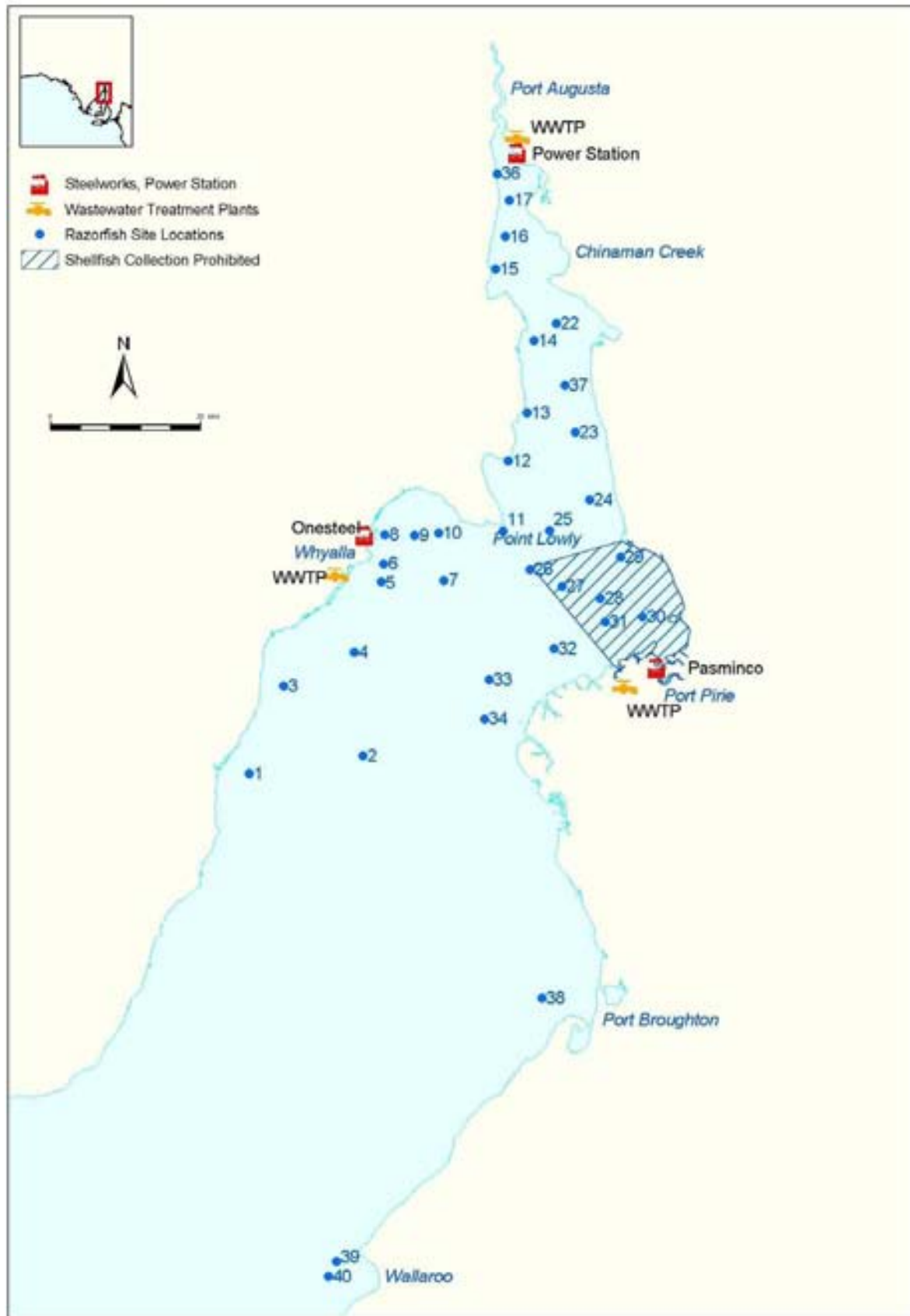


Figure 4 Razorfish collection sites

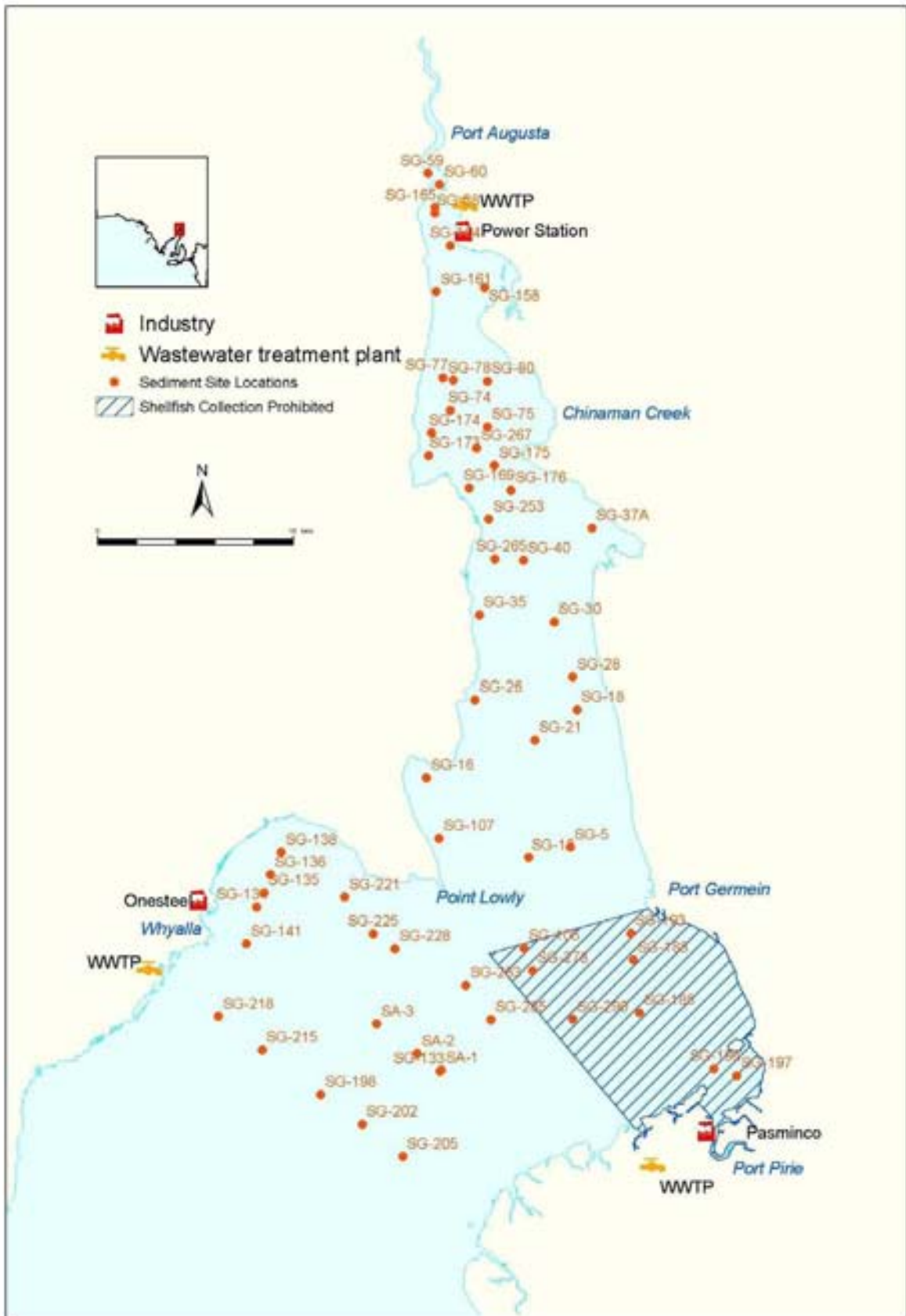


Figure 5 Sediment collection sites

6.2 Sediments

Survey design

From 1976 to 1981 a baseline study of seafloor geology and geophysics was carried out by Dr JR Hails and Dr VA Gostin from the Department of Geology at the University of Adelaide (Hails & Gostin 1984). During this period 330 seafloor sediment cores were retrieved from the area bounded by Whyalla, Port Pirie and Port Augusta.

Dr W Maher from the Department of Chemistry, University of Adelaide, and Dr Gostin later determined metal concentrations of the top 2 cm of 59 of these cores. These results have not been published previously. The locations of the 59 sites are shown in figure 5.

Field methods

The sediment cores were collected using a vibrocore, which is generally used in unconsolidated sediments. The vibrocore consists of a long tube with a vibrating device attached to it that assists in vertical penetration of the tube into the sediment.

Laboratory analytical methods

Sediment from the top 2 cm of each core was analysed following a hotplate digestion method. This involved the addition of perchloric acid (HClO₄) and hydrogen fluoride (HF) to the sediment samples, followed by heating to 200°C on a hotplate and the addition of hydrochloric acid (HCl). The samples were then analysed using atomic absorption spectrophotometry (AAS). The concentrations of cadmium, chromium, copper, lead, nickel and zinc were calculated and are expressed as mg/kg dry weight. The lowest reportable concentrations are listed in Appendix 2.

Several methods are available for extracting metals from sediments, and they vary substantially in recovery efficiency. The ANZECC guidelines suggest a dilute-acid extraction method for comparison with the sediment guidelines as this gives a better indication of the metals likely to be biologically available. It is important to note that the method used to analyse the sediment data presented in this report is a more aggressive extraction method that removes all metal from the sediments, including those bound in detrital minerals that are unlikely to become bioavailable under normal circumstances.

7 Data analysis

7.1 Descriptive statistics

Measurements of contaminants from most natural environments are highly variable, so descriptive statistics are used to summarise the data. The mean, 95% confidence interval, standard deviation, median, and 10th and 90th percentiles have been calculated for each metal analysed in both the razorfish and the sediments. Spearman's rank correlations were performed to investigate relationships between metal concentrations and distance from source.

7.2 Classification of data

To simplify the presentation of the data collected during this survey, a method has been developed which broadly summarises the data and provides a useful and relatively simple means of classifying the metal concentrations in razorfish tissue and sediment samples. These classifications allow ready comparison of sites and provide information that can be used to support management decisions.

Although the classifications of metal concentrations at each site have been assigned as good, moderate or poor, no formal national standards for these classifications exist. They have been developed using the *Australia New Zealand Food Standards Code* (FSANZ 2003) to classify razorfish tissue and the *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* (ANZECC 2000) to classify sediment data.

Food standards and metals in razorfish

At the time of sampling the *Australian Food Standards Code* consisted of two separate codes, volume 1 containing the older *Australian Food Standards Code* and volume 2 the new joint *Australia New Zealand Food Standards Code* (FSANZ 2003). On the 20 December 2002 the new code took precedence and all food sold in Australia and New Zealand must now comply with these new food standards.

In the new code, defined 'maximum levels' (MLs) are used to manage risks to human health. They have only been designated for food-metal combinations that provide a significant contribution to the total dietary exposure (>5% exposure). Those contaminants for which MLs have not been established, such as copper, selenium and zinc, are considered to be low risks to public health (FSANZ 2003). However, as a general rule, levels of all contaminants should be kept as low as is reasonably possible.

To provide guidance for those food-metal combinations for which MLs have not been established, a set of 'generally expected levels' (GELs) have been developed. Unlike MLs, GELs are not legally enforceable and exceeding a GEL does not necessarily indicate health risks. They are an indication of the concentration of metals found in some foods that reflect best practice. These GELs are expressed as a median and 90th percentile concentration. A sample value higher than the reported 90th percentile indicates that the sample being investigated is higher than 90% of all samples tested to produce the GEL. In this instance, further investigation is warranted.

The MLs and GELs are calculated for the edible content of the food that is normally consumed; in the case of razorfish, this is the posterior adductor muscle. However, people have been known to consume other parts of the razorfish and it is possible that the

concentration of some contaminants may be higher in other tissues. Therefore, it is important to note that comparison with food standards is only valid for the consumption of the adductor muscle, and does not provide any guidance for the consumption of other tissues. MLs and GELs are presented as mg/kg wet weight.

Classification of metal concentrations in razorfish against food standard maximum levels (MLs)

To assess the metal concentrations in razorfish tissues collected in this survey, adductor muscle samples are classified according to standard 1.4.1—Contaminants and natural toxicants—of the *Australia New Zealand Food Standards Code* (FSANZ 2003). MLs for food-metal combinations in molluscs are detailed in table 2.

Table 2 Maximum levels of cadmium, mercury, lead and inorganic arsenic in molluscs as listed in the *Australia New Zealand Food Standards Code* expressed as mg/kg wet weight

	Cadmium	Mercury	Lead	Arsenic (inorganic)
Maximum level	2.0	0.5	2.0	1.0

In the *Australia New Zealand Food Standards Code* (FSANZ 2003) the maximum level (ML) is defined as ‘the maximum level of a specified contaminant, or specified natural toxicant, which is permitted to be present in nominated food’ and is applicable to the edible portion normally consumed. Each composite sample of razorfish will be classified as either good or poor according to the ML of the metals:

GOOD	Metal concentration in the composite sample is equal to or less than the maximum level (ML) specified in the <i>Australia New Zealand Food Standards Code</i> (FSANZ 2003).
POOR	Metal concentration in the composite sample is greater than the maximum level (ML) specified in the <i>Australia New Zealand Food Standards Code</i> (FSANZ 2003).

Classification of metal concentrations in razorfish against generally expected levels (GELs)

GELs for various food-metal combinations are detailed in table 3. Copper, selenium and zinc have been assigned GELs as they do not contribute significantly to dietary exposure and are considered to pose little risk to public health (FSANZ 2003). These GELs have been established using studies conducted in Queensland and Western Australia and one national study (Hambridge, pers. comm.). The studies used to generate GELs were believed to have occurred in areas with no known pollution sources. Targeted surveys, or those where samples were taken from known contaminated sites, were not included in the data sets used to generate GELs.

The copper GELs are applicable to molluscs in general as they were derived from studies on ten different mollusc species (including razorfish) with a total of 234 values. The values for selenium have been derived using data from both crustacean and mollusc species (at

least five different species, 119 values) while the zinc GELs are specific to oysters (20 values) (Hambridge, pers. comm.).

The mode and rate of uptake, metabolism and excretion of each metal can vary between species of molluscs. As these GELs are not specific to razorfish, they are only used in this report as a guide to the concentrations that might be found in razorfish in uncontaminated sites. Further specific studies would need to be conducted to determine how applicable these GELs are to razorfish in South Australia.

Table 3 Generally expected levels (GELs) for copper, selenium and zinc in molluscs and crustaceans as listed in the *Australia New Zealand Food Standards Code* expressed as mg/kg wet weight

	Copper (mg/kg)	Selenium (mg/kg)	Zinc (mg/kg)
Median	5	0.5	130
90th percentile	30	1	290
Food category	Molluscs	Crustacea and molluscs	Oysters

Unlike those metals for which MLs exist, the concentrations of copper, selenium and zinc in the razorfish samples have not been classified. Instead, the results have been simplified by presenting the number of samples with concentrations below the median value, between the median and 90th percentile, and above the 90th percentile.

Comparisons of metal concentrations in sediments against sediment guidelines for the protection of marine ecosystem values

Guidelines for metal concentrations in marine and estuarine sediments, provided by the ANZECC guidelines for fresh and marine water quality (ANZECC 2000), are summarised in table 4. These figures are based on a review of contaminated marine and estuarine sediment studies by Long et al. (1995), and they summarise the findings of negative impacts on fauna and flora at different metal concentrations. In 10% of these studies there was a negative impact at low metal concentrations and in 50% a negative impact at high metal concentrations. The low and high guideline levels have been developed to provide information regarding the likelihood of negative impacts occurring to the aquatic organisms inhabiting the sediment.

There are limitations in using these trigger values—they were generated from toxicity tests using just one or two species of aquatic organisms, mostly amphipods, and they do not take into account the synergistic or antagonistic effects that can occur between metals.

Metal concentrations below the low value indicate that organisms inhabiting the sediment are unlikely to be significantly affected by that metal; concentrations between the low and high values indicate a possibility of a negative impact upon the organisms; and a concentration above the high value indicates that negative impacts are more likely to occur.

Table 4 ANZECC guidelines for metal concentrations in sediments expressed as mg/kg dry weight

	Low trigger value (mg/kg)	High trigger value (mg/kg)
Cadmium	1.5	10
Chromium	80	370
Copper	65	270
Lead	50	220
Nickel	21	52
Zinc	200	410

Classifications for these metal concentrations have been designed to ascertain the quality of the sediment. Three classification classes have been established: good, moderate and poor. The classification of metal concentrations in sediments for the protection of marine ecosystems have been assigned as follows in comparison with the appropriate guideline value:

<i>GOOD</i>	Metal concentration of the sample is less than or equal to the low trigger value.
<i>MODERATE</i>	Metal concentration of the sample is greater than the low trigger value but less than the high trigger value.
<i>POOR</i>	Metal concentration of the sample is equal to or greater than the high trigger value.

8 Metal concentrations in razorfish

8.1 Distribution of heavy metals in razorfish across the northern Spencer Gulf

A statistical summary of the heavy metal concentrations (dry weight) detected in razorfish adductor muscles is presented in table 5.

Table 5 Dry weight metal concentrations of 105 composite razorfish adductor muscle samples from the northern Spencer Gulf

	Mean (mg/kg)	95% confidence interval (mg/kg)	Standard deviation (mg/kg)	Median (mg/kg)	10th percentile (mg/kg)	90th percentile (mg/kg)	Minimum (mg/kg)	Maximum (mg/kg)
Arsenic	54.4	50.8–57.9	18.3	49.8	38.0	71.4	28.8	128.2
Cadmium	1.08	0.99–1.17	0.45	0.97	0.68	1.57	0.38	3.47
Copper	1.40	1.26–1.54	0.71	1.16	0.75	2.48	0.40	4.04
Lead	1.22	0.94–1.50	1.46	0.73	0.18	2.45	0.01	7.74
Mercury	0.038	0.034–0.041	0.019	0.034	0.014	0.067	0.005	0.098
Selenium	3.59	3.27–3.91	1.64	3.16	1.94	5.97	1.60	9.82
Zinc	655.5	554.6–756.4	521.3	473.2	238.3	1182.2	125.3	2769.1

The metals have been investigated individually and the distribution of each metal detected in razorfish collected in the northern Spencer Gulf is presented in figures 6 to 12. The values represent the mean concentrations measured in the three composite samples collected from each site in the study area.

No discernible patterns were seen for the distribution of arsenic, cadmium, copper or mercury across the northern Spencer Gulf. Concentrations of arsenic in razorfish adductor muscle were in the range 28.8–128.2 mg/kg (table 5). The lowest concentrations were seen at the two sites near Wallaroo, which are the furthest south in the study area (figure 6). The highest concentration was seen at a site on the edge of the prohibited zone. This high value was measured in one of the composite samples but the other two collected at this site had much lower concentrations of arsenic (51.7 and 47.4 mg/kg).

Cadmium concentrations in razorfish were in the range 0.38–3.47 mg/kg (table 5). The lowest concentration was detected in a sample just north of the prohibited area in Germein Bay and the highest concentration at the site near Port Broughton (figure 7). The other two composite samples collected from this site had just over half this concentration, both recording 1.89 mg/kg.

The concentrations of copper measured in razorfish samples were in the range 0.40–4.04 mg/kg (table 5). The lowest concentration was measured from a site in the centre of the prohibited area. There was substantial variation between the three composite samples collected from this site, with recordings of 0.40, 0.74 and 2.00 mg/kg (figure 8). The site at Point Lowly was another to show substantial variation between the three composite samples, with copper concentrations of 1.38, 2.76 and 4.04 mg/kg measured.

Mercury concentrations were in the range 0.005–0.098 mg/kg (table 5). The lowest concentration occurred at a site in the prohibited area (figure 10). The highest concentration recorded at this site was 0.028 mg/kg and this concentration was exceeded at the two sites near Wallaroo. These two sites were chosen in this study because it was believed that concentrations of heavy metals would be at or near background levels at this distance from the known sources of metal pollution.

Elevated concentrations of lead, selenium and zinc were seen mainly around Port Pirie and Whyalla. Concentrations of lead detected in the adductor muscle of razorfish were in the range 0.01–7.74 mg/kg (table 5). Elevated levels of lead were detected in razorfish collected from sites throughout the prohibited area. All composite samples collected from the site closest to Pasmenco recorded lead concentrations above 7 mg/kg and included the highest recorded concentration of 7.74 mg/kg. The lowest concentration was detected from a site near Wallaroo (figure 9). There was substantial within-site variability in lead concentrations between the composite samples collected at one site in the northern section of the study area near Port Augusta, with concentrations in the range 0.64–5.58 mg/kg.

The highest concentration of selenium (9.82 mg/kg) was measured in razorfish collected from the site closest to the Pasmenco smelter and the lowest concentration was measured in samples collected from one of the sites near Wallaroo. Many of the samples collected from inside the prohibited area, as well as some samples from between Port Pirie and Port Augusta, had elevated concentrations of selenium (figure 11). Between July 2001 and June 2002 NPI records show that almost all selenium entering the gulf, either through air emissions or discharge direct to water, came from the Pasmenco smelter.

