THE DISTRIBUTION OF METAL INDUSTRY WASTES IN INTERTIDAL SEDIMENTS NEAR WHYALLA, IN UPPER SPENCER GULF, SOUTH AUSTRALIA

A thesis for the degree of
Master of Environmental Studies
at The University of Adelaide

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March, 1980

Awarded 12th September 1980

THE DISTRIBUTION OF METAL INDUSTRY WASTES IN INTERTIDAL SEDIMENTS NEAR WHYALLA, IN UPPER SPENCER GULF, SOUTH AUSTRALIA.

ABSTRACT

Intertidal sediments near the B.H.P. steelworks at Whyalla, on the west coast of Spencer Gulf, were analysed by Atomic Absorbtion spectrometry to determine sedimentary, geochemical, and biological factors controlling the distribution and mobility of metals in the nearshore environment. Selective extraction procedures were used in an attempt to distinguish metals likely to be available to biota under a range of surface water conditions, from the total metal content of sediments.

The region is characterized by intertidal mudflats up to 2 km wide, with extensive mangrove vegetation, high day temperatures, low but often torrential rainfall, and high salinity in shallow water. Wind data and subtidal topography shown in aerial photographs suggest prevailing longshore transport of sediments to the north. Sheltered conditions favour the deposition of fine particulates and associated metals, while wide fluctuations in pH, salinity, and temperature may enhance the impact of metals on intertidal organisms.

The results show that zinc in surface sediments is particularly mobile. Cadmium, chromium, copper, and some lead could become available at lower pH, or under oxidizing conditions, but the 'scavenging' action of suspended iron and manganese particulates may exert some control on the concentration of other metals in the overlying water.

Mangrove swamps may provide optimum conditions for the accumulation of metals. They also shelter juvenile stocks of commercial fish species, which could be affected if metals are released from disturbed sediments.

STATEMENT

The thesis contains no material which has been accepted for the award of any other degree or diploma in any university, nor does it contain any material previously published or written by another person, except where due reference has been made in the text.

I.P. Harbison

I.P. HARBISON.

ACKNOWLEDGEMENTS

I am indebted to Dr. V. Gostin for his guidance and supervision in the sedimentary aspects of the study, and for making the facilities of the Department of Geology, The University of Adelaide, available for all laboratory work.

The staff of this department have kindly assisted with many practical problems. Dr. K. Turnbull and Mr. P. McDuie are particularly thanked for helpful discussion and advice on laboratory procedures throughout the project.

My external supervisor, Dr. H. Veeh at the School of Earth Sciences, Flinders University of South Australia, provided valuable advice on analytical techniques, and I am most grateful for his criticism of the geochemical section of the manuscript, and of my interpretation of the data.

The study was partly supported by a grant from the Broken Hill Proprietary Company Ltd (B.H.P.) at Whyalla. The co-operation and assistance of company personnel, particularly Mr. S. Abdelmalek, Mr. B. Hassel, and Mr. A. Lang, was very much appreciated.

Finally, I sincerely thank Miss Joy McCann for her patient and capable deciphering of my notes, and typing of the manuscript.

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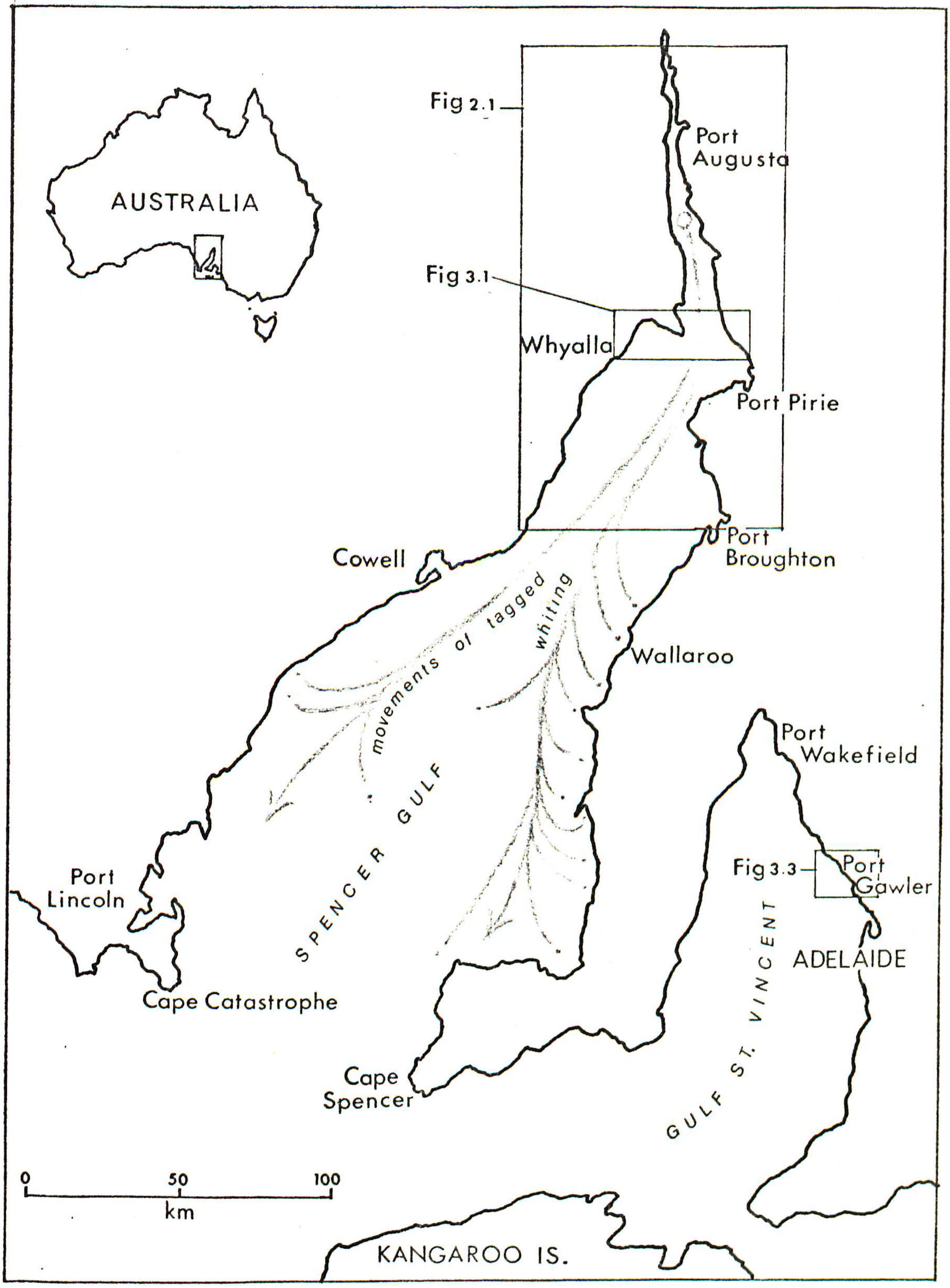


FIG. 1.1 Location of study areas in Spencer Gulf and Gulf St. Vincent. Movement of tagged whiting in Spencer Gulf adapted from Department of Agriculture and Fisheries (1979).

1 INTRODUCTION

1.1 Rationale

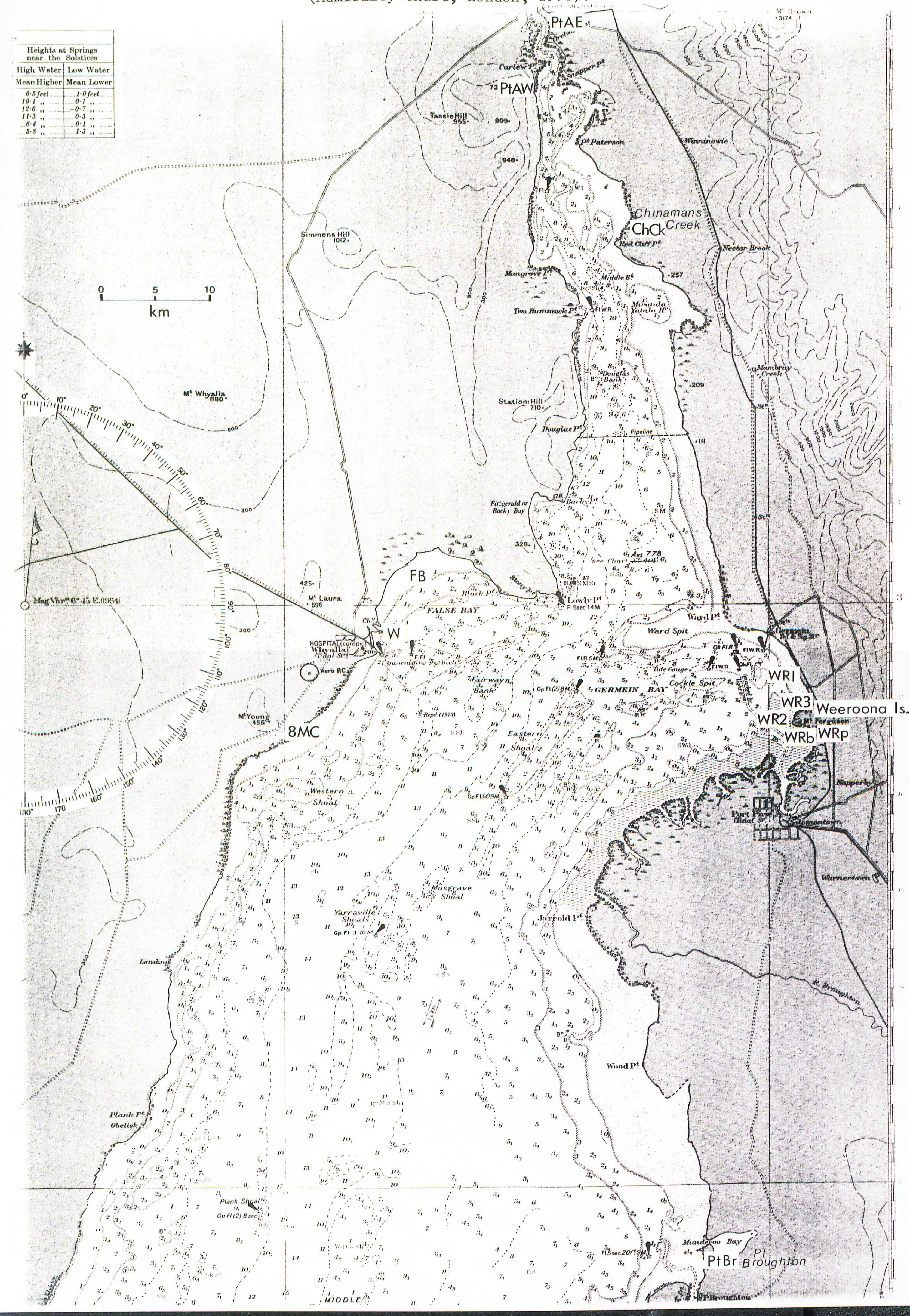
The most recent investigation into the inshore commercial marine scale fish industry in South Australia was confined to Spencer Gulf, because "it is in this region that the major percentage of landings of the important fish are made" (Jones, 1979). The mangrove swamps and seagrass beds in Spencer Gulf are also considered to be an important nursery ground for these fish species (Robertson, 1977).

The disastrous pollution which effectively closed fisheries in the Derwent estuary (Bloom, 1975) has made Australian Government departments acutely aware of the need for assessment of potential hazards from heavy metals in our own fishing grounds. Any detrimental impact of metal wastes on the marine life of northern Spencer Gulf could damage the most important commercial fishery in South Australia (Fig. 1.1).

A survey initiated by the then Minister of Works, the Hon. J.D. Corcoran, M.P., to enquire into the sources of marine pollution in Spencer Gulf was carried out by P.L. Deland and R.M. Jones in 1973. Industrial, urban, and shipping sources of pollution were identified, and recommendations made, which included a chemical survey and assessment of the potential hazard to the marine environment of the wastes from the B.H.P. steelworks at Whyalla. A similar study was also recommended to evaluate the effects of waste water from the B.H.A.S. lead and zinc smelters at Pt. Pirie (Deland and Jones, 1973). An extensive study based on the latter recommendation is at present being carried out for the International Lead Zinc Research Organization (I.L.Z.R.O. Venture Analysis LH-230/2H-212/CH6 and Project CH-6/ZH-212) by a multidisciplinary task force set up by the Commonwealth Scientific and Industrial Research Organization in 1978 (C.S.I.R.O., 1979).

In November 1978, the B.H.P. company at Whyalla provided funds for a study of the impact of steelworks discharges in the marine environment, and this grant supported the present assessment of the distribution and availability of heavy metals in intertidal sediments and shallow water at Whyalla. It is hoped that an appreciation of factors influencing the distribution of heavy metals in sediments, and their availability to marine organisms through geochemical and trophic pathways, will make potential hazards to the marine environment predictable, and the impact of future construction and discharges possible to assess, so that development can be carried out with the minimum disturbance to the ecology of Spencer Gulf.

FIG. 2.1 Northern Spencer Gulf showing sampling sites. (Admiralty Chart; London, 1978).



2 SPENCER GULF

2.1 Physical environment

Spencer Gulf, in South Australia, is an elongated triangle of water enclosed by the coastline extending from Cape Catastrophe on southern Eyre Peninsula, north to Pt. Augusta, and south to Cape Spencer on Yorke Peninsula (Fig. 1.1). The southern part of the gulf is deepest, from 20-40 m, and 60 m at the entrance, but the northern region, apart from central channels 20 m deep, is relatively shallow, with intertidal mud flats and mangrove swamps up to 6 km wide (Pls 2.1.1 and 2.1.2). South of Cowell on the west coast and Wallaroo on the east, a clockwise current system carries water from the open sea north along the western coast of the gulf, and south along the eastern side (Tronson, 1974 and Bullock, 1975). Water circulation in the extreme north of the gulf, however, is very limited, and the region north of Pt. Lowly and Ward Spit is virtually a closed system (Jones, 1979), retained by the very wide sand bar which extends 4-5 km out into the gulf from Ward Point toward Pt. Lowly (Fig. 2.1).

A limited circulation, high evaporation rate, low annual rainfall, and lack of river input would all contribute to the extremely high salinities recorded at the apex of the gulf. The salinity range at Pt. Augusta recorded by the S.A. Department of Fisheries Research Branch is 44-49‰ (unpublished data). Higher salinities have been recorded in surface pools on the intertidal area: 53‰ at Chinamans Creek (Fig. 2.1), and 59‰ in False Bay (present study). Salinity in the southern waters of Spencer Gulf ranges from 35.75-37.6‰ (Jones, 1979).

The northern half of the gulf has wide intertidal sand and mud flats, with dense mangrove stands in sheltered areas, and extensive seagrass beds just offshore. One of the largest remaining mangrove communities in the State is found at Chinamans Creek, and extends over 3000 acres, including more than 50 miles of tidal creeks (Reilly, 1977).

PLATE 2.1. Intertidal flats in False Bay with steelworks in the background.

PLATE 2. 2 Intertidal flats on the south side of Weeroona Island near Pt. Pirie.

Between Pt. Augusta and Whyalla, old mangrove trees occur in boulder beaches considered to be a relict of higher Pleistocene sea levels (Hails and Gostin, 1978). These substrates are in contrast to the prograding mud flats on the eastern shore, and predictably lack the dense growth of young seedlings found in the latter sediments.

Other relict sediments outcropping at Chinamans Creek and Eight-Mile Creek consist of very compact fine-grained black mud, with remnant stumps and wood fibre. At Chinamans Creek, the old mangrove substrate is covered by the coarse yellow sand of the present intertidal flat, while at Eight-Mile Creek (Fig. 2.1) it projects on the seaward side of a stranded beach ridge (present study).

2.2 Sources of metals in Spencer Gulf

One of the largest centres of population in the upper gulf is Pt. Pirie, 220 km north of Adelaide on the eastern side of the gulf at 138°E and 33°10'S (Fig. 2.1). This is the site of the B.H.A.S. lead/zinc smelting operation, which discharged zinc in waste water at a rate of 1,000 tons Zn/year (Deland and Jones, 1973). Data from B.H.A.S. (reported by these authors) gave the total metal content of the waste water discharged into No. 1 drain as

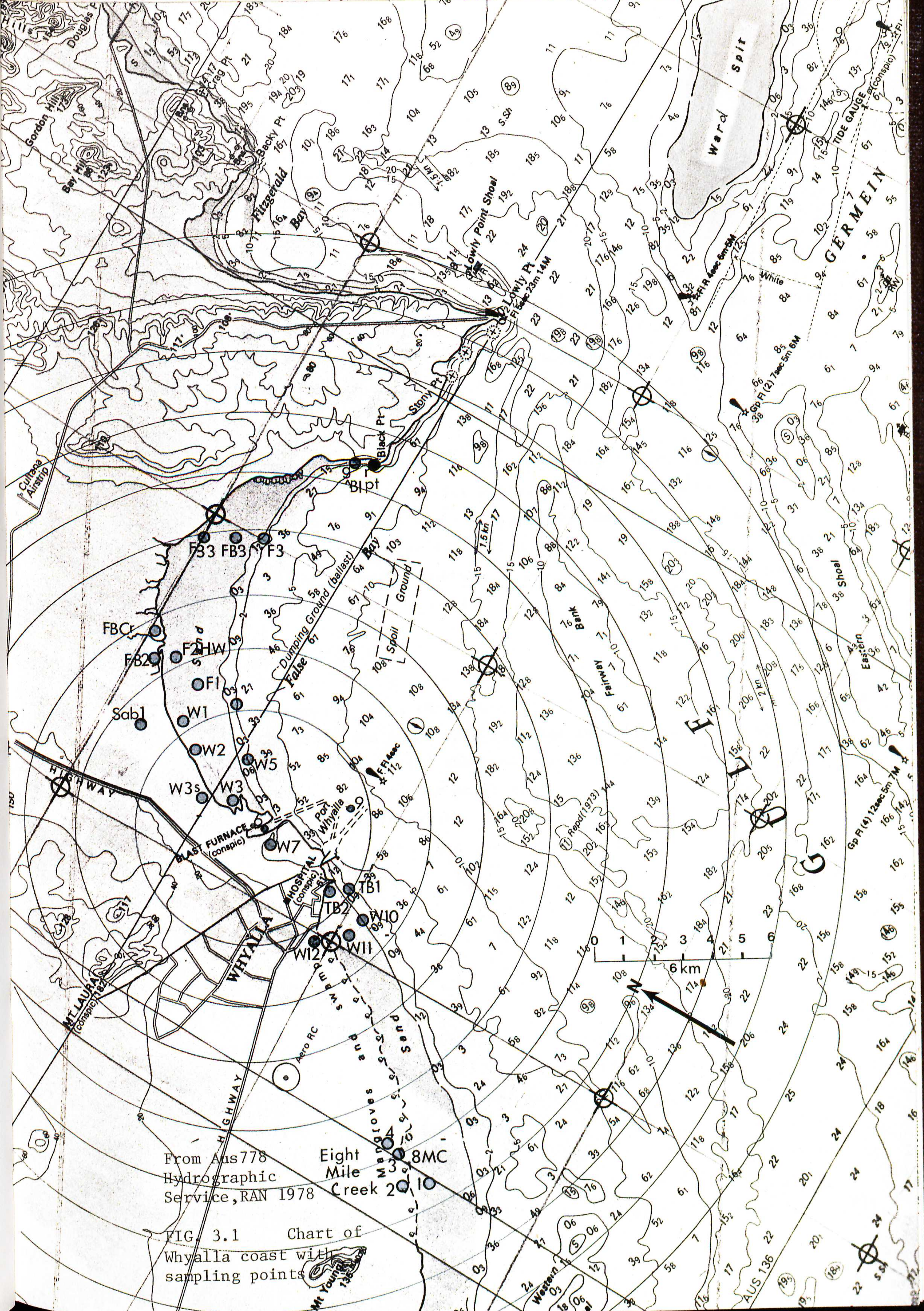
zinc	20	mg/1	
cadmium	0.2	mg/1	
arsenic	0.05	mg/1	
antimony	0.05	mg/1	
lead	1	mg/1	(Deland and Jones, 1973)

Pt. Pirie is considered to be the major source of lead, zinc and cadmium in Spencer Gulf (Warren, 1979).

The regional accumulation of lead and zinc in sediments is being mapped by the C.S.I.R.O., and results to date show that metals of recent origin are enriched in the top 10 cm of sediment, rather than distributed more uniformly down the core, as is the case for unpolluted sediments. Sediments high in lead are also found in shallow water well away from the main zone of pollution, the shipping channel. No direct relationship with surface water concentration of lead has been found (Warren, 1979, I.L.Z.R.O. Venture Analysis LH-230/2H-212/CH6).

The Playford Power Station, 5 km south of Pt. Augusta (Fig. 2.1), burns Leigh Creek coal, and discharges ash mixed with water into large salt ponds east of the plant. Water draining from the ash ponds eventually reaches the sea. The fly ash is considered a potential source of metals in the gulf, but analyses carried out by C.S.I.R.O., together with plume dispersion measurements, indicated that the contribution to metal concentrations in the Pt. Pirie area would be insignificant (Williams, 1979, I.L.Z.R.O. Project Ch-6/ZH-212). The main impact of the power station is considered to be the rise in sea temperature caused by the discharge of cooling waters at a rate of 17,000,000 gal/hour, at a temperature 6-8^{o}C higher than the ambient water temperature. The metal content of water draining from the fly ash may be responsible for the elevated metal concentrations recorded for sediments taken from the eastern waterfront in Pt. Augusta, compared with those from areas more distant from the power station (samples Pt A.E. and Pt A.W. Table A6, appendix).

The Whyalla steel works is the third important source of metal wastes in northern Spencer Gulf, and will be described in more detail as the selected study area.



From Aus778 Hydrographic Service, RAN 1978

FIG. 3.1 Chart of Whyalla coast with sampling points

3 THE STUDY AREA

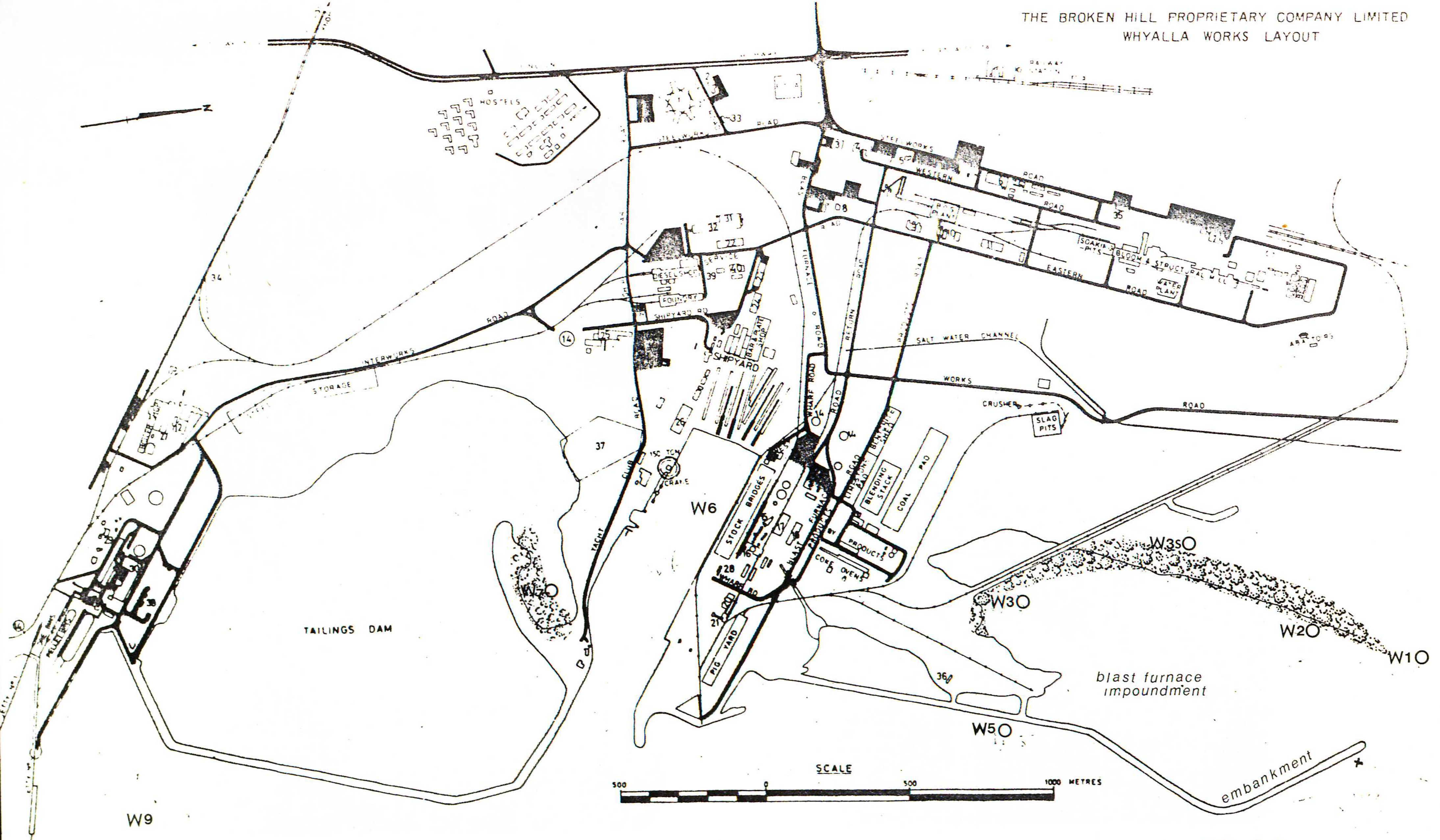
3.1 Whyalla

The area sampled to determine the distribution of metal wastes from the Whyalla steelworks extends from Black Point at the eastern end of False Bay ($137^{o}43'$E and $32^{o}59'$S), around the bay to include the work's shoreline, and south of the town to Eight-Mile Creek ($137^{o}31'$E and $33^{o}10'$S), (Figs. 2.1 and 3.1).