There was a general distribution of elevated zinc concentrations laterally across the gulf between Port Pirie and Whyalla (figure 12). The highest concentration of 2769.1 mg/kg was detected in razorfish collected from a site at Point Lowly, and the lowest of 125.3 mg/kg was detected in a composite sample collected from a site approximately 20 km south of Whyalla.

Metal concentrations measured in the razorfish indicated substantial variation at some sites between the three composite samples. This variation may be due to differences in the age or size of the organisms that made up each composite sample. These results have emphasised the need to collect several razorfish from the one site and ensure that the sample size is large enough to include any variation that may occur.

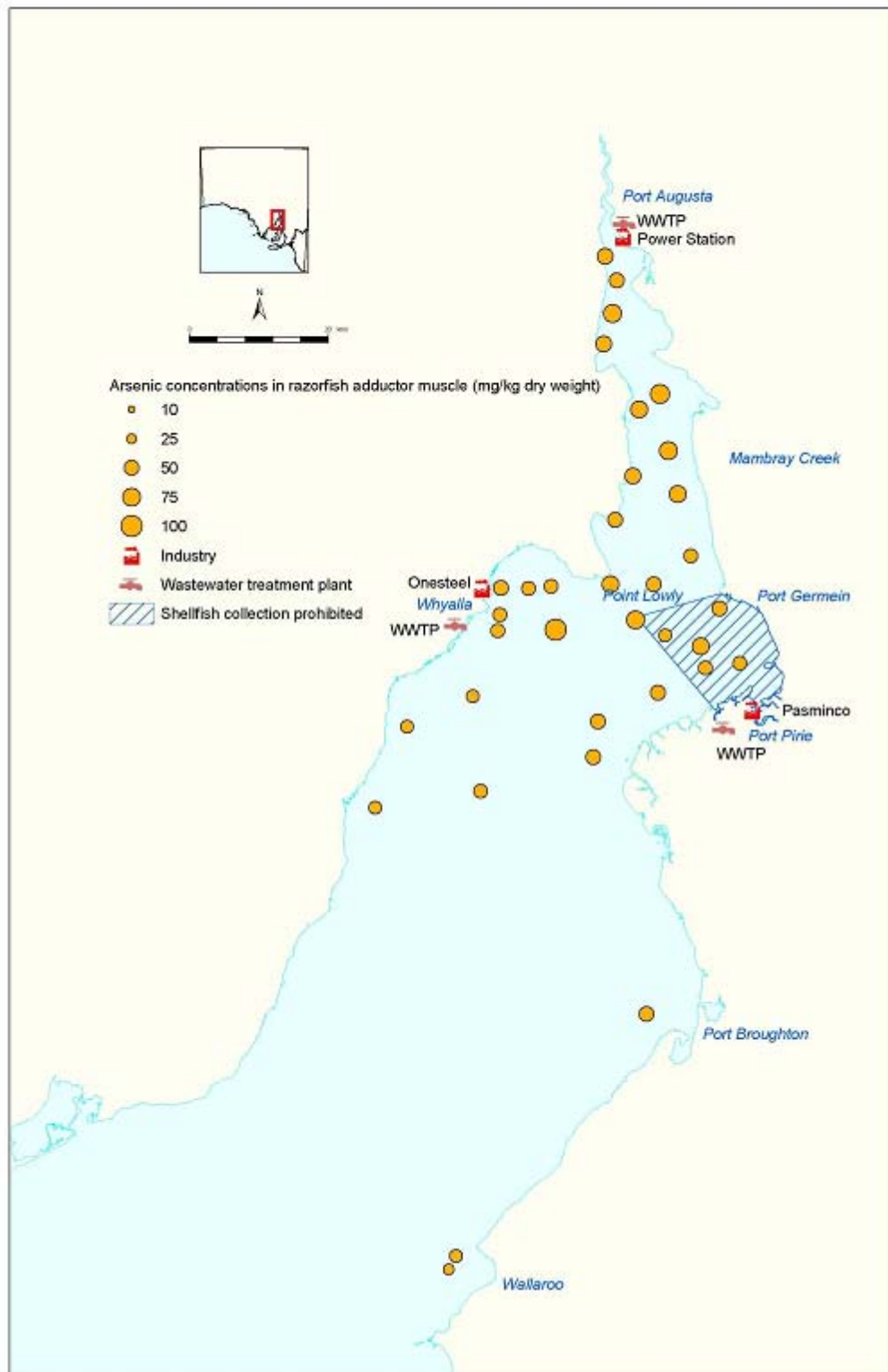


Figure 6 Total arsenic concentrations (dry weight) present in razorfish adductor muscle collected from the northern Spencer Gulf

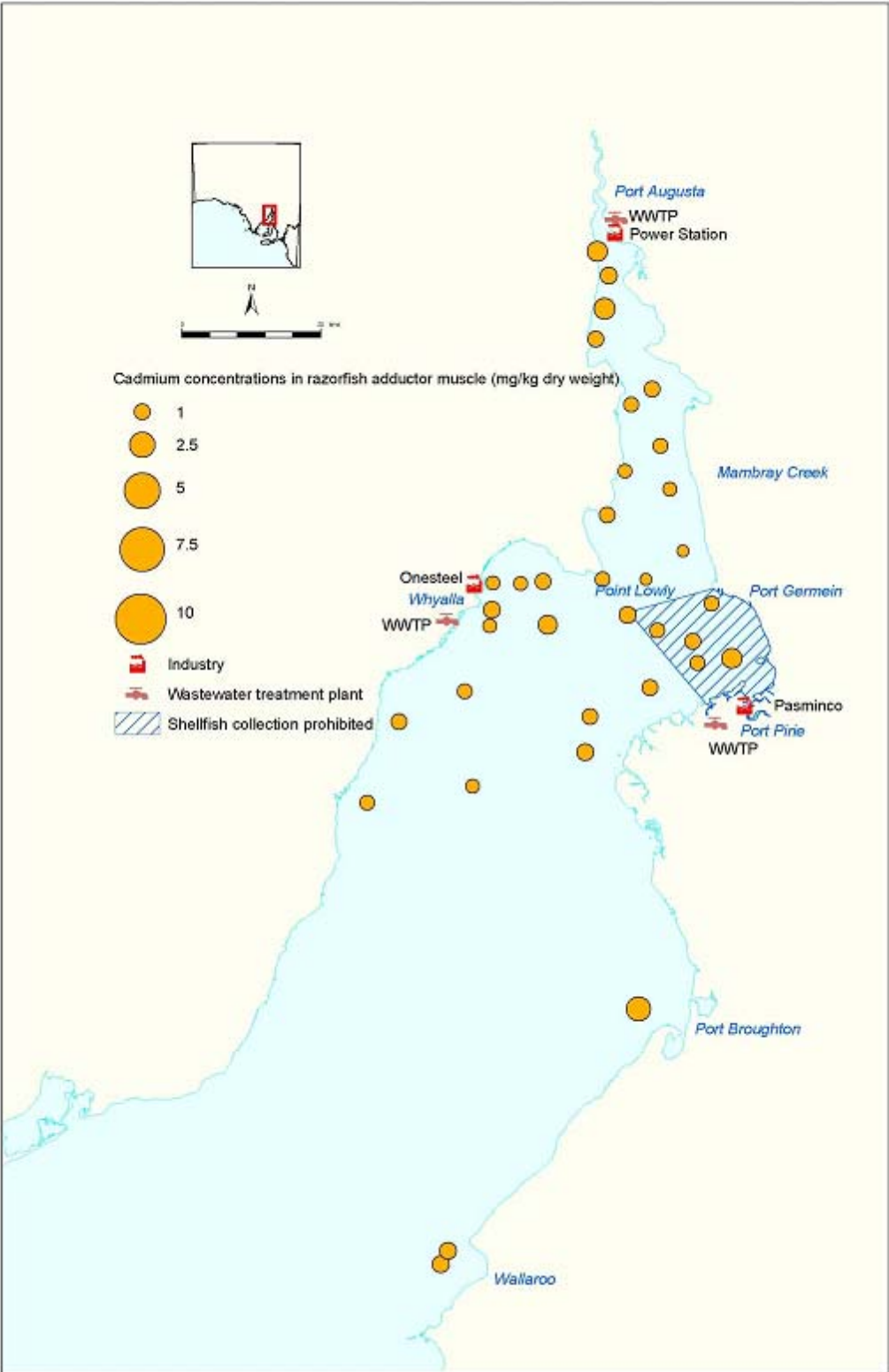


Figure 7 Cadmium concentrations (dry weight) present in razorfish adductor muscle collected from the northern Spencer Gulf

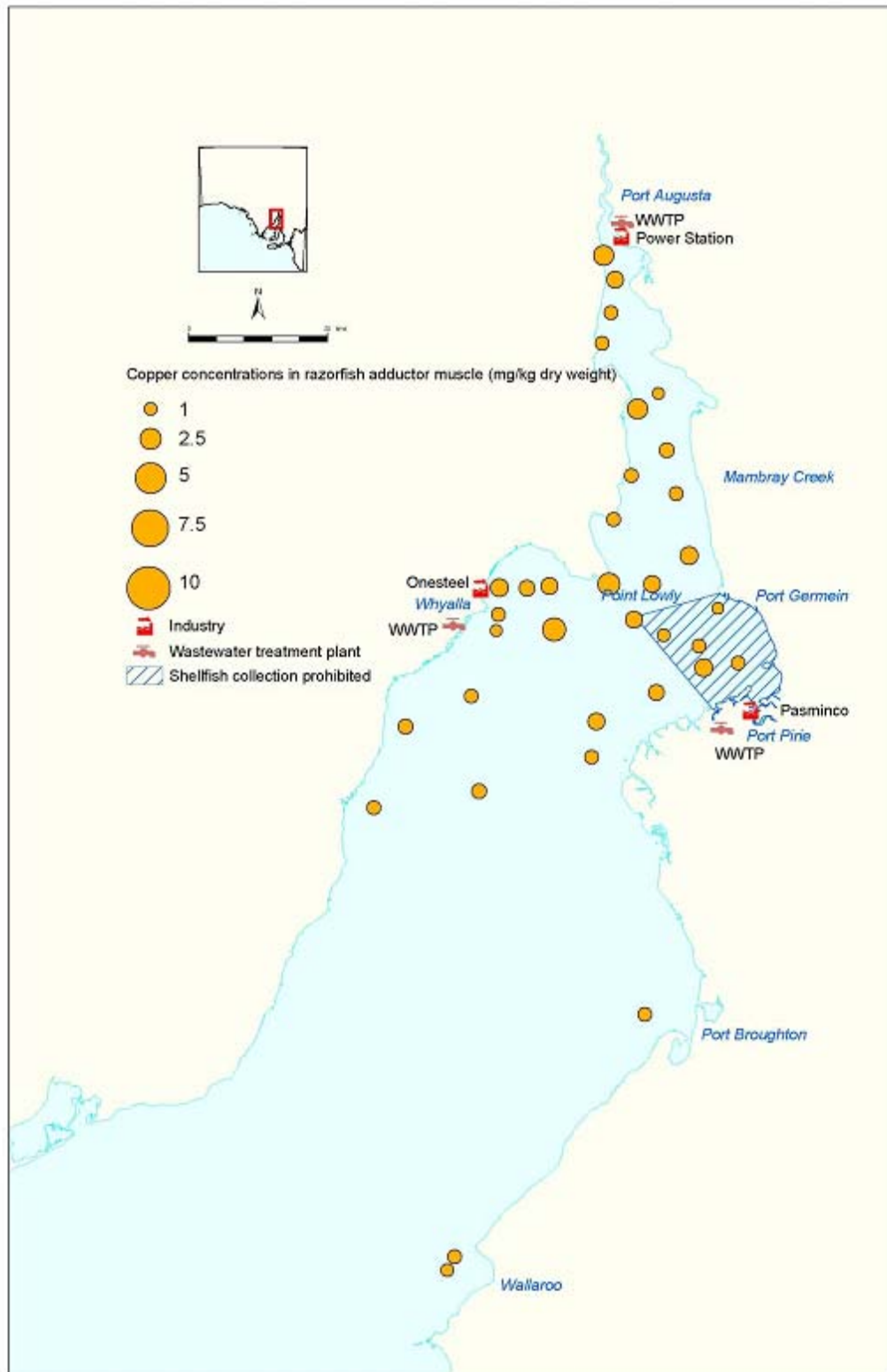


Figure 8 Copper concentrations (dry weight) present in razorfish adductor muscle collected from the northern Spencer Gulf

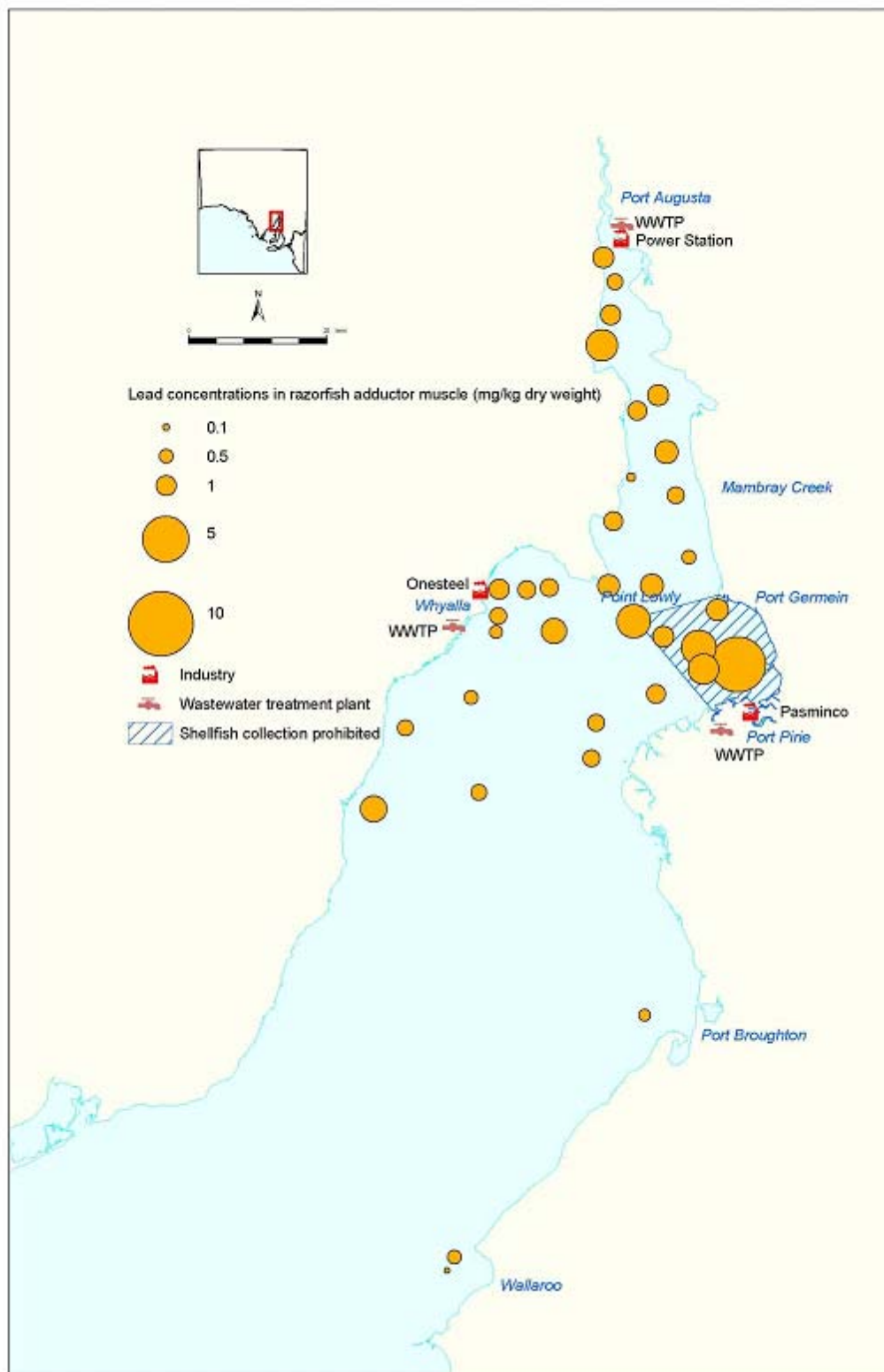


Figure 9 Lead concentrations (dry weight) present in razorfish adductor muscle collected from the northern Spencer Gulf

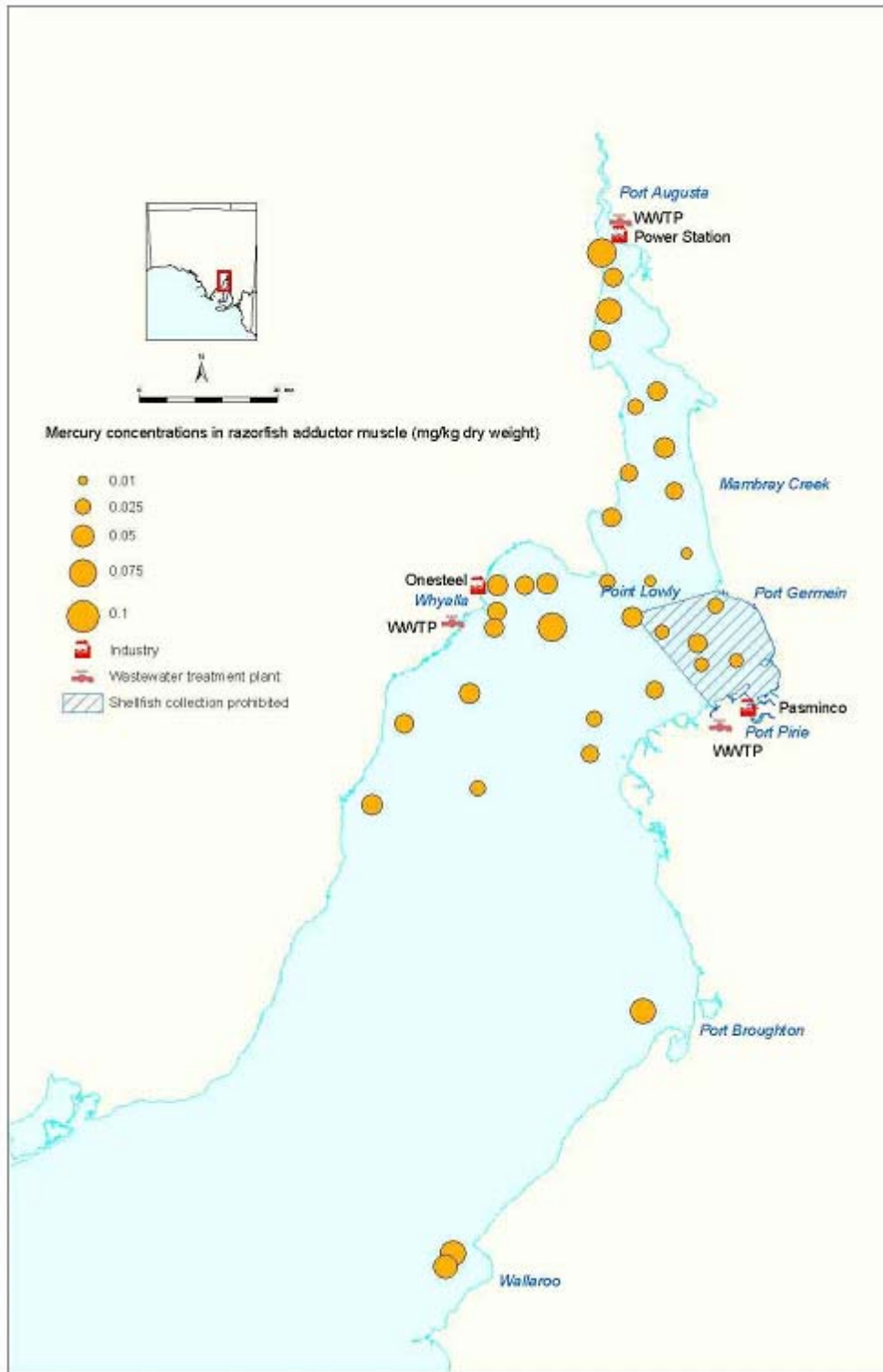


Figure 10 Mercury concentrations (dry weight) present in razorfish adductor muscle collected from the northern Spencer Gulf

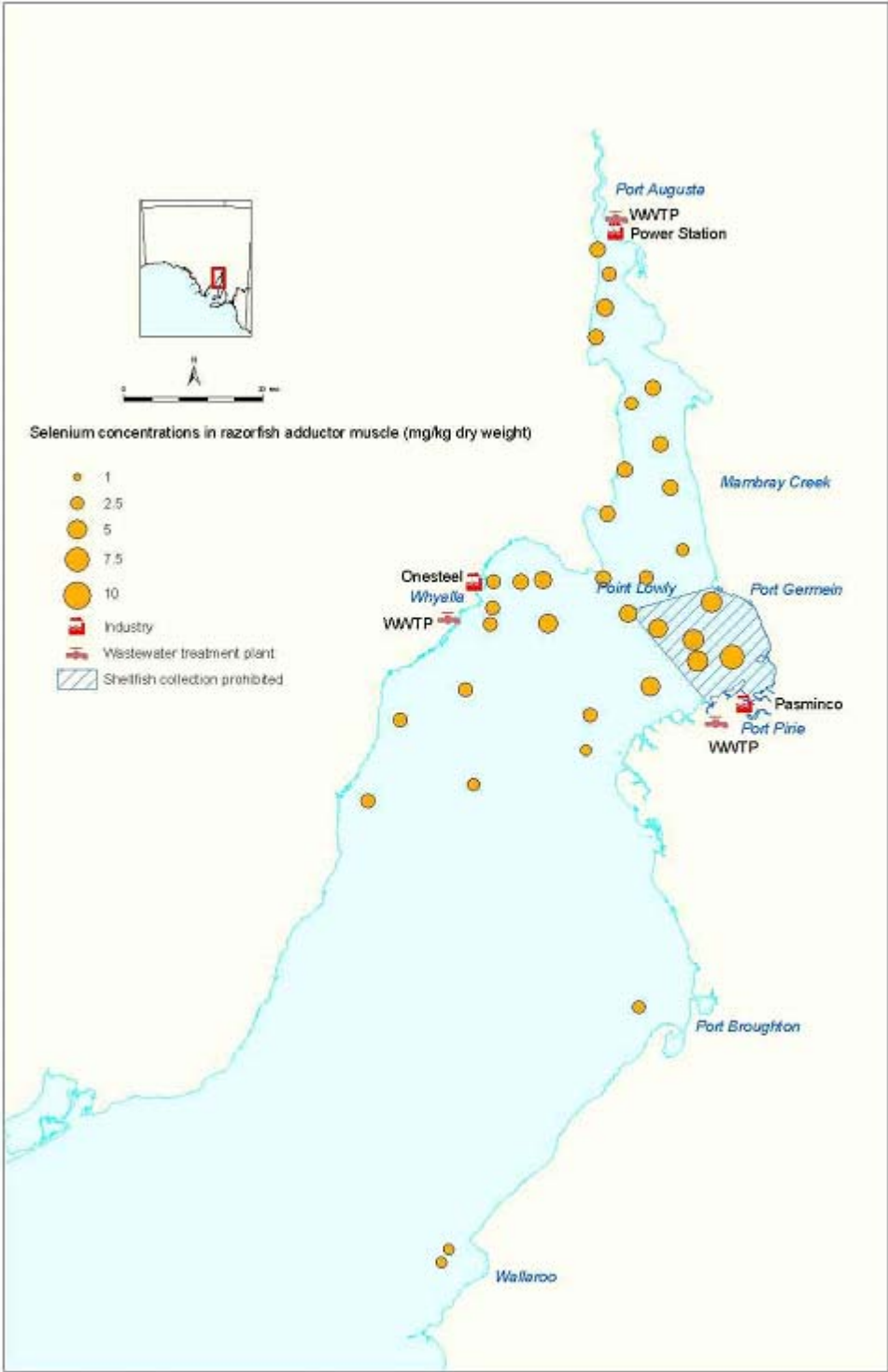


Figure 11 Selenium concentrations (dry weight) present in razorfish adductor muscle collected from the northern Spencer Gulf

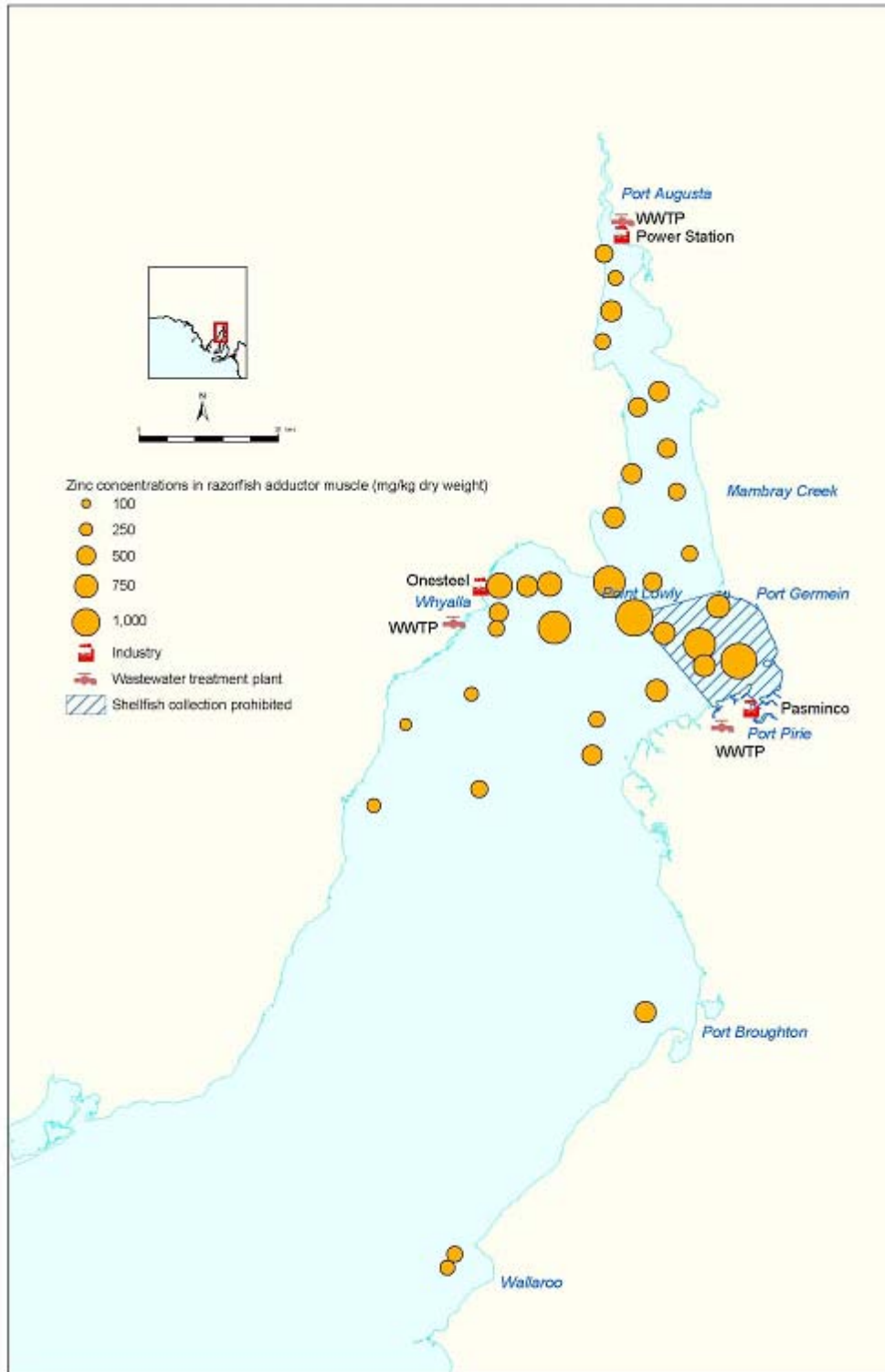


Figure 12 Zinc concentrations (dry weight) present in razorfish adductor muscle collected from the northern Spencer Gulf

Relationship between heavy metal concentrations in razorfish and distance from point sources

The relationships between concentrations of metals found in razorfish and distance from the Pasmenco lead smelter, a known source of heavy metals, were investigated using Spearman's rank correlations. The sites chosen for use in this investigation are those that are closer to Pasmenco than other point sources and those considered least likely to be affected by other known sources of metal pollution, such as OneSteel at Whyalla. Spearman's rank correlations were conducted using the dry weight concentrations of all metals analysed in razorfish adductor muscle and the reciprocal of the distance between each site and the Pasmenco smelter. The r^2 value produced by these correlations indicates how much of the variability in metal concentrations is explained by distance from a point source. Scatterplots showing the relationship for each metal are presented in figures 13 and 14.

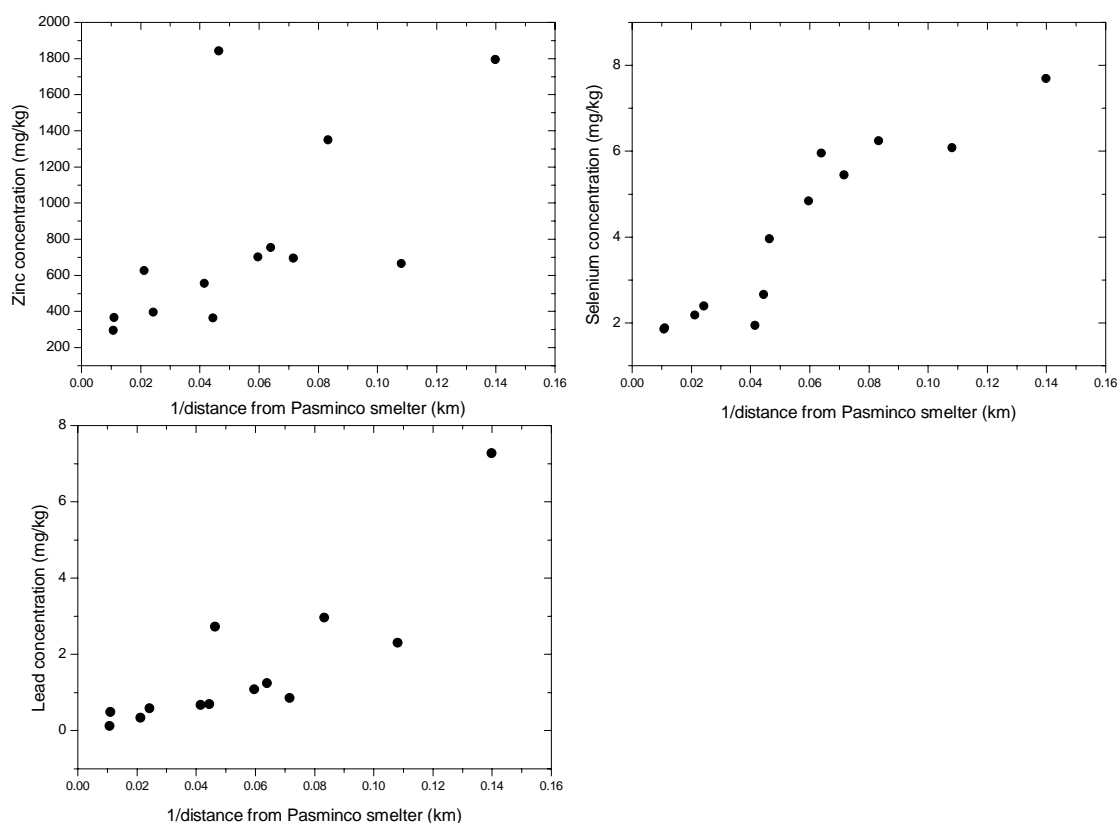


Figure 13 Relationship of distance from the Pasmenco smelter and metal concentration for zinc, selenium and lead

Zinc, lead and selenium concentrations were found to be spatially correlated with the Pasmenco smelter, with r^2 values of 0.550 ($p < 0.01$), 0.832 ($p < 0.001$) and 0.946 ($p < 0.001$) respectively, indicating a decrease in concentration of these metals away from the smelter. The correlation value for zinc is slightly less than for the other metals, possibly due to some influence from OneSteel at Whyalla; however, sites in False Bay near Whyalla were not used in the correlation assessment as these sites were closer to OneSteel than Pasmenco.

There were poor correlations between distance from source and concentrations of each of copper, arsenic, mercury and cadmium ($r^2 = 0.008, 0.107, 0.442$ and 0.082 respectively).

Ward et al. (1982) also found that cadmium levels were not spatially correlated with distance from the Port Pirie smelter. The present study found that mercury and cadmium increased as the distance from Pasmenco increased. This phenomenon was more obvious for mercury ($r^2 = 0.442, p < 0.05$), than for cadmium ($r^2 = 0.082$). The elevated concentrations of mercury in the gulf, particularly at the sites near Wallaroo, could possibly be derived from natural geological sources.

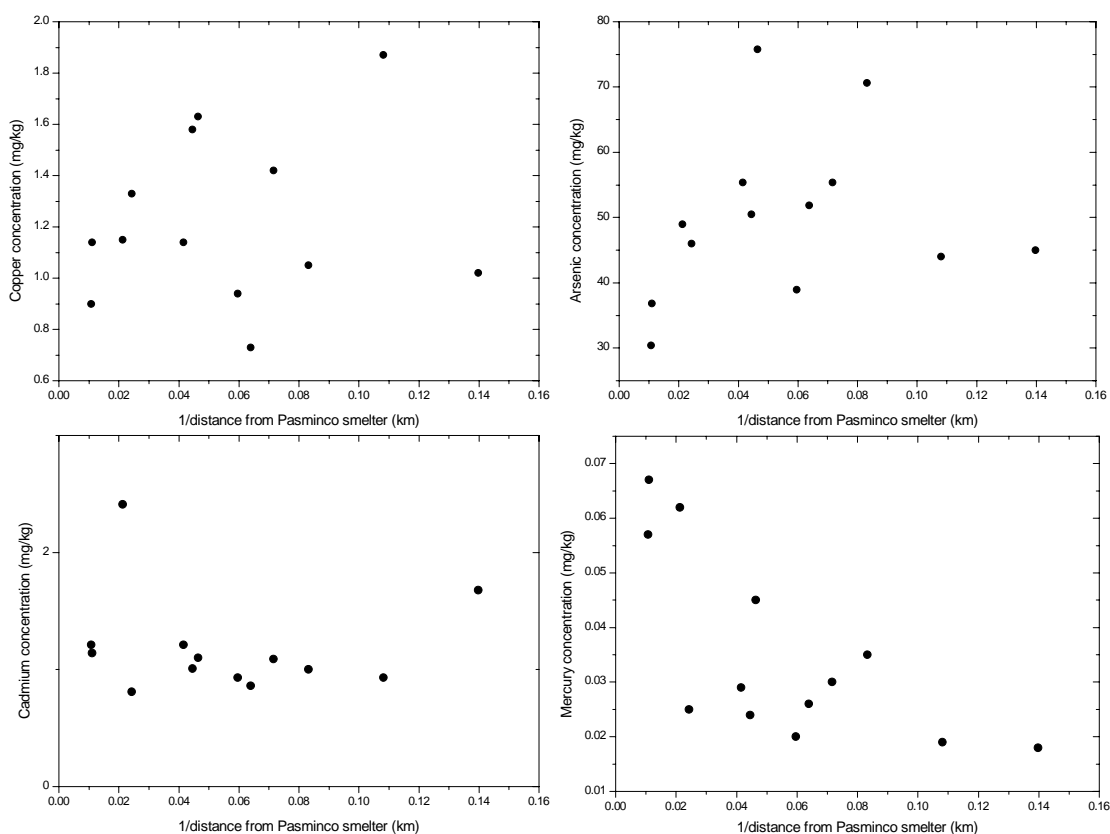


Figure 14 Relationship of distance from source and metal concentrations for copper, arsenic, cadmium and mercury

The lack of a relationship between distance from source and copper, arsenic, cadmium and mercury concentrations is possibly due to metal concentrations near the source being at or near background levels. Another possibility is that razorfish may not accumulate these metals as readily as they accumulate zinc, lead and selenium, and therefore may not be very good indicators of the distribution of these metals.

No appreciable relationship was seen between metal concentration and distance from source when investigating OneSteel at Whyalla. The best correlation occurred for zinc, with an r^2 value of 0.183. Harbison and Wiltshire (1998) suggested that seasonal patterns in currents determine the metal concentrations in the gulf around Whyalla and cover up any gradients in concentration.

8.2 Comparison of metal concentrations in razorfish with food standards

The metal concentrations in razorfish have been compared with the MLs and GELs for each metal to assess the levels of metal contamination occurring in razorfish at selected sites in the northern Spencer Gulf. The concentration measured in each of the three composite samples collected at 35 sites across the gulf has been compared with food standards. A summary of the wet weight metal concentrations measured in the razorfish samples is presented in table 6.

Table 6 Summary of metal concentrations (wet weight) of 105 composite razorfish adductor muscle samples from the northern Spencer Gulf

	Mean (mg/kg)	95% confidence interval (mg/kg)	Standard deviation (mg/kg)	Median (mg/kg)	10th percentile (mg/kg)	90th percentile (mg/kg)	Minimum (mg/kg)	Maximum (mg/kg)
Arsenic	14.8	13.8–15.7	5.0	13.8	9.9	19.6	7.1	35.3
Cadmium	0.29	0.27–0.31	0.11	0.26	0.18	0.41	0.11	0.78
Copper	0.38	0.34–0.42	0.19	0.32	0.21	0.67	0.11	1.10
Lead	0.34	0.26–0.41	0.41	0.20	0.05	0.68	0.01	2.21
Mercury	0.0103	0.0094–0.0113	0.0048	0.0092	0.005	0.0166	0.0045	0.0261
Selenium	0.98	0.89–1.07	0.47	0.86	0.52	1.65	0.40	2.81
Zinc	177.4	150.6–204.3	138.5	134.0	65.8	315.9	32.2	698.2

Comparison of razorfish samples with maximum levels (MLs) for cadmium, mercury, lead and arsenic

Two sets of razorfish samples were collected. The first set of 105 samples consisted of three composite samples collected from 35 sites; for each composite sample the adductor muscles of five razorfish were combined and analysed together. The second set of samples comprised 53 individual razorfish of varying size collected from four sites, with between 10 and 15 animals from each site. These two groups have been investigated separately and have been termed 'composite samples' and 'individual samples'.

Composite samples

Table 7 summarises the classifications of cadmium, mercury and lead concentrations (wet weight) in razorfish tissue. No samples exceeded the ML for cadmium (2.0 mg/kg) or mercury (0.5 mg/kg). Only two composite samples showed lead concentrations elevated above the specified ML of 2.0 mg/kg, resulting in a 'poor' classification (table 7). This occurred at the site closest to the Port Pirie lead smelter (figure 15), which is within the prohibited zone in Germein Bay and is also close to the area where dumping of contaminated dredge spoil from the Port Pirie River has occurred. Two of the three composite samples had concentrations above the ML of 2.0 mg/kg (i.e. 2.03 and 2.21 mg/kg). The other sample collected at that site had a concentration of 1.98 mg/kg, which is only just below the ML.

Table 7 Classification of cadmium, mercury and lead concentrations of razorfish adductor muscle tissue with food standard maximum levels for 105 samples across 35 sites in the northern Spencer Gulf

	Cadmium	Mercury	Lead
Good	105	105	103
Poor	0	0	2

The highest detected cadmium concentration, of 0.78 mg/kg, was recorded from one sample collected at the site closest to Port Broughton and another sample collected from the site closest to Port Pirie. This value is approximately 40% of—and well below—the food standard. Only four samples were higher than 0.5 mg/kg, which is one-quarter of the ML, while 48 samples were 0.25 mg/kg or less, one-eighth of the ML.

The highest mercury concentrations were two readings of 0.026 mg/kg, about one-twentieth of the food standard guideline. Sixty percent of the samples were 0.01 mg/kg or less, which is only one-fiftieth of the ML. The highest concentrations were seen at a site just south of the power station in Port Augusta and at a site on the outskirts of Germein Bay. The mercury recorded south of the power stations may be from natural sources or it may have been derived from the Northern Power Station in past years. Between July 1998 and June 1999 NPI records show that 17 kg of mercury was released direct to water. Since then the amount of mercury discharged from the power station each year has significantly declined; however, residual mercury may be present at this site. It is important to note that even at the sites with the highest mercury concentrations, the levels were still only half that of the food standard ML.

The toxicity of arsenic is strongly influenced by the chemical form in which it is present; the more toxic form is inorganic arsenic. In this study total arsenic was measured in razorfish; however, an ML has only been established for the inorganic form and there is no reliable way to estimate the proportion of inorganic arsenic present in total arsenic. As the predominant form of arsenic in seafood is organic (FSANZ 2002), comparing total arsenic with the ML for inorganic arsenic is a substantial overestimation of the risk associated with consumption of the razorfish. All recorded concentrations of total arsenic in the composite samples were greater than the ML for inorganic arsenic (1.0 mg/kg), with results in the range 4.2–35.3 mg/kg; however, it is unknown how much was in the organic form and how much in the inorganic form. Due to the difficulty in interpreting the importance of the arsenic concentrations found in the razorfish, these results have not been classified.