Whyalla is situated at the south-western corner of False Bay, on a low-lying coastal plain, with intertidal sandflats extending more than 1 km seaward from a line of mangroves, backed by low beach ridges and samphire vegetation. South of the town, the mangrove communities are dense, and form an almost continuous belt as far south as Cowell.

From 1900-1937, 'Hummock Hill' was used as a port for the shipment of iron ore from the Iron Knob leases, and in 1920 was renamed Whyalla (McLennan, 1975). The shipyard was established in 1939, the first ship launched in 1941, and a new blast furnace 'blown in' the same year. Blast furnace operations were continued on a small scale until 1958, when the decision to build an integrated steelworks was made. This was to include the coke oven battery, a second larger blast furnace, an oxygen steel plant, and billet mill. In 1968 a magnetite plant was established to convert low-grade haematite ore to magnetite pellets by a reducing roast process. In 1975, the works reached a production level of 1 million tons/year, the town having a population of 32,000.

Discharges from the works are released both north and south of the ship basin (Fig. 3.2). Waste from the pellet plant consists mainly of cooling water, with large quantities of fine suspended iron oxides. This is discharged into a tailings dam which is now enclosed by a wall of rock overburden and slag extending south from the ship basin to No. 2 jetty (Fig. 3.2). Water from the open sea percolates freely



THE BROKEN HILL PROPRIETARY COMPANY LIMITED
WHYALLA WORKS LAYOUT

1	ADMINISTRATION OFFICES
2	CAFETERIA
3	MEDICAL CENTRE
4	LABORATORY
5	RECEPTION CENTRE
6	STEELWORKS STORE
7	STRUCTURAL OFFICE & AMENITIES
8	TRAFFIC CONTROL OFFICE
9	OXYGEN PLANT
10	PRECIPITATORS
11	DIRECT METAL FOUNDRY
12	FITTING & TURNING APPRENT SHOP
13	
14	OIL TANKS
15	N° 1 BLAST FURNACE
16	N° 2 BLAST FURNACE
17	BOILER HOUSE
18	POWER HOUSE
19	
20	LADLE SERVICING
21	PIG MILL
22	ELECTRICAL WORKSHOP
23	TIMBER SHED
24	BOILERM APPRENT TR SHOP
25	BRICK PLANT
26	FITTING OUT SHOP
27	MACHINE SHOP (LIGHT)
28	SHIPPING OFFICE
29	GEOLOGICAL OFFICE
30	PELLETIZING PLANT
31	MEDIUM MACHINE SHOP
32	HEAVY MACHINE SHOP
33	E D P BUILDING
34	NURSERY
35	CONSTRUCTION OFFICE
36	BRECKETS
37	DIMET AREA
38	MAGNETITE PLANT
39	PAINT STORE
40	CARPENTERS SHOP

LEGEND

ROADS	▬
CAR PARKS	█

FIG. 3.2
B.H.P. works area, Whyalla, showing sampling points.

ADM. 873

PLATE 3.1 Tailings dam wall.

PLATE 3.2 Mangrove seedlings inside the tailings dam (Pellet Plant in background).

through the wall, so that tidal fluctuations within the dam follow the normal pattern. The wall seems to act as an effective filter for the suspended iron-oxides, which are deposited as a fine red mud on the intertidal flats inside the dam, and coat rocks and algae on the inside of the wall (Pl. 3.1). The water flowing out under the wall is clear, and the outer rocks are colonized by the usual zonation of intertidal organisms. A vigorous growth of young mangrove trees and seedlings is established in the sheltered north-east corner of the dam nearest the yacht club (Pl. 3.2).

North of the ship basin, a long embankment projecting north partly encloses the shallow sandy mud flats where waste water from the blast furnace area is discharged (Fig. 3.2). The embankment was intended to extend to the opposite shoreline, impounding waste waters in the same manner as the tailings dam south of the ship basin. However, this impoundment was considered a threat to the extensive mangrove community there, so the wall was left incomplete to maintain full tidal circulation in that area. Even so, changes in the former pattern of sediment movement have resulted.

Waste water from the steelworks area is used, after sedimentation, to quench coke from the coking ovens. The excess is run into a pond behind the railway embankment and seeps under this embankment to the semi-enclosed intertidal area (Fig. 3.2). A dense growth of young mangrove seedlings appears to be flourishing in the dark sandy mud in this corner of the blast furnace area (Pl. 3.3), and a series of photographs taken from the same point by Mr. Reece Edwards shows continued healthy growth over the last 3 to 4 years. Cooling water and gas scrubber effluent from the blast furnace runs through 'under and over' weirs to trap floating material, and allow suspended matter to settle, before reaching the main effluent channel running along the inside of the embankment (Fig. 3.2). The final weir on the channel has been reduced to a rocky 'race' which agitates and aerates water before it discharges into the main lagoon. The strong current which sweeps around the

PLATE 3.3 Young mangroves, <1 m high, in the rapidly accreting corner of the blast furnace lagoon (W3), January 1979.

incomplete end of the embankment may confine the waste water to the lagoon as the tide rises but, diluted with tidal water, a considerable part of the lagoon contents would be removed with the outgoing tide.
Aerial fallout from flue dust and fine iron oxide may contribute to surface sediment metal concentrations, and also to the fine dust which covers mangrove leaves in the tailings dam and blast furnace area.

The shipping channel and basin, lying between the blast furnace area and the pellet plant, is dredged periodically to a depth of approximately 10 m, as is a channel to No. 2 ore jetty, south of the tailings dam. The dredged spoil is dumped in deeper water in the centre of False Bay, just off the edge of the sand bank (Fig. 3.1). It is possible that fine particulates from the dredged material would be deposited with intertidal sediments on the False Bay shoreline.

There are no discharges associated with the steelworks in the area south of the town jetty. Treated effluent from the sewage works south of 'town beach' is released into a large creek in dense mangrove swamps. A path of green 'sludge' where the creek discharges into the sea indicates some enrichment of nutrients in the area, but the contribution is unlikely to have any significant impact on the marine environment (Deland and Jones, 1973). The same authors consider that seepage from the nearby town rubbish dump is unlikely to enter the sea. The intertidal areas at the south end of town beach and at Eight-Mile Creek, with wide expanses of sandy mud flats exposed at low tide, and a coastal fringe of mangrove swamps, are very similar to the shoreline north of the works. These areas were included in the study as 'control' or 'clean' areas.

3.2 Other sampling areas

Sediment samples, some intertidal organisms, and mangrove leaves were collected from other areas in Spencer Gulf, and Gulf St. Vincent, to compare metal concentrations with those of the Whyalla material. These sampling areas are located as follows:

Spencer Gulf (Fig. 2.1) -

(1) At Snapper Reach on the western side of the gulf, just south of the Pt. Augusta power station on the opposite shore (137°45'E and 32°35'S).

(2) On the eastern shoreline in Pt. Augusta, on the beach just below the Yacht Club, where mangroves colonize red clayey mud.

(3) At Chinamans Creek, near Redcliff point (137°50'E and 32°41'S), where very wide sand flats are exposed seaward of the mangroves, and overly relict black mangrove muds.

(4) At Weeroona Island (Mt. Ferguson), 138°3'E and 33°6'S, near the Pt. Pirie navigation channel. On the south side of the bluff opposite the smelters mangroves extend inland for 2 to 3 km, and have extensive stagnant creeks which are inundated only on high spring tides.

(5) At Pt. Broughton (137°55'E and 33°35'S), just inside Munderoo Bay, where very large old mangrove trees grow in sheltered sandy muds.

Gulf St. Vincent (Fig. 1.1). Sampling sites were located

(1) On the bank of the Pt. Wakefield river, near its entry to the sea (138°6'E and 34°10'S).

Fig 3.2

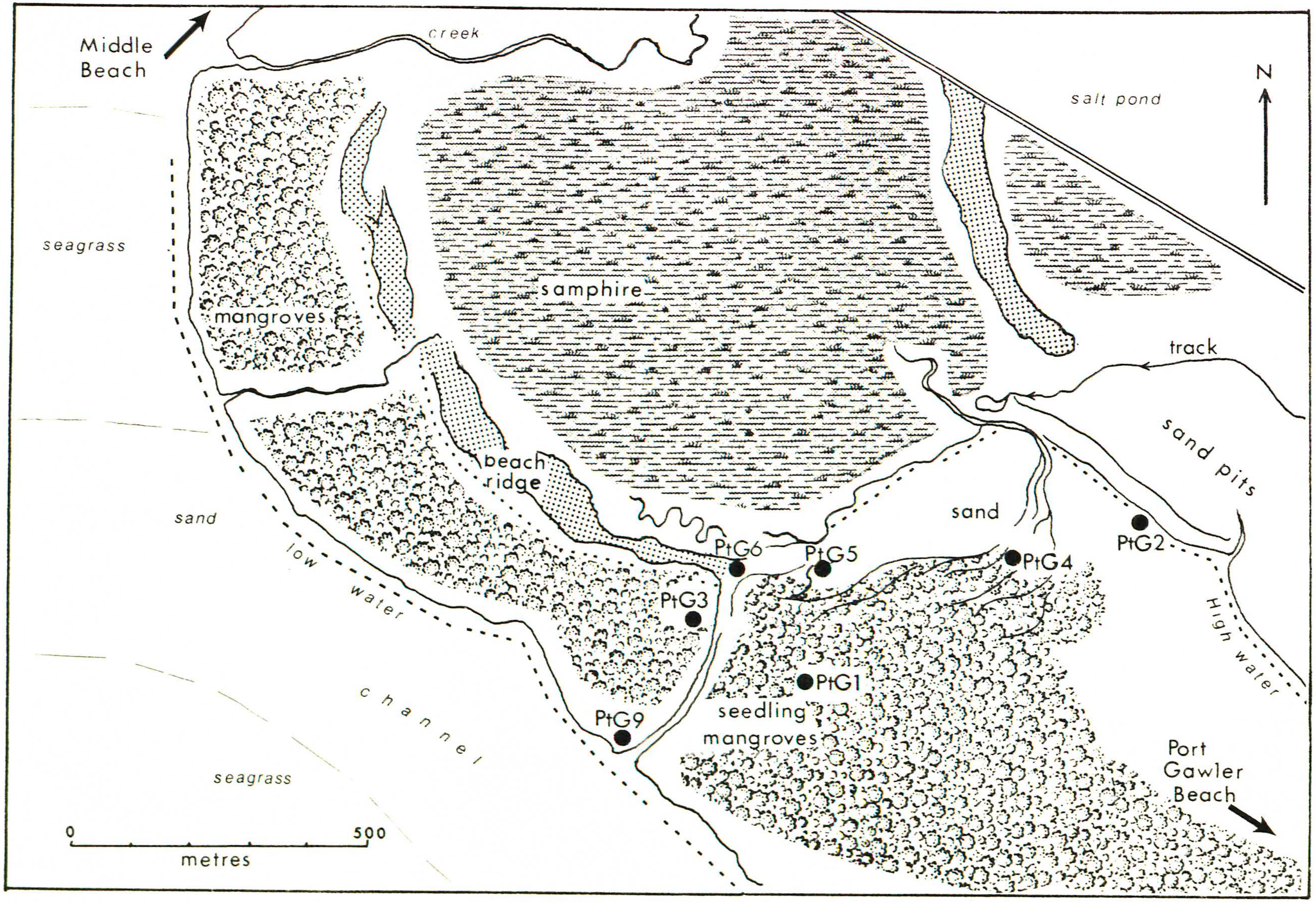


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FIG. 3.3 Map of Pt. Gawler study area.

(2) In mangroves beside the channel at Pt. Wakefield harbour, nearby.

(3) Further south, the Pt. Gawler area ($138^{o}28'$E and $34^{o}40'$S) was chosen for a more detailed study of sediments and surface water parameters (Figs 1.1 and 3.3).

Pt. Gawler has wide intertidal sand and mud flats, densely colonized with mangrove trees (Fig. 3.3). Several small creeks discharge onto the intertidal area, north of the main Gawler River. This study area is similar to the Eight-Mile Creek area south of Whyalla, but has greater fresh water input.

The intertidal zone at Pt. Gawler seems to be rapidly accreting, much of the fine dark brown sediment being transported by the river and creeks. New stands of mangrove seedlings and young trees have colonized offshore bars parallel to the beach. The area was chosen for the measurement of surface water parameters because of its easy access in all types of weather and tidal conditions.

4 METHODS

4.1 Fieldwork

4.1.1 Aerial photographs

The Whyalla study area was initially surveyed from a light aircraft in May 1978, and the many oblique photographs taken in conventional colour recorded the features of the shoreline and shallow water zone. On the basis of black and white photographic surveys flown by the Department of Lands, and conventional colour surveys made by the B.H.P. company in 1978 and 1979, the larger shoreline features, direction of littoral drift, wave encroachment, and sediment accumulations were defined.

Aerial photographs are considered to show more details of the configuration of coastal features and circulation patterns than can be discerned from field surveys of the coastline (El-Ashry, 1977). They also provide a convenient reference in the interpretation of field and laboratory data. In this study they were used initially to select sampling points, and later to aid in the interpretation of the distribution of metal concentrations in sediments.

4.1.2 Wind data

The direction of wave encroachment, and the wave energy available for the transport of sediments, is influenced by the prevailing wind direction and velocity in the coastal zone. A record of wind speeds and directions at Whyalla was made over a full year, from December 1973 to December 1974, by Schwerdtfeger and Williams, of the Flinders Institute for Atmospheric and Marine Sciences, to allow computation of local air mass trajectories as a basis for town planning decisions. Air temperatures obtained by the Bureau of Meteorology were compared with mean values to show that "the year 1974 was not too atypical" (Schwerdtfeger, 1975). These data were used to support data from aerial photographs in interpreting patterns of littoral transport in the vicinity of Whyalla.

4.1.3 Selection of sites for sampling

The study of aerial photographs and wind roses for the Whyalla area suggested sampling stations to assess the distribution of sedimentary accumulations of waste material from the works. The 'control areas', likely to be free of the effects of discharges, were chosen south of the town, at the south end of town beach and at Eight-Mile Creek, as the net direction of longshore transport appeared to be north. Most of the coastline here, as at False Bay, has wide sand flats exposed at low spring tides, but covered at high spring and neap tides. In both areas, sampling stations were chosen at the seaward edge of the sand flat, or low tide level, as well as at the seaward margin of the mangrove stands, and at the upper limit of high tide, or slack water, within the mangroves. In the works area samples were taken within the mangrove stands, on sand bars offshore, and in rapidly accreting and apparently eroding areas. The northern limit of the Whyalla sample sites was Black Point, at the north-eastern end of False Bay (Fig. 3.1).

4.1.4 Coring of sediments

Most sediment samples were collected in the intertidal zone at low tide, so that cores would be reasonably intact, maintaining the sequence of sedimentary and chemical horizons. Short lengths (50 cm) of plastic water piping 7 cm diameter (recommended by Dr. K. Tiller of the C.S.I.R.O. Division of Soils) were well washed with the ambient sea water at each site. The tubes were then pushed as far as possible into the mud or, in some cases, hammered in with a wooden mallet. The top end of the tube was then capped, and a hole dug beside the tube down to the level of the lower end. A hand was then pushed under the end of the tube, capping the lower end while the whole tube was carefully withdrawn. Site details and orientation were written on the outside of each tube with a marking pen. The tubes were stored with ice in an "Esky" while collection was in progress, but were taken at the end of each day to the "Golden North" depot at Whyalla for freezing.

All frozen cores were transported back to the laboratory packed in dry ice, and were kept deep frozen until prepared for analysis.

4.1.5 Biological material

The ability of some marine organisms to concentrate metals above the ambient available level has been used in many parts of the world to monitor, or indicate water concentrations of particular metals (Goldberg, 1975; Phillips, 1978; Barbaro and others, 1978).

In the present study the variety of organisms at each sampling location was first observed, in an attempt to find one organism which might occur at all sites. A number of different ones were collected for preliminary analysis in November 1978, and in May 1979.

All samples were collected in plastic bags, previously thoroughly washed in ambient seawater. After collection, the organisms were washed several times in the ambient water to remove adhering particulate matter, drained thoroughly, and stored on ice for transport to the laboratory. The material was not frozen, to avoid maceration of the soft parts. Results of the analyses of some samples have been included in section 5.1, but no one species was found under similar conditions at all stations, or in sufficient numbers, to make any regional comparison possible.

Mangrove leaves were collected from trees at all sampling stations to investigate the possibility that they might indicate the concentrations of available metals in the sediments, and also suggest any role in making sedimentary metal concentrations available to organisms as detritus. The largest healthy green leaves were collected from the terminal 10 cm of branches of trees growing close to the sampling station. Usually, the trees at any one station were fairly uniform in size, being "old" (Obviously many years, with thick gnarled trunks), "small mature" (usually 2 metres high with trunks 5-10 cm diameter), or 'seedlings' (<1 m tall, often <0.5 m). Leaves from each station were stored in plastic bags well washed with seawater, and kept cold, but not frozen, for transport to the laboratory.

4.1.6 General observations

The variety of invertebrates, larger animals, and feeding habits was observed wherever possible at sampling sites, to suggest trophic pathways which might be available for the distribution of sedimentary metal accumulations. The general health of mangrove communities was noted in relation to the shoreline environment north and south of the town, and the subtidal benthic community was studied in the False Bay area.

4.1.7 Surface water parameters

The solubility of metal compounds is probably most important in determining the availability of toxic concentrations to marine organisms. The parameters controlling the concentration of available metals are the pH of the overlying water (Zirino and Yamamoto, 1972; Rubin, 1974; Payne and Pickering, 1975; and others), the oxidation state of sediments and water (Rubin, 1974), the salinity (‰) (McElvie, 1979), and the presence of other complexing molecules (Rubin, 1974; Davis and Leckie, 1978).

The actual toxicity of these metal concentrations to marine organisms is also affected by the salinity and temperature of the water in which they are encountered (O'Hara, 1973 and Jones, 1975). Jones (1975) and Sullivan (1977) recorded the greatly increased toxicity of cadmium to small crustaceans at lower salinities and higher temperatures, probably due to increased ion uptake during osmoregulation at lowered salinity, and a higher metabolic rate at higher temperatures.

To establish the range of fluctuation in surface water parameters of the intertidal marine habitat, the pH, salinity, temperature, and H_2S in solution were measured under a variety of tidal and climatic conditions throughout the year.

4.1.7.1 Temperature

Temperatures were recorded with the centigrade thermometer provided with the Hatch DR-EL/2 portable test kit for water analysis, the pH and conductivity meters being adjusted accordingly.

4.1.7.2 Salinity

In this report, the term salinity is used to mean 0.03 + 1.8050 Cl (Riley and Chester, 1971). Chlorinity (Cl‰) is defined as "the mass in grammes of chlorine equivalent to the mass of halogens contained in 1 kg seawater" (Riley and Chester, 1971). Chlorinity is determined by titration with silver nitrate. The electrical conductivity of seawater is roughly proportional to salinity, as defined above, and for large numbers of field measurements in shallow surface water, a portable conductivity salinometer is more convenient than laboratory determination.

Salinity was measured with a Townson portable conductivity meter 2103A, with full temperature compensation, calibrated for use with .5 M potassium chloride. The conductivity cell used was a TAO type CG210-p (K=10). In addition to the linear conductivity scale, the instrument has a salinity scale reading 0-40‰. In many cases the salinity of surface water exceeded 40‰, and conductivity only was recorded. Salinity was later estimated from the approximately linear relationship between the two around the range of normal seawater (35‰). This method may be slightly inaccurate in highly saline waters, but was considered adequate to demonstrate the range of surface water parameters for this study.

The measurements were made in surface pools on the intertidal sand flats, mangrove muds and seagrass beds at Pt. Gawler throughout 1979. The pools were marked on an aerial photograph and the same sites were used for measurements each time (Fig. 3.3). The wide range of parameters recorded is listed in the appexidx (Table A1). The variations are shown in Fig. 5.3 of the text.

4.1.7.3 pH

pH measurements were made with a metrohm AG CH-9100 Herisau E588 portable pH-meter, using a combined electrode assembly. The instrument was calibrated against commercial buffers at pH 5 and pH 7, immediately before field use, and the calibration rechecked afterwards. The instrument proved extremely reliable under a variety of weather conditions.

4.1.7.4 Hydrogen sulphide

Hydrogen sulphide, in the range 0-5 mg/1 in solution, was measured by the lead sulphide method developed for the Hach portable test kit. This is a very simple test which relies on a colour comparison with test paper colours produced by prepared standards (Hach Chemical Co., 1976). While its sensitivity is extremely limited, it does allow immediate field measurement of hydrogen sulphide in water taken directly from the source being tested. The presence of hydrogen sulphide and black colour were used to identify reducing conditions in the sediment. The procedure was probably adequate to identify anoxic horizons without the problems associated with field measurements of redox potential by electrodes (Zobell, 1946; Whitfield, 1971; Hallberg, 1974).

4.1.8 Photographs

Conventional colour photographs were taken throughout the year to record observations of mangrove flora and fauna, tidal flooding, and other phenomena relevant to the study. These have been reproduced in the report where appropriate. An aerial survey of mangrove communities with infra-red film was undertaken by the company as part of a normal bi-annual survey flight, but as yet no data is available.

4.2 Laboratory methods

4.2.1 Sediment cores

Plastic tubes removed from freezer storage were left on the laboratory bench for a short period of time to allow the outer casing to reach room temperature. At this stage, the still frozen core could be gently extruded from the tube onto an acid-washed plate glass slab. The core then remained intact while completely thawing out.

Horizons were visually identified in most cores, on a basis of distinct colour or texture of sediments, i.e., either chemical or sedimentary horizons, or both. Each horizon was described, and measured, before proceeding further. Special features such as the presence of organic debris, stones, shells, or smell of hydrogen sulphide were also noted. Slices approximately 5 cm thick were then cut from the centre of each horizon with a stainless steel knife thoroughly washed with distilled water.

In order to assess the total metal content of the sediment and its interstitial water, it was decided not to remove any water from the samples, nor to attempt to remove chlorides by washing with distilled water. All core 'slices' were consequently placed in evaporating dishes, and allowed to dry for several days in a drying oven at 60-80°C. The low temperature was selected to avoid losses of volatile metals during drying (Fourie and Peisach, 1977).
Water content for many samples was calculated by weighing before and after drying. After final weighing, the sediment was broken up with an agate mortar and pestle, and sieved through a coarse nylon mesh sieve to remove shell fragments and pebbles. The sediment was then carefully mixed again in the mortar and stored in labelled glass jars. The purpose of the grinding was to disaggregate the dried material, rendering it sufficiently homogeneous to allow a representative sample to be taken for analysis, without reducing the predominant grain size of the sediment.

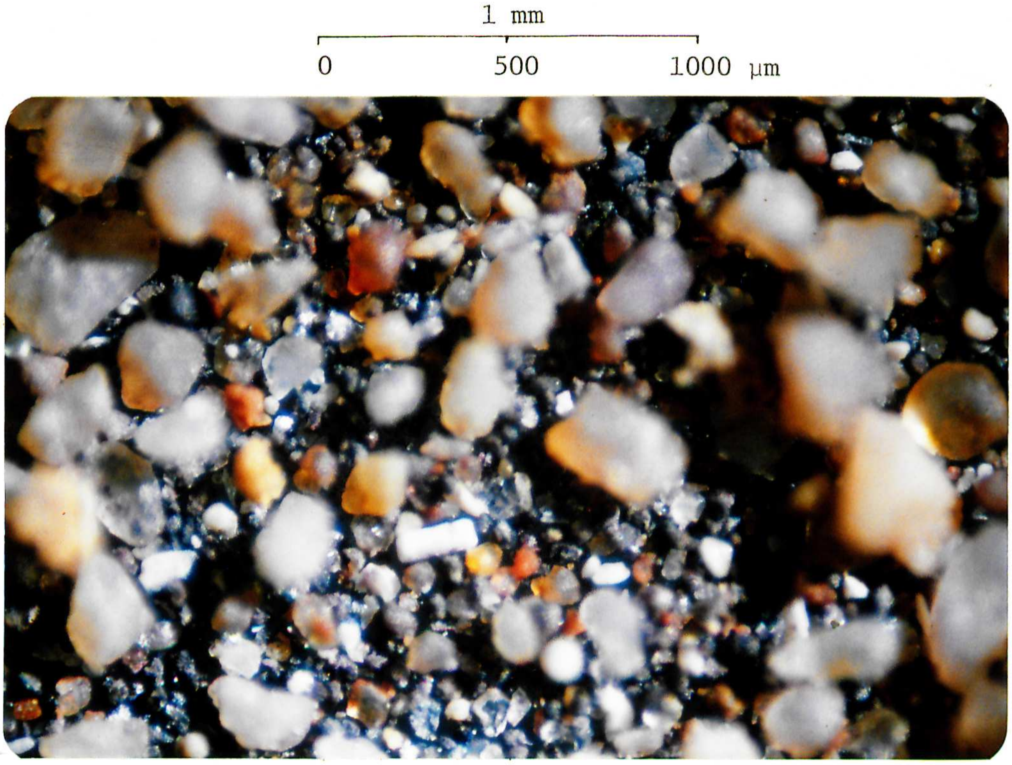


PLATE 4.1 Poorly sorted very fine and medium sand with conspicuous metal fragments.

(Smear slide: Core W1A)

PLATE 4.2 Medium sand.