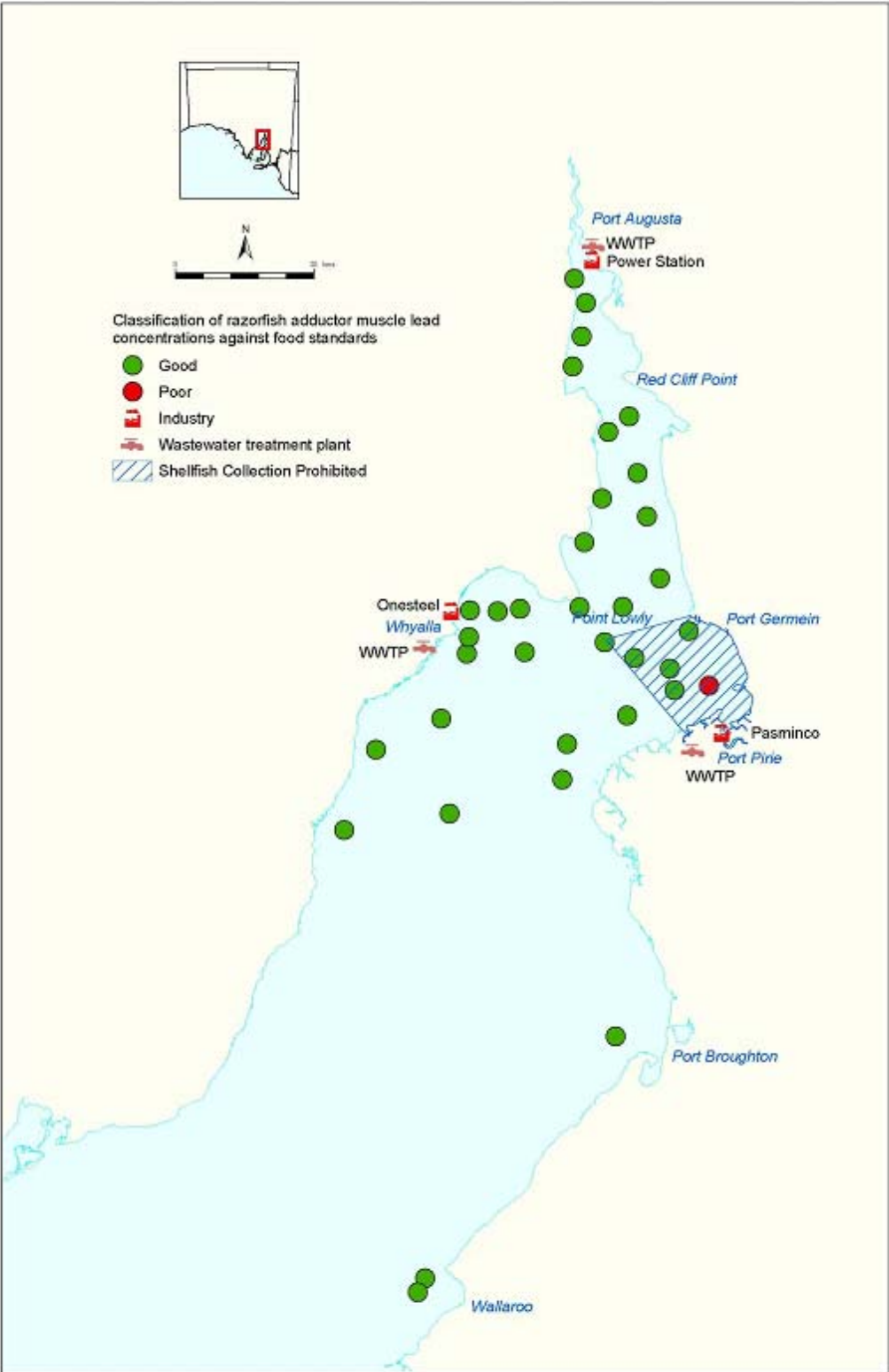


Figure 15 Classifications of razorfish adductor muscle lead concentrations in the northern Spencer Gulf against food standards

Individual samples

In addition to the composite samples, between 10 and 15 individual razorfish were collected from each of four sites in the northern Spencer Gulf to examine the relationship between the length of razorfish shells and metal content in the adductor muscles. Examination of these individual razorfish shows that all samples had mercury and cadmium concentrations substantially below the MLs set for these metals, and concentrations were classified as good. All razorfish samples at sites 8, 12 and 40 contained lead at concentrations below the ML and were classified as good. However, at site 30, 7 of the 15 razorfish collected exceeded the ML for lead and were classified as poor (table 8). The highest concentration recorded was 7.17 mg/kg, approximately 3.5 times the ML. Site 30 was also the site where the two poor classifications were recorded for the composite samples. This site is inside the prohibited zone and just over 7 km north of the smelter in the vicinity of the dredge spoil dumps.

Table 8 Classification of cadmium, mercury and lead concentrations in individual razorfish adductor muscle tissue from the northern Spencer Gulf

		Cadmium	Mercury	Lead
Site 8	Good	14	14	14
	Poor	0	0	0
Site 12	Good	10	10	10
	Poor	0	0	0
Site 30	Good	15	15	8
	Poor	0	0	7
Site 40	Good	14	14	14
	Poor	0	0	0

Comparison of razorfish samples with generally expected levels (GELs) for copper, selenium and zinc

Composite samples

Copper concentrations detected in the adductor muscle of the razorfish were all below the median GEL of 5 mg/kg (table 9).

Table 9 Summary of copper, selenium and zinc concentrations in razorfish adductor muscle tissue in comparison with the generally expected levels (GELs) for 105 samples from 35 sites in the northern Spencer Gulf

	Copper	Selenium	Zinc
<Median	105	8	50
>median but <90th percentile	0	62	41
>90th percentile	0	35	14

Selenium concentrations in almost all samples exceeded the median GEL (0.5 mg/kg), with only eight samples having selenium concentrations below the median GEL (table 9). Of the 105 composite samples tested, 35 (33%) exceeded the 90th percentile GEL (1 mg/kg).

Of the total 105 composite samples tested, 50 (48%) had zinc concentrations below the median GEL (130 mg/kg), 41 (39%) were between the median and 90th percentile values, and 14 (13%) exceeded the 90th percentile GEL (290 mg/kg) (table 9). Most sites with zinc concentrations above the median GEL were situated in either Germein Bay near Port Pirie or False Bay near Whyalla, indicating that zinc is entering the marine environment from both sides of the gulf.

Individual samples

All additional razorfish samples collected from the gulf and analysed individually contained copper at concentrations below the median GEL (table 10).

Table 10 Summary of copper, selenium and zinc concentrations in razorfish adductor muscle tissue in comparison with the generally expected levels (GELs) in individual razorfish samples collected from four sites in the northern Spencer Gulf

		Copper	Selenium	Zinc
Site 8	<Median	14	1	7
	>median but <90th percentile	0	9	6
	>90th percentile	0	4	1
Site 12	<Median	10	0	5
	>median but <90th percentile	0	4	3
	>90th percentile	0	6	2
Site 30	<Median	15	0	1
	>median but <90th percentile	0	1	6
	>90th percentile	0	14	8
Site 40	<Median	14	1	14
	>median but <90th percentile	0	12	0
	>90th percentile	0	1	0

Elevated selenium concentrations were seen at all four sites, including site 40 in Wallaroo Bay, the site furthest south in the study area (table 10). Concentrations at this site were lower than at the other sites, exceeding the 90th percentile GEL value in only one individual razorfish. The highest concentration of selenium (2.81 mg/kg) was found at site 30, the site closest to the Pasmenco smelter. Of the 15 razorfish collected at this site, 14 contained concentrations of selenium above the 90th percentile GEL (table 10).

At site 40, the site furthest south, zinc concentrations in all razorfish were below the median GEL (table 10). At the other three sites zinc concentrations above the median GEL were detected in some of the razorfish, particularly at site 30 in Germein Bay. Of the 15 individual razorfish collected at this site, eight samples contained zinc in concentrations above the 90th percentile GEL (table 10). Some elevated concentrations of zinc were seen at sites 8 and 12; both are on the western side of the gulf near Whyalla and Port Bonython (table 10).

8.3 Summary of heavy metal concentrations in razorfish

Results for cadmium and mercury were significantly below their corresponding MLs for all composite and individual razorfish samples and were classified as good. The highest cadmium concentrations were seen at the site closest to the Pasminco discharge point near Port Pirie and also at the site closest to Port Broughton. The highest mercury concentration (wet weight) was found at the site closest to Port Augusta; however, even at this location mercury levels were only one-twentieth of the food standards and were classified as good.

The ML for lead was exceeded in two composite samples at the site closest to Pasminco at Port Pirie (site 30), situated in the prohibited zone. At this same site 7 out of a total 15 individual samples also exceeded the ML and were classified as poor. The 12 highest recordings of lead came from this site. Some samples collected from the other sites in the prohibited area near Port Pirie also showed slightly higher concentrations of lead in comparison to sites outside the prohibited zone, although none of these exceeded the food standards. The variability in lead concentrations in razorfish seen at site 30 (in the range 0.37–7.17 mg/kg, with 7 of the 15 razorfish exceeding the ML) shows the need to test several razorfish specimens when assessing concentrations of contaminants against food guidelines.

Copper concentrations in all composite and individual razorfish samples were below the median GEL. The highest copper concentrations were recorded in individual razorfish from the site closest to Whyalla, although these were still only half the median GEL.

Razorfish from the sites in the prohibited area near Port Pirie contained the highest concentrations of selenium, particularly site 30, closest to Pasminco, where 14 of the 15 individual razorfish samples had concentrations exceeding the 90th percentile GEL. Of the 105 composite samples, a concentration less than the median GEL occurred in less than 8% of samples and a concentration greater than the 90th percentile was found in 33% of samples.

The highest zinc concentrations detected in the razorfish are grouped in the prohibited zone near Port Pirie, across the gulf towards Whyalla and in False Bay at Whyalla (figure 12). Of the 105 composite samples, a concentration less than the median GEL was measured in 48% of samples and a concentration greater than the 90th percentile was detected in 13% of the samples. As with lead, site 30 had the highest number (8 out of 15) of individual razorfish with elevated concentrations of zinc (greater than the 90th percentile).

9 Metal concentrations in sediments

9.1 Distribution of heavy metals in sediment samples across the northern Spencer Gulf

A statistical summary of metal concentrations found in sediment samples taken from the northern Spencer Gulf is presented in table 11, and the distribution of the metals across the gulf is presented in figures 16 to 21.

Table 11 Dry weight metal concentrations of 59 sediment samples from the northern Spencer Gulf

	Mean (mg/kg)	95% confidence interval (mg/kg)	Standard deviation (mg/kg)	Median (mg/kg)	10th percentile (mg/kg)	90th percentile (mg/kg)	Minimum (mg/kg)	Maximum (mg/kg)
Cadmium	1.84	0.73–2.95	4.27	0.50	0.20	2.80	0.20	25.10
Chromium	15.1	0.7–19.6	17.0	11.0	3.0	27.2	3.0	105.0
Copper	7.0	4.3–9.7	10.4	3.0	2.0	13.0	2.0	66.0
Lead	30.8	7.4–54.3	90.1	10.0	4.0	40.4	3.0	638.0
Nickel	4.6	3.6–5.7	4.0	3.0	2.0	9.2	1.0	25.0
Zinc	82.7	26.3–139.2	216.7	33.0	10.0	122.8	4.0	1560.0

The distribution of most of the heavy metals analysed in the sediments indicates the presence of 'hot spots' throughout the northern region of the gulf, where elevated concentrations of some metals were detected. Zinc, with concentrations in the range 4–1560 mg/kg, was the only metal to show any spatial patterns in its distribution across the gulf. Slightly elevated concentrations of zinc occurred throughout the gulf, particularly in the prohibited zone near Port Pirie and in False Bay near Whyalla (figure 21).

The highest concentrations of cadmium (25.1 mg/kg), lead (638 mg/kg) and zinc (1560 mg/kg) were all recorded at the same site, which was the closest to Pasmenco, just under 5 km north of the smelter. Two other sites contained high concentrations of cadmium: a site 34 km north of Port Pirie and a site near Red Cliff Point approximately 56 km north of Port Pirie (figure 16). The latter site also exhibited high concentrations of lead and zinc (figures 19 and 21), indicating that it may be a regional deposition area.

The lowest concentration of cadmium, 0.2 mg/kg, was recorded at ten sites scattered throughout the gulf. The lowest concentration of lead was 3.0 mg/kg, recorded from a site near Whyalla.

The highest concentrations of chromium, copper and nickel were all recorded from the one site, in the middle of the gulf between Port Pirie and Whyalla (figures 17, 18 and 20). This site is not near any known source of heavy metal pollution. Chromium concentrations were in the range 3–105 mg/kg, with the lowest recorded at seven sites. Copper concentrations were in the range 2–66 mg/kg, with the lowest recorded at 22 sites, some of which were located within the prohibited zone in Germein Bay. Nickel

concentrations were in the range 1–25 mg/kg, with the lowest recorded at four sites. One of these sites is just 58 m from the site that recorded the highest concentration.

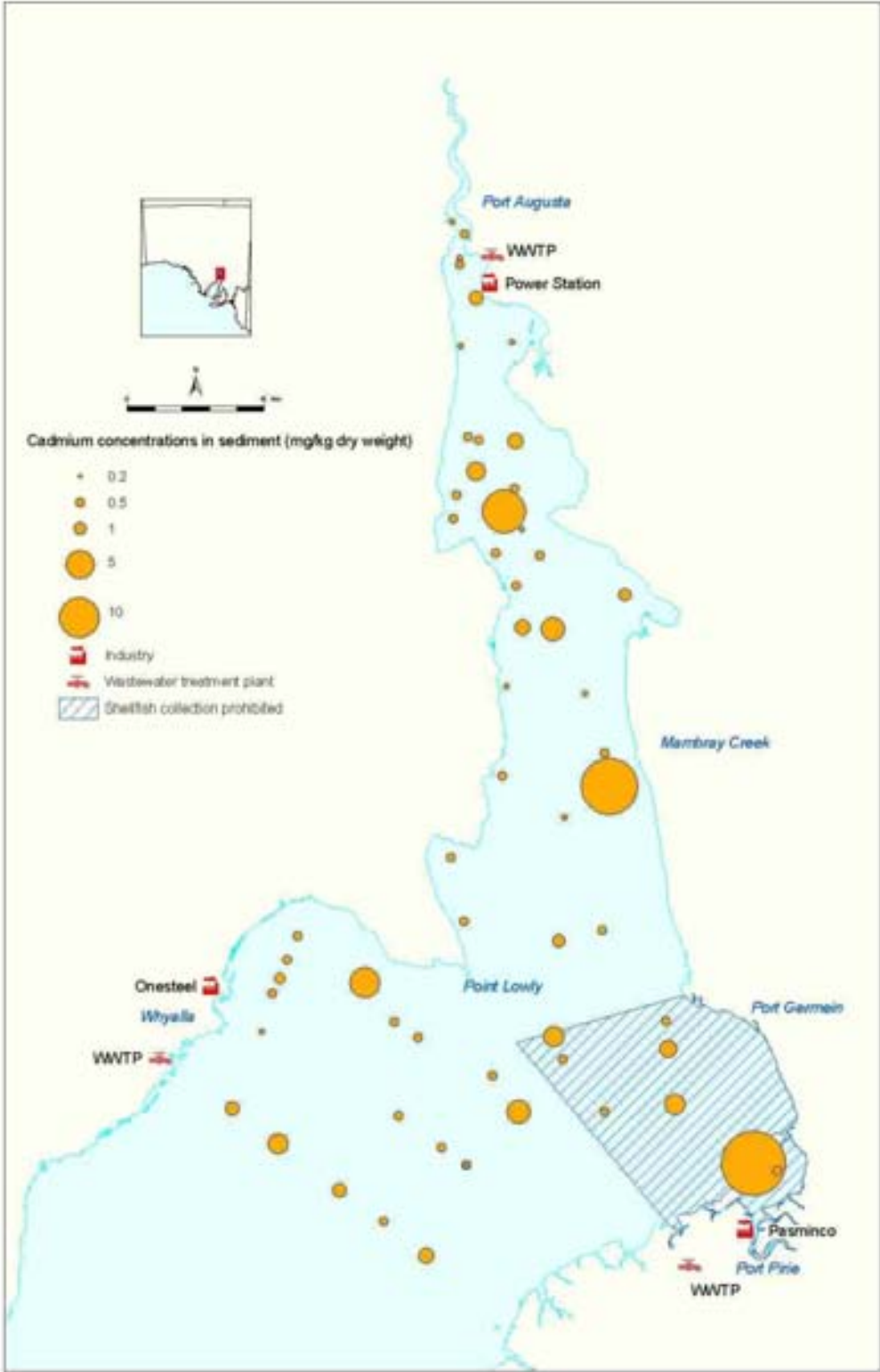


Figure 16 Cadmium concentrations present in marine sediments in the northern Spencer Gulf

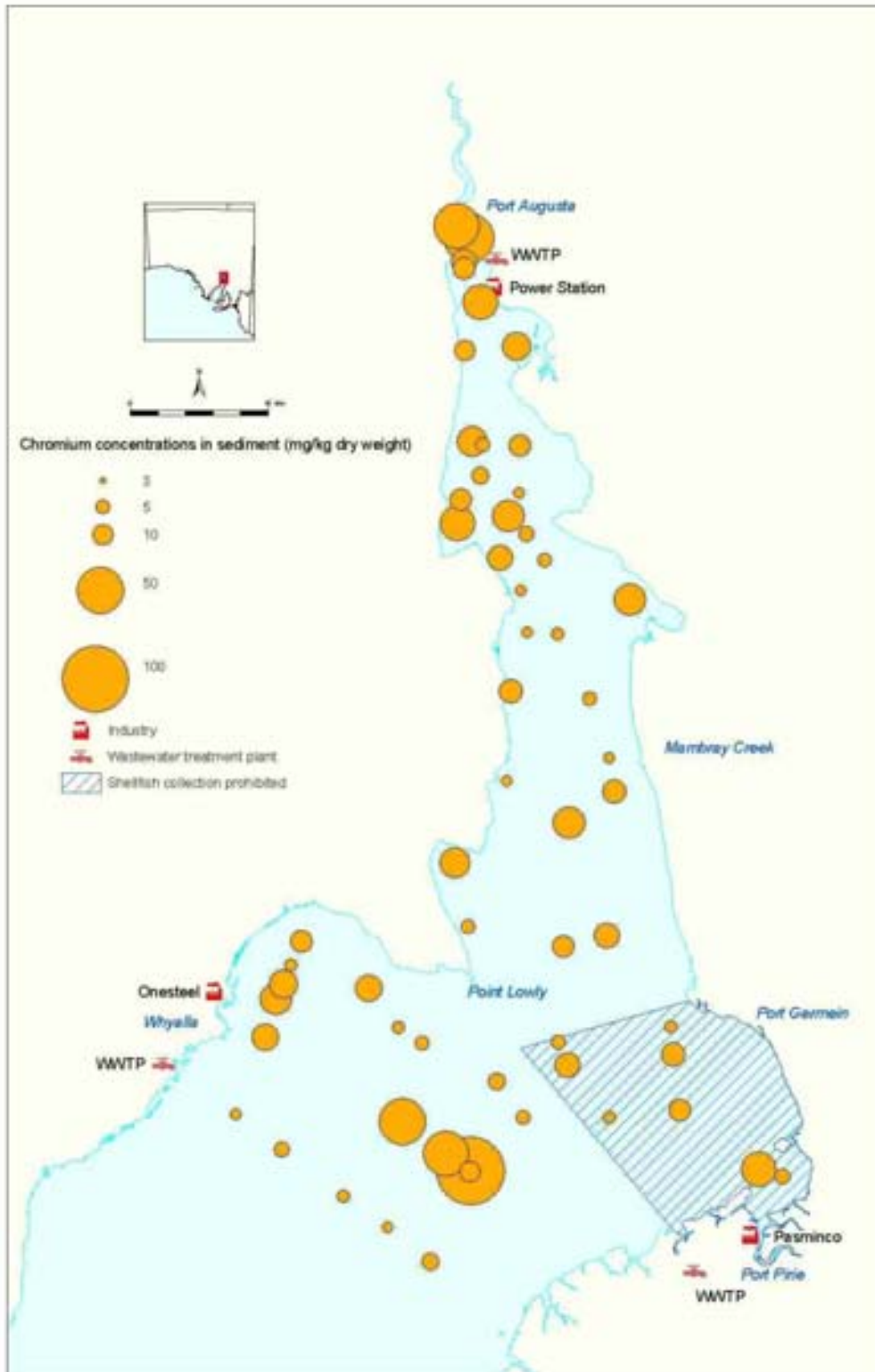


Figure 17 Chromium concentrations present in marine sediments in the northern Spencer Gulf

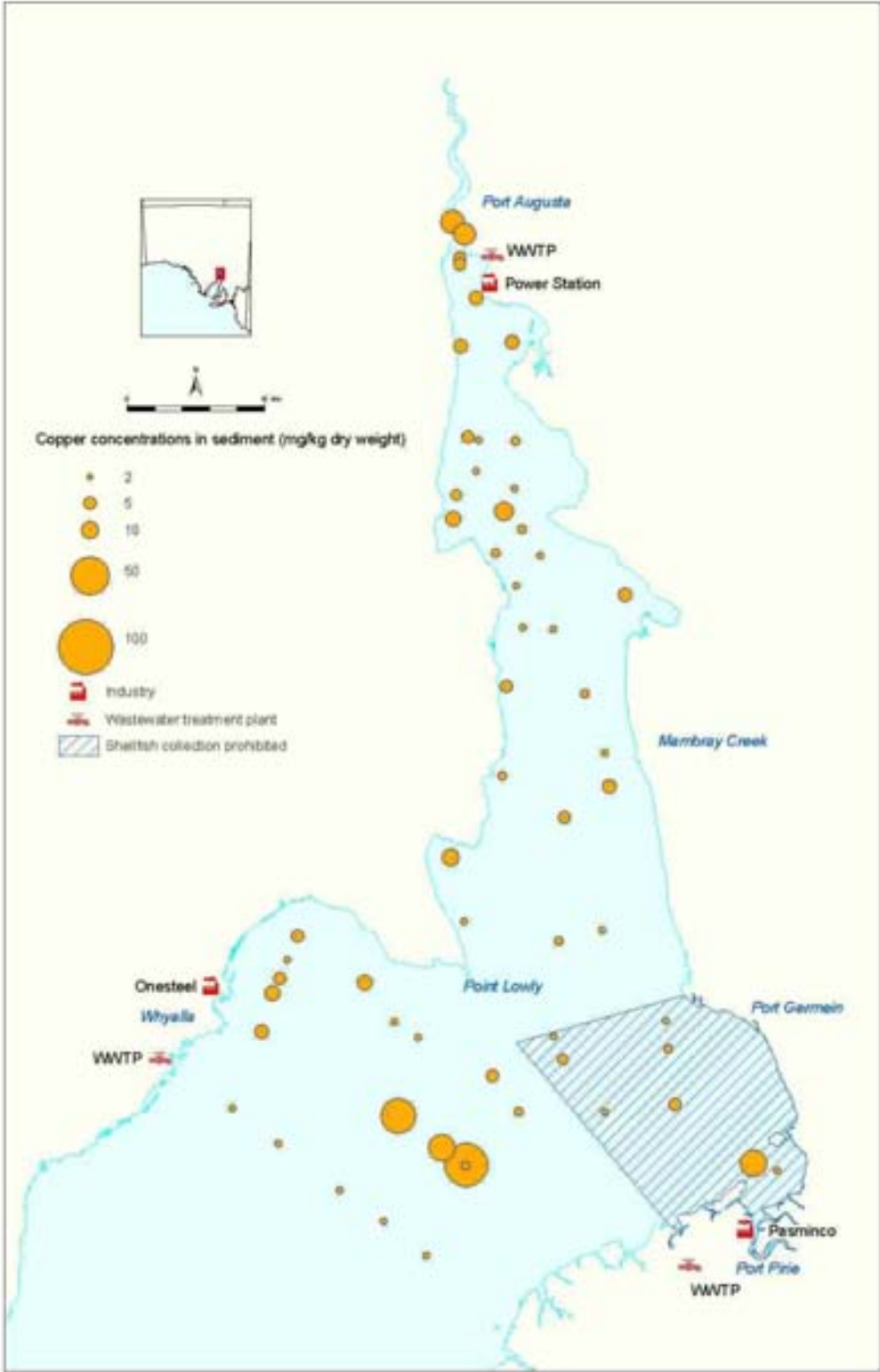


Figure 18 Copper concentrations present in marine sediments in the northern Spencer Gulf

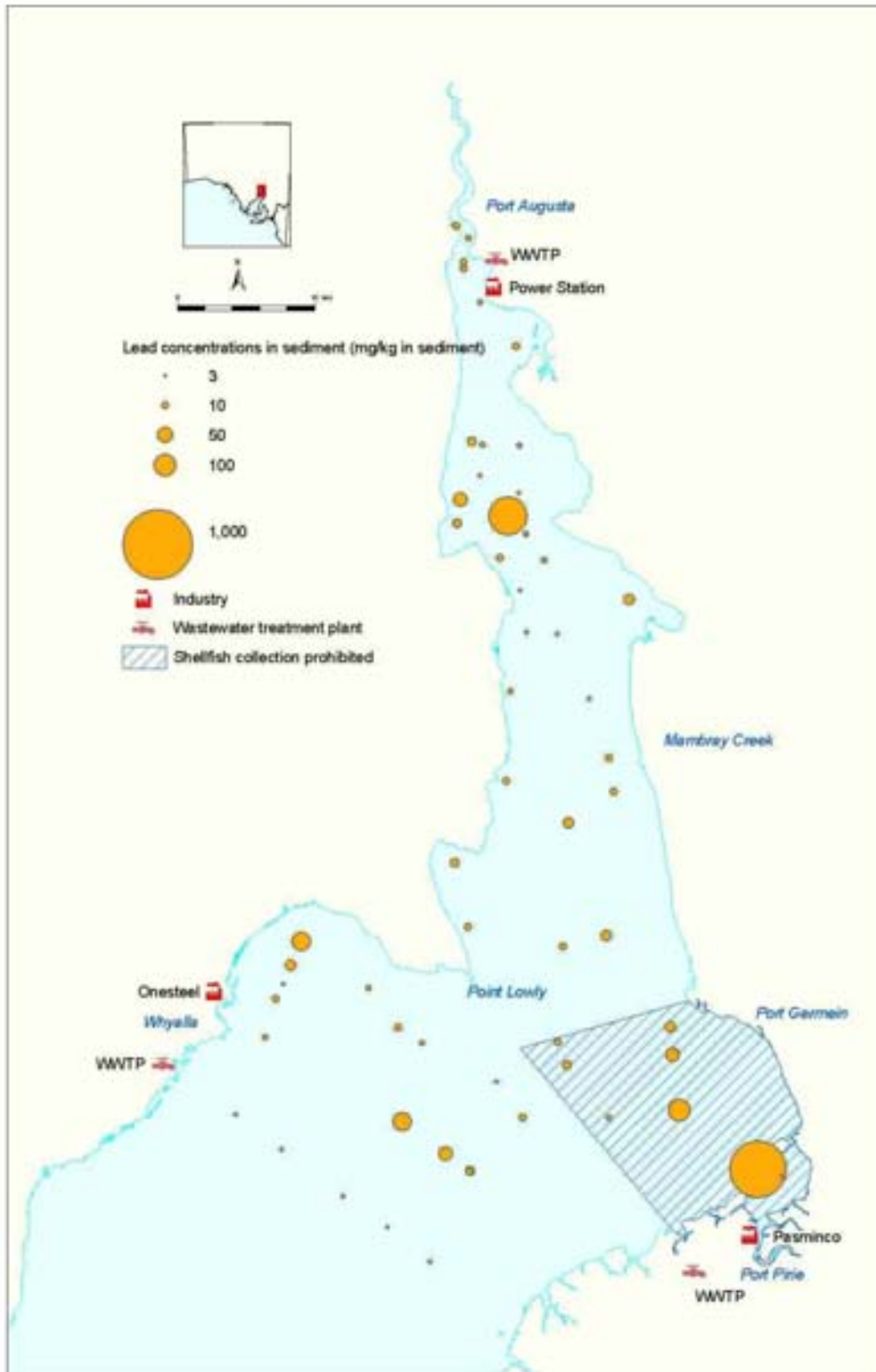


Figure 19 Lead concentrations present in marine sediments in the northern Spencer Gulf

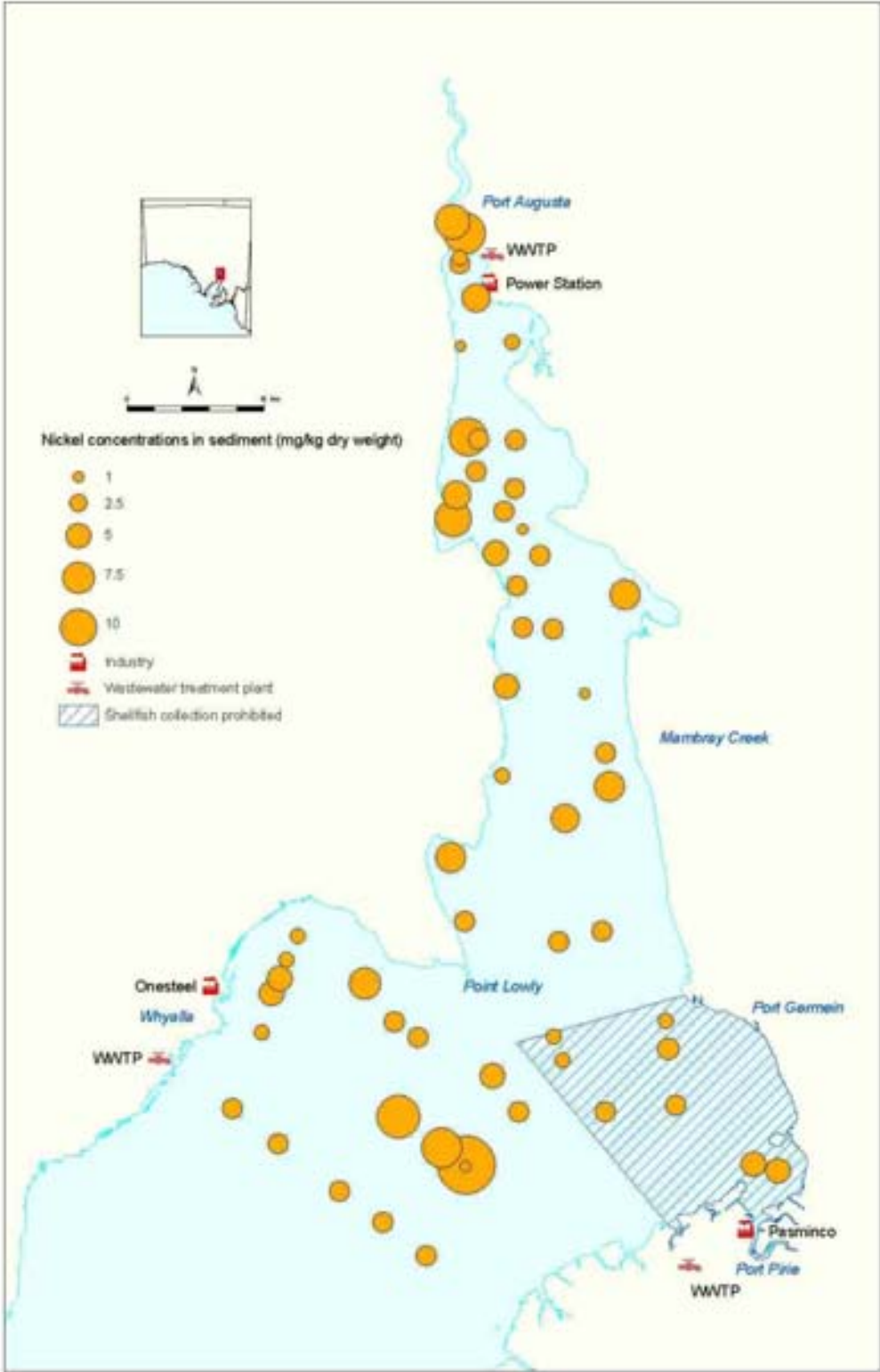


Figure 20 Nickel concentrations present in marine sediments in the northern Spencer Gulf

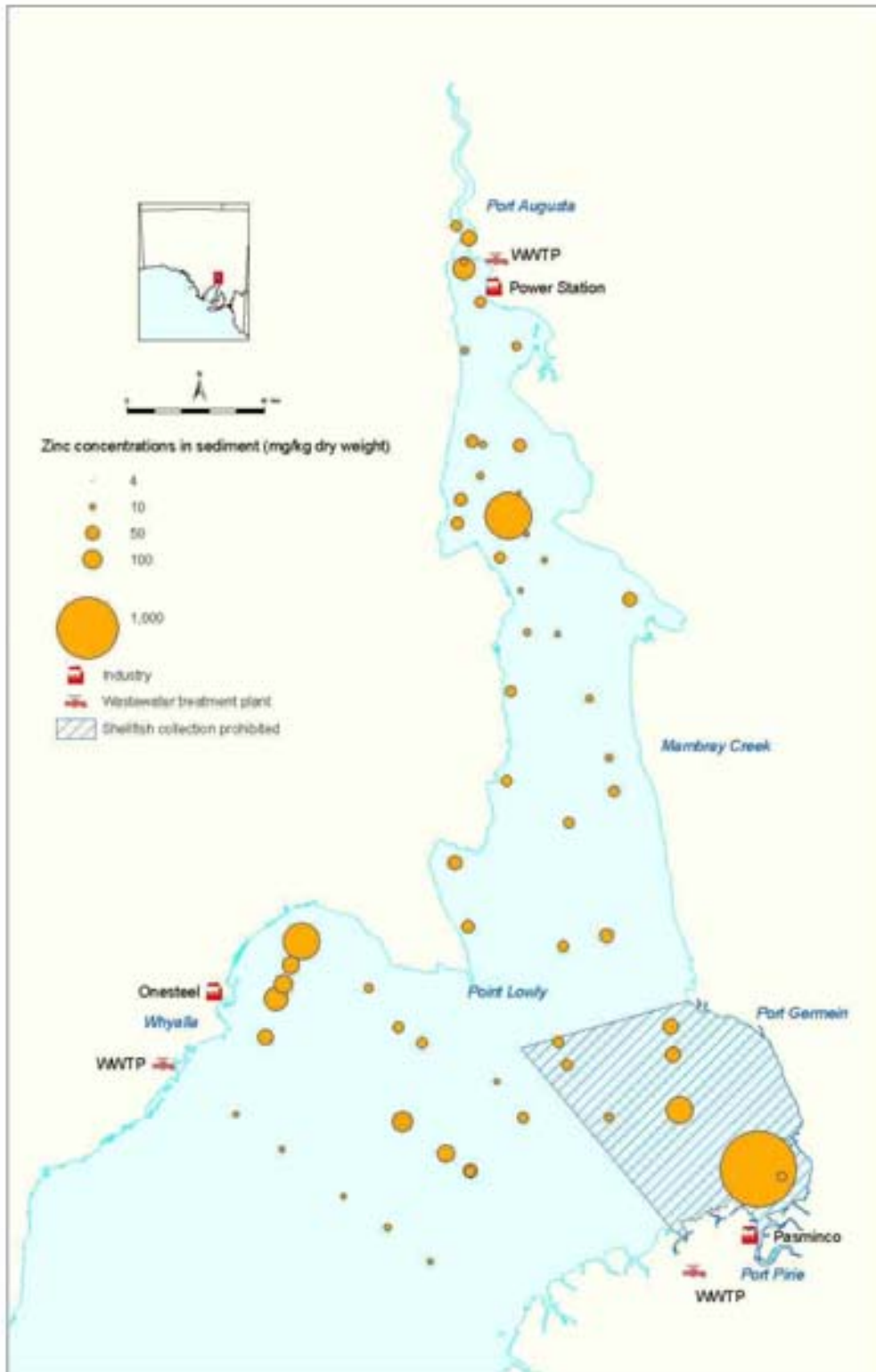


Figure 21 Zinc concentrations present in marine sediments in the northern Spencer Gulf

9.2 Comparison of metal concentrations in sediments with ANZECC guidelines for the protection of marine ecosystems

Concentrations of heavy metals in the sediments were classified as good at most sites. Poor classifications were recorded for three of the metals analysed: cadmium, lead and zinc. There were no poor classifications for chromium, copper or nickel, although they were each classified as moderate on one occasion (table 12).

Table 12 Classification of sediment metal concentrations of samples collected during 1976–81 at 59 sites across the northern Spencer Gulf

	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
Good	45	58	58	54	58	56
Moderate	11	1	1	3	1	1
Poor	3	0	0	2	0	2

Cadmium concentrations were classified as poor at three sites. This was the highest number of poor classifications for all the metals tested (table 12). These three sites were not situated near one another; one was near Pasmenco, one approximately 34 km north of Port Pirie and the other near Red Cliff Point, approximately 56 km north of Port Pirie. The latter two sites are not near discharge outlets from any industrial or wastewater treatment plants. Of the other sites investigated, eleven sites had cadmium concentrations high enough to be classified as being moderate. These sites were also scattered throughout the gulf, mainly in an area around Red Cliff Point, and spread laterally across the gulf between Port Pirie and Whyalla (figure 22).

Lead and zinc concentrations were classified as poor at two sites each (table 12), one situated close to the Pasmenco smelter and the other further north near Red Cliff Point (figures 23, 25). It is unclear why this latter site had such high concentrations, particularly as the other sites around it did not.

Lead concentrations were classified as moderate at three sites, one situated in the prohibited area around Port Pirie, one in False Bay near Whyalla and one in the middle of the gulf just south of Whyalla (figure 23). Only one site, in False Bay near Whyalla, was classified as having moderate levels of zinc (figure 25). This site also had moderate levels of lead.

The moderate classification for each of copper, chromium and nickel occurred in the same location, in the middle of the gulf just south of Whyalla (figure 24). At all other sites concentrations of these metals were classified as good. The classification of sites for all heavy metals tested is provided in figure 26.

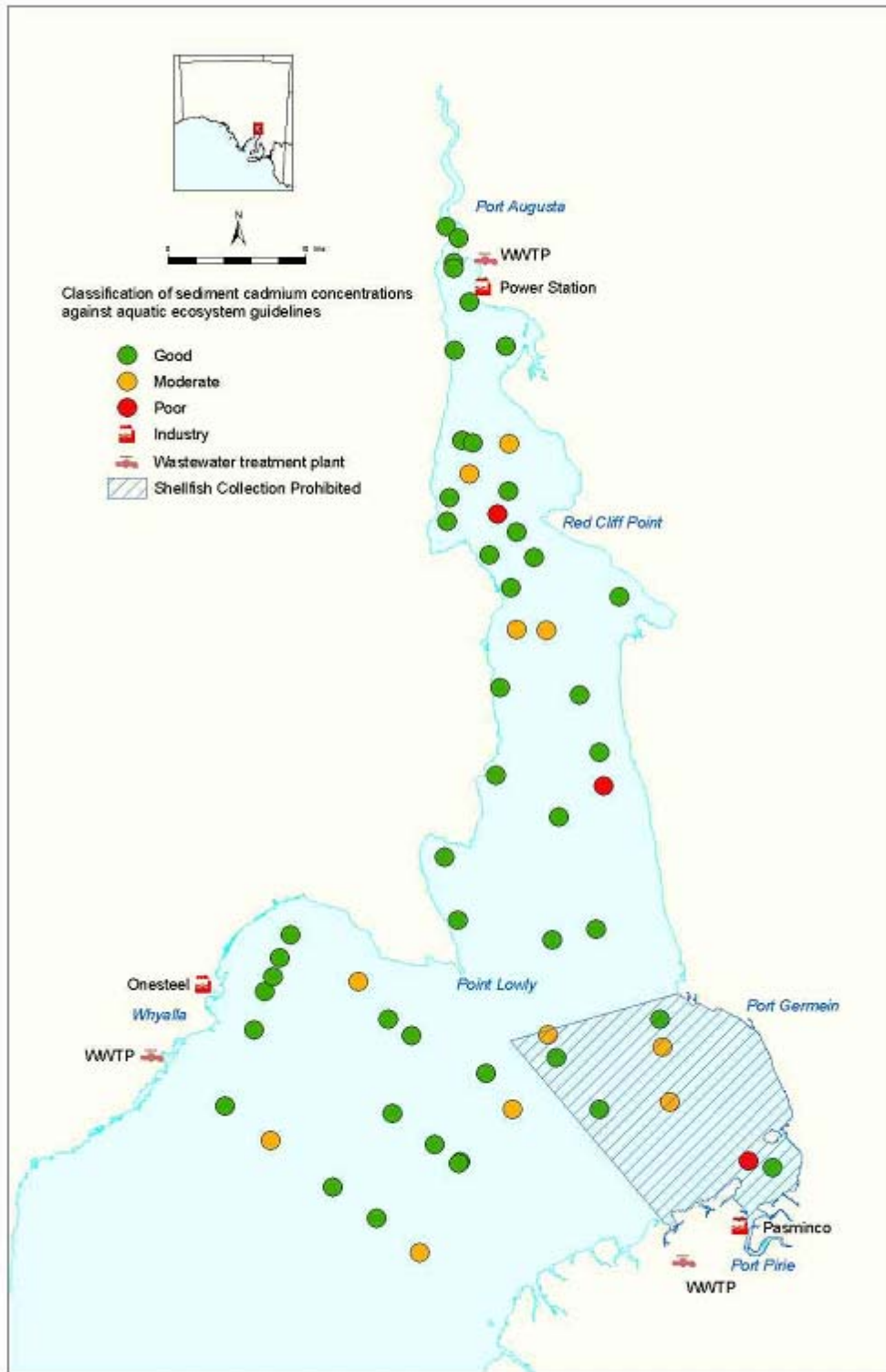


Figure 22 Classifications of marine sediment cadmium concentrations in the northern Spencer Gulf against aquatic ecosystem guidelines