(Smear slide: Core W1B)

0 500 1000 µm

1 mm

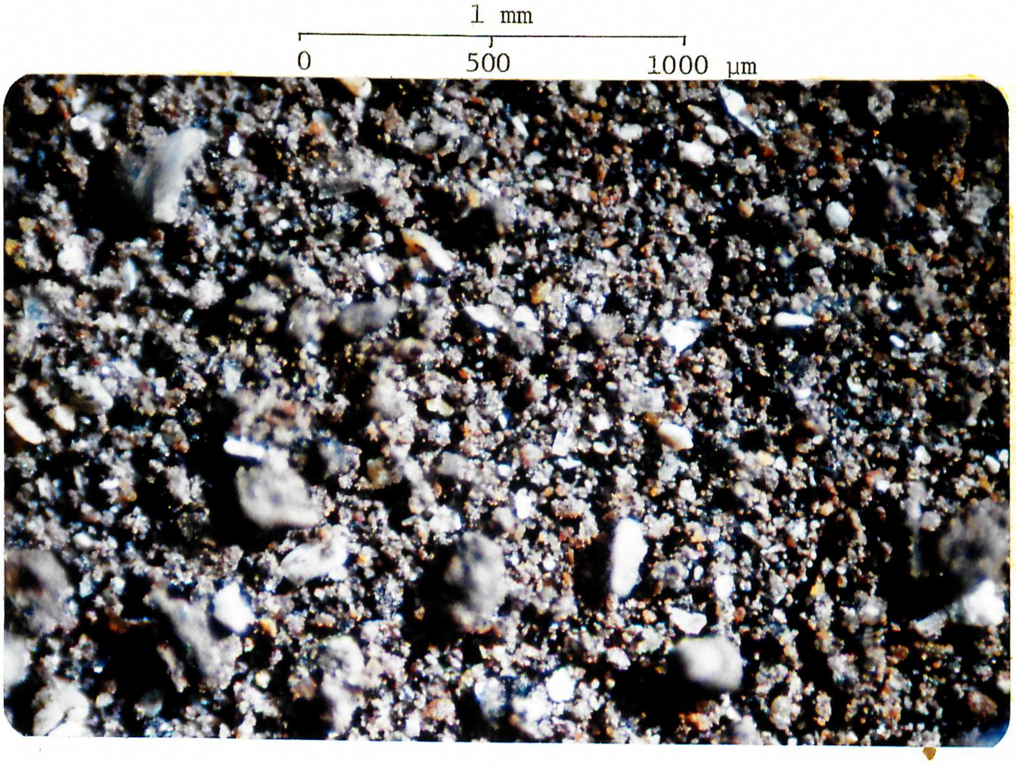


PLATE 4.3 Poorly sorted silt with metal particles.

(Smear slide: Core W1C)

PLATE 4.4 Fine shelly sand.

(Smear slide: Core W1D)

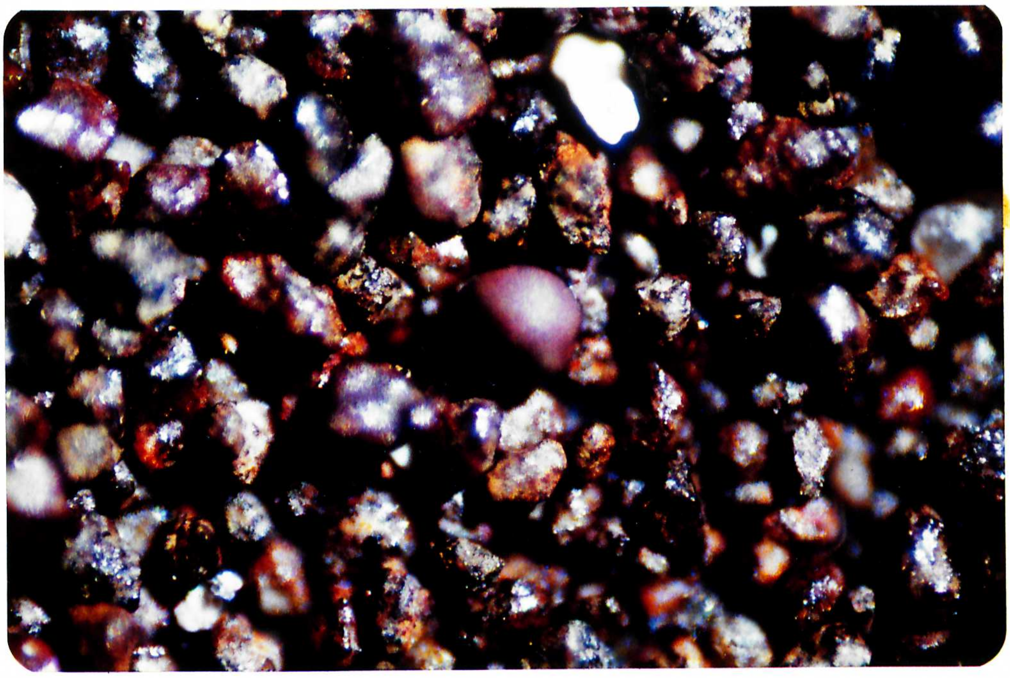
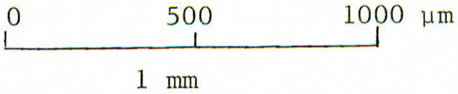


PLATE 4.5 Sand from W5A showing grains apparently coated with iron minerals.



4.2.2 Sediment characteristics

While removing sections from each horizon in the core, a small sample of each was placed on a labelled glass microscope slide. These samples were later dispersed on the slide with a drop of distilled water, dried, and covered with EUKITT mounting medium and a glass cover slip. The microscope slides were then used to determine the texture, content, and predominant grain size of sediments using a 1 mm stage graticule divided into microns. The smear slides and graticule were photographed on Kodak EPY Tungsten 50 ASA colour slide film. All sediment classifications were repeated and checked by projecting the slides onto a white paper screen, on which the projected graticule scale had been marked in black ink. The content of shell, quartz, and plant detritus, sediment colour, coating of grains with metal, and degree of sorting were all clearly visible by this latter method (Pls 4.1-4.4 and Pl. 4.5).

Sediments were classified as sand, silt, or mud, according to the grain size predominating in each horizon.
The size classes used were based on Folk's classification (1968).

coarse sand	500-1,000 microns
medium sand	250-500 µm
fine sand	100-250 µm
silt	20-100 µm
mud	<20 µm

The term clayey-mud was used for muds with an obvious "sticky" quality.

The characteristics of all sediment samples are listed in Table A2 of the appendix. Other terms used in the table are:

depth	cm below the surface, at the middle of the horizon
colour	sediment colour in wet core
feature	observed inclusions, or other features

organic C (%)	weight loss on ignition at 500°C
total carbonate (%)	weight loss 500-1,000°C (inaccurate for clayey materials)
location	(in relation to tide levels or environment) High Water (HW), Low Water (LW), Mid-littoral (Mid), Subtidal (Sub), Mangroves (Mang.), Boulder Beach (BB)

4.2.3 Organic carbon and total carbonate

The organic carbon content of sediments was estimated using the method described by Dean (1974). This is a simple weight loss on ignition for 1 hour at 550°C. Hallberg (1974), and Skei and Paus (1978) also used this method. Hallberg (1974) verified that interference from the dehydration of clay minerals is negligible below 500°C. Organic carbon estimates made by this method were reproduced in duplicate samples, and correlated well with observed characteristics of sediments. The estimates for organic carbon in fine grained sediments, however, could be exaggerated by the loss of some residual water at 500°C, as sediments were oven dried at less than 100°C to avoid loss of volatile elements. Dean (1974) also recommended a further ignition for one hour at 1,000°C to determine total carbonate in sediments. This method, however, is only reliable for calcareous sediments, as the interlayer water from clays would contribute a significant percentage of the weight loss in clayey sediments. The data are listed with other sediment characteristics in the appendix (Table A2), but were not used in any conclusions except where other observations, such as microscopic examination, supported the estimates. Total carbonate estimates did prove useful in separating terrestrial and marine sediments, in conjunction with microscope observations.

4.2.4 Selective extraction of metals from sediments

4.2.4.1 Definition of fractions

The metal fractions most relevant to this study, obtained by different acid digestion procedures, are defined below:

Total metals -

Hydrofluoric, nitric and perchloric acids were used to dissolve all sediment constituents, including silicate minerals. Analyses of these solutions represent the total metal content of sediments, the natural lode plus the metal derived from industrial wastes.

'Industrial' metals -

A hot nitric acid/hydrogen peroxide leach dissolves all non-silicate components of the sediment, but does attack some clay minerals (Agemian and Chau, 1976). This fraction includes authigenic metal, such as sulphides, formed in the sediment from solution, as well as adsorbed and particulate metals, transported from industrial sources. Some iron and manganese from natural sources will be extracted from unpolluted sediments, but concentrations of cadmium, chromium, copper, lead and zinc will be very low in these samples. This fraction represents the upper limit of metal potentially available to biota, and should be a close estimate of industrial input.

Available metal -

A mixture of ammonium oxalate and oxalic acid at pH 3 was used to extract easily reducible metal compounds from the sediment. This fraction includes iron as amorphous oxide phases, as well as metals adsorbed or co-precipitated with these (Schwertmann, 1964). It represents the more mobile elements in the industrial deposits, which could be released from sediments under normal environmental conditions.

Mobile fraction (%) -

This represents the proportion of the 'Industrial' metal which is easily available, or mobile, under natural fluctuations in environmental conditions ($\frac{\text{Available metal}}{\text{'Industrial' metal}} \times 100$)

Two other extraction procedures were used on a limited number of samples. A cold dilute acid extraction (.5N hydrochloric acid) was used to assess the possibility that metals could be released from sediments at the low pH found in animal digestive tracts.

A cold alkaline leach at pH 9.5 was used on surface sediment samples to investigate the mobility of metals from surface sediments under the high pH conditions found in sunlit surface waters with algal or seagrass growth.

The extraction methods used, and their action on sediments, are summarized in Table 5.4, in section 5.6. The laboratory procedures are detailed in the following section (4.2.4.2-6).

4.2.4.2 Extraction of total metals

This method of digestion was recommended by Agemian and Chau (1975), who considered that it fulfilled the important conditions of (1) dissolving the silica matrix of the sediment, (2) destroying the organic matter, and (3) taking all the metals into solution without introducing any interfering ions. A sealed bomb digestion was considered to eliminate losses due to volatilization. 0.1 g of finely powdered sediment was used for digestion in a teflon cup with 2 ml concentrated nitric, 1 ml perchloric, and 4 ml hydrofluoric acids. The teflon cup was enclosed in a stainless steel pressure bomb, and digested at 140°C overnight. After cooling, the contents of the teflon cup was poured into 30 ml saturated boric acid solution and allowed to stand for two hours to dissolve any insoluble fluorides. The solution was then made up to 50 ml with distilled water in a volumetric flask, and stored in a polypropylene bottle. Thirty representative samples were digested by this method, to compare the total metal content of sediments with the amount extracted by other leaching methods.

4.2.4.3 Nitric acid/Hydrogen peroxide extraction

The procedure described by Krishnamurty and Shpirt (1976) was used to extract all metals not incorporated in acid resistant silicates.

Bloom (1975) tested four commonly used combinations of nitric, hydrochloric, and perchloric acids, and found the nitric acid digestion as effective as any combination of acids in extracting metals from sediments of the Derwent estuary. 1 g sediment samples were weighed into 100 ml Erlenmeyer flasks, and 1 ml distilled water added to each. Two drops of Octan-2-ol were also added to reduce frothing. 20 ml concentrated nitric acid was added to each flask, and heated for 2 hours on a hotplate at ~100°C. The flasks were then removed and cooled for 15 minutes before adding 5 ml 30% hydrogen peroxide very slowly. At this stage some sediments froth vigorously and may overflow the flask. To prevent this the base of the flask can be dipped into a large beaker of iced water. Heating was then continued for another hour, with intermittent swirling of the flask. The cooled digestate was then poured, with careful rinsing, into a volumetric flask and made up to 100 ml with distilled water. Filtering was necessary because of the considerable residue of resistant material. The diluted samples were filtered through Whatmans 54 filter paper, and stored in 120 ml polypropylene bottles. This digestion was used for all sediment samples and biological material. A selected number of sediment samples was compared with bomb digestions to assess the percentage of each element removed by this method (Table 5.4).

4.2.4.4 Cold acid extraction

A few samples were treated with .5N hydrochloric acid at room temperature. 1 g samples were placed in 100 ml Erlenmeyer flasks with 20 ml .5N hydrochloric acid, shaken for 2 hours on a mechanical shaker, and left standing overnight. Samples were then made up to 100 ml, and filtered, as in the previous procedure.

4.2.4.5 Reducing leach

To some extent, this extraction reproduces conditions found in mangrove swamps at night, when large quantities of decaying seagrass material can reduce the pH of surface waters. Schwertmann (1964) considered that acid ammonium oxalate under dark conditions would dissolve only amorphous iron oxides, whereas in the presence of sunlight or UV light, some crystalline iron oxides would dissolve. Dark conditions were chosen for this leach because

(a) it separates the most active fraction of iron oxides (Schwertmann, 1964), and

(b) sunlight usually produces a high pH in intertidal surface waters due to the presence of photosynthetic algae.

1 g samples of sediment were weighed into 100 ml Erlenmeyer flasks which were then completely wrapped in aluminium foil to exclude light. 50 ml of a mixture of .2M ammonium oxalate and .2M oxalic acid at pH 3 were added to each flask (approximately 11 ml of the oxalic acid and 15 ml ammonium oxalate give a mixture at pH 3). The flasks were gently shaken on a mechanical shaker for 2 hours. Each solution was then rinsed into a volumetric flask, made up to 100 ml with distilled water, and filtered through Whatmans 54 filter paper into a 120 ml polypropylene bottle. A blank disgestion was included with every batch of 10 flasks as for the nitric acid digestion. After dilution, the pH was still close to 3, so it was not considered necessary to further acidify the solution.

4.2.4.6 Alkaline leach

The very high pH conditions, up to pH 9.8, found in surface water of intertidal flats in sunlight were also modelled using a buffered solution at pH 9.4, containing 50 ml .2M boric acid, 50 ml .2M potassium chloride and 32 ml .2M sodium hydroxide, diluted to 200 ml. 1 g samples of dried, ground sediment were weighed into 100 ml Erlenmeyer flasks, and 30 ml of the above solution was added. The flasks were shaken for 2 hours at room temperature on a mechanical shaker. The solutions were then made up to 100 ml with distilled water in a volumetric flask, filtered through Whatmans 54 filter paper into 120 ml polypropylene bottles, and acidified with approximately 1 ml (4 drops) of 1:1 nitric acid.

4.2.5 Biological material

4.2.5.1 Mussels

These were usually in clumps and, having 'hairy' outer shells, incorporated a considerable amount of extraneous material. Each clump was thoroughly but quickly washed under running distilled water. Ten individuals having shells 3 to 4 cm long were then removed from each clump, washed again, and carefully opened with a stainless steel knife. The soft parts were dried at 60^{o} for four days, powdered, and stored in glass jars.

4.2.5.2 Barnacles

Where possible, barnacles were extracted from the washed shells with a small stainless steel probe, and dried in the same manner as the mussels. The barnacle growing in the ship basin at Whyalla, *Balanus amphitrite*, was large enough to extract the animal from the shell completely. *Elimnius modestus*, the very small barnacle growing on mangrove stems and leaves, proved impossible to separate from the shell without contamination from extraneous matter, and was not used for subsequent analysis.

4.2.5.3 Snails

The small air-breathing snail, *Salinator fragilis*, was found in most mangrove swamps. A large number (more than 50) was collected from each area. In the laboratory the snails were washed rapidly with running distilled water in a nylon sieve. However, it proved very difficult to entirely free the snails from adhering sediment, and it is possible that some sediment was included in the final sample. Because of the small size, the whole snail including shell was crushed, dried, and finally ground to a fine powder in an agate mortar. The problem of obtaining large specimens, free of sediment, probably precludes *Salinator* as an indicator organism, although it was present in most sampling stations.

4.2.5.4 Bivalves

The small sand cockle of the genus *Katelysia* was also present in many localities, but could not be found where sediment metal concentrations were high. The soft parts could easily be extracted from larger specimens, but in some areas the individuals were less than 1 cm in diameter.

4.2.5.5 Mangrove leaves

These were removed from the plastic bag to a nylon sieve, and thoroughly washed under running distilled water. Leaves were then oven dried at about 80°C for six days. The dried leaves were then crushed to homogeneous size fragments (about 2 mm^2) and stored in glass jars. Finer crushing was not attempted after an initial trial sample because the fine yellow powder produced adhered to the sides of the glass beaker and proved difficult to collect. All dried powdered biological material was digested with nitric acid and hydrogen peroxide, as for sediment samples. 1 g samples were weighed into flasks, moistened with 1 ml distilled water, and digested for 2 hours with 20 ml concentrated nitric acid at 100°C. After cooling, 5 ml hydrogen peroxide was added and the flasks heated again for 2 hours. After cooling again, the volume was made up to 100 ml with distilled water, and the solution was filtered through Whatmans 54 filter paper into 120 ml polypropylene bottles.

4.2.6 Water samples

Some analyses of acidified water samples were made early in 1979 by the B.H.P. company as part of their regular monitoring programme. These are included, in the appendix (Table A3.1). A separate analysis of water and particulate matter was carried out in December 1979. Five litres of water were collected at the end of the blast furnace embankment at low tide, the current at the time flowing north parallel to the wall. The sample was immediately filtered through .08 μm Millipore filter. The content of suspended particulate matter was 6.1 mg/l. The filtrate was acidified immediately, and the metal content of both fractions determined. The results of these analyses are included in Table A3.2 of the appendix, and discussed in section 5.7.

4.2.7 Reliability of analytical methods

All measurements of metal concentrations in solution were made with a Varian Techtron Atomic Absorption Spectrophotometer A.A.6, with simultaneous hydrogen lamp background correction for non-atomic absorption. Initially the accuracy of analytical methods was checked by the analysis of two U.S.G.S. standards. MAG-1 (a marine mud), and SCo-1 (Cody shale). A nitric/perchloric/hydrofluoric acid digestion was used, similar to that described in the reference paper (U.S.G.S. professional paper 840, p.119), and solutions were analysed by atomic absorbtion spectrometry. Few A.A. measurements are available for these new standards, and the range shown in Table 4.1 includes A.A. measurements with other quantitative spectrographic data.

TABLE 4.1

Analyses of U.S.G.S. samples carried out in present study, compared with range of values published.

Element	Sample	Present study (ppm)	Range (ppm) published
Cr	MAG-1	134	87.5-140
	SCo-1	110	48.9-72
Cu	MAG-1	26	27.5-52
	SCo-1	24	27.5-35
Mn	MAG-1	690	705-1100
	SCo-1	390	393-678
Ni	MAG-1	50	30.0-79.7
	SCo-1	30	24.6-33.9
Zn	MAG-1	126	94.4-155
	SCo-1	107	89.2-125

Pb was not present in MAG-1, and the 15 ppm listed for SCo-1 was not detectable at the dilutions used (1g/100 ml). Data for Fe and Cd were not available for these U.S.G.S. materials.

In general, the agreement between the total metal content found in this laboratory, and the published values for MAG-1 and SCo-1, is satisfactory for the purpose of the present study.

Other checks used were:

Blank samples -

Prepared for all types of digestion with each batch of approximately 10 samples. Initially zinc contamination was traced to glass fibre filter papers. No further contamination was found when these were replaced by Whatmans 54 and 541 papers. Considerable contamination was found for iron and chromium in stainless steel pressure bomb digestions and these consistent levels were deducted from the final concentrations. Iron levels were sufficiently high for the deduction to be insignificant but, in the case of chromium, negative results were obtained for some samples where low concentrations should have been present in the sediment.

Duplicate digestions and analyses -

These were carried out for all methods of digestion. The concentrations are tabled below. Duplicates were prepared at another time, rather than with the original batch of samples. Results are reasonably consistent for the same procedure, carried out on the same sample at different times.

TABLE 4.2

Analyses of duplicate nitric acid and oxalic acid extractions of sediment samples

Sample	Cd		Cr		Cu		Fe(%)		Mn		Pb		Zn	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Nitric Acid Leach														
W2MA	6	5	42	42	19	20	4.70	5.40	981	not measured	623	645	2710	2860
F1A	2.5	2.5	25	29	13	14	4.13	4.07	810		445	450	2880	2890
W12MA	0	0	29	33	10	10	1.20	1.13	90	93	32	32	100	104
WR2A	23	22.5	20	20	13	13	0.82	0.75	148	142	330	338	1090	1110
PtG4A	0	0	48	40	21	20	2.02	1.66	105	104	8	14	43	42
(MC2A	0	0	17	17	0	0	0.16	0.15	30	30	0	0	4	4
Oxalic Acid Leach														
W12MA	0	0	0	0	3	2	.466	.458	17	17	0	0	52	52
W12MB	0	0	0	0	2	0	.127	.123	7	7	0	0	81	88

Elements in ppm except Fe (%)

1 and 2 replicated extractions

Repeat cores -

Cores were taken at the same locations in January 1979 and again in May 1979. Nitric acid digestions are compared for the two samples in Table 4.3 below.

TABLE 4.3

Analyses of cores taken from W2 and W12 in January and May, 1979.

		Elements in ppm (nitric acid extraction)							
Core	Depth*	Cd	Cr	Cu	Fe	Mn	Pb	Zn	Org. Carbon (%)
W2A J	4	6	20	18	69,200	908	480	2,280	12
M	10	6	42	19	54,100	981	645	2,800	13
W2B J	14	2	10	8	15,540	274	110	456	6
M	26	0	21	17	12,460	236	32	150	7
W2C J	28	1	13	13	5,320	72	3	19	4
M	39	0	33	7	10,040	76	0	16	5
W2D J	38	1	18	15	6,360	28	50	202	3
M									
W12A J	4	1	9	8	11,010	95	7	182	26
M	1	0	31	10	11,960	90	32	103	20
W12B J	12	1	16	10	21,800	110	32	268	21
M	7	0	17	6	2,900	65	9	130	10
W12C J	30	1	12	1	1,560	60	3	2	4
M	24	0	13	0	1,920	35	0	2	5
W12D J									
M	40	0	17	0	1,290	35	0	0	5

*Depth = Depth at Mid-horizon (cm)

J = January

M = May

TABLE 5.1

Salinator fragilis - Possible metal uptake
(ppm dry weight)

Area	Sample	Date of Collection	Cr	Cu	Pb	Zn	Note
W2	Surface sediment	1.79	16	18	480	2280	few, very small
	Snails	1.79	-	14	88	436	
W3	Surface sediment	1.79	125	27	1076	8280	few, small
	Snails	1.79	16	10	195	928	
W3S	Surface sediment	1.79	168	31	345	8280	few, small
	Snails	1.79	23	13	125	928	
W12	Surface sediment	1.79	19	8	7	182	many, medium size
	Snails	1.79	4	11	3	57	
PtG3	Surface sediment	1.79	28	14	12	47	many, large
	Snails	1.79	4	24	0	76	
	Snails	6.79	0	25	13	91	

There are changes apparent in the depth and number of visually distinct horizons. This could have been due, in the case of the heavily contaminated sediment W2, to the anoxic layer being closer to the surface in the summer, with a much shallower layer of oxidized surface sediment. The existence of a distinct surface layer 1 cm thick in the May core at W12 was due to a surface algal mat which was not apparent in January, and appears to have concentrated lead and chromium. Generally, however, thereis broad agreement in the overall metal content of the cores collected in the two separate periods.

4.2.8 Identification of residue

'Complete' dissolution of sediment samples with nitric, perchloric and hydrofluoric acids, either as an open digestion in a teflon beaker, or sealed in a stainless steel pressure bomb, left a persistent residue from the sediments nearest the blast furnace outlet. The heavy grey sediment remained in the bottom of beakers after all methods of digestion. The residue gave an X-ray diffraction pattern similar to hematite and ilmenite and appears, on the basis of X-ray fluorescence analysis, to be predominantly iron, with a substantial amount of zinc, and detectable chromium, arsenic and manganese. This fraction of the sedimentary metal content was considered to be unavailable to marine organisms, and was not further investigated.

5 RESULTS AND DISCUSSION

5.1 Biological material

Mussels, barnacles, snails and sand cockles were collected in intertidal regions in November 1978, and January and May 1979. However, it was not possible to obtain any comparable data, due to the variety of species, and variation in condition within each species.

5.1.1 Snails

The air-breathing snail, *Salinator fragilis*, common on intertidal mangrove mudflats, did appear to take up chromium, copper, lead, and zinc in concentrations related to sediment levels, but the possibility of contamination from sediments discussed in section 4.2.5.3 makes the results of little value unless this source of error can be eliminated by improved technique. Results so far suggest that the snails' possible merit as an indicator organism would be in their wide distribution, and their apparent ability to take up chromium, but much further work would be necessary to establish this. The uptake of chromium by this species was, however, also noted by Bloom (1975).

The snails appear to feed on the surface algal film, which could also provide a site for metal binding and concentration (Ferguson and Bubela, 1974; C.S.I.R.O.-I.L.Z.R.O. Project CH-6/ZH-212, May 1979). The present investigation found that surface sediment at Chinamans Creek, which was bound with an algal mat, contained much higher levels of nickel, lead, and zinc than surface sediment with no algae (Table 5.2).

TABLE 5.2

Metal content of surface sediment (ppm)

	Algal mat	Bare surface
Ni	10	2
Pb	29	-
Zn	57	21

The snails found in polluted areas were mostly very small, and few in number. However, as a variety of wading birds on the mud flats seem to be eating them, they may provide a pathway between heavy metal accumulations in the mangrove muds and higher vertebrate consumers.

5.1.2 Cockles

Small sand cockles (*Katelysia sp.*) (Cotton, 1961), collected at Pt. Gawler appeared to have higher zinc concentrations than the sediment, as did larger cockles from Eight-Mile Creek. These were prevalent in all unpolluted mangrove and sandy intertidal areas, but were not found in the polluted sediments. No further samples were collected, although further work could show them to be a useful indicator of zinc and possibly copper and nickel.

5.1.3 Barnacles

The small barnacles, *Elimnius modestus* (Underwood, 1977), found on mangrove leaves, trunks, and pneumatophors, proved too thick-shelled to crush whole, and too small to separate soft parts, so no further specimens were used. The larger *Balanus amphitrite*, attached to wharf piles and grilles of the powerhouse water inlet in the ship basin, appears to accumulate cadmium, copper, and very high levels of zinc, but were not found in any other areas of study, so no data could be compared. However, continuous monitoring of this species could indicate the concentration of available metals in this area. Bloom (1975) found another species of barnacle, *Catophragmus polymerus*, to be a sensitive indicator of cadmium contamination in the Derwent estuary.

5.1.4 Mussels

Three different species of mussels were found in the study area and all appeared to accumulate copper and zinc to similar levels. It was noted by D'Silva and Kurensky (1978) that the uptake of copper and zinc for the green mussel (*Mytilis viridis*) was linear for the first 5 weeks of exposure but then appears to reach a steady concentration. In Table 5.3, cadmium, copper, manganese and zinc concentrations are listed for soft parts of the three species in different areas. All were full healthy looking specimens, although dissimilar in size.

TABLE 5.3

Metal concentrations in Mussels

Whyalla area	Date	Cd ppm	Cu ppm	Mn ppm	Zn ppm	Species
W6	1.79	1	10		85	*Mytilus hirsutus*
Ship basin	5.79	2	10	30	77	*Mytilis hirsutus*
W9						
Beacon	5.79	2	3	10	64	*Mytilus planulatus*
Beacon	5.79	1	3	9	65	*Mylitus hirsutus*
Old jetty	5.79	1	3	9	62	*Mylitus hirsutus*
W11	1.79	1	10	16	80	*Austromytilis erosus*

A. erosus grows almost completely submerged in mud in the mangrove area and could possibly be contaminated by sediments. The most potentially useful results are probably those from the ship basin and W9, where the mussels grow on constructions in deep water, above the sediment surface. However, as mussels were not available under these conditions in other areas, no further samples were analysed.

D.J.H. Phillips (1977), reviewing the usefulness of biological indicators, concluded that macroalgae and bivalve molluscs were the most efficient. However, he also suggested that the results of such surveys may be unreliable because of a wide range of sampling and environmental variables which have so far mostly been overlooked. Variables such as breeding season, age, weight and size of the individuals, salinity, water temperature, and the coexistence of several metals, have all been shown to significantly affect the uptake and concentration of metal in the organisms studied (Phillips, 1977).

While it is possible to eliminate some of these variables by carefully controlled sampling, in an area where the abundance and variety of species is very limited, such controls would lead to so limited a number of samples that few worthwhile conclusions could be drawn. Bloom (1975) collected and analysed many different species of shellfish from the Derwent estuary, and was able to compare and rank the organisms in order of their ability to accumulate a particular metal. The data could be used to assess the hazard in consuming a particular species of shellfish from an area contaminated by a known metal, but also provides a guide in selecting the most potentially useful organism as a biological indicator of contamination by a particular metal, if the variables discussed by Phillips (1977) can be controlled.

5.1.5 Mangrove leaves

The concentration of all elements, in ppm on a dry weight basis, is shown for mangrove leaves and sediment in Table A4 of the appendix. The copper and zinc content shows the most consistent relationship to available metal in sediments (Figs 5.1.1 and 5.2).

The concentrations of zinc in mangrove muds show such a wide range that the low values cannot be studied when plotted on the same scale as the high values. The range is shown for sediment concentrations plotted on a normal scale in Fig. 5.1. The values for zinc concentrations (ppm) in sediments and mangrove leaves are plotted on a logarithmic scale in Fig. 5.1.1, so that the relationship between sediment and leaf concentrations in unpolluted areas can be appreciated.

Lead was detected only in leaves from young trees at W3 and W3S. These sampling stations are very close to tracks having continuous movement of heavy vehicles, and the lead was possibly derived from this source. Cadmium and chromium were not detected in leaves even when their concentrations in nearby sediments were high. The results of leaf analyses suggest that mangrove leaves may indicate sedimentary accumulations of copper and zinc, and also contribute to the availablity of these metals in detritus, as well as to the cycling of iron and manganese. Leaves of young trees in polluted areas appear to have higher levels of metals than older trees. In unpolluted areas, the reverse situation is possible. However, more samples are needed to confirm these observations.

5.1.6 General observations

5.1.6.1 The subtidal habitat

The nearshore sea-bed at Whyalla appears to support a seagrass community similar to that in other parts of Spencer Gulf having no industrial input. One exception, however, is the subtidal area between the northern end of the blast furnace embankment and the ship basin. Here there is little seagrass or algal growth, and the seafloor is covered with fine red particulate material.

On 29.4.79, more than sixty stingrays were observed in about 20 minutes from a boat moving slowly southward, about 500 m out from the embankment, in water about 3 m deep. The large number of rays suggests some disturbance to the ecology of the area, in favour of this species. Snedaker (1978) attributes similar observations to the settling of large amounts of flocculated material in areas where current velocity is low, the associated organic matter providing food for scavenging animals such as rays, flatfish and crabs. Further study of the benthic community at Whyalla would be necessary to establish the significance of this observation, and any related circumstances.

5.1.6.2 The conservation of mangrove trees

Since the maintenance of recreational and some commercial fisheries at Whyalla is desirable, the conservation of the large areas of mangrove swamps is essential. So far, the area of mangroves threatened by the impoundments for waste water is very small compared with the large areas of healthy trees south of the town. However, an increase in salinity of the substrate, for any reason, can be a serious threat to the survival of mangrove trees. This can occur wherever tidal flow is restricted, sediment levels are raised, or freshwater runoff from the land is impeded (Snedaker, 1978). At several points around False Bay the construction of salt pond embankments, or the dumping of dry material, has truncated creeks or impeded surface drainage which would normally feed freshwater runoff into the mangrove swamps after heavy rain. This runoff helps to keep the salinity of the substrate at a tolerable level, and contributes an important supply of nutrients.

It is possible that salt pond embankments present a more serious threat to the perpetuation of the mangrove stands than the metal content of the sediments. Any further proposals to construct salt ponds should include some means of maintaining the free flow of terrestrial drainage creeks, such as linking ponds with large pipes to span these channels. The creeks are clearly visible on aerial photographs, which could be used to advantage in planning the construction of salt ponds in any area where mangroves lie between the proposed ponds and the sea.

5.2 Aerial photography

Aerial photographs of the intertidal and subtidal zones between Eight-Mile Creek and Pt. Lowly, were used to assess the direction of sediment movement along the coast. Although this could vary with different weather conditions, the established pattern of shoreline features visible in recent and older photographs suggests that the net direction of longshore transport is northward.

5.3 Wind data

A study of wind roses for the Whyalla area supports the evidence of bottom topography. The prevailing south winds in summer produce incident waves at right angles to this direction, which strike the approximate north-south shoreline below Whyalla at an angle which will tend to move suspended materials in a net northerly direction. Wind data for the winter months

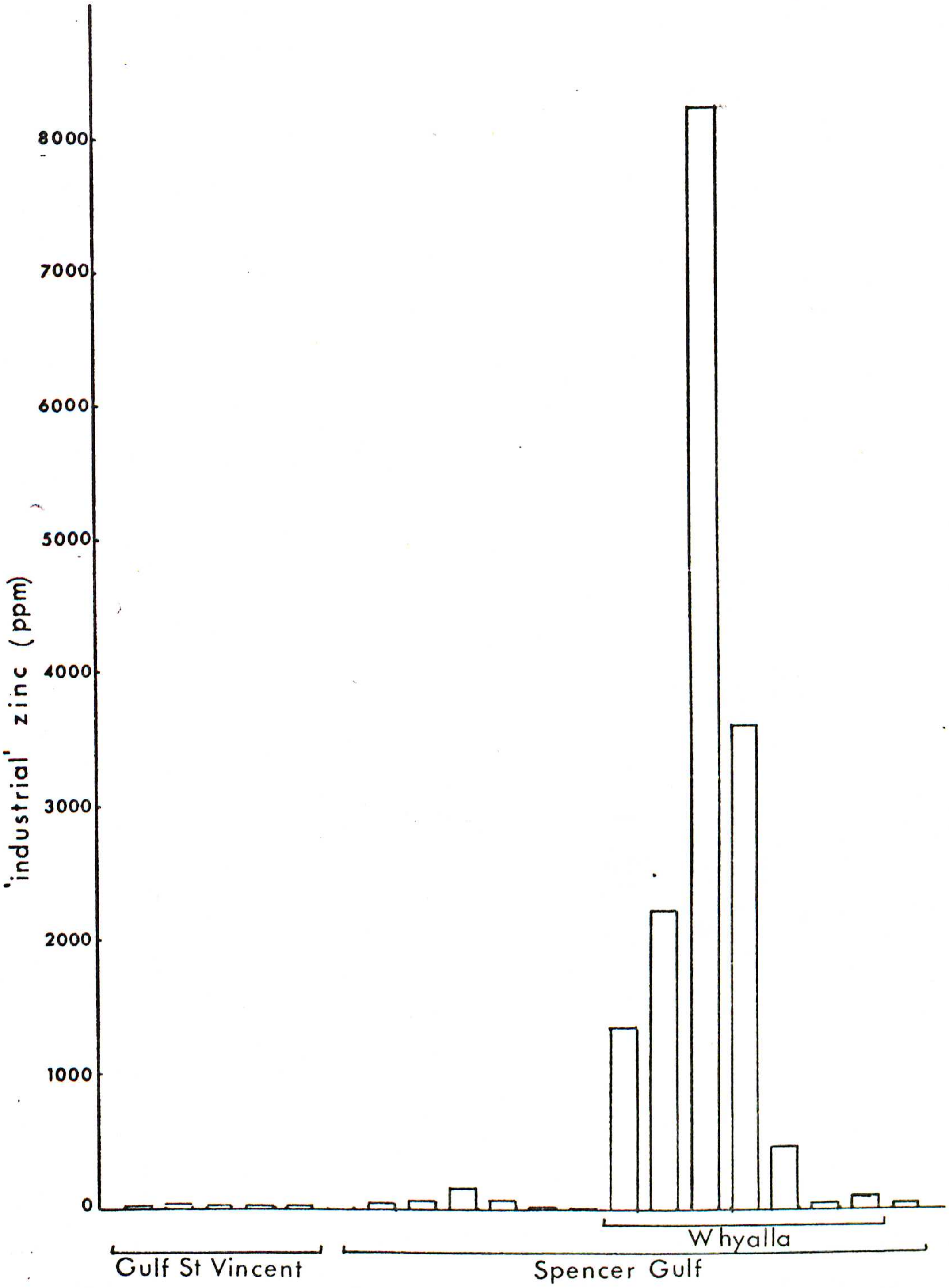


FIG. 5.1 Range of zinc concentrations in mangrove sediments (normal scale).

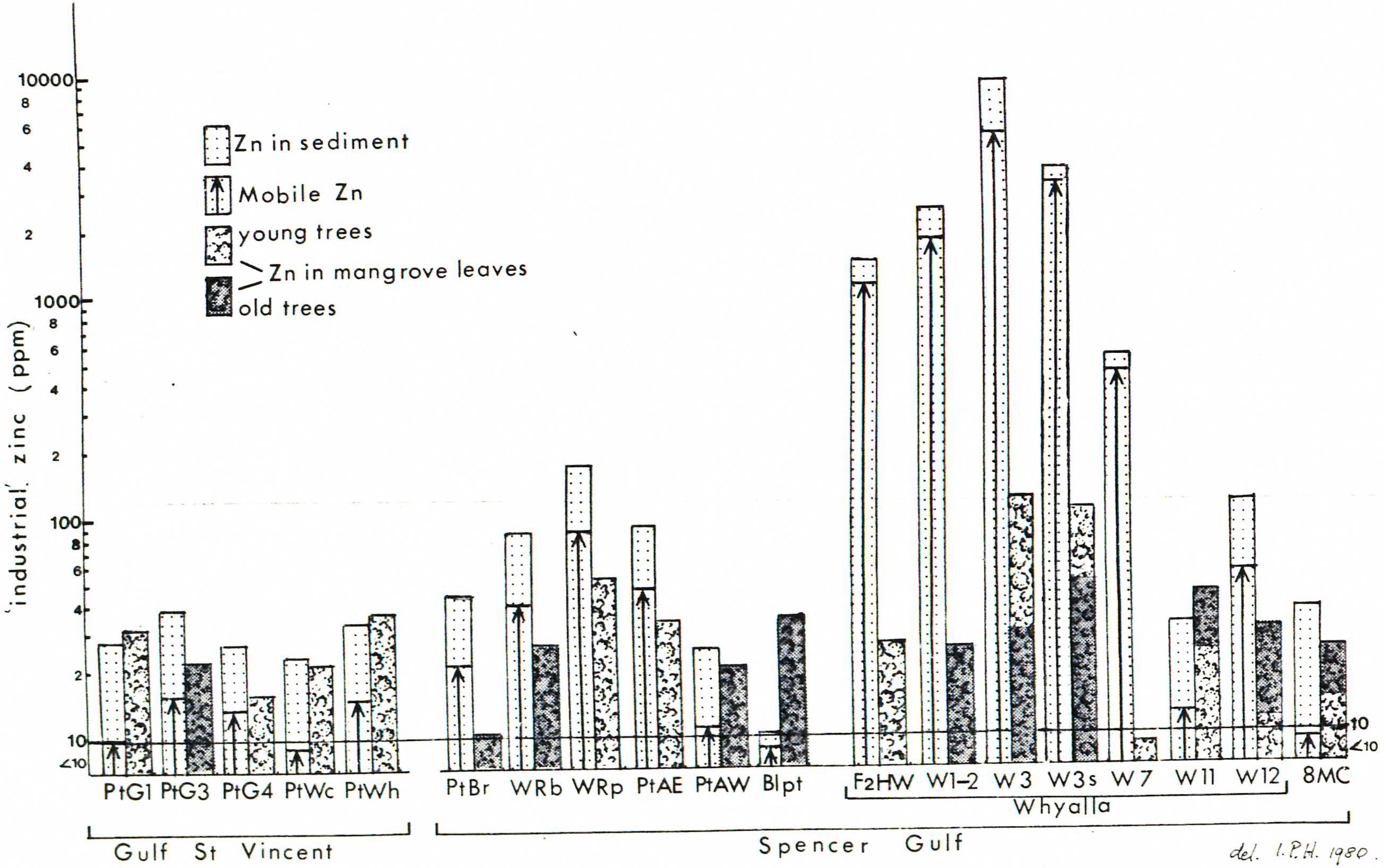


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FIG. 5.1.1 Zinc concentrations in mangrove leaves and sediments (logarithmic scale).

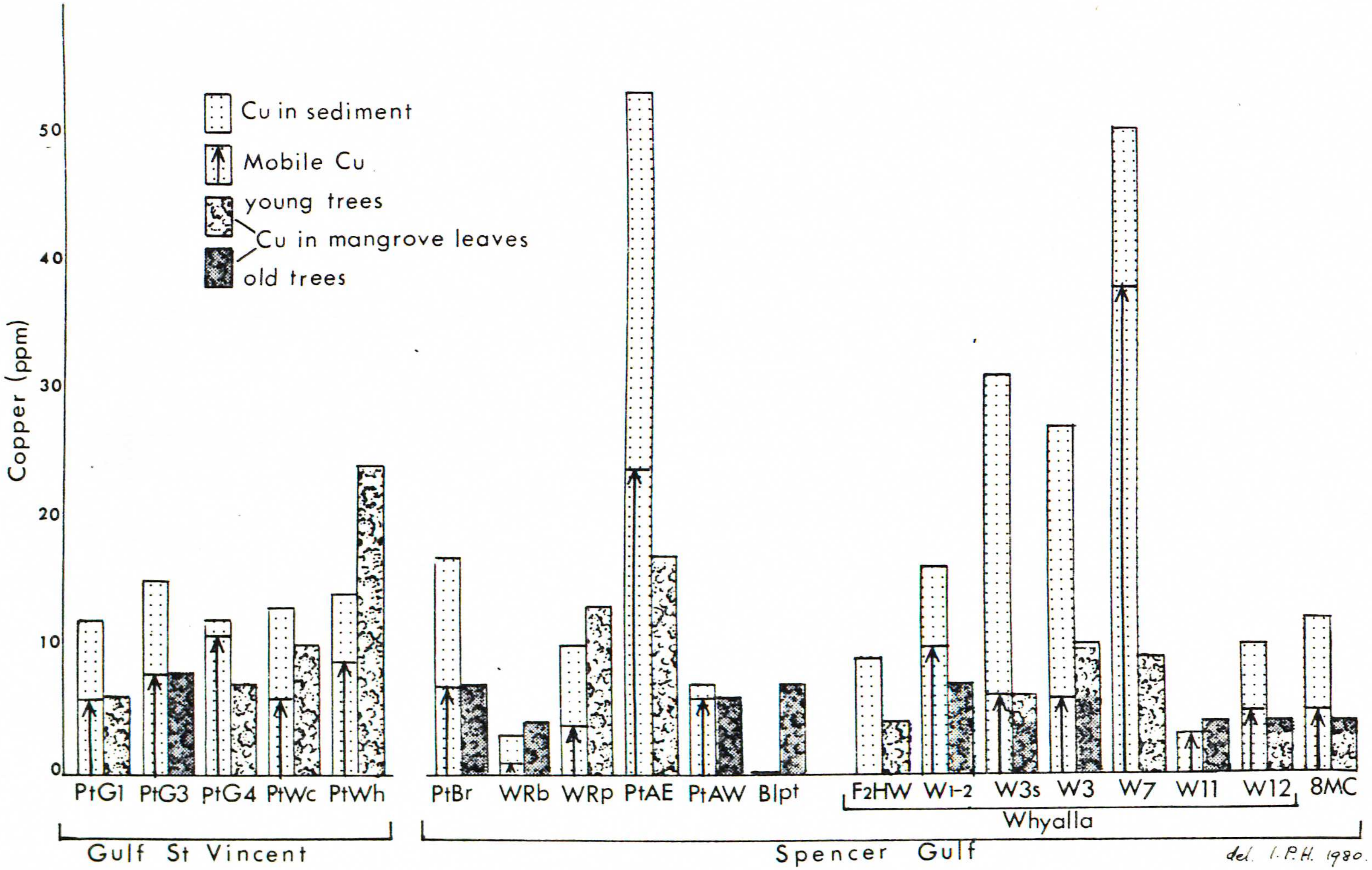

FIG. 5.2 Concentrations of copper in mangrove leaves and sediments.

show a consistent westerly land breeze. These winds have a lower speed than the prevailing south wind in summer (Schwerdtfeger, 1975). The influence of any wind on sediment transport will depend on the size of the waves generated, which in turn depends on the fetch, or distance of open water over which the waves travel. Reference to the map (Fig. 2.1) will show that only the south and south-east winds have sufficient fetch (about 90 km) to generate waves large enough to influence sediment transport.

North of the works, where the False Bay shoreline curves in an easterly direction, the incident waves are nearer parallel to the coast, and a very wide shelf of intertidal sand has accumulated (Fig. 3.1). Prior to the construction of the blast furnace embankment, material discharged from the blast furnace area probably followed the general trend of the longshore current, accumulating in the intertidal and subtidal sediments on the western side of False Bay. After construction of the embankment projecting towards the shoreline to leave a relatively narrow opening for tidal movement at this end of the bay, aerial photographs show wave diffraction around the open end of the wall.

This has resulted in transported material from outside being carried into the impoundment, instead of across to the opposite shoreline (Pl. 5.1). The narrowed opening has apparently also increased tidal scouring along the shoreline opposite the end of the wall, with obvious erosion of about 20 cm of material from the roots of young and old mangrove trees (Pls 5.2.1 and 5.2.2). The overall effect of the embankment appears to be to direct the movement of material <u>into</u> the impoundment. The rapid accretion of very soft deep sediments is apparent in the inner corner of the wall, where mangrove seedlings are rapidly colonizing the mud (Pl. 3.3).

PLATE 5.1: Aerial photograph of steelworks at Whyalla
1:40000
(Department of Lands Survey 2393-000, 10.3.79)

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PLATES 5.2.1 and
5.2.2

Erosion around
mangrove trees at
W1.

5.4 Sediment characteristics

As cores were extruded, the colour of separate horizons was noted, as this sometimes changed rapidly after the material was exposed to the air. Hallberg (1974) attributed the colours of these horizons to the presence of different iron minerals. These observations, together with estimates of predominant grain size, were used to place the variety of sediment samples into broad categories. A description of sediments in terms of this classification has been included in Table A2 in the appendix.

5.5 Surface water parameters

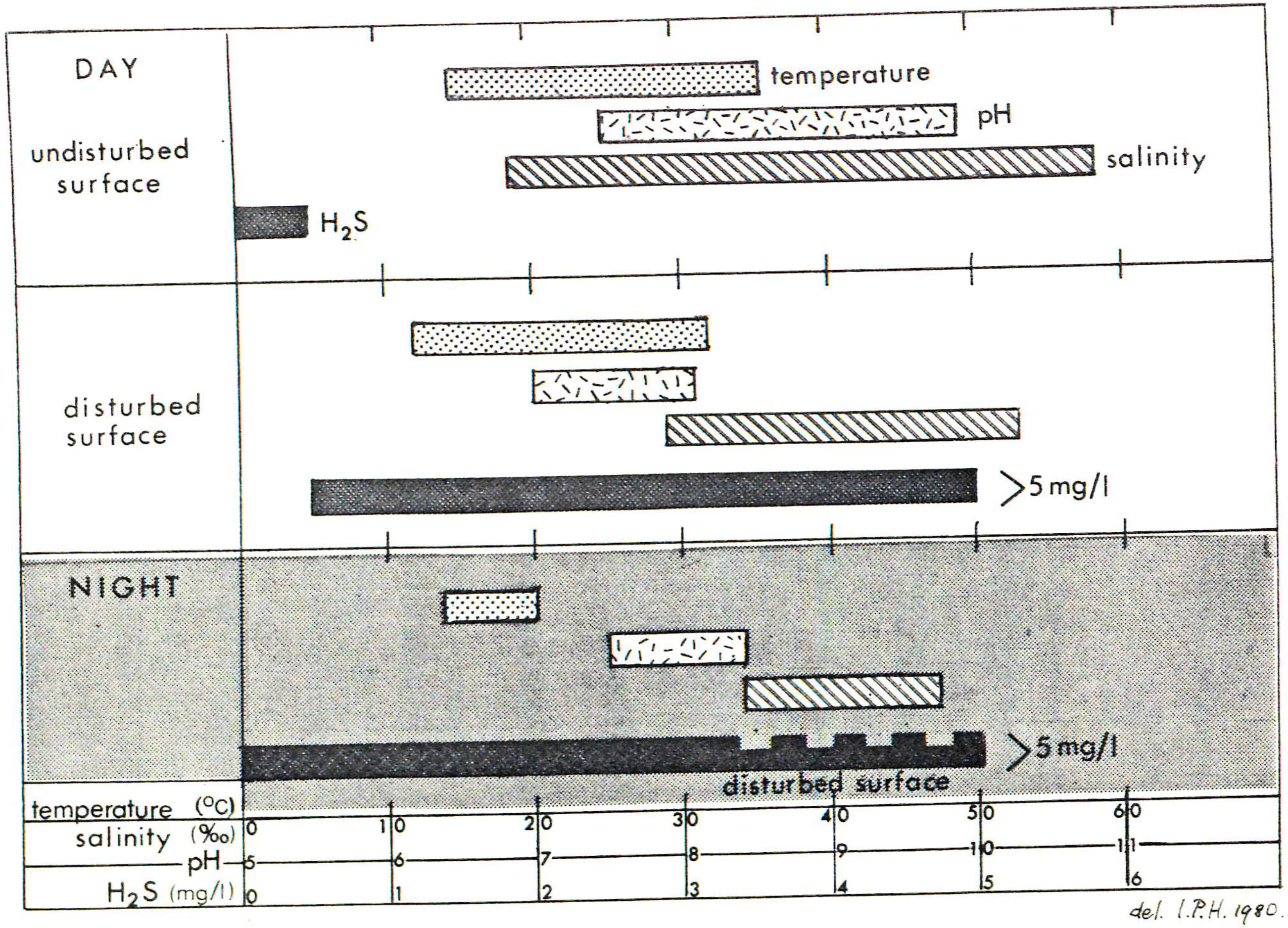
These are presented in Fig. 5.3. pH, temperature, salinity (from conductivity), and in some cases hydrogen sulphide content of water in mg/l were measured in mangrove swamps in Pt. Gawler, and other areas where leaf samples were taken in Spencer Gulf. Readings in other areas lay within the range measured throughout the year at Pt. Gawler.

5.5.1 Temperature

The temperature of surface water ranged from 15-33°C for winter-summer months, with the lowest recorded in a hole 20 cm deep, close to a dense mangrove tree, which was marked and used for readings throughout the year. The temperature of very shallow water was found to be generally higher by 2 or 3°C over dark-coloured muds and sands than over pale or white sand and mud. Below the sediment surface the temperature of interstitial water showed less variation than water in surface pools.

5.5.2 Salinity

Salinity, based on electrical conductivity, ranged from 15‰ in heavy rain to more than 50‰. Measurements taken in surface water during or after rain are included in Fig. 5.3.



del. I.P.H. 1980.

FIG. 5.3 The range of surface water parameters.

5.5.3 pH

pH measurements ranged from near 6.0 units just below the surface, in footprints, core holes, and in water containing decaying plant debris, to 9.8 units in pools with algal growth, at noon in sunlight. Generally lower pH measurements were recorded at night, and there was less variation due to algal growth. Similar variations have been reported by Gnaiger and others (1978). In the main sandy channels, where tidal water ebbs and flows, the pH of water draining the tidal flats was generally high, about 9.5, while the incoming tidal water from the sea measured pH 8.5. The change in pH could influence the direction of metal migration at the sediment/water interface during the period of slack tide over algal flats (Lu and Chen, 1977), and the concentration of metal available to intertidal organisms.