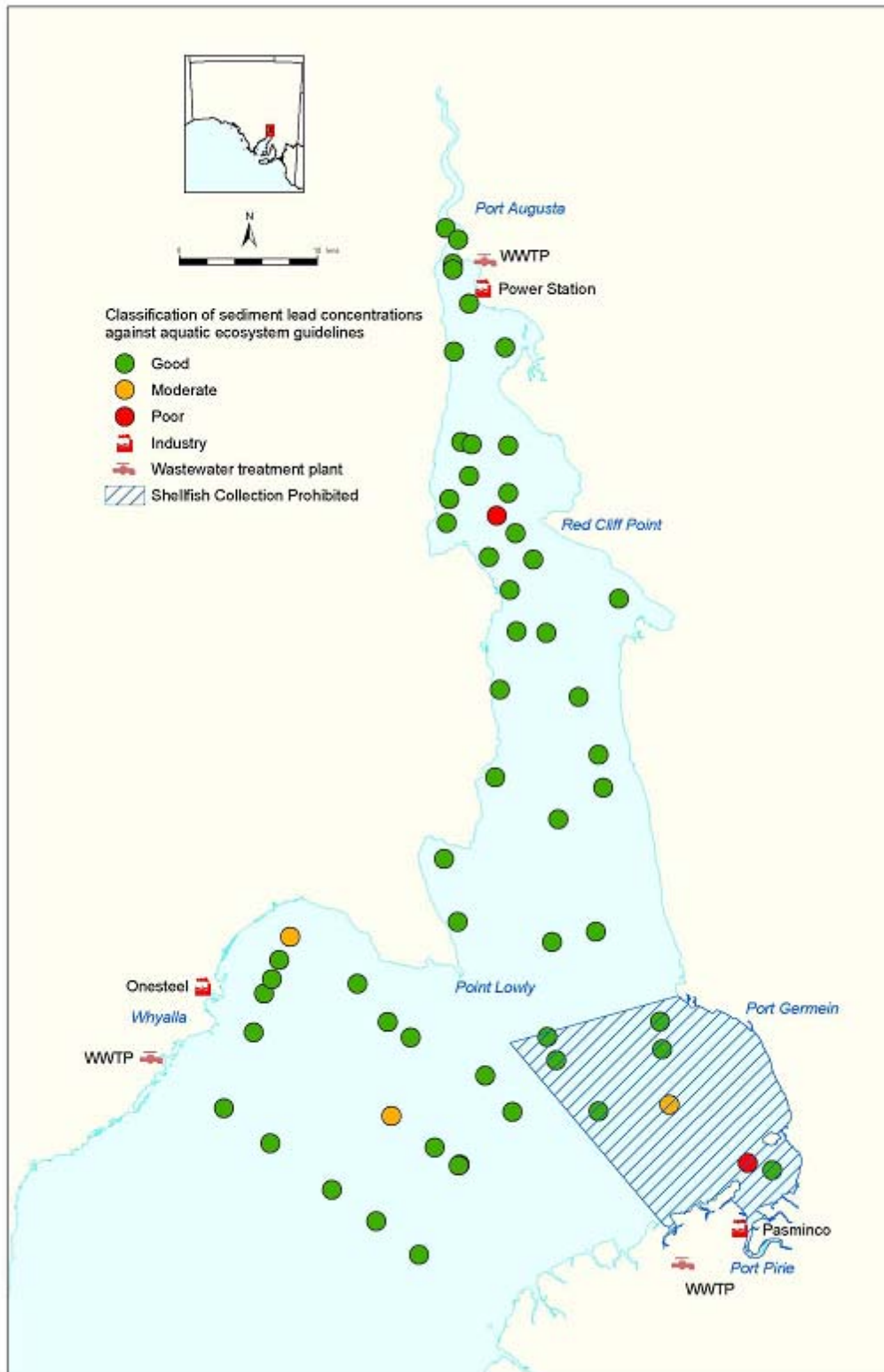


Figure 23 Classifications of marine sediment lead concentrations in the northern Spencer Gulf against aquatic ecosystem guidelines

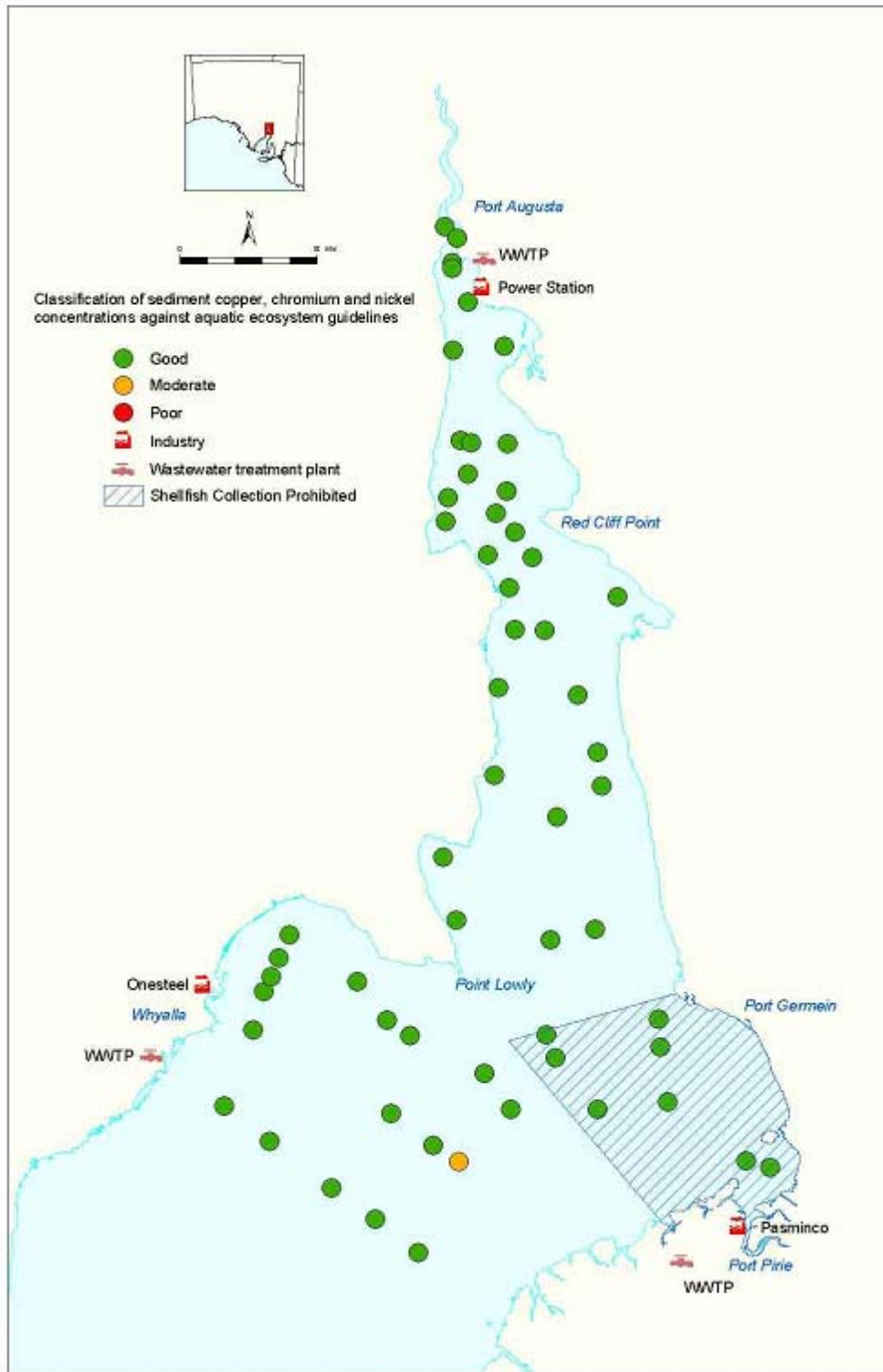


Figure 24 Classifications of marine sediment copper, chromium and nickel concentrations in the northern Spencer Gulf against aquatic ecosystem guidelines

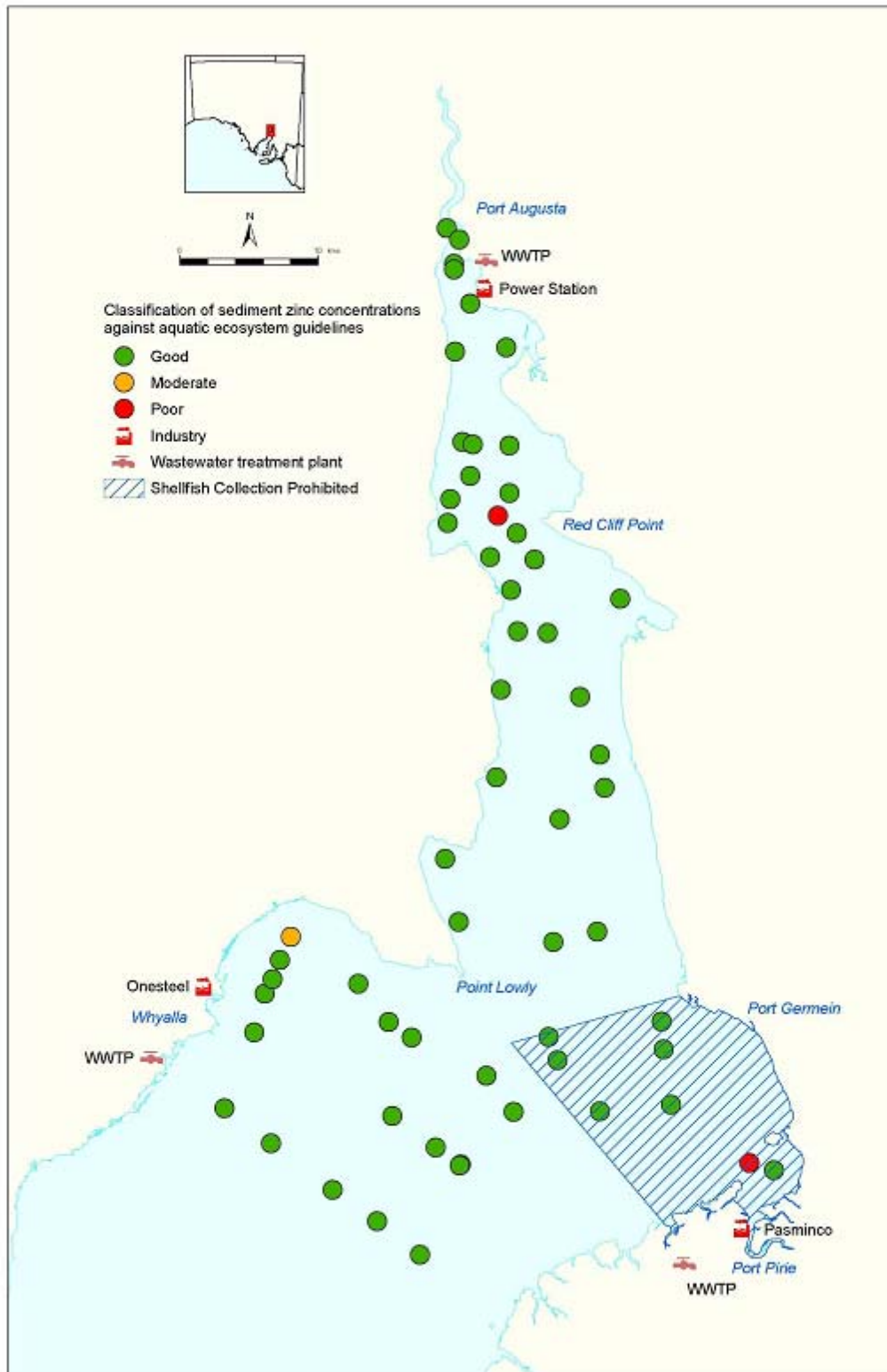


Figure 25 Classifications of marine sediment zinc concentrations in the northern Spencer Gulf against aquatic ecosystem guidelines

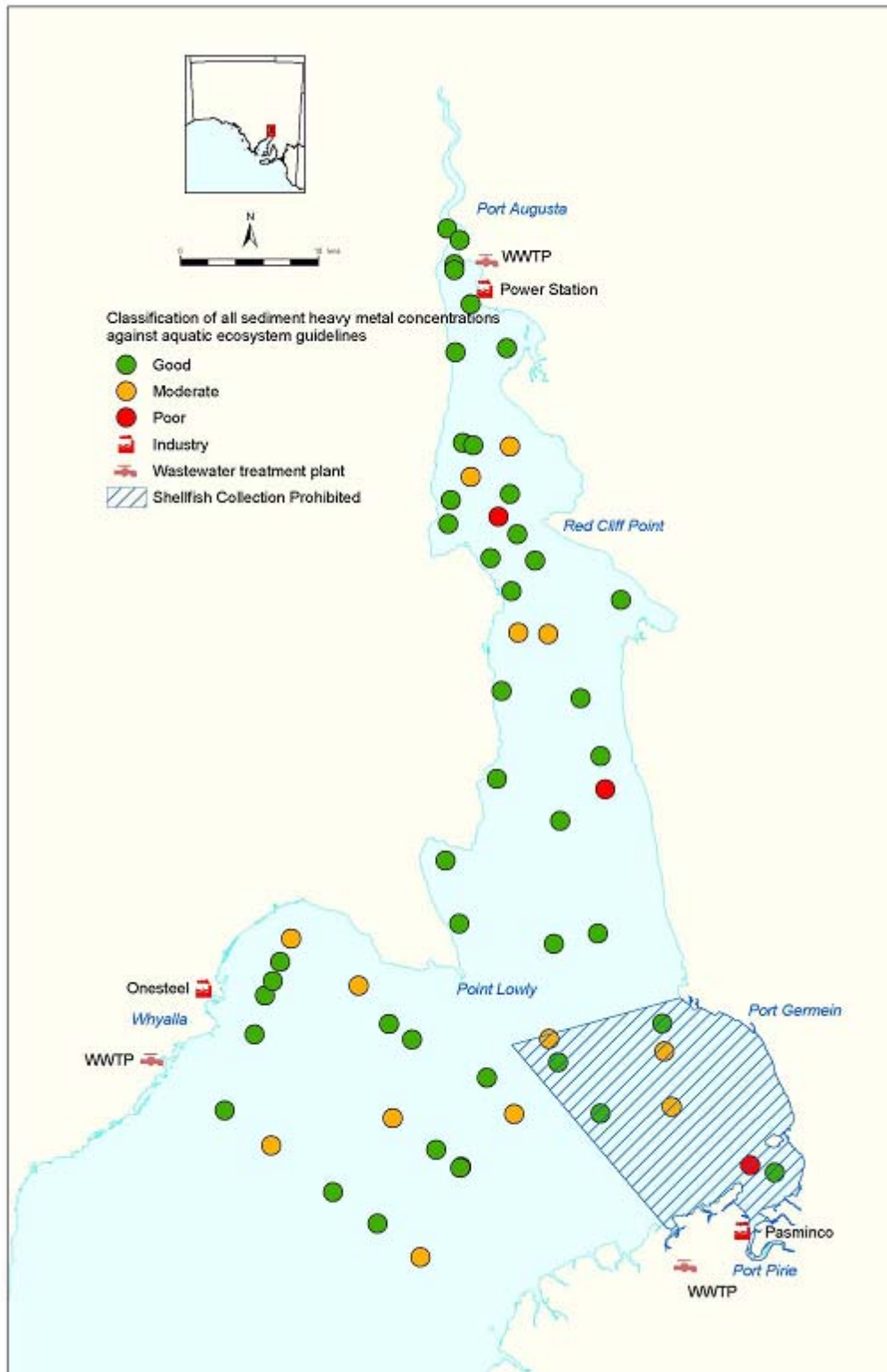


Figure 26 Classifications of marine sediment for all heavy metal concentrations tested in the northern Spencer Gulf against aquatic ecosystem guidelines

Relationship between heavy metal concentrations in sediments and distance from metal point sources.

The relationships between concentrations of metals found in sediment and the distance from the Pasmenco lead smelter, a known source of heavy metals, were investigated using Spearman’s rank correlations. The sites chosen for use in this investigation were those situated closer to Pasmenco than other point sources and those considered to be least affected by other known sources of metal pollution. Spearman’s rank correlations were conducted using the concentrations of all metals analysed in the sediment and the reciprocal of the distance between each site and the Pasmenco smelter. The r^2 value produced by these correlations indicates how much of the variability in metal concentrations is explained by the distance from the smelter (figure 27).

No appreciable relationship could be seen between the distance from the Pasmenco smelter and the metal concentration in the sediment. The best relationship occurred when investigating zinc, with an r^2 value of 0.166.

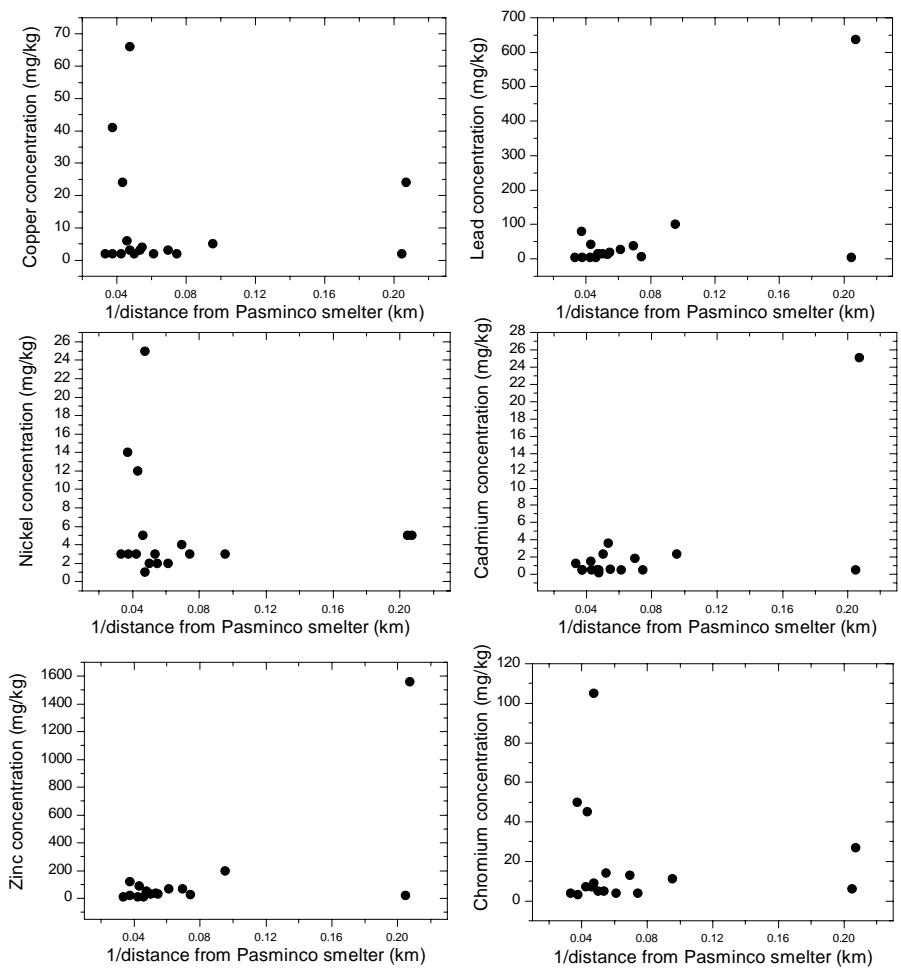


Figure 27 Relationship of distance from source and metal concentration for all metals analysed in sediment

10 Conclusions

Studies by Ward et al. (1982, 1986) show that contamination of the Germein Bay area with heavy metals from the Port Pirie smelter is substantial. In addition to this historical pollution, NPI data shows that currently the main contributor of heavy metals to the northern Spencer Gulf region is the Pasminco lead smelter at Port Pirie. For example, in the year 2001–02 Pasminco reported discharging 74,000 kg of lead to air and 11,000 kg to water, and 82,000 kg of zinc to air and 38,000 kg to water. Both the historical and recent pollution has been reflected in this study through the concentrations of heavy metals found in the razorfish and the sediments in the area surrounding Port Pirie. NPI data shows that OneSteel at Whyalla is also contributing a significant amount of zinc into the gulf (240 kg to air and 2800 kg to water in the year 2001–02). Elevated concentrations of zinc were detected in the adductor muscle of razorfish at some sites near Whyalla.