5.5.4 Dissolved hydrogen sulphide

Dissolved hydrogen sulphide, in mg/l, was measured using the Hatch portable test described in section 4.1.7.4. In many sediments, a black layer was clearly defined just below the surface, and interstitial water showed 3-5 mg/l hydrogen sulphide in field measurements, supporting the visual identification of the anoxic horizon (Zobell, 1946).
Generally, no hydrogen sulphide was present in surface water during daylight hours. An exception to this was found in stagnant water among mangroves behind Weeroona Island at the upper limit of high tide. Here algal mats had lifted, probably due to accumulating gases in the anoxic sediment beneath, and released hydrogen sulphide into the surface water. The concentration was measured at 3 mg/litre. High concentrations of >5 mg/l were found in holes and footprints at Pt. Gawler, where surface algal films were disturbed, and interstitial water from anoxic sediments had seeped to the surface. Lower concentrations, distinctly recognizable by smell, were also found in shallow surface water over undisturbed sediments, among mangroves at night. Similar observations were reported by Hansen and others (1976). Apart from the exception noted

in stagnant water, hydrogen sulphide was not found in surface water during daylight unless the surface was disturbed (Pls 5.4 and 5.5). Bella (1972) also noted periodic concentrations of 1-2 mg/1 free sulphide when surface sediment was disturbed by an ebbing tide, levels which far exceed those found toxic to a variety of desirable intertidal species (Bella and others, 1972). Many areas of coastal mangrove mudflats in South Australia are now subject to large scale disturbance of the surface mud by trail bikes, dune buggies, and other recreational vehicles. The concentration of hydrogen sulphide recorded in tyre tracks and footprints in the present study suggests that such activity could result in a substantial increase in the concentration of free sulphides in the shallow water covering these flats at high tide, which might be detrimental to benthic fauna and young fish.

PLATE 5.3 Channels draining surface water from algal flat, PtG1 (Fig. 3.3).

PLATE 5.4 Disturbed surface sediment. (Water in tyre tracks had 2 mg/l H_2S.)

PLATE 5.5 Ebbing tidal water with anoxic sediment released from footprints.

TABLE 5.4

Summary of extraction methods

Metal extracted by hot HNO_3/H_2O_2 expressed as a proportion of TOTAL metal ($HNO_3/HClO_4/HF$). Other extractions are a proportion of 'Industrial' metal.

Extraction Procedure	Proportion of metal removed from sediment
Total metals	
$HNO_3/HCLO_4/HF$ under pressure	All metals, except very small amount of insoluble residue from blast furnace area (section 4.2.8).
'Industrial' metal	
Hot concentrated HNO_3 and H_2O_2	~45% total Cu; 25% total Cr ~45% total Fe; 60% total Mn ~80% total Pb; 80% total Zn Cd concentration at Whyalla was too low to measure in bomb digestion, but result for WR2A (Pt. Pirie) suggests that all of Cd removed by this leach.
Cold .5N HCl (pH 0.3) (cf. digestive tract)	~75% Cd; 15% Cr; 60% Cu; 12% Fe; 55% Mn; 80% Pb; 80% Zn.
Available metal	
Cold oxalic acid and am. oxalate at pH 3 (dark) (cf. nocturnal conditions in tidal swamps)	no Cd; ~50% Cr; ~6% Cu; ~40% Fe; 45% Mn from polluted sediments, but only 11% from unpolluted. ~12% Pb from polluted sediments, none from unpolluted at Whyalla. >75% Zn from polluted sediments.
Alkaline leach, buffered boric acid, pot chloride and sodium hydroxide at pH 3. (cf. shallow water over algal mat in sunlight)	up to 3% of Fe, Mn and Zn, but not other metals (Table A7, appendix)

5.6 Metal concentration in sediments

The action of the various procedures for extracting metals from sediments is summarized in Table 5.4. Zinc is seen to be the most mobile element under all conditions, while the mobility of others is pH dependant, or related to the different chemical species in sediments near the works, and in relatively unpolluted areas. A complete list of 'Industrial' and easily available metals is given in Table A6 of the appendix. The distribution and availability of individual elements is discussed below.

5.6.1 Cadmium

The 'Industrial' concentration in sediments ranges from <0.1 ppm at W11A to 14 ppm in W3A, and seems closely related to a point source (W3). In individual cores, the higher concentrations correlate with higher organic carbon content, which seems more important than the grain size of sediments. Cadmium is not released from sediments by the reducing leach. This does not agree with the findings of Burrows and Hulbert (1975) who found cadmium in the reducible fraction of polluted sediments. However, cadmium is released, almost 100%, by the .5N hydrochloric acid leach (Table 5.5), which suggests that it may be available to organisms which pass sediment through their digestive tract. The high concentrations in the blast furnace impoundment might thus be available to a variety of benthic in fauna, or to larger vetebrates feeding on these. The concentration of cadmium in mussels and barnacles from the ship basin (W6) and beacon at W9 suggest that small amounts could be available in the water (Table A5). The highest concentration is 6 ppm in W6 barnacles, low compared with that in mussels from the Derwent estuary (Bloom, 1975). That paper reports a cadmium concentration of 9.3 ppm in the sediment at site 72, comparable to the level at W3 of the present study. Site 72 has 0.1 ppm of cadmium in suspended particulates, and 28 ppm of cadmium in mussels. Bloom found that the concentration of cadmium in filtered water was generally at least five times higher than that in suspended particulate matter,

TABLE 5.5

Proportion of 'Industrial' metal extracted by cold acid leach
compared with metal available by oxalic acid leach

	Sample		Cd			Cr			Cu			Fe			Mn			Pb			Zn		
			1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Polluted	FB1	ppm	3	2	-	13	4	8	13	4	-	11200	2300	5080	340	290	100	240	125	8	1210	1070	860
		%		66	-		30	61		30	-		20	45		85	29		89	3		88	71
	W1C	ppm	4	6	-	16.5	-	13	20	16	4	52000	6700	26400	630	470	360	402	202	-	1584	1340	1360
		%		100	-		-	78		80	20	1	13	51		74	57		50	-		85	86
	W2A	ppm	6	5	-	20	-	8	18	14	-	69000	6000	35000	908	570	510	480	510	-	2280	1910	1740
		%		83	-		-	40		77	-		9	51		63	56		100	-		83	76
	W3SB	ppm	9	8	-	181	92	110	23	10	-	46000	3720	14200	560	110	190	603	670	16	3620	3880	3170
		%		90	-		51	61		43	-		8	31		20	34		100	3		100	87
	W5A	ppm	1	-	-	30	-	13	3	4	-	166000	12300	64200	3330	1670	1600	607	590	270	3240	2530	2560
		%		-	-		-	43		100	-		7	39		50	48	97	94	44		78	79
Unpolluted	W12B	ppm	1	-	-	15	4	8	10	-	-	21800	1360	9900	110	37	4	32	9	-	268	280	210
		%		-	-		26	53		0	0		6	45		34	4	28	-	-		100	78
	PtG3	ppm	-	-	-	27	4	8	13	7	4	12500	2200	1900	110	58	16	10	-	-	39	23	16
		%					15	30		54	30		18	15		53	15		-	-		60	41

..continued

TABLE 5.5 (continued)

	Sample		Cd 1	Cd 2	Cd 3	Cr 1	Cr 2	Cr 3	Cu 1	Cu 2	Cu 3	Fe 1	Fe 2	Fe 3	Mn 1	Mn 2	Mn 3	Pb 1	Pb 2	Pb 3	Zn 1	Zn 2	Zn 3
–Unpolluted–	PtG4	ppm	1	-	-	27	-	4	15	7	-	9930	1825	1540	86	45	10	7	12	-	27	14	10
		%					-	15		47	-		18	16		52	12		100	-		52	37
	PtG6	ppm	-	-	-	8	-	-	4	2	-	1800	230	880	74	60	10	-	-	-	15	12	9
		%					-	-		50	-		13	49		81	14					80	60

1 = 'Industrial' metal (HNO_3/H_2O_2) (ppm)

2 = Metal extracted by .5N HCl - possibly mobilized in digestive tract (ppm)

3 = Easily available metal (oxalic acid extraction) (ppm)

% = Proportion of 'Industrial' metal

probably due to the strong association of cadmium with chloride ions, unaffected by pH (Zirino and Yamamoto, 1972). No edible mussels grow in the blast furnace area at Whyalla, where the highest sediment concentrations are found, and where the highest water concentrations would be expected.

5.6.2 Chromium

Total concentrations of chromium in sediments could not be reliably estimated by the pressure bomb dissolution, due to contamination. Earlier samples treated by open digestion in Teflon beakers with nitric, perchloric and hydrofluoric acids, and compared with samples treated with the nitric acid leach, suggested that approximately 22% of chromium is extracted by the latter method.

TABLE 5.6

Proportion of total chromium*extracted by nitric acid/hydrogen peroxide.

Sample	Total Cr $HNO_3/HClO_4/HF$	HNO_3/H_2O_2	Proportion extracted %
W1C	84	17	23
SCO-1	110	23	21
MAG-1	134	28	20

*Cr concentration in ppm

The chromium concentrations recorded for the nitric acid leach from all sediment samples, used here as an estimate of industrial input, may represent only $^1/_5$ of the gross concentration in the sediment. The remaining fraction, resistant to the nitric acid digestion, is unlikely to be available to marine organisms.

The concentration of 'Industrial' chromium ranges from 8 ppm on the eastern side of False Bay, to 180 ppm at W3, and 30 ppm south of 'town beach'. In individual cores, higher chromium concentrations are found in the finest sediment fractions, and also in those with high organic carbon content.

The most conspicuous exception is W5A, where the highest concentration of chromium is associated with the coarse red sand found in the surface sediment (Pl. 4.5), rather than in the fine, black mud below. This agrees with the report of Gupta and Chen (1975) who found most of the non-residual chromium incorporated in ferro-manganese nodules and iron oxides in the sediments. They also found that the lithogenous proportion of total chromium in different sediment types varied between 60-74%, which supports the findings in Table 5.6 above. Where chromium concentrations are very high, more than 50% seems to be easily available under reducing conditions. However, chromium was not found to be concentrated in any of the marine invertebrates with the exception of *Salinator fragilis*, nor was it found in mangrove leaves, which suggests that it is not readily incorporated in the biological cycle.

Hem (1977) suggests that in groundwater systems where iron is abundant, chromium will tend to be immobilized, but he records a high concentration of hexavalent chromium in groundwater with high pH (8.5-9) and oxidizing redox potential. The chromate was thought to be derived from the oxidation of trivalent chromium in soil minerals. The shallow surface water in parts of the blast furnace lagoon has a very high pH, >8.5, in sunlight due to the photosynthesis of algae and seagrasses, which might provide similar conditions for the release of chromate to surface water. However, chromium was not released from surface sediments by the alkaline (pH 9.4) leach in the laboratory.

The highest concentrations of cadmium, chromium and copper in the study area all occur together at W3 and W3S. Negilski (1976) found that these elements showed increased toxicity to the Yellow Eye Mullet (*Aldrichetta forsteri* C & V), if all three were present. A higher concentration of any one element alone was tolerated, but together there was a synergistic effect.

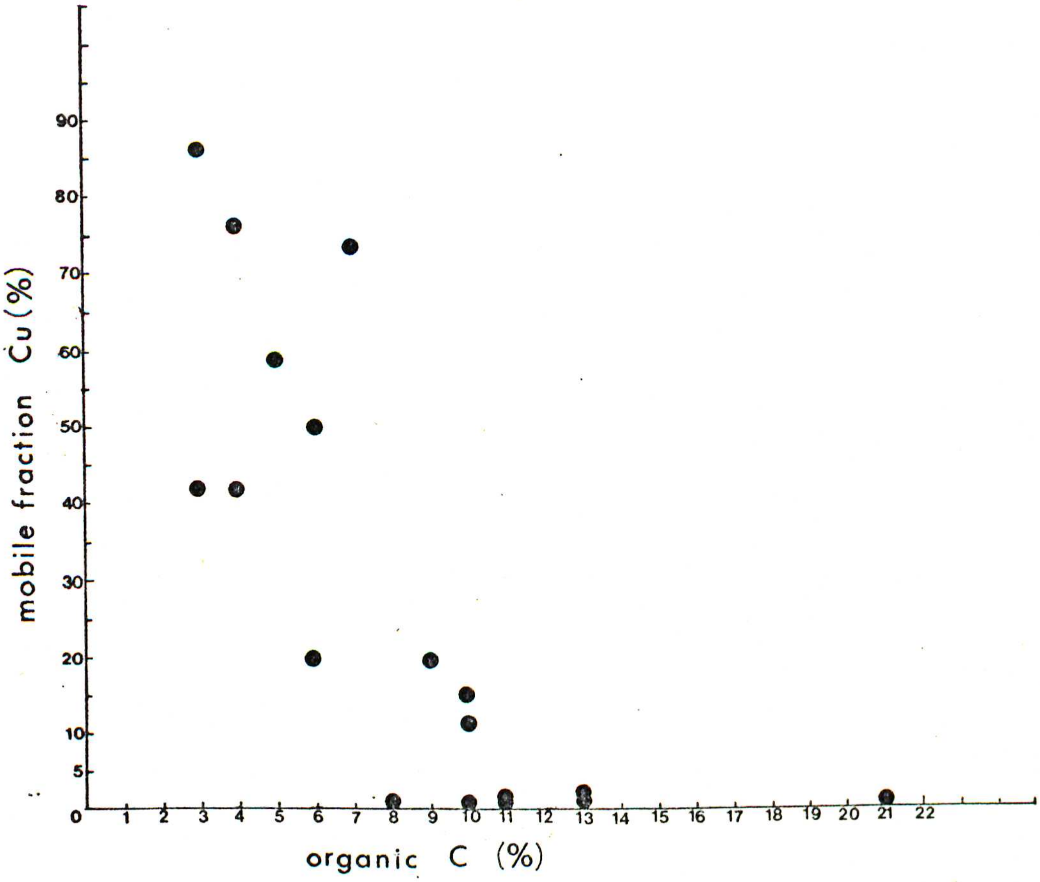


FIG. 5.4 Mobile fraction of copper related to organic carbon content of sediments.

5.6.3 Copper

A concentration of 30 ppm occurs in the immediate area of the outfall (W3) but is highest in the fine red mud of the tailings dam, 50 ppm. 'Industrial' copper in individual cores correlates with the finest, anoxic, and most organic sediments, and more than 60% is extracted by the reducing leach from the most polluted samples. If the mobile fraction of copper is compared with the organic carbon content of False Bay sediments (Fig. 5.4) an inverse relationship is suggested. Less copper is available from sediments with a high organic carbon content, suggesting that copper, like lead, is more firmly bound in these sediments, perhaps as sulphide. A higher proportion of copper is available with a .5N hydrochloric acid extraction (Table 5.5) which suggests that a considerable amount could be available through ingestion of sediments. It is also taken up by mangrove leaves (Fig. 5.2), and could become available, through leaf fall, to detritus feeders.

5.6.4 Iron

Since iron ore is processed at the Whyalla works, large concentrations of suspended iron oxides are to be expected in the discharged waters. In areas near the blast furnace, total iron concentrations in sediments reach 10-16%, while the coarse sands eroded from the embankment at W5A show 36% iron. Total concentrations of iron measured by pressure bomb digestion were unreliable in samples with low concentrations, as corrections made to allow for contamination reduced the concentration of total iron to less than, or equal to, that of the nitric acid soluble iron. In sediments with a very high iron content, such as W2MA and W3A (12%), W2A (16%), and W5A (36%), a comparison of the two extracts suggest that approximately 50% of the iron is incorporated in silicate minerals, and would not be available for sedimentary cycling by natural chemical or biological processes.

The oxalic acid leach at pH 3 used in darkness, is reported by Schwertmann (1964) to dissolve only X-ray amorphous iron oxides, the most surface-active fraction of free iron oxides. Where the iron content of sediments is related to natural weathering and terrestrial run-off, the proportion of amorphous iron oxides appears to be fairly low, as seen in the relatively low proportion of iron (mobile fraction Table 5.7) removed by this leach.

TABLE 5.7

Mobile fraction of iron in sediments from other areas.

Sample	'Industrial' Fe (ppm)	Available Fe (ppm)	Mobile fraction* (%)
B1PtRed	1100	90	8
Grey	790	120	15
Sab 1A	5360	880	16
Sab 1B	19260	2500	13
TB1A	1120	210	19
W1OA	1630	250	15
8MC1A	1600	170	11
WR1A(Pt.Pirie)	2510	680	27
WR2A(Pt.Pirie)	8160	1530	19
PtG1A	10840	1910	18
PtG3S	12500	1900	15
PtG9A	1930	380	20
W7A (pellet plant)	60800	9030	15

$$^{*}\text{Mobile fraction} = \left(\frac{\text{Available metal}}{\text{'Industrial' metal}} \times 100\right)$$

Where pellet plant (concentrating low grade iron ores to magnetite) wastes are run into the tailings dam, the mobile fraction of Fe is generally low, 15% at W7A (Table 5.7). However, this fraction rises abruptly in surface sediments adjacent to the steelworks discharges (Table 5.8).

TABLE 5.8

Mobile fraction of iron in works sediments

Sample	'Industrial' Fe ppm	Available Fe ppm	Mobile fraction* (%)
F1A	41330	23400	57
FB1 (subtidal)	11200	5080	45
W1A	6900	3150	46
W1B	4200	2480	59
W1C	52000	26400	51
W2A	69200	35300	51
W2MA	46990	29300	62
W3A	50000	31000	62
W3SA	34140	23530	69
W5A	166000	64200	39
W5B	36720	23950	65

$$^{*}\text{Mobile fraction} = \left(\frac{\text{Available metal}}{\text{'Industrial' metal}} \times 100\right)$$

The coarse red surface sand at W5A is derived from wave erosion of the embankment, constructed of blast furnace slag, and probably has a high proportion of iron held as silicates. This would account for the lower proportion of amorphous iron oxides here. W5B, however, a fine soft black mud, possibly pre-dates the wall and may represent the previous direct input to the shoreline from the blast furnace drain. Here the proportion of available iron is >60%, as in the other sediments immediately adjacent to the outfall (W2MA, 3A, 3SA).

Amorphous iron oxides are considered to provide a large surface area for the adsorption or 'scavenging' of trace metals, removing them to the sediments (Troup and Bricker, 1975; Davis and Leckie, 1978). If this is so, the high concentration of amorphous iron oxides in the sediments adjacent to the blast furnace would provide for extensive removal of trace metals in wastes to the sediment sink. However, this may not occur to the extent to which it is theoretically possible because of competition for adsorption sites from other complexing ligands. Davis and Leckie (1978) note that trace concentrations of cyanide have this effect on the adsorption of silver by amorphous iron oxide. B.H.P. analyses of water samples taken inside the embankment wall in March, 1979, shows free cyanide present in concentrations ranging from 0.040 ppm to 0.075 ppm at different points within the lagoon. This may be sufficiently high to suppress the adsorption of some trace metals by the available iron oxides. The same authors reported similar competition from chloride, if present in high concentrations of 0.1 M. The chloride concentration of shallow water at Whyalla would be very close to 1 M, 10 times the concentration necessary to make chloride an effective competitor for co-ordination surfaces. However, organic matter may provide an enhancing effect on the association of trace metals with sediments, in the presence of amorphous iron oxides. Davis and Leckie (1978) consider that metal ions may have a larger affinity for co-ordination with the chelating groups of adsorbed humic or fulvic acids than with the oxide surface sites themselves, the presence of the organic matter thus enhancing adsorption of trace metals. In the absence of adsorption sites, however, these acids may enhance availability of trace metals in solution. Rashid and Leonard (1973) found that the presence of humic acids in media which otherwise had favourable conditions for the precipitation of metals as carbonates, hydroxides or sulphides, prevented the formation of insoluble metal salts.

Further competition for adsorption on amorphous iron oxide surfaces, particularly at Whyalla, may come from the high concentrations of available manganese which commonly co-precipitates with iron. The effectiveness of iron oxide then, as an agent to remove trace metals to sediments, may be reduced by the presence of other complexing ligands or ions associated in the discharges at Whyalla, particularly chloride, cyanide and manganese. Co-precipitation of iron and manganese is suggested by the general agreement between the mobile fractions of iron and manganese in sediments where the concentration of both is high (Table 5.9).

TABLE 5.9

Mobile fractions* of iron and manganese (in %) in works area.

Sample	Fe	Mn
W1A	46	41
W1C	51	57
W2A	51	56
W2B	43	49
2MA	62	43
W3A	62	63
W39A	69	55
W5A	39	48

* Mobile fraction = $\left(\frac{\text{Available metal}}{\text{'Industrial' metal}} \times 100\right)$

No similar agreement with the mobile fraction of iron is shown for any of the other metals studied.

5.6.5 Manganese

Manganese oxide, if present in sufficient concentrations to provide a large surface area for adsorption, may become the dominant sink for trace metals in the blast furnace waste, if the findings of Theis and Richter (1979) for ash-pond leachates can be extrapolated to the situation which exists in the blast furnace lagoon at Whyalla. These authors found that a surface area of manganese oxide approaching 10^{-2} hectares/litre begins to exert an influence on soluble metals due to its large sorptive capacity, while iron oxide needs a greater surface area concentration to be effective. They concluded that manganese oxide, if present in large enough quantities, was capable of becoming the dominant sink for all the metals studied (cadmium, chromium, copper, lead, nickel and zinc). In fact, the especially large sorptive capacity of manganese oxide was considered a potential control procedure for fly-ash seepage ponds. If these oxides were present naturally in the fly-ash, they would provide an ameliorating effect which could be taken into acount in

TABLE 5.10

Metal extracted by HNO_3/H_2O_2 as a proportion (in %) of total metal content of some sediment samples (cadmium and chromium not included)*

		Cu			Fe			Mn			Pb			Zn	
Sample	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
FB2	15	6	40	8220	4170	51	105	67	64	105	96	91	750	670	90
W1C	40	20	50	116000	52000	45	1100	630	57	630	402	64	1940	1584	82
W2MA	30	19	63	110000	46990	43	1505	981	65	680	635	93	3500	2800	80
W3A	53	27	51	116000	50000	43	1875	1200	64	1570	1076	69	9500	8280	87
W3SA	53	31	58	91000	34140	38	1675	1075	64	364	345	95	3400	2440	72
W5A	30	3	10	361000	166000	46	7500	3330	44	770	607	79	5250	3240	62

1 = Total metal (ppm)

2 = HNO_3/H_2O_2 extraction (ppm)

3 = Proportion extracted (%)

* Cd concentrations were too low to detect in .1 g/50 ml dilution
Cr contamination made values unreliable

proposed control measures. The same potential to remove trace metals to sediments could exist in the blast furnace lagoon at Whyalla, where total manganese exceeds 1,600 ppm, and readily reducible manganese as oxides is greater than 600 ppm. The deliberate use of iron and manganese oxides for heavy metal control would necessitate an oxidizing soil environment in ash-ponds (Theis and Richter, 1979). However, this should not be a problem in the extremely shallow water of the blast furnace lagoon.

Apart from the blast furnace area, the distribution of manganese in sediments at Whyalla conforms to levels found in other areas reasonably free of industrial discharges. Other sampling stations in Spencer Gulf and Gulf St. Vincent all show concentrations less than 200 ppm, with the exception of Weeroona Island (WR2A) which has a large industrial discharge nearby from the B.H.A.S. lead/zinc smelters. South of the town jetty in Whyalla, sediment concentrations of manganese are less than 100 ppm, with is also true of the sediments on the eastern side of False Bay (Table A6, appendix).

5.6.6 Lead

A comparison of the total lead concentrations in sediments with those obtained by nitric acid digestion suggests that almost 100% of the lead is removed by the latter method (Table 5.10).

Lead accumulation in the False Bay sediments ranges from 8 ppm at the eastern end of the bay (F3) to 1,076 ppm in the blast furnace lagoon (W3), with no detectable lead in 'town beach', and W10 and 11 sands. 32 ppm was associated with the fine muds at the upper tidal limit in mangroves south of the town. In most cases the highest concentrations are associated with a high content of organic matter, and with dark coloured anoxic sediments. The notable exception is the coarse red brown sand eroded from the outside of the blast furnace embankment (W5A) which has a low content of organic matter. In this case, the 'mobile fraction' of lead, removed by the reducing acid leach (44%), closely parallels the iron and

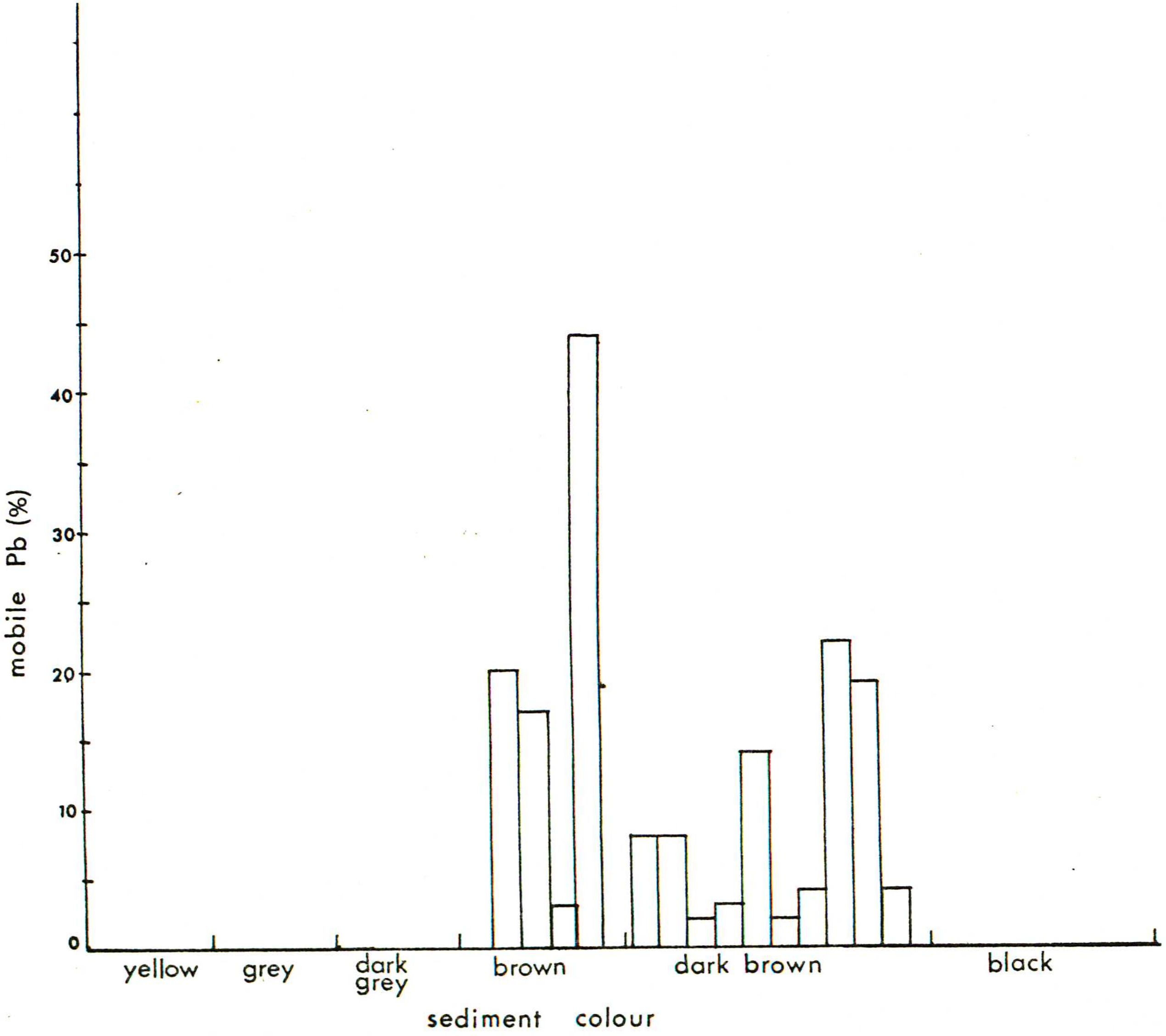


FIG. 5.5 Mobile fraction of lead related to colour of sediments.

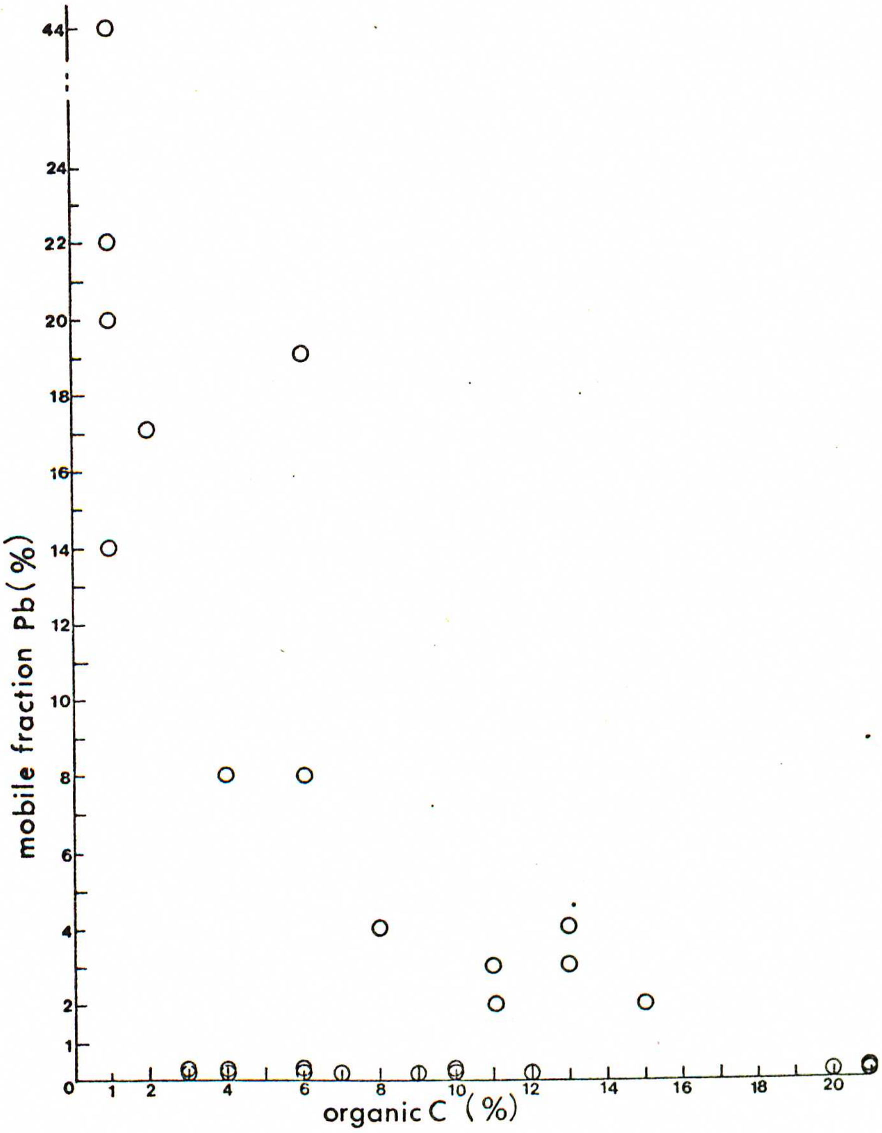


FIG. 5.6 Mobile fraction of lead related to organic carbon content of sediments.

manganese extracted by the same method (39% and 48%), suggesting an association with these oxides. The correlation between available lead and all brown sediments (Fig. 5.5) also suggests a similar association.

The lead associated with horizons having a high organic content and a sulphide smell in the blast furnace area is only available in small amounts (4-20%)(Fig. 5.6), while lead is not available at all from 'clean' sediments south of Whyalla by a reducing leach (Table 5.11). Sediments at Weeroona Island, which have 200 to 300 ppm lead, probably derived from the B.H.A.S. smelters at Pt. Pirie, also do not release any of this accumulation under reducing conditions, suggesting its retention as insoluble sulphides in the sediments.

The association of lead with highly organic sediments could be significant for its possible methylation. Wong, Chan and Luxon (1975) report the bacterial formation of tetramethyl lead in a similar process to the methylation of mercury, with more rapid uptake and greater toxicity to green algae than inorganic lead. The microbial methylation of lead and mercury is facilitated by temperatures suited to bacterial growth, and the provision of a constant source of carbon, conditions likely to be optimum in intertidal sediments. However, the small fraction of lead removed by the reducing leach suggests that the apparent association of lead with organics may be due to the formation of the sulphide mineral in anoxic sediments with high organic content. In Table 5.11, sediment horizons having >30 ppm 'Industrial' lead (which would include the sulphides) are used to compare the amount of this lead with that removed by the reducing oxalic acid leach (adsorbed and exchangeable lead), and the organic carbon content.

TABLE 5.11

'Industrial' and available Pb related to organic carbon content of Whyalla sediments containing more than 30 ppm Pb

Sample	'Industrial'Pb (ppm)	Available Pb (ppm)	Mobile fraction* (%)	Organic carbon (%)
FB2	96	8	8	4
F2HWA	200	15	8	6
FBCrB	36	0	0	5
F1A	448	8	2	11
FB1	240	8	3	11
W1A	111	15	14	1
W1B	74	15	20	1
W1C	402	0	0	9
W2A	480	0	0	12
W2B	110	0	0	6
W2D	50	0	0	3
W2MA	635	15	2	13
W2MB	32	0	0	0
W3A	1076	42	4	13
W3B	189	42	22	1
W3C	700	138	19	6
W3D	47	8	17	2
W3SA	345	0	0	10
W3SB	603	16	3	13
W3SC	215	8	4	8
W5A	617	270	44	1
W12A	32	0	0	21
W12MA	32	0	0	20

$$* \text{ Mobile fraction} = \left(\frac{\text{Available metal}}{\text{'Industrial' metal}} \times 100\right)$$

The comparison between organic carbon and mobile lead (Fig. 5.6) suggests that a higher proportion of lead is readily available from sediments with low organic content, or conversely, lead is more tightly bound, perhaps as sulphide, in the sediments with high organic content and is only removable with a hot strong oxidizing leach. The implication for the environment here is that lead may accumulate to a greater extent in organic muds, but is more likely to be biologically available from fine sands with a low organic content.

5.6.7 Zinc

The distribution of 'Industrial' zinc is primarily related to the point source of discharge, being highest in sediments in close proximity to the effluent drains in the blast furnace area. The diagrammatic map (Fig. 5.7) shows the very localized nature of the distribution, as well as the direction of littoral transport inferred from aerial photographs and wind data. The highest concentrations in each core range from 30 ppm in surface sand at Black Point, on the eastern side of False Bay, to a maximum of 8280 ppm or 0.8% inside the blast furnace lagoon, and as low as 10-18 ppm in mangrove muds and sand, south of the town.

In most cores, the highest accumulations of 'Industrial' zinc are in surface sediments, with rapid decreases in concentration at a depth of 40 cm. (The reverse is true in cores at Eight-Mile Creek, where the highest concentrations are found in the bottom 10 cm of the 50 cm cores. These higher levels are possibly associated with accumulation of zinc in wood fibre from relict mangrove sediments just below the present beach, or represent a history of much larger discharges many years ago, not necessarily from Whyalla. The available zinc from these horizons is low, <25%, suggesting a long residence time in the sediment.)

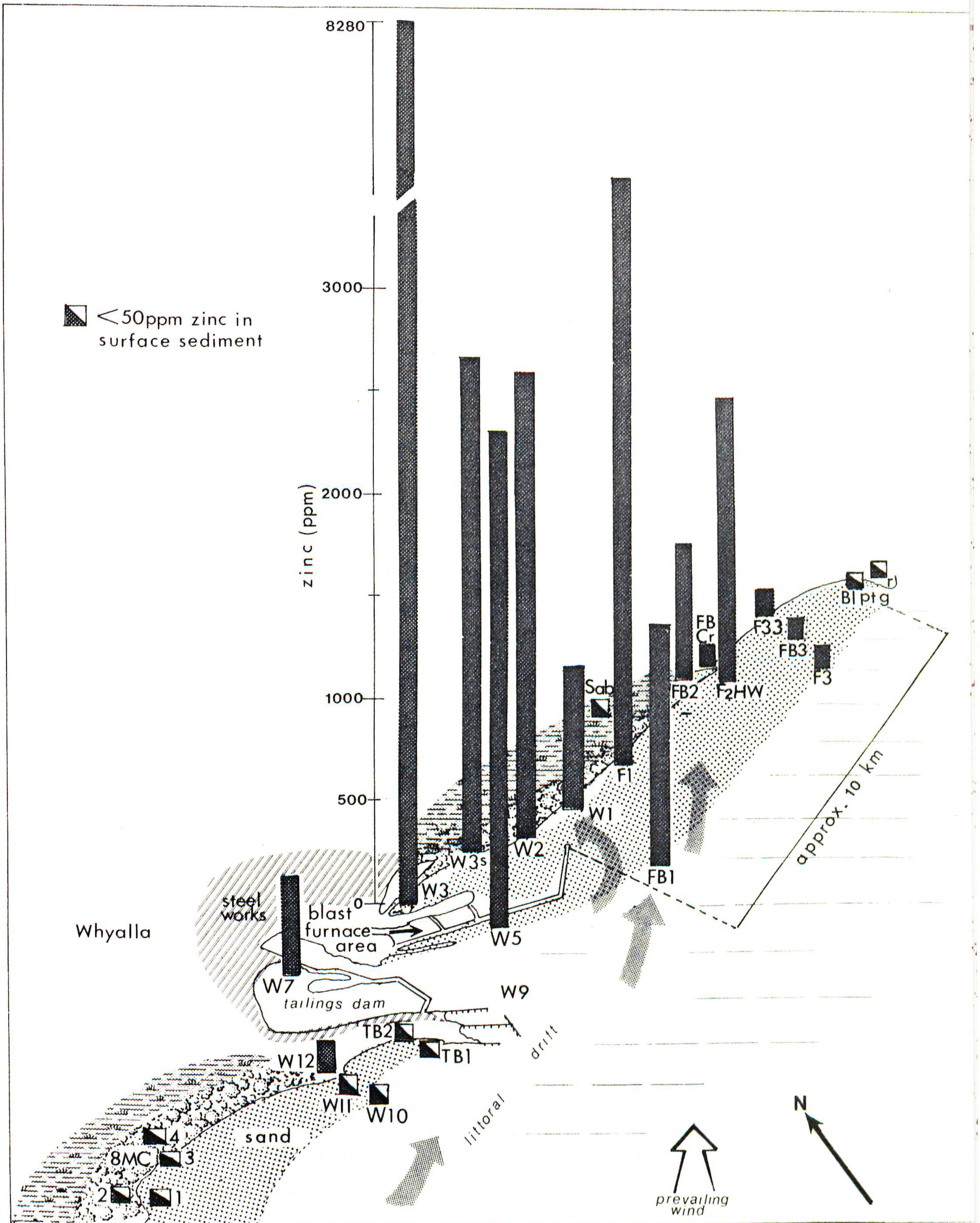


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FIG. 5.7 The distribution of zinc in intertidal sediments at Whyalla.

High concentrations of zinc in deeper horizons are found in cores from FBCr, F3 and W1A, and may be related to the change in littoral transport after the embankment was built. Some erosion of surface material is now occurring at W1, with material accreting at W3 (Pl. 5.1 and Fig. 6.2). The B horizon at FBCr and the C horizon at W1 are both dark brown in colour and have 84%and 86% available zinc respectively. This suggests that they are related to the blast furnace discharge, like the W2 and W3 surface accumulations, but probably predate the embankment, when sediment transport moved around False Bay from the blast furnace area. The recent surface accumulations are lower at W1 because sediment is now deflected around the end of the embankment (Pl. 5.1).

The dark brown sediments near the works release 70-90% of the 'Industrial' zinc with a reducing leach. These brown sands are low in total carbonates, and the colour is not related to the organic content. Sands on the east side of False Bay, and south of the town are shelly, with high total carbonate, and when dark in colour, a high organic carbon content. About 50% zinc is available from unpolluted sediments, and is unrelated to the organic content. Grey, anoxic sediments appear to release slightly more zinc than oxic sands, irrespective of grain size, but the mobile fraction zinc is fairly constant at about 50%.

In the blast furnace area, a higher fraction of available zinc corresponds with the mobile fraction of iron and manganese in surface sediments, but not for deeper layers. Zinc may be associated with amorphous oxides of iron and manganese in the surface layers, but must be released from some other loosely bound, perhaps exchangeable form in lower, anoxic horizons. Table 5.12 shows the distribution of 'Industrial' and mobile zinc (%), and the mobile fraction of iron and manganese in the blast furnace area, and also for two cores at Eight-Mile Creek, which have much older accumulations in deeper layers.

TABLE 5.12

'Industrial' zinc, and mobile fractions of zinc, iron and manganese (for Available metal see Table A6, appendix).

Core	'Industrial' Zn (ppm)	Mobile fraction (%)* Zn	Fe	Mn
W2A	2280	76	51	56
W2B	456	69	43	49
W2C	19	47	5	24
W2D	19	36	3	36
W2MA	2800	81	62	43
W2MB	150	67	17	27
W2MC	16	25	4	21
W3A	8280	61	62	63
W3B	1674	94	35	100
W3C	1850	94	69	100
W3D	202	78	73	68
8MC1A	3	33	11	16
8MC1B	1	50	7	42
8MC1C	35	26	4	9
8MC1D	48	6	1	6
8MC2A	4	100	11	16
8MC2B	1	100	8	16
8MC2C	14	21	8	20

$$^{*}\text{Mobile fraction} = \left(\frac{\text{Available metal}}{\text{'Industrial' metal}} \times 100\right)$$

The very low fraction of available iron, combined with the high fraction of available zinc at 8MC2 suggests that zinc is not associated with iron or manganese oxides here.

Zinc is also released from sediments with the alkaline leach at pH 9.4, similar to the shallow water midday conditions on the intertidal flats. The high salinities typical of this situation also favour an increase of zinc in solution (McElvie, 1979). Mangrove leaves show concentrations of zinc which are proportional to the available metal in sediments, further supporting the possibility that zinc is the most mobile of all metal wastes in the intertidal zone and, if toxic, the most likely to constitute a threat to the marine environment.

5.7 Metal concentration in water and suspended matter

Results of routine analyses of water from blast furnace discharges, and of samples taken inside and outside the embankment were made available by the company (Tables A3.1, A3.2, appendix). An additional analysis of suspended particulate matter from a filtered water sample taken at the northern end of the embankment, with the current flowing north, was made in December 1979. With the exception of zinc, the metal content of filtered water was less than 0.04 ppm. The zinc content was 0.25 ppm, indicating the mobility and general availability of this element. The chromium concentration in the filtered water was 0.04 ppm, confirming the findings from sediment analyses of its mobility where sediment concentrations are high.

The metal content of the suspended solids was much higher, 3000 ppm zinc, 400 ppm lead and 6000 ppm chromium, resembling, except for cadmium and chromium, the respective metal concentrations in surface sediments at W5A and W2A (Table A6, appendix). These points are south and north of the water sampling point, on the path of longshore sediment transport.

TABLE 5.13

Metal content of suspended solids and filtered water (ppm)

Sample	Cd	Cr	Cu	Fe	Mn	Pb	Zn
water	.001	.04	<.02	<.02	.03	.014	.25
solids	<100	6000	<100	49000	6200	400	3000
W5A	1.0	30	3	166000	3330	345	2440
W2A	6.0	20	18	69200	907	480	2280

The high metal concentrations found in the suspended solids, which measured 6.1 ppm of the total water sample, suggest that particulate matter could be the principle transport medium for these elements, and may represent a significant source of metal to filter feeding organisms such as mussels, barnacles, tube worms, and razor fish. The concentration of a metal in molluscs or barnacles has been compared with the concentration in the surrounding water to derive a 'concentration factor' for an element by a particular organism (Barbaro and others, 1978). The metal available to the organism, however, could consist of either the dissolved or the particulate lead, or both. As the degree of adsorption onto particulates varies for different elements, any 'concentration' factor would depend on the distribution of the element between dissolved and particulate phases, as well as on the feeding habit of the organism.

Bloom (1975) also suggests that the initial concentration of trace metals by adsorption onto particulate matter could account for much of the accumulating capability formerly attributed to shellfish alone.

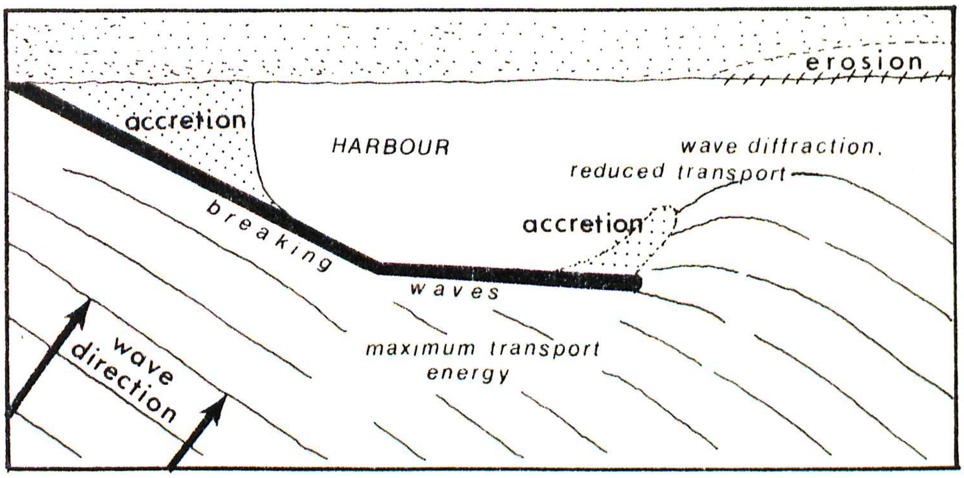

FIG. 6.1 The effect of a shore-connected breakwater on sediment transport. Adapted from Johnson (1956).

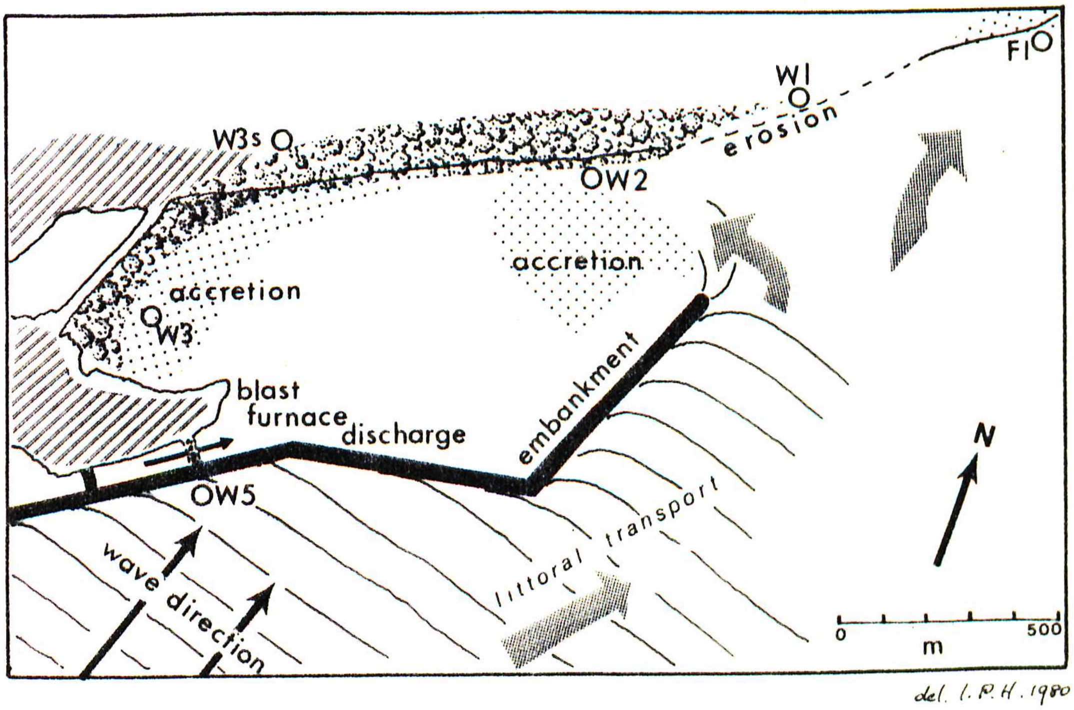

FIG. 6.2 The effect of the blast furnace embankment on longshore transport at Whyalla.

6 FACTORS INFLUENCING THE DISTRIBUTION AND AVAILABILITY OF METALS IN INTERTIDAL SEDIMENTS

6.1 Sedimentary factors

6.1.1 Littoral transport

If metals are released in solution or suspension in industrial waste water, they will be transported in the water body in directions associated with the existing pattern of sediment transport. At Whyalla, a net northerly movement parallel to the coast has been inferred from aerial photographs of bottom topography and surface waves, and from wind data (Schwerdtfeger, 1975). This net direction of littoral drift should explain the accumulation of a wide sand bank at the top of False Bay which extends out into the bay for more than 2½ km. Suspended material from the steelworks would also be expected to accumulate on the False Bay shoreline, carried by the same wave and wind action. The concentrations of waste material should decrease around the bay, as they are diluted with natural littoral material.

Similarly, sediments dredged from the harbour approaches and deposited in deep water just off the sand bank should, if they reached shore, be deposited along the northern shoreline of the bay. The stands of mangroves extending along the shoreline from the blast furnace area also indicate the net accretion of sediments. The much higher surface concentrations of metals at F3 and F3.3, at the eastern side of the bay, compared with surface accumulations at 'town beach' just south of the works, also suggest the northerly direction of drift (Table A6, appendix).

The higher accumulation of metals in mangrove sediments at W12 and W12M, compared with W11 and W10 and 'town beach' (TB1 and 2) can be explained in terms of the depositional environment. Although W12 is further from the source, the sheltered conditions at upper slack water which facilitate mangrove colonization also encourage the deposition of the finest particulate matter. The greater surface area presented for metal adsorbtion by this material results in a greater load of metals being deposited under slack water conditions further enhanced by the growth of mangroves. Ellaway (1978) found 60-80% of the total metal content of sediments from the Yarra River, Victoria, in the <2 μm grain size fraction. Inclusion of the <20 μm fraction accounted for 90-100% of the metal content.

6.1.2 The effect of the blast furnace embankment

If the general direction of wave incidence is interrupted by a construction which impedes the waves, a change in the direction of littoral transport will occur. Shore-connected breakwaters are considered by Johnson (1956) to be one of the basic types of man-made coastal structures which function as barriers to the established pattern of littoral transport, with predictable changes in the pattern of deposition (Fig. 6.1).

A structure which extends seaward from the shore across the littoral zone will 'dam' littoral material on the updrift side until the shoreline is built out to the point where sediments can bypass the end of the breakwater. This situation is clearly visible in the aerial photograph taken above the blast furnace embankment at Whyalla (Pl. 5.1). Sediments have built up on the seaward side of the last section of the wall, and extended across the entrance, so that some material is already bypassing the end of the wall and being carried to the False Bay shoreline. At the tip of the wall, waves are refracted and deflected with loss of turbulence, and material is deposited in the lee of the breakwater (Fig. 6.2). This predictable event is also clearly visible in Pl. 5.1. If a narrow entrance is created by the breakwater, the increased velocity of the confined tidal current will erode a channel and a silted tidal delta may form in the semi-enclosed area with a new distribution of the sediments. Erosion of the shoreline opposite the tip of the embankment is likely to occur (Fig. 6.1 and Pl. 6.1). A study of the aerial photograph (Pl. 5.1), will show that all of the changes predicted by Johnson (1956) have occurred since the

PLATE 6.1 Erosion at W1 opposite the end of the shore-connected embankment (Fig. 3.2 and Plate 5.1). January 1979.

blast furnace embankment was constructed.