The following conclusions can be drawn from this study:

- Cadmium, mercury and copper concentrations measured in both the composite and individual razorfish samples all complied with food standards.
- Lead concentrations in two composite razorfish samples exceeded the food standard maximum levels. Both of these occurred at a site close to the Port Pirie smelter, near an area of historical dumping of dredge spoil. Seven out of 15 individual razorfish samples collected from this same site had lead concentrations that exceeded food standards. Lead concentrations in razorfish at all other sites were classified as good.
- Elevated concentrations of selenium and zinc were detected in razorfish at many sites throughout the gulf. The highest concentrations of selenium occurred in razorfish collected from Germein Bay near Port Pirie and elevated concentrations of zinc were detected in razorfish collected from both Germein Bay and False Bay, near Whyalla.
- A strong relationship was found between the concentrations of zinc, lead and selenium in razorfish and the distance from the Pasminco smelter, with concentrations decreasing as the distance from Pasminco increased. Mercury concentrations were found to be higher in razorfish collected from sites further away from the Pasminco smelter than from those collected near the smelter. It is likely that this mercury is from natural geological sources.
- Copper, nickel and chromium concentrations in sediment were classified as good at all but one site located in the middle of the gulf between Port Pirie and Whyalla, approximately 22 km from Port Pirie. This site was classified as moderate for each of these three metals.
- Of all metals tested in the sediments, cadmium had the highest number of poor ratings, with three out of 59 sites rated poor; one site was situated near Pasminco, one 34 km north of Port Pirie and the third 56 km north of Port Pirie, near Red Cliff Point.
- Poor ratings for lead and zinc concentrations in sediment were seen at two sites that also rated poor for cadmium. These were sites near Pasminco and near Red Cliff Point.
- There was no appreciable relationship between heavy metal concentrations detected in the sediment samples and the distance from the Pasminco smelter.

Ward et al. (1982) reported elevated concentrations of lead and zinc around Port Pirie. They suggested that the zinc concentrations appeared to remain high outside their chosen

study area, for a considerable distance away from the Pasminco lead smelter. The present study also found elevated lead concentrations near Port Pirie, particularly at one site 7 km from the Pasminco smelter; and confirmed that zinc concentrations in razorfish were elevated across the gulf, stretching from Port Pirie to Whyalla.

Appendix 1: Relationships between razorfish length and metal concentrations

In some species of bivalve a relationship exists between age of the organism and metal concentration in the soft tissue. This occurs when metals are accumulated at a greater rate than their loss from the animal. If size is related to age then there may also be a relationship between the size of the shell and the metal concentration present in the soft tissue of the bivalve.

Walker et al. (1982) showed that the concentration of mercury and cadmium found in the commercial scallop *Pecten alba*, collected from Port Phillip Bay, Victoria, was partially determined by their length. Other studies have shown that there is no relationship between size of bivalve and metal concentration, or that the relationship varies for different metals. Ritz et al. (1982) tested metal concentrations of two different size classes of the blue mussel and found that the smaller mussels had higher levels of copper but lower levels of cadmium and lead than the larger mussels, and no obvious difference in zinc concentrations. Some work has even indicated that smaller animals have higher concentrations of contaminants. Walker (1982) found that length was not important to the concentration of mercury in the black lip abalone or the blue mussel.

To determine if these relationships occur in the razorfish *Pinna bicolor*, an additional 10–15 razorfish were collected from four sites across the gulf. These sites were chosen to include some where contaminated animals were expected to be collected as well as some where metal concentrations were expected to be near background levels. From this data it can be determined if any relationship between size and metal concentration exists for razorfish.

If a relationship between size and metal concentration can be confirmed in razorfish, assessing metal concentrations in the gulf using razorfish of different sizes becomes unreliable. Recruitment of razorfish is known to be irregular, with large and successful recruitment events occurring intermittently, interspersed with years of poor recruitment (Butler 1987). It is therefore difficult to ensure that animals of the same size are collected at each sampling site.

Methods

Sampling and analytical methods follow those described in section 6.1 of the report.

Razorfish were collected from sites 8 (closest to Whyalla—contaminated site), 12 (just north of Point Lowly—possibly contaminated), 30 (closest to Pasmenco discharge area—contaminated) and 40 (in Wallaroo Bay—uncontaminated). Relationships between the shell length (measured in cm) and metal concentration (measured as mg/kg dry weight) were investigated at each site for seven metals: arsenic, cadmium, copper, lead, mercury, zinc and selenium.

Relationships were assessed using Spearman's rank correlation. The r^2 value explains how much the variability in one parameter can be explained by the other. For example, an r^2 value of 0.33 indicates that 33% of the variation in parameter 1 can be explained by parameter 2. While r^2 values indicate the strength of the relationship between two variables, they do not reveal the statistical significance of this relationship. The present study has also reported the statistical significance against a criteria of $p = 0.05$ for a two-tailed comparison. These r^2 values have been reported along with a statistical summary for each metal at each site (figures A1.1–1.7; tables A1.1–1.7).

Results

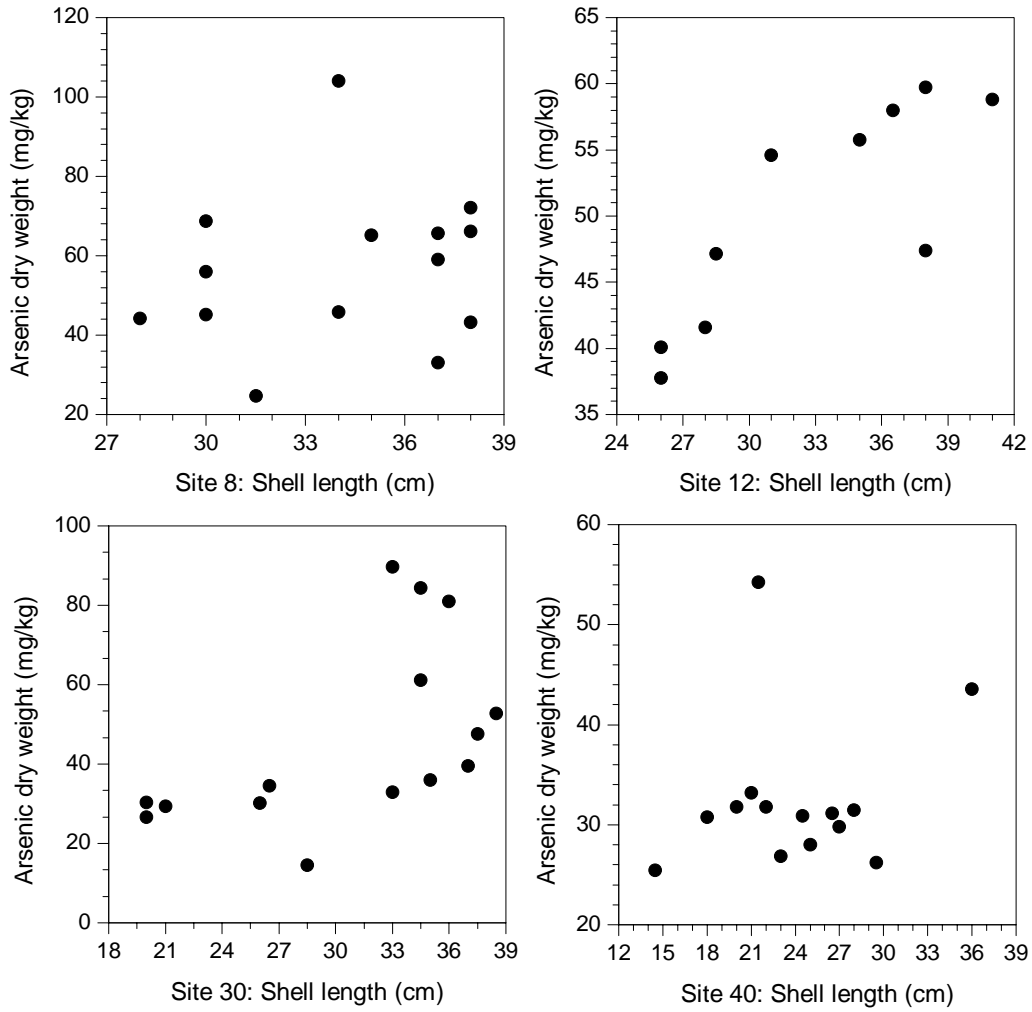


Figure A1.1. Length–arsenic relationship in razorfish at four sites in the northern Spencer Gulf

Table A1.1. Statistical summary of arsenic concentrations in razorfish and length–arsenic relationships at four sites in the northern Spencer Gulf

	Mean (mg/kg)	95% confidence interval (mg/kg)	Standard deviation (mg/kg)	Median (mg/kg)	10th percentile (mg/kg)	90th percentile (mg/kg)	Number of samples	Correlation of length: dry weight (Spearman's r ²)
Site 8	56.6	45.25–67.99	19.7	57.49	36.09	71.10	14	0.04 (ns)
Site 12	50.1	44.12–56.03	8.3	50.98	39.84	58.88	10	0.78 (sig 0.002)
Site 30	46.0	33.24–58.80	23.1	35.93	27.70	82.99	15	0.45 (sig 0.005)
Site 40	32.5	28.11–36.90	7.6	31.00	26.42	40.43	14	0.00 (ns)

Note: ns = not statistically significant at $p = 0.05$, sig = statistically significant at p value provided.

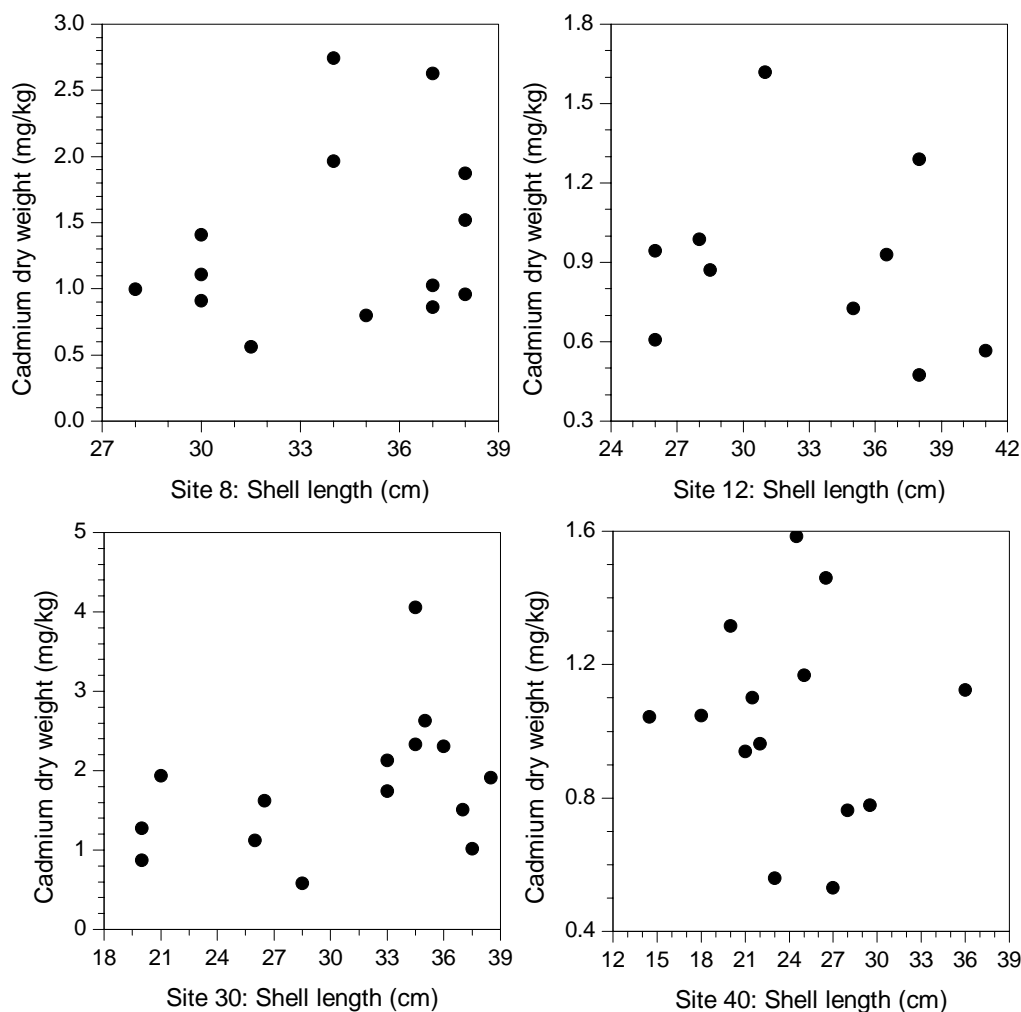


Figure A1.2 Length–cadmium relationship in razorfish at four sites in the northern Spencer Gulf

Table A1.2 Statistical summary of cadmium concentrations in razorfish and length–cadmium relationships at four sites in the northern Spencer Gulf

	Mean (mg/kg)	95% confidence interval (mg/kg)	Standard deviation (mg/kg)	Median (mg/kg)	10th percentile (mg/kg)	90th percentile (mg/kg)	Number of samples	Correlation of length: dry weight (Spearman's r ²)
Site 8	1.38	0.99–1.78	0.68	1.07	0.82	2.43	14	0.03 (ns)
Site 12	0.90	0.65–1.15	0.35	0.90	0.56	1.32	10	0.08* (ns)
Site 30	1.80	1.33–2.28	0.86	1.75	0.93	2.51	15	0.13 (ns)
Site 40	1.03	0.85–1.20	0.31	1.05	0.62	1.42	14	0.02* (ns)

Note: ns = not statistically significant at $p = 0.05$, * Spearman's r^2 value is negative for this analysis.

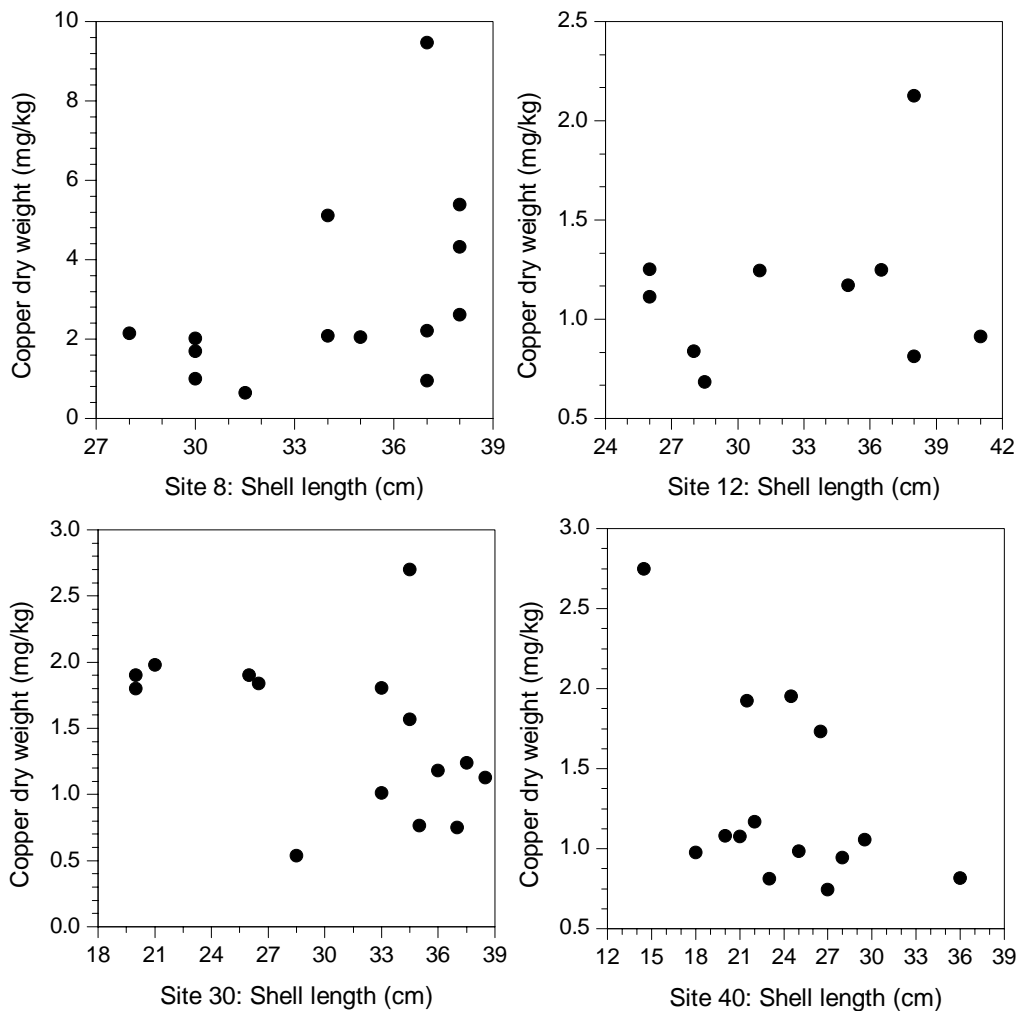


Figure A1.3 Length–copper relationship in razorfish at four sites in the northern Spencer Gulf

Table A1.3 Statistical summary of copper concentrations in razorfish and length–copper relationships at four sites in the northern Spencer Gulf

	Mean (mg/kg)	95% confidence interval (mg/kg)	Standard deviation (mg/kg)	Median (mg/kg)	10th percentile (mg/kg)	90th percentile (mg/kg)	Number of samples	Correlation of length: dry weight (Spearman's r ²)
Site 8	2.97	1.60–4.35	2.38	2.11	0.96	5.30	14	0.31 (sig 0.05)
Site 12	1.14	0.85–1.43	0.40	1.14	0.80	1.34	10	0.00 (ns)
Site 30	1.47	1.15–1.80	0.59	1.57	0.75	1.95	15	0.27* (ns)
Site 40	1.29	0.95–1.62	0.58	1.06	0.81	1.94	14	0.24* (ns)

Note: ns = not statistically significant at $p = 0.05$, sig = statistically significant at p value provided, * Spearman's r^2 value is negative for this analysis.

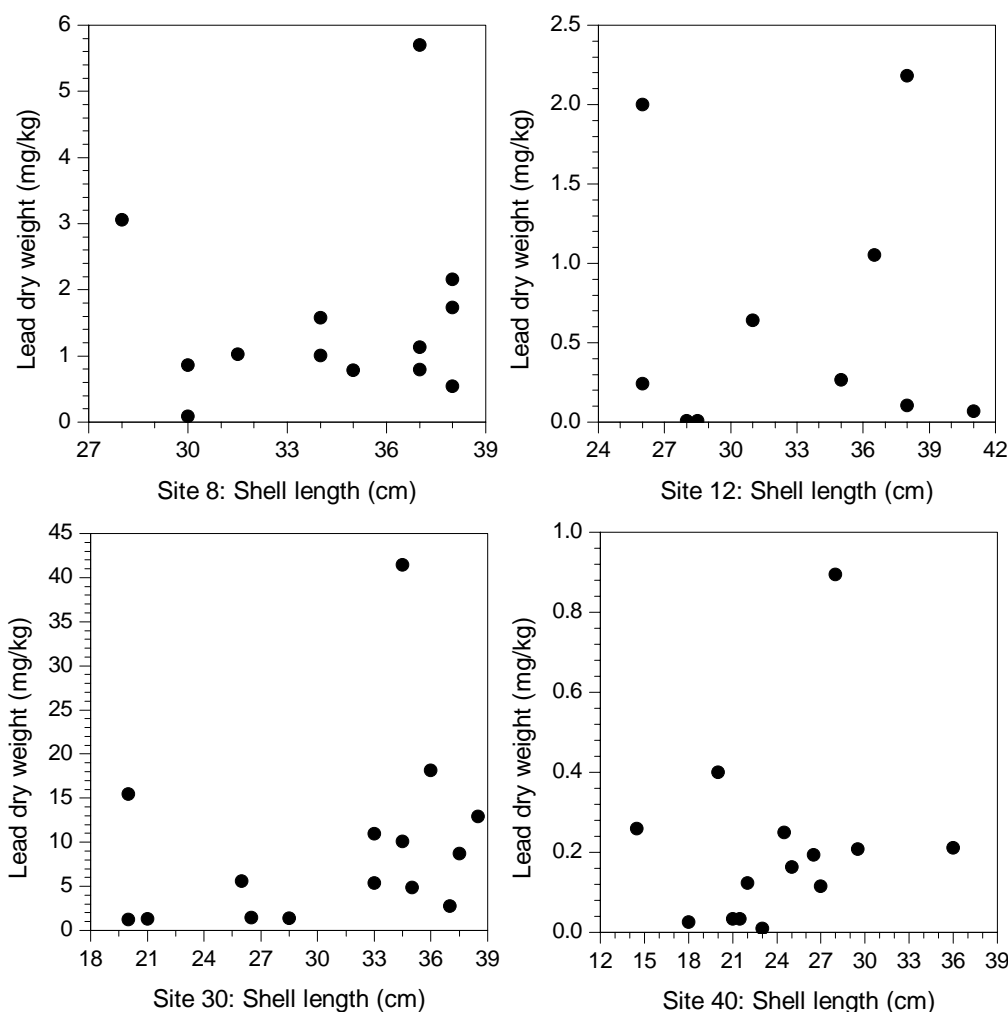


Figure A1.4 Length–lead relationship in razorfish at four sites in the northern Spencer Gulf

Table A1.4 Statistical summary of lead concentrations in razorfish and length–lead relationships at four sites in the northern Spencer Gulf

	Mean (mg/kg)	95% confidence interval (mg/kg)	Standard deviation (mg/kg)	Median (mg/kg)	10th percentile (mg/kg)	90th percentile (mg/kg)	Number of samples	Correlation of length: dry weight (Spearman's r ²)
Site 8	1.52	0.71–2.34	1.41	1.02	0.62	2.79	14	0.02 (ns)
Site 12	0.66	0.07–1.25	0.82	0.25	0.01	2.02	10	0.00 (ns)
Site 30	9.45	3.70–15.20	10.39	5.58	1.34	17.07	15	0.17 (ns)
Site 40	0.21	0.08–0.34	0.23	0.18	0.03	0.36	14	0.05 (ns)

Note: ns = not statistically significant at $p = 0.05$.