At present, the build up of littoral material on the seaward side of the wall, and the effect of wave refraction at the tip, results in material being transported into the lagoon. Two sources of this material appear to be the wave erosion of the outer surface of the wall itself, where undercutting is clearly visible, and the erosion of the shoreline opposite the end of the wall (Pl. 6.1). The material eroded by wave action on the outside of the wall is Breckets fines, a slag which forms the coarse red sand sampled close to the wall at W5. Surface material eroded from the opposite shoreline would consist of the normal littoral deposits, plus the surface load of metal wastes which accumulated there before construction of the embankment (Pl. 4.1). The metal content of this material should resemble that of W2A, and W2MA, on the north-western shoreline, just inside the lagoon (Table A6, appendix).

This net movement of material <u>into</u> the lagoon would lead to the retention of the present discharges in the lagoon, rather than deposition, in decreasing quantities along the northern shoreline in False Bay (Fig. 3.1). The earlier pattern of transport and deposition is probably indicated by the higher concentrations of metals in the C horizon of the core, taken at W1, where erosion is now severe. However, further cores would need to be taken along this shoreline to support such a conclusion. The present pattern of sediment transport, however, suggests that the blast furnace lagoon will have a more rapid rate of accretion than it did prior to the construction of the wall. Pl. 3.3 shows young mangroves rapidly colonizing the accreting sediments in the sheltered inner corner of the lagoon, while Pls 5.2.1 and 5.2.2 show the severe erosion around roots of older and young trees in area W1. The high surface concentration of metals in the core taken at F1 (Table A6, appendix) suggests deposition is occurring there, possibly due to the resumption of littoral transport bypassing the wall. Sediments from W5 would accumulate at F1, as well as material from the blast furnace discharges. Many young mangrove seedlings are colonizing the intertidal mud flat, also suggesting a net accretion of sediments on this shoreline.

The material transported from W5 and W1 to the growing tidal delta inside the entrance to the lagoon (Pl. 5.1) may have a greater potential to affect marine organisms in its new situation. The material transported will belong to the finest fractions, which potentially carry the greatest load of adsorbed metals on their much greater surface area. The deposition of this material will be encouraged by the dense growth of algae and fine seagrasses which have already colonized the sand banks inside the entrance. Sediments from W5 contain high concentrations of metals, of which 43% chromium, 44% lead, and 75% zinc are easily released to overlying water. At low tide, the surface water over the tidal delta is only 5-10 cm deep, and subject to wide diurnal fluctuations in pH, and also in salinity during heavy rain. Since the degree of adsorption of metals on fine particulates is pH dependant, and in some cases affected by salinity, the metals in these sediments may be more mobile on this tidal delta than in their original location outside the wall, in comparatively deep water. The higher temperatures and salinity fluctuations likely to be encountered in the very shallow water, can also enhance the toxicity to invertebrate organisms of any metals released (O'Hara, 1973; Jones, 1975; O'Sullivan, 1977).

The overall effect of the blast furnace embankment, then, is a change in sedimentation, with erosion of the opposite shoreline, and an increased rate of accretion in the lagoon. The retention of organic material from the mangroves, together with the accumulation of fine sediments from outside, should result in the concentration of metal wastes within the lagoon, with very little spread north-east, around False Bay. However, this accumulation may have greater potential for release, and transport in solution out into the bay, because of the shallow conditions and likely fluctuation in surface water parameters inside the lagoon. If the wall was completed, sediments would be retained inside, but the input from longshore transport would be reduced. The wall would probably act as an efficient filter, like the wall of the tailings dam. However, if constructed of slag, like the present embankment, there would still be a concentrated source of metals available for potential release to the marine environment.

6.2 Geochemical factors

Although analysis of total metal concentrations is frequently used to assess the degree of pollution of marine sediments, the potential impact on marine organisms depends on the amount likely to become available as soluble compounds, free ions, or adsorbed on the particulates which form the food items of detritus feeders. Once these metals become available, their actual impact or toxicity will be determined by ambient water conditions, synergistic effects of temperature and salinity, or the presence of other metals concurrently.

The potential availability of metals from sediments will depend upon the chemical environment, influenced by the mineralogy, organic content, redox potential and degree of bacterial activity at various depths.

6.2.1 Mineralogy

6.2.1.1 Silicates

The origin of the metals is important when total metal concentrations are considered. Metals derived from the natural weathering of rock materials, or from crushed ores, are often incorporated in crystal lattice structures of silicate minerals, which are only soluble in hydrofluroic acid, or other extreme chemical conditions unlikely to be encountered in the environment. These are classified as 'detrital' (Loring, 1976; Skei and Paus, 1979), or residual, and are considered to be 'removed' from the system (Troup and Bricker, 1975). Preliminary analyses of sediments from the works area at Whyalla showed that a strong oxidizing leach of nitric acid and hydrogen peroxide removed a high proportion of most metals from the sediments (Tables 5.4 and 5.6). These results suggest that about 80% of chromium is unlikely to be available, presumably because it is incorporated in lattice structures or other resistant minerals, and that the wastes from the steelworks have about 50% of iron incorporated in silicates, and hence removed from the system. However, up to 100% of the cadmium total, 90% zinc and lead, 50-60% manganese and copper, and 20% chromium are apparently not associated as silicates, and could, under extreme environmental conditions, become available to marine organisms.

6.2.1.2 Carbonates

A sedimentary environment of warm shallow water can facilitate the precipitation of carbonates in regions where the photosynthesis of algae and seagrasses causes wide diurnal fluctuations in the pH (Williams and Barghoom, 1959). This range has been measured at 7.5-9.8 (Table A1, appendix) on seagrass meadows in intertidal areas of Gulf St. Vincent and Spencer Gulf. If sufficient carbonate is present, it is possible that some trace metals may also be precipitated with calcium carbonate. Cadmium is precipitated as carbonate at an optimum rate at pH 9.2 (Rubin, 1974), in the range of the measured pH in surface water over intertidal flats with a surface algal mat (present study). Lead was removed from brine solution by co-precipitation with carbonate phases in the simulated sedimentary system set up by Bubela and others (1974) to model the genesis of ore deposits in metal-rich highly saline environments. The carbonate in sediments at Whyalla appears to be derived from shell material, and is confined to the coarse sands in relatively unpolluted areas on the eastern side of False Bay, and south of the town. There seems to be no direct relationship with high metal concentrations which, because of their terrestrial origin and the accumulation of ore dust and slag, are found in sediments with a very low carbonate content.

6.2.1.3 Clays

Clay minerals found in natural systems can act as 'scavengers' for trace metal transport (Koppelman and Dilland, 1975), and their deposition at the margins of inlets, rather than in deep water (van Straaten and Kuenen, 1958) contributes to the high level of metal accumulation in the intertidal zone. Natural clays, such as kaolinite, illite and montmorillonite adsorb heavy metal ions at exchange sites and by specific bonding, the capacity varying with pH and the nature of the clay mineral (Farrah and Pickering, 1976). As pH increases above 6, increasing proportions of all metal ions can be bound as hydroxy complexes on suspended particulates, and deposited under slack water conditions in intertidal sediments. These metals are held while pH remains high, in surface conditions, but could be released at the low pH which can occur in anoxic sediments with microbial activity, or in the presence of humic and fulvic acids derived from plant detritus. Much of the effectiveness of clays in removing trace metals from water is due simply to the surface area presented. McKelvie (1978) found a surface area of 1 m^2/g for sandy sediments compared with 21.5 m^2/g for sediments with a high clay content, with could account for the distribution of metal concentrations independently of the mineralogy. Clay horizons in Whyalla sediments were usually the deepest section of the core, and had low metal concentrations, probably predating the blast furnace discharges. As a transport medium, suspended clays are more likely to be important in the estuarine situation, where there is considerable terrestrial input. High metal concentrations at Whyalla related to fine sediments, rather than to clays as such.

6.2.1.4 Iron and manganese minerals

The influence of these minerals has been discussed in the report on iron and manganese concentrations in sediments at Whyalla, and their importance as a 'sink' for heavy metals noted (Theis and Richter, 1979).

The behaviour of iron-rich sediments observed during leaching experiments at high pH may be relevant to their value as 'scavengers' of other elements.

At pH 9.5, fine red sediments remained in suspension for several hours, but immediately settled to the bottom of the tube when the pH was reduced to 8. In situations where surface water is shallow, over algal mats, fine particulate iron minerals may remain dispersed in the water at the high pH attained in bright sunlight, but would be removed to the sediments, carrying adsorbed minerals, when the pH of surface water decreased at night. Their presence in large quantities in the steelworks discharges could be a natural control measure on the dissipation of other trace metals in the marine environment, provided that these quantities are sufficient to allow for the competing effect of other complexing ligands such as cyanide. It is likely that the concentration of both these elements, as hydrated oxides, is sufficiently high to reduce water concentrations of both cyanide and metal to acceptably low levels, and provide a 'built in' control on the impact of these wastes on the marine environment at Whyalla.

6.2.1.5 Sulphides

Anoxic conditions are common a few centimetres below the surface in low energy environments, such as intertidal mud flats and mangrove swamps. The deposition of fine particulates in these situations restricts circulation beneath the surface layer, and the accumulated organic debris facilitates intense microbial activity, with the production of hydrogen sulphide. Metals such as lead, copper and zinc can then be precipitated as sulphides. With the exception of the sulphides of iron and manganese, these are generally insoluble, and unlikely to become available unless sediments are disturbed. Results of the present study suggested that much of the 'Industrial' lead and copper had accumulated in the sediments as sulphides and was relatively unavailable to marine organisms. The sulphides of iron and manganese are more mobile, and subject to vertical migration in the sediment column. Such diagenetic processes leave a record of coloured bands in unconsolidated sediments which indicates the migration of compounds in solution, and their precipitation in forms related to the stratified chemical environment (Sharma, 1971). The present study separated core horizons on colour and other sediment characteristics such as grain size. Colour was also used by Hallberg (1974) to differentiate layers in intertidal sediment cores. He attributed the colours to the presence of different iron minerals, ranging from brown (oxyhydroxides) to black (a mixture of sulphides) and grey (mainly pyrite).

Data from the present study (Table 6.1) shows that most lead is available from brown sediments (oxyhydroxides, according to Hallberg (1974), and generally not from black or grey sediments. Sulphides are not dissolved by the oxalic acid leach at pH 3, used to assess available metals.

TABLE 6.1

Mobile fraction of lead and sediment colour

Core horizons having 20 ppm lead	'Industrial' lead (ppm)	Mobile * fraction (%)	Colour of sediment
FB33A	28	0	Yellow sand
FB2	96	8	Dark brown sand
F2HWA	200	8	Brown surface on black sand
FBCrB	36	0	Black sand
F1A	448	2	Dark brown sand
FB1	240	3	Dark brown mud
W1A	111	14	Red brown sand
W1B	74	20	Dark brown sand
W1C	402	0	Dark brown mud
W2A	480	0	Red/black mud
W2B	110	0	Light brown sand
W2D	50	0	Grey sand
W2MA	635	2	Red/black sand
W2MB	32	0	Mottled black sand
W3A	1076	4	Dark brown mud
W3B	189	22	Dark brown sand
W3C	700	19	Dark brown mud
W3D	47	17	Mottled brown sand
W3SA	345	0	Black mud
W3SB	603	3	Brown sand
3SC	215	4	Red/brown sand
W5A	607	44	Red/brown sand
W5B	482	0	Black mud
W5C	150	0	Dark grey sand

$$^{*}\text{ Mobile fraction} = \left(\frac{\text{Available metal}}{\text{'Industrial' metal}} \times 100\right)$$

Fig. 5.5 shows the distribution of mobile lead in relation to sediment colour.

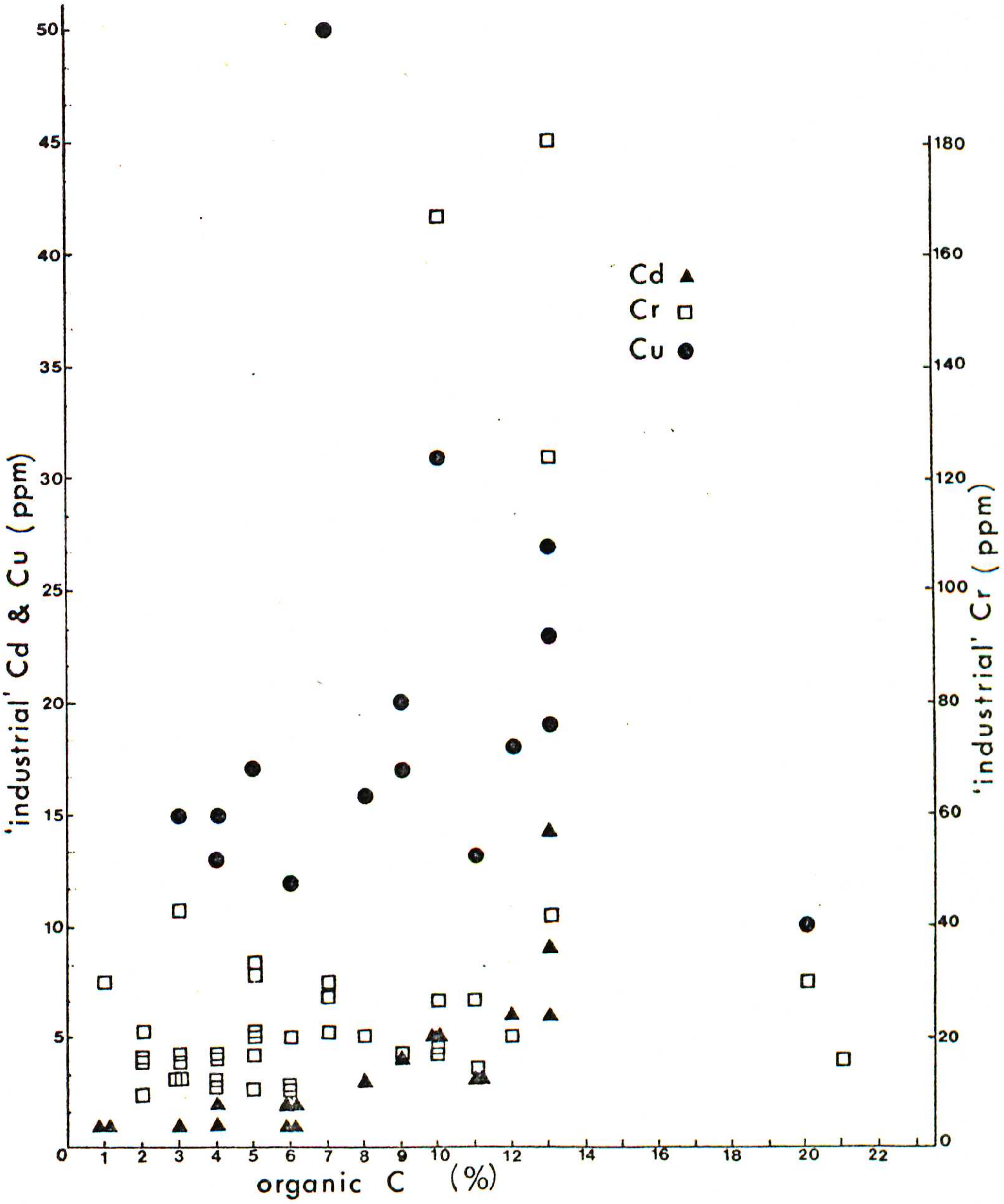

FIG. 6.3 'Industrial' cadmium, copper, and chromium related to organic carbon content of sediments.

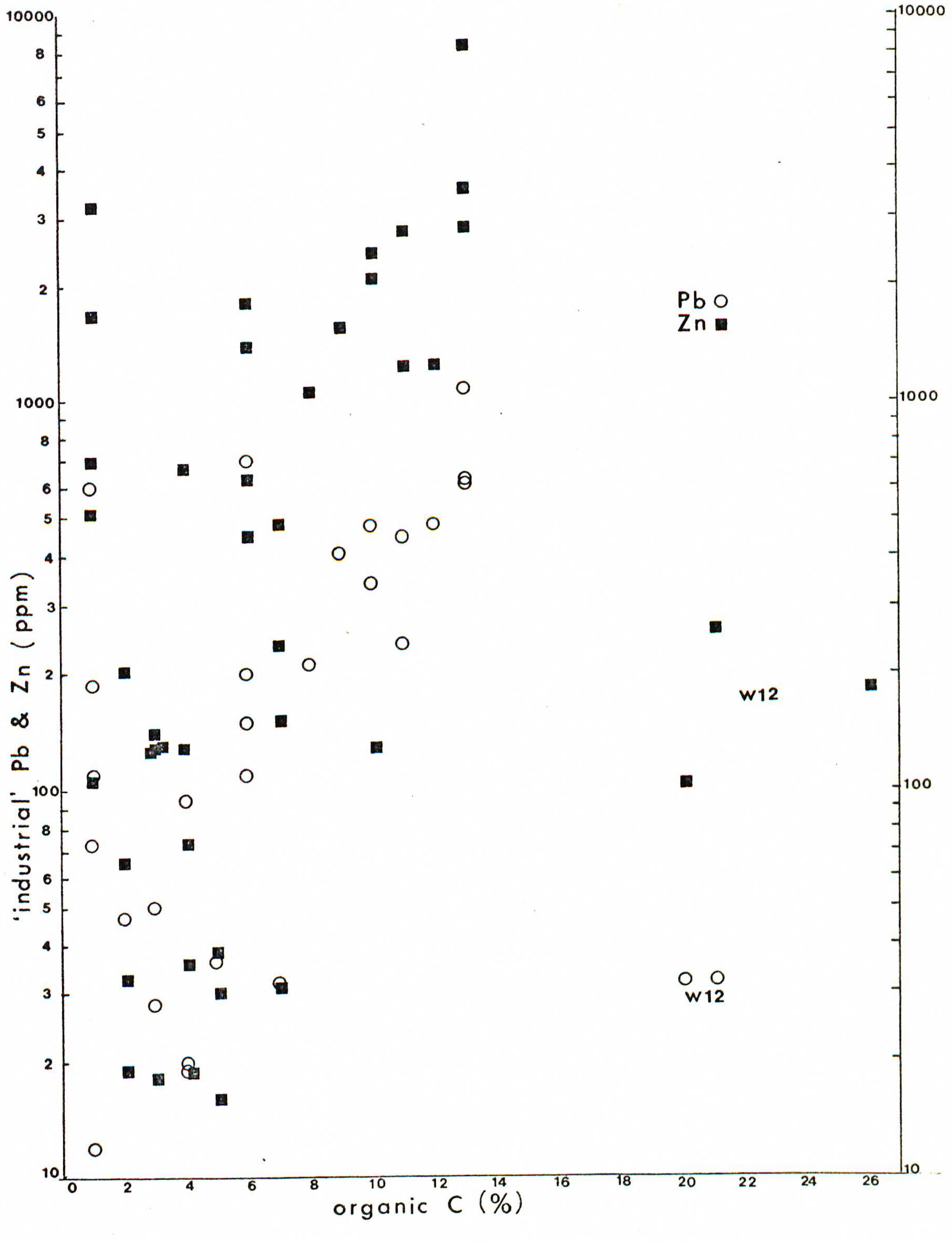

Fig. 6.4. "Industrial" lead and zinc related to organic carbon content of sediments.

6.2.1.6 Organic carbon

The correlation found by many authors for heavy metals such as zinc, cadmium and lead with organic matter in sediments was also found to a certain extent in Whyalla sediments. The highest concentrations of strong acid soluble or 'Industrial' metal, other than iron and manganese, are shown related to the organic carbon content of the horizon in Figs 6.3 and 6.4.

The relationship of available metals to organic carbon is inverse for lead, and to a lesser extent, copper, suggesting the formation and precipitation of sulphides in these horizons, which are not then easily remobilized. Some of the relationship between organic carbon and 'Industrial' metal concentrations is probably secondary due to the correlation between grain size and organic carbon (Loring, 1976). This is probably true where industrial discharges are high, and residence time in sediments has been too short for the accumulation of sulphide minerals. It probably also explains the higher metal accumulations in mangrove sediments, with high organic carbon, rather than in beach sands with a lower organic content, and larger particle size. Although methylated forms of lead and mercury were not investigated at Whyalla, the greatest environmental significance of organic carbon in sediments, as distinct from grain size, could be in providing optimum conditions for the microbial methylation of these elements, with increased toxicity to higher consumers (Sommers and others, 1974; Wong and others, 1975; Lindberg and Harris, 1974; Ratkowsky and others, 1975).

6.2.2 Chemical parameters

6.2.2.1 pH

The pH of surface and interstitial water has been established by many workers as the most important factor in the speciation and availablility of metals in aquatic environments (Zirino and Yamamoto, 1972; Farrah and Pickering, 1976; Hem, 1976; McKelvie, 1979 and many others). In seawater the speciation of copper, zinc and lead is dependent on pH. Copper forms complexes with hydroxide and carbonate ions, zinc with hydroxide and chloride ions, and lead with carbonate and chloride (Zirino and Yamamoto, 1972). At pH 9, copper would be mainly complexed as hydroxide, with a small amount of carbonate present, which decreases at higher pH. For lead, carbonate is the dominant species at high pH.

The high pH measurements recorded in surface water during the present study of intertidal sediments suggest that this factor could influence the precipitation of metal species in surface sediments, and their availability in shallow water. Most metals are adsorbed on particulates in increasing quantities at high pH values, but may be released from sediments with decaying plant material, or other organic material which lowers the pH of interstitial water. The wide diurnal fluctuations in pH of surface water could thus produce corresponding variations in the concentration of metals in the overlying water.

Possibly one of the most direct influences on the availability of metals is the lowered pH of the first stage of digestion in many invertebrate and higher organisms. Benthic organisms such as polychaete worms and molluscs, and bottom-feeding fish all ingest large quantities of particulate matter as, or with, food items. A lowered pH inside the digestive tract would then favour the release of adsorbed metals from the particulates. An acid first stage of digestion is common to most animals, from unicellular organisms such as *Paramoecium* having pH 1.4 in the food vacuole, to bony fishes such as *Pleuronectes*, the plaice, with pH 1.5 in the stomach (Jennings, 1965).

The effect of .5N hydrochloric acid on the release of metal from sediments shown in Table 6.2 indicates that cadmium, which is not released from the sediments by the oxalic acid reducing leach, is removed by the hydrochloric acid leach. This also applies, to a lesser extent, to lead and copper. The reduced pH in the digestive tract could thus release quantities of metals such as cadmium which might otherwise not be available from sediments.

TABLE 6.2

The effect of lowered pH on extraction of metal from sediments

Sample	Extraction method	Cu	(ppm) Cd	Pb
FB1	1	13	3	240
	2	4	2	215
	3	0	0	8
W1C	1	20	4	402
	2	16	6	202
	3	4	0	0
W2A	1	18	6	480
	2	14	5	510
	3	0	0	0
W3SA	1	23	9	603
	2	10	8	670
	3	0	0	16

1 = Hot HNO_3/H_2O_2

2 = Cold .5N HCl at pH 0.3

3 = Cold oxalic acid at pH 3

The pH of the cold hydrochloric acid was probably somewhat lower than the digestive tract pH of any animal, but a comparison of the two cold leaches does indicate that metals which do not appear to be available under ambient seawater conditions, may become available if the sediments are ingested.

6.2.2.2 Salinity

The competing effect of chloride for the adsorption sites on iron and manganese oxides has also been noted for clay minerals and other particulate matter. McKelvie (1979) investigated the factors affecting zinc adsorption on sediment particulates from Lake Wellington, Victoria. He found that the adsorption of zinc decreased from 85-90% at 0‰ salinity to about 60% at 35‰ (standard seawater). It is possible that adsorption could be further decreased in the waters of upper Spencer Gulf, where salinity can be 40‰ in shallow waters for long periods, and exceeds 50‰ in surface water on intertidal mud flats (Thomas and Edmonds, 1955; and present study). Since cadmium is complexed mainly with chloride ions, and its speciation is not affected by pH, the availability of chloride may affect that of cadmium in seawater.

Wide fluctuations in salinity could influence the impact of metal wastes on intertidal organisms. When heavy rain falls on these exposed habitats, the salinity of surface water can drop from >40‰ to <20‰ in a few minutes (present study). Apart from any increase in the solubility of some sediment components, this change results in an increased uptake of ions by intertidal organisms in the process of osmoregulation (O'Hara, 1973; Sullivan, 1977). Any metal ions released from the sediments will then have a greater toxicity due to their rapid uptake. Tidal flats in upper Spencer Gulf have little rainfall, but when it does rain, the falls are often very heavy, with the possibility of the effects described if potentially toxic materials are present in surface sediments.

6.2.2.3 Temperature

The high temperatures recorded in shallow water over intertidal sediments in summer (>32°C) are likely to increase the concentration of dissolved substances in the water, and decrease the solubility of gases. The rise in temperature will also affect the rate of metabolic processes in intertidal organisms, making them more vulnerable to changes in the composition of surface water. The synergistic effect of temperature on the toxicity of some metals has already been noted (O'Sullivan (1977) and others). The effect of sediment colour on surface water temperature, noted over black, brown and light coloured sands, is particularly relevant in intertidal regions at Whyalla, where the darkest coloured sediments have the highest metal concentrations, and are likely to have the highest temperature in surface water.