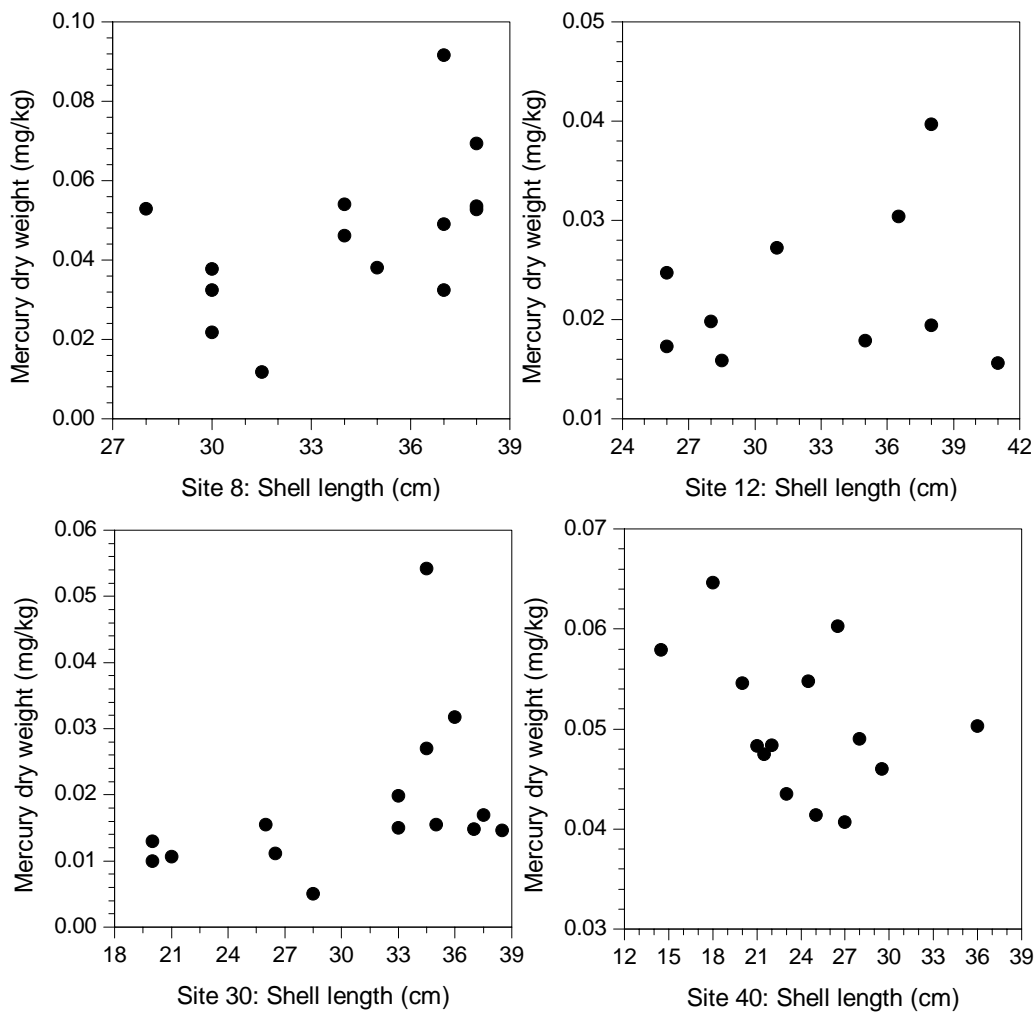


Figure A1.5 Length–mercury relationship in razorfish at four sites in the northern Spencer Gulf

Table A1.5 Statistical summary of mercury concentrations in razorfish and length–mercury relationships at four sites in the northern Spencer Gulf

	Mean (mg/kg)	95% confidence interval (mg/kg)	Standard deviation (mg/kg)	Median (mg/kg)	10th percentile (mg/kg)	90th percentile (mg/kg)	Number of samples	Correlation of length: dry weight (Spearman's r ²)
Site 8	0.0460	0.0345 – 0.0574	0.0198	0.0475	0.0249	0.0648	14	0.26 (ns)
Site 12	0.0228	0.0172 – 0.0283	0.0078	0.0196	0.0159	0.0313	10	0.00 (ns)
Site 30	0.0183	0.0117 – 0.0249	0.0119	0.0150	0.0103	0.0298	15	0.28 (sig 0.05)
Site 40	0.0505	0.0464 – 0.0546	0.0071	0.0487	0.0420	0.0596	14	0.14* (ns)

Note: ns = not statistically significant at $p = 0.05$, sig = statistically significant at p value provided, * Spearman's r^2 value is negative for this analysis.

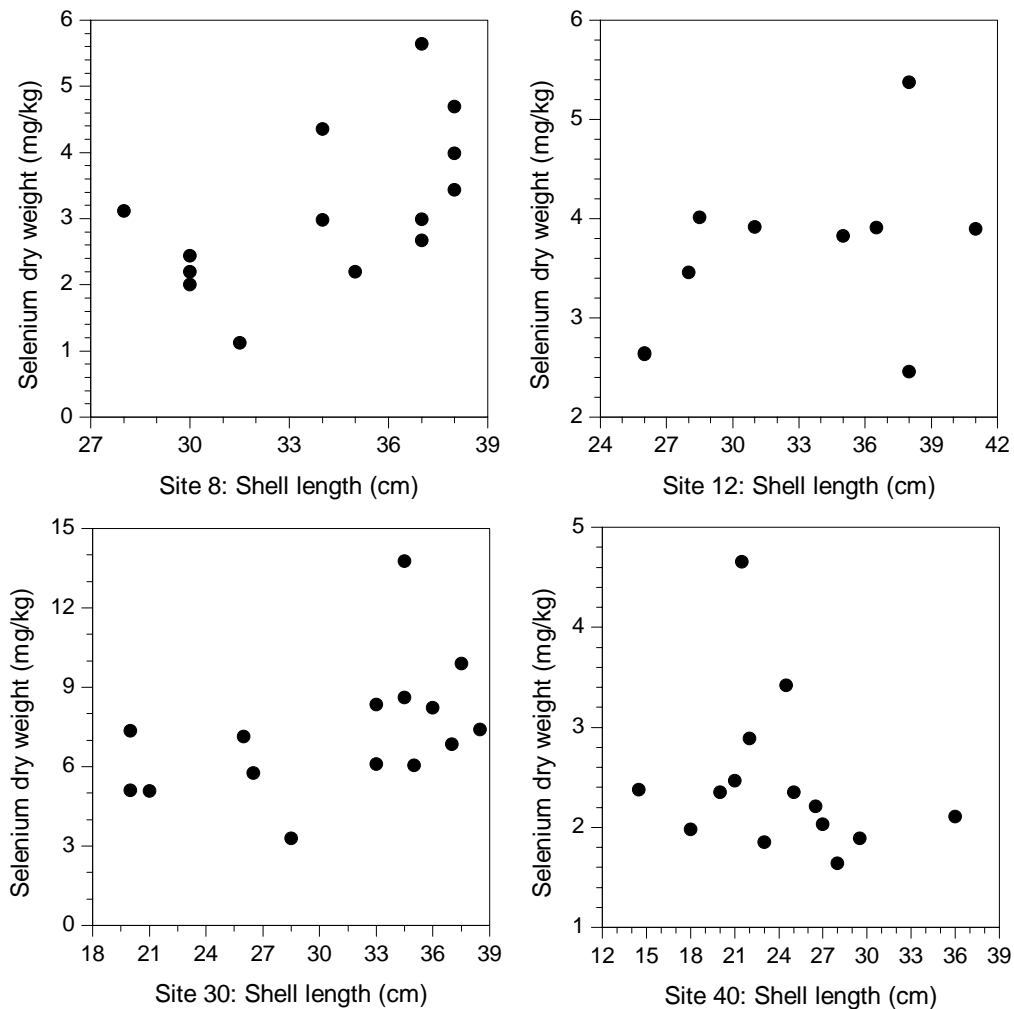


Figure A1.6 Length–selenium relationship in razorfish at four sites in the northern Spencer Gulf

Table A1.6 Statistical summary of selenium concentrations in razorfish and length–selenium relationships at four sites in the northern Spencer Gulf

	Mean (mg/kg)	95% confidence interval (mg/kg)	Standard deviation (mg/kg)	Median (mg/kg)	10th percentile (mg/kg)	90th percentile (mg/kg)	Number of samples	Correlation of length: dry weight (Spearman's r ²)
Site 8	3.13	2.44–3.83	1.20	2.99	2.06	4.59	14	0.33 (sig 0.05)
Site 12	3.61	2.99–4.24	0.87	3.86	2.61	4.15	10	0.10 (ns)
Site 30	7.27	5.91–8.62	2.44	7.13	5.10	9.38	15	0.28 (sig 0.05)
Site 40	2.44	1.99 –2.89	0.78	2.28	1.87	3.26	14	0.22* (ns)

Note: ns = not statistically significant at $p = 0.05$, sig = statistically significant at p value provided, * Spearman's r^2 value is negative for this analysis.

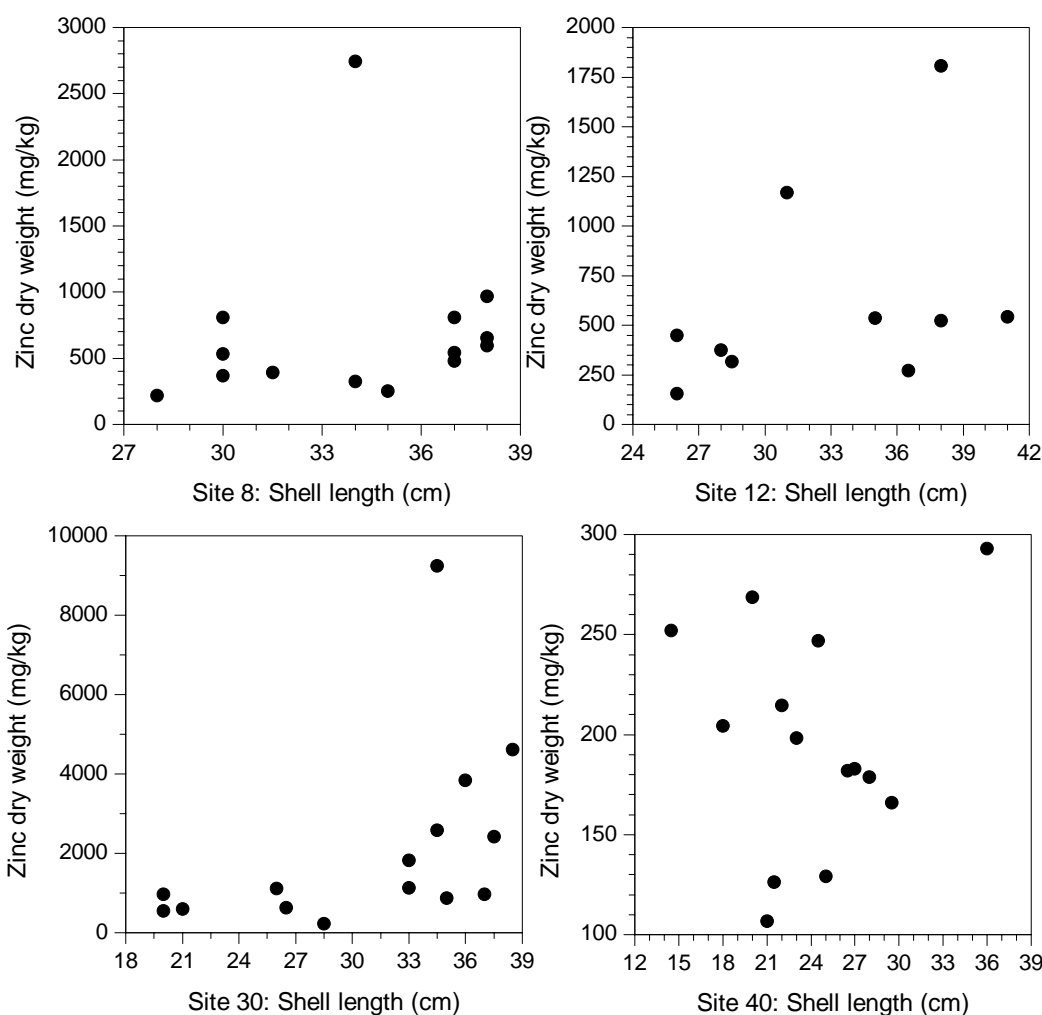


Figure A1.7 Length–zinc relationship in razorfish at four sites in the northern Spencer Gulf

Table A1.7 Statistical summary of zinc concentrations in razorfish and length–zinc relationships at four sites in the northern Spencer Gulf

	Mean (mg/kg)	95% confidence interval (mg/kg)	Standard deviation (mg/kg)	Median (mg/kg)	10th percentile (mg/kg)	90th percentile (mg/kg)	Number of samples	Correlation of length: dry weight (Spearman's r ²)
Site 8	691.4	327.2–1055.6	630.8	538.4	271.3	918.1	14	0.23 (ns)
Site 12	613.7	256.3–971.1	499.6	485.8	259.8	1230.2	10	0.34 (ns)
Site 30	2103.2	803.1–3403.3	2347.7	1105.1	567.2	4306.1	15	0.38 (sig 0.02)
Site 40	196.4	164.5–228.3	55.3	190.7	127.1	263.8	14	0.02* (ns)

Note: ns = not statistically significant at $p = 0.05$, sig = statistically significant at p value provided, * Spearman's r^2 value is negative for this analysis.

Discussion

Arsenic provided the strongest positive correlation value at site 12 ($r^2 = 0.78$) and a substantial correlation at site 30 ($r^2 = 0.45$). These correlations were both statistically significant and at these sites the arsenic concentrations appeared to increase with length. However, the correlations at sites 8 ($r^2 = 0.04$) and 40 ($r^2 = 0.00$) were both poor and neither were statistically significant.

There was no evidence of a relationship at any site between length and cadmium concentration (r^2 from 0.02 to 0.13) or length and lead concentration (r^2 from 0.00 to 0.17).

The relationship between copper concentration and length was statistically significant at site 8 ($r^2 = 0.31$); however, the relationship was not statistically significant at the other three sites and was negative at sites 30 and 40. Mercury correlated significantly with length at site 30 ($r^2 = 0.28$) but not at the other three sites, and the relationship was negative at site 40. Selenium showed statistically significant positive correlations with length at sites 8 ($r^2 = 0.33$) and 30 ($r^2 = 0.28$), but the correlations at sites 12 and 40 were not statistically significant and at site 40 the correlation was negative. Zinc correlated significantly with length at site 30 ($r^2 = 0.38$), the site that had the highest level of zinc contamination. Relationships at the other three sites were not statistically significant.

It is interesting to note that there were no statistically significant correlations between metal concentrations and razorfish length at site 40, the location furthest from significant point sources of metals, while at site 30, the location closest to the Port Pirie smelter, four out of seven correlations were significant. This suggests that where metal concentrations are elevated it is more likely that there will be a relationship between length and concentration.

Conclusions

These results do not provide evidence of consistent relationships between adductor muscle metal concentration and razorfish length across the northern Spencer Gulf. However, they suggest that at some sites there may be a relationship, and the likelihood of this is greater at sites that have elevated metal concentrations. Collecting razorfish within a restricted size range minimises the variability in metal concentrations due to razorfish size and therefore the possibility of obscuring spatial patterns in metal concentration.

Appendix 2: Laboratory reporting limits

Table A2.1 Limit of reporting for analysis of metal concentrations in razorfish expressed as dry weight

Element	Dry weight limit of reporting (mg/kg)
Arsenic	0.05
Cadmium	0.01
Copper	0.05
Lead	0.01
Mercury	0.005
Selenium	0.05
Zinc	0.05

Table A2.2 Lowest reported concentrations for analysis of metal concentrations in sediments expressed as dry weight

Element	Lowest concentration reported (mg/kg)
Cadmium	0.2
Chromium	3.0
Copper	2.0
Lead	3.0
Nickel	1.0
Zinc	4.0

Glossary

anoxic – (an environment) lacking oxygen.

antagonistic – where one chemical reduces or counteracts the effects of another such that the resulting effect is less than would be expected if the chemicals were acting independently of one another.

bioaccumulation – the net uptake of chemicals in an individual organism through air, water and food where the rate of uptake is greater than the rate of excretion.

biomagnification – the accumulation of chemicals up the food chain.

benthic – living on or in the sediment.

bioavailability – where a chemical that can be readily absorbed by an organism is available to exert physiological effects.

bivalve – a class of mollusc that has two valves or shells hinged together; examples include razorfish, oysters, scallops, cockles, mussels and clams.

epifauna – organisms that attach themselves to and grow on substrates such as seagrass leaves, shells of razorfish and rocks.

filter-feeder – an organism that filters water to remove suspended particles as a food source.

generally expected levels (GELs) – levels of particular chemicals determined by the Australian and New Zealand Food Authority using survey data from areas where ‘normally expected’ levels of contamination would be found. Food-metal combinations exist for those metals which had maximum levels under the old food standards but not under the current food standards. GELs are not legally enforced values but are set as a guide.

half-life – the time taken for a chemical to decay through physical, chemical or biological processes to half its initial concentration.

intertidal – the zone between the low tide level and the high tide level.

limit of reporting (LOR) – the lowest concentration of a chemical or physical parameter reported by a laboratory for a particular analysis; the lowest concentration that can be routinely measured by a laboratory in a consistent and reliable manner. This is influenced by the nature of the analytical method and the media being tested.

mean – the average of a data set, calculated by adding all the values in the data set and dividing by the total number of values. The mean is a good estimate of central tendency when a sample is symmetrically distributed; however, if the distribution is skewed, the mean should be used with caution.

median – the middle value of a data set arranged in ascending order, also known as the 50th percentile. If the data set contains an even number of values, the median is then the average of the middle two numbers of that data set. The median is a more robust estimate of central tendency than the mean when a data set is skewed by outliers.

ML (maximum level) – the maximum allowable level of a particular chemical in food to be sold in Australia or New Zealand for human consumption, as set by the Australian and New Zealand Food Authority. Food-metal combination MLs have only been designated for those combinations that provide a significant contribution to the total dietary exposure.

mollusc—a type of animal with a soft body that is usually enclosed in a hardened shell. Molluscs include such animals as the ordinary garden snail, marine snails, abalone and bivalves such as mussels, oysters and razorfish.

sessile—an organism that does not move around but remains fixed in the one position, e.g. seagrass, oysters and razorfish.

seston—particles that are suspended in sea water and may include living organic matter such as plankton, dead organic matter, or inorganic matter such as silt.

standard deviation—a measure of the spread of the values in a data set around the mean of the data set.

subtidal—the marine or estuarine environment that is below the average low tide level.

supratidal—the zone just above the high tide mark that is only inundated during storm conditions.

synergistic—where chemicals work together in such a manner that the resulting effect is greater than would be expected if the chemicals were acting independently.

trophic level—a level in a food chain defined by the manner in which the organism obtains food. Primary producers such as plants, bacteria and algae are lower level trophic organisms, herbivores are at a middle level, and carnivores are at a high trophic level.

90th and 10th percentiles—a means of describing the range of a data set instead of using the minimum and maximum. If a data set is arranged in ascending order, the lowest 10% of the data set falls under the 10th percentile, the largest 10% falls above the 90th percentile and the middle 80% falls between the 10th and 90th percentiles.

95% confidence interval of the mean an indication of the precision of the estimate of the population mean for normally distributed data. For example, a sample mean of 15 mg/kg with a 95% confidence interval of 10–20 mg/kg indicates that there is a 95% chance that the true, or population mean, falls between 10 mg/kg and 20 mg/kg.

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