6.2.2.4 Redox conditions in sediment

Redox potential, as measured by an electrode, indicates the electron demand or the electron availability within the solution or sediment, and depends on the ratio of oxidized to reduced forms in the system (Whitfield, 1971). In sediments, the measurement can be used to identify horizons having a reducing environment. Black colour, and the presence of hydrogen sulphide, which also indicate reducing conditions (Zobell, 1946; Giamatteo, 1975) were used in the present study to identify anoxic horizons.

The preferential or more rapid accumulation of certain trace elements in anoxic sediments (Calvert and Price, 1970; Richards, 1971; Aston and Chester, 1976; Hodder, 1978) has been noted in many studies of sedimentary metal accumulation. Lu and Chen (1977) considered redox conditions the principal factor controlling the direction of metal migration across the sediment/water interface, a view supported by A. Eaton's (1978) work on the release of manganese from sediments under anoxic summer conditions in Chesapeake Bay. Anoxic conditions associated with bacterial degradation of organic matter and sulphate reduction favour the precipitation of metal sulphides, particularly those of copper, lead and zinc (Baas Becking and Moore, 1961; Ben Yaakov, 1973; Bauld, 1979).

The sulphides of iron and manganese are more soluble than the oxides, hence iron and manganese may be released to the overlying water as sediments become anoxic (Eaton, 1978). The low solubility of copper and lead sulphides can result in extremely low levels of these metals in water containing hydrogen sulphide (Riley and Chester, 1971). Surface water samples were collected from mangrove swamps at Pt. Gawler over the unbroken mud surface, and in a footprint which released hydrogen sulphide from the anoxic sediment just below the surface. The water contained >5 mg/1 hydrogen sulphide, and no detectable zinc, copper or lead. Manganese was present at a concentration of 0.01 ppm over the undisturbed surface, but 0.14 ppm in the water from the footprint (present study). Surface sediments contained 14 ppm copper, 98 ppm manganese, 12 ppm lead and 47 ppm zinc (PtG3A, Table A6, appendix).

High concentrations of organic matter and fine particulates are characteristic of, and contribute to, the reducing conditions in anoxic sediments, by providing the substrate for intense microbial activity, and restricting the circulation of water and gases. These conditions are generally found in the extensive mangrove swamps of upper Spencer Gulf, and probably provide a significant sink for metals released into gulf waters.

PLATE 6.2 Rapidly accreting sediments at Pt. Gawler (young mangroves <1 m).

PLATE 6.3 Drifting algal and seagrass debris trapped by pneumatophores (PtG4). Mangroves <1 m.

6.3 Biological factors

These factors influence the distribution and availability of metals through their modification of the sedimentary and chemical environment.

6.3.1 Mangroves

The mangrove seedlings colonizing accreting sediments (Pl. 6.2) produce rows of pneumatophores which project 10-20 cm above the sediment surface, and trap floating seaweed and debris brought in by the tide (Pl. 6.3). The baffle effect on tidal flow leads to the deposition and trapping of fine particulate material in the slack water environment. Anoxic conditions are usually found just below the surface, due to the lack of circulation in the fine sediments, and the accumulation of decaying organic matter. An ideal 'sink' for the accumulation of metal wastes is thus created, where slack water facilitates the settling of the fine particulates carrying the most adsorbed metals, and anoxic highly organic muds enhance sulphide precipitation.

Zinc and copper, as well as iron and manganese are taken up by the roots of the trees, and accumulate in the leaves. When these leaves fall and decay this metal becomes available to detritus feeders. Since some of the detritus feeders are young stages of our commercial fish species, which shelter and feed in mangrove swamps, this may be a significant pathway for a wider distribution of metals from the sediment. Johnson (1974) considered that 61% of particulates at the sediment/water interface were potential food items. The potential threat of metal accumulations to the scale fishery is probably not the actual metal-content of the fish itself, as most metals other than mercury accumulate in the liver and kidney, and not in the muscle which is used as food. However, if high concentrations of toxic metals become available in the shallow tidal swamps where juvenile fish feed and shelter, mass deaths could significantly affect the population size two or three years later.

6.3.2 Algae

Blue green algae, which grow on the surface of intertidal muds, also trap fine particulates in their gelatinous matrix so that a dense mat, mostly impermeable to larger molecules, is formed on the surface with black anoxic sediments directly beneath. These mats are common on the wide intertidal flats all around Spencer Gulf, and also in Gulf St. Vincent (Pl. 6.4). Their role in the accumulation of heavy metals, and as a limiting membrane at the sediment/water interface, has been examined in a simulated sedimentary system reported by Bubela (1979). The underlying anoxic sediments provide a site for the sulphide precipitation of uncomplexed metals which can pass through the mat, and the restricted passage of gases prevents oxidation of the sediments.

The impermeability of the mats to gases was noted by Bubela (1979) when pieces of the mat were detached by the pressure of gases generated beneath the mat. A similar condition was observed in stagnant surface pools in mangroves near Weeroona Island in Spencer Gulf (Fig. 2.1). In one pool, having a water temperature of 30°C (noted on 1.11.79, present study), large sections of the mat had broken free revealing the greyish black sediments underneath. The pH of water immediately beneath this dislodged mat was 6.8, and the surface water of the pool had pH 7.2. Salinity was 50‰. Large numbers of dead young fish, about 3 cm long, were lying on the bottom of the pool. A Hatch test for hydrogen sulphide in the water showed a concentration of 3 mg/l. A similar pool, slightly deeper, close by, had a considerable growth of green algae, probably *Enteromorpha sp.*, but the bottom algal mat was not detached. Water temperature was 30°C, salinity 40‰, and pH 7.8. Hydrogen sulphide was not detected in the water. A large number of apparently healthy young fish were swimming in the pool. The lower salinity suggested that this pool had been flushed by the tide more recently than the other. The other differences in water quality, however, may have been due to the lifting of the mat, and the release of hydrogen sulphide from the sediments beneath. The high concentration of hydrogen sulphide suggests a low availability of oxygen

PLATE 6.4 Dense mat of seagrasses and blue green algae on intertidal flat, Pt. Gawler. Mangroves 0.5-1.5 m.

Metal concentrations in a mud sample taken nearby obtained by digestion with hot nitric acid were: chromium 26 ppm, copper 10 ppm, lead 329 ppm and zinc 170 ppm. Organic carbon was estimated by ignition to be 17%. (Sample WRp, Table A6, appendix.)

6.3.3 Concentration by organisms

The uptake of heavy metals from water by plankton, bacteria, macro-algae, and molluscs has been noted in many reports (Calvert and Price, 1970; Bloom, 1975; Brinckman and Iverson, 1975; Talbot and others, 1976; Foster, 1976). These concentrations are returned to the water or sediment on the death and decay of the organisms, and may form pockets of enrichment in the sediments where the dead material is accumulated by tidal currents. Alternatively they may be distributed to consumer organisms with increased concentration at successive trophic levels (Ratkowsky and others, 1975). This 'food chain concentration', although limited to certain species and particular metals such as cadmium in the edible mussel, *Mytilus edulis*, zinc in oysters, and mercury in fish (Bloom, 1977) is probably the most significant aspect, for man, of heavy metal accumulation in the marine environment. In the Whyalla area, shellfish are not grown or harvested commercially, so metal contamination is not likely to present the problem it has done for the Derwent oyster and mussel fisheries (Bloom, 1975; and others).

6.3.4 Micro-organisms

The established toxicity of methylated forms of heavy metals also directs attention to the sedimentary environment which facilitates this process, and it has been demonstrated by Sommers and others (1974) that at optimum sediment temperatures in the 15-25°C range, with a continuous supply of organic carbon, the rate of microbial transformation of inorganic mercury to the methylated form is proportional to the total mercury available to the system. Presumably the methylation of lead (Wong and others, 1975) would proceed in a similar environment, readily available in intertidal regions of Spencer Gulf. The role of marine bacteria in the deposition of zinc and cadmium was also noted by Holmes and McLerran (1974). Two pathways were involved. The greatest proportion of metal was precipitated out of solution due to the large amounts of hydrogen sulphide produced by the bacteria. A smaller proportion (20%) was directly associated with bacterial cells. Bacterial growth, hydrogen sulphide production, and zinc and cadmium deposition were all at a maximum in summer. Optimum conditions for the deposition of metals by these biological pathways, and the others already suggested, exist in upper Spencer Gulf for most of the year.

7 CONCLUSIONS

7.1 The impact of steelworks discharges on the marine environment

The sedimentary accumulations of zinc at Whyalla are highly mobile, and readily available in solution or, associated with particulate matter, as food material.

Water quality on the tidal flats is likely to be strongly influenced by fluctuations in pH, salinity and temperature, and so is the toxicity of any available metals. For this reason zinc accumulation in mangrove swamps could be a potential hazard for marine species. The presence of several elements together is also known to enhance the toxicity of any one element alone.

Cadmium, chromium, copper, and lead are not so readily available in solution, but could be released from detritus at low pH during the acid stage of digestion in most animals.

The affinity of transition metals for fine particulate matter, which forms a major food item for benthic organisms, could be the most important factor in making sedimentary metal accumulations available in the marine environment.

Iron and manganese could be valuable in removing other metals to the sediments but have an undesirable blanketting effect which may reduce the productivity of benthic algae and mangrove leaves.

The presence of large numbers of stingrays in the shallow water offshore from the works (W4-W6) suggests some disturbance to the ecology of the area in favour of this species.

The mangrove stands between W1 and W3 do not appear to be threatened by the sedimentary accumulation of metals. However, opposite the end of the blast furnace embankment, severe erosion has rendered many trees unstable, and prevented the establishment of seedlings.

Older trees at W3S, and young ones at W3 and W7, may be affected in the future by the rapid accumulation of sediments, leading to the build up of a highly saline substrate, but seepage under the railway embankment at W3 may prolong the survival of these young trees by maintaining water movement through the sediment.

The changes in littoral transport associated with the blast furnace embankment will increase deposition inside the wall and across the entrance. Once this bar is established, littoral material will again be deposited on the shoreline at F1 and F2. The growth of young mangrove seedlings observed in October 1979 suggests that sediment is already accumulating in this area.
Eventually littoral transport should by-pass a sand bar across the mouth of the blast furnace lagoon, with the same end result as completion of the wall. The mangroves at W2 may die as the substrate is built up and water circulation is reduced, but a new vigorous stand should become established between F1 and F2.

7.2 The particular role of mangrove swamps in the distribution of heavy metals

A large proportion of the coastline in northern Spencer Gulf is colonized by mangroves (*Avicennia marina var. resinifera*). These trees grow rapidly in intertidal mudflats which are sheltered and have a net accretion of sediments. Once established, their network of horizontal roots below the surface, and the projecting pneumatophores above the sediment, further reduce current velocities and scouring, stabilizing the sediment, and facilitating the deposition of the finest particulate matter. A large quantity of plant detritus is often trapped by the pneumatophores, and eventually contributes, with other organic material brought in by the tide, and leaf fall, to the high organic carbon content of the sediment.

The low permeability of the fine muds, and the accumulation of organic material, with associated micro-organisms, leads to the development of black, anoxic sediments just below the surface. Open areas between the trees are often colonized by mats of blue green algae, and fine sea-grasses. The photosynthetic activity of these plants raises the pH of surface water to 9.8 during periods of maximum light intensity, and creates conditions favourable to carbonate precipitation. These four environmental parameters:

finest particulates
anoxic sediments having a
high pH in surface water and
high organic carbon content

favour the accumulation and precipitation of heavy metals, making the mangrove swamp a major sink for metal industry wastes. Mangrove swamps also shelter and feed a variety of marine organisms, including some commercial species, which could be endangered if toxic metals became available from the sediments. Most of these organisms are detritus feeders, consuming the fine particulate matter. Metals can be released from particulate material if the pH is lowered. Very low pH (6.8) has been recorded in surface water in the mangrove swamps, where pools are shaded by trees, and have accumulated seagrass debris (present study). Low pH is also characteristic of the digestive tract of most organisms.

Shallow intertidal areas are also subject to high summer temperatures and wide fluctuations in salinity during heavy rain. Low salinity and high temperature, together or separately, have a synergistic, or compounding effect on the toxicity of metals.

In these intertidal swamps, it is possible for a combination of low tides, summer rain, and overcast or nocturnal conditions to produce a shallow water environment having high temperature, lowered salinity, and low pH which could favour the release of easily available metal from sediments (particularly zinc), with maximum toxicity to marine organisms.

The mangrove swamp provides optimum conditions for the accumulation of metals, coinciding with the possibility of natural climatic and tidal conditions favouring the release of these metals in a situation where the impact on marine organisms could be at a maximum.

8 RECOMMENDATIONS

8.1 Zinc is a highly mobile element in the marine environment and should, if possible, be removed from aerial and aquatic discharges.

8.2 Iron and manganese oxide particulates could be an asset in impoundments, where they aid the removal of other metals from solution to sediments.
Fine suspensions discharged into air or open water, however, should be reduced to avoid the blanketting of mangrove leaves and algae, with loss of productivity in the marine community.

8.3 The known principles of littoral transport should guide decisions relating to the construction of embankments, and siting of discharge pipes.
Effluents should, if possible, be directed to deep, well-circulated offshore water, or inland into sabkhas, rather than into shallow intertidal areas.

8.4 The maintenance of recreational and limited commercial fishing at Whyalla requires the continued productivity of mangroves and seagrass beds south of the town. If solar salt ponds are constructed on the landward side of mangrove swamps, the terrestrial creeks should not be truncated, but by-passed with pipes. This occasional input of fresh water is necessary to keep salinity of the substrate at a tolerable level, and maintain a nutrient supply to the trees and subtidal area.

8 RECOMMENDATIONS (continued)

8.5 The use of trail bikes and other recreational vehicles on intertidal mangrove mudflats should be discouraged. The change in water quality resulting from disturbance to the surface layer of sediment could be detrimental to many intertidal organisms and juvenile stages of commercial fish species.

8.6 In Spencer Gulf there should be no further industrial development of a type likely to discharge potentially toxic materials, by design or accident, into intertidal or subtidal areas, north of Ward Spit and Point Lowly. The restricted circulation and vast area of mangrove swamps at the northern end of the gulf would enable waste materials to accumulate with the greatest potential threat to marine life.

9 APPENDIX TABLES

TABLE A1 APPENDIX

Range of surface water measurements on intertidal flats

		Undisturbed surface		Disturbed surface
		night	day	
Temperature °C	High	20	36	29
	Low	15	15	12
pH	High	8.4	9.9	8.1
	Low	7.5	7.5 (ebbing tide)	6.5
Salinity ‰	High	47	58.5	53
	Low	34	19 (rain)	29 (rain)
H_2S mg/l	High	>5 mg/l	1 mg/l (dense mangrove)	>5 mg/l
	Low	0	0	0.5 mg/l

TABLE A2

APPENDIX

Sediment characteristics

False Bay

Sample	Location	Depth cm	Colour	Size Class	Feature	Organic Carbon %	$CaCo_3$ %	Water %
BlptR	BB.mang.	5	red	m.sand	quartz	1	2	22
BlptG	Mid.	10	grey	m.sand	shell	2	13	19
FB33A	HW	1	yellow	f.sand	shell	3	33	22
B		9	grey	f.sand	sulphide	4	40	27
C		30	yellow	sand	shell grit	2	25	26
F3A	LW	1	white	f.sand	shell	3	38	29
B		11	grey	f.sand	shell	3	38	31
C		30	white	c.sand	shell	3	38	34
FB2	HW	5	brown	sandy mud	fibre	4	6	37
FB3	Mid.	5	yellow	f.sand	shell	3	35	27
F2HWA	HW	6	brown	sandy mud		6	12	22
B		21	grey	f.sand		3	20	27
C		38	grey	f.sand	fibre	4	29	35
FBCrA	HW	3	brown	c.sand	quartz	1	5	21
B		11	black	m.sand		5	15	32
C		24	pink	m.sand	shelly	2	14	23
D		35	pink	f.sand	whole shells	4	22	34
FB1	Sub.	5	brown	silt	fibre	11	20	50
F1A	Mid./Mang.	5	brown	f.sand		11	16	32
B		16	grey	m.sand	stones & shells	2	23	25
C		34	grey	c.sand	shell & fibre	3	31	34

..continued

TABLE A2 (continued)

Sample	Location	Depth cm	Colour	Size Class	Feature	Organic Carbon %	CaCo$_3$ %	Water %
SAB1A	Sabkha	5	yellow	sandy mud	clay	10	20	29
B		18	yellow	clayey mud	clay	5	5	36
C		38	yellow	m.sand	shell	3	40	32

TABLE A2 (continued) APPENDIX

Steelworks area

Sample	Location	Depth cm	Colour	Size Class	Feature	Organic Carbon %	$CaCo_3$ %	Water %
W1A	LW	3	brown	m.sand	metal	1	3	
B		13	d.brown	m.sand	quartz	1	3	
C		26	d.grey	silt	metal	9	9	
D		39	l.grey	f.sand		4	6	
W2A	LW/Mang.	4	black	mud	metal	12	8	
B		14	brown	m.sand		6	9	
C		28	grey	silt		4	11	
D		38	grey	silt & pebbles		4	2	
W2MA	LW/Mang.	11	black	m.sand		13	7	
B		16	grey/ black	m.sand	stones & shells	7	19	
C		39	grey	sandy mud		5	12	
W3A	Mid./ Mang.	1	brown	m.sand	metal	13	6	
B		7	brown	m.sand	metal	1	1	
C		27	brown	silt		7	6	
D		43	grey/ brown	silt		2	1	
W3SA	HW/Mang.	3	black	clayey mud	algae	10	12	
B		13	brown	silt	fibre& metal	13	22	
C		29	brown	silt	fibre	8	19	
D		42	grey	clayey mud	clay	7	2	
W5A	LW	8	brown	m.sand	nodules	1	2	
B		20	black	silt	metal	10	16	
C		28	grey	silt		6	18	
W7A	HW/Mang.	5	red/ brown	silt		8	4	
B		24	red	f.sand	metal	1	1	
C		42	grey	clayey mud	metal	3	3	

TABLE A2 (continued)

Whyalla, south of steelworks

Sample	Location	Depth cm	Colour	Size Class	Feature	Organic Carbon %	$CaCo_3$ %	Water %
TB1A	LW	10	l.grey	c.sand	sulphide	2	41	39
B		25	grey	m.sand	shell	2	41	36
TB2A	HW	1	l.grey	m.sand	seagrass	5	34	49
B		8	grey	f.sand	shell	4	37	37
C		18	grey	c.sand	gravel	2	23	25
W10A	LW	1	l.grey	f.sand	shell	3	34	
B		13	grey	f.sand	shell	3	35	
C		28	grey	silt	shell & fibre	5	34	
W11A	Mid.	6	l.grey	f.sand	shell & fibre	5	31	
B		18	grey	silt	shell	6	32	
C		29	l.grey	f.sand	shell & fibre	4	33	
W12A	HW/Mang.	4	grey	sand	shell & debris	26	21	
B		12	l.grey	f.sand		21	23	
C		31	l.grey	silt	shell	4	34	
W12MA	HW/Mang.	1	l.grey	sandy mud	algal film	20	19	58
B		7	grey	silt	fibre	10	29	48
C		24	l.grey	silt	sulphide	5	36	34
D		40	l.grey	sandy mud	shell	5	34	39
8MC1A	LW/Mang.	8	grey	m.sand	shell	3	30	30
B		18	grey	m.sand	shell	3	26	28
C		25	grey	silt	fibre	3	4	28
D		38	pink	clay/ mud		4	2	26

..continued

TABLE A2 (continued)

Sample	Location	Depth cm	Colour	Size Class	Feature	Organic Carbon %	CaCo₃ %	Water %
8MC2A	HW/Mang.	8	grey	m.sand	shell	3	28	29
B		20	grey	m.sand	shell	2	25	23
C		33	grey	silt	fibre	10	19	45
8MC3A	Mid.	6	mottled	m.sand	clay	5	27	32
B	(relict sed.)	21	brown	m.sand	shells	8	17	52
C		35	grey	m.sand	wood fibre	4	33	42

TABLE A2 (continued) APPENDIX

Other areas

Sample	Location	Depth cm	Colour	Size Class	Feature	Organic Carbon %	$CaCO_3$ %	Water %
PtAe	Mid.	10	red/ brown	silt	bioturbation	12	3	44
PtAw	Mid.	10	grey	silt		7	6	42
ChCkBA	Mid.	1	yellow	m.sand		6	4	30
B		24	d.grey	mud	relict mang.	6	5	42
ChCkStA	HW	5	pink	silt	algal film	21	17	45
B		15	grey	f.sand	shell	2	16	22
C		32	yellow	m.sand		1	5	19
WR1A	Mid	7	yellow	m.sand	shell	2	14	17
B		28	yellow	f.sand	clay	3	6	17
WR2A	LW/ Seagrass	10	black	silt	seagrass	10	21	55
B		28	grey	f.sand	sulphide	5	25	37
WR3A	HW/Mang.	8	grey	silt	clay	6	6	34
B		23	black	f.sand	roots	5	4	32
WRp	HW/Mang.	5	d.grey	silt	sulphide	2	23	50
WRBch	Mid	5	grey	m.sand	shell	17	19	30
PtBr	LW	5	grey	silty sand	seagrass	17	8	70
PtG1A	Mid./ Seagrass	5	d.grey	silt	algal film	15	14	
B		23	grey	silt	shell	3	32	
C		40	d.grey	f.sand	fibre	3	24	
PtG2A		4	d.grey	m.sand	shell	6	29	
B		17	grey	c.sand	shell	5	27	

..continued

TABLE A2 (continued)

Sample	Location	Depth* cm	Colour	Size Class	Feature	Organic Carbon %	CaCo$_3$ %	Water %
PtG3A	Mid./ Mang.	2	black	silt	sulphide	19	15	
B		10	d.grey	f.sand	sulphide	8	21	
C		27	grey	f.sand	plant debris	4	30	
PtG3S	Mang.	5	grey	mud		21	17	74
PtG4S	Mang.	5	d.grey	silt		12	17	58
PtG4MA	Mid./ Mang.	3	black	f.sand		19	8	71
B		18	d.grey	silt	shell	12	15	59
C		35	grey	silt	shell & fibre	4	21	35
PtG6	HW	5	yellow	m.sand	shell	5	31	32
PtG9A	LW	3	grey	m.sand	shell	2	21	32
B		14	black	m.sand	shell	2	22	31
PtGSA	Upper HW	5	yellow	mud	algal film	6	22	37
B		23	yellow	silt	shell	2	20	30

l.grey = light grey
d.grey = dark grey
d.brown = dark brown

f.sand = fine sand
m.sand = medium sand
c.sand = coarse sand

*Depth at Mid-horizon (cm)

TABLE A3.1

Water analyses (B.H.P.)

Water samples analysed by B.H.P. at Whyalla

(metal concentrations in ppm)

Date	Location	pH	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Cn$^-$(total)
17.1.79 unfiltered	W4		<.002			.116			.049	.394	
	W3S core hole		<.002			.990			.133	.109	
	W12		<.002			.006			<.002	.007	
	W12				.009	<.01	<.005	<.001	<.002	.111	
	W7				.026	.110	.800	.001	<.002	.013	
31.1.79 filtered	W2 core				.064	1.900	3.09	.014	.111	.40	
	W2 surface				.06	<.01	.02	<.001	.02	.035	
	W1 core				.096	21.5	2.69	.008	.38	3.65	
	W10 core				.02	<.01	<.005	.001	.006	.012	
7.3.79 unfiltered	Blast Furnace										
	outflow	7.1			.05		<.01		.16	.79	.045
	dam	7.3			.04		.01		.25	.90	.075
	race	7.4			.08		<.01		.23	.82	.08
	lagoon	7.7			.01		.01		<.01	.03	.03
	W5	7.7			.03		.06		<.01	.09	.077
	W5-6	8.0			.03		.12		.01	.01	.033

continued

TABLE A3.1 (continued)

Date	Location	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Hg
30.5.79 filtered	W6 surface	.001	.01	.03		.05	.008	.018	.01	.0083
	F1 surface	.003	.06	.006		.36	.009	.18	1.11	.0004
	W12 surface	.001	.03	.008		.13	.01	.06	.04	.0004
	W2 surface	.001	.03	.001		.10	.009	.04	.10	.0004
3.9.79	W6 surface	.001	.04	.03		.01	.02	.005	.04	.00005

TABLE A3.2

Metal content of suspended solids and filtered water*

One five litre sample filtered through .08 µm Millipore filter
Suspended solids: 6.1 ppm.

	Cd	Cr	Cu	Fe	Mn	Pb	Zn
Metal content of solids, (ppm)	<100	6000	<100	49000	6200	400	3000
Equivalent metal in sample	<0.0006	0.0366	<0.0006	0.299	0.0378	0.0024	0.018
Metal content of filtered water, (ppm)	0.001	0.04	<0.02	<0.02	0.03	0.014	0.25
Total metal content of sample, (ppm)	0.001	0.08	<0.02	0.31	0.068	0.016	0.27

* Sample collected and analysed by B.H.P. staff, Whyalla

TABLE A4

Metal concentrations (ppm) in sediments and mangrove leaves

Sample	Cu					Fe					Zn					Mn				
	Sediment		Leaves from trees			Sediment		Leaves from trees			Sediment		Leaves from trees			Sediment		Leaves from trees		
StV.Gulf	'Ind.'	Avail	<1m	>1m	Old	'Ind.'	Avail	<1m	>1m	Old	'Ind.'	Avail	<1m	>1m	Old	'Ind.'	Avail	<1m	>1m	Old
PtG1	12	6	6			10840	1910	380			28	10	31			129	20	111		
PtG3A	14	8			9	12500	1900			106	39	16			23	102	17			48
PtG4S	12	11	4	7		20230	2330	300	121		27	14	11	14		86	10	98	52	
PtWCr	13	6		10		19580	4000		300		24	4		22		197	72		78	
PtWH	13	9		24		14900	5300		106		34	15		38		123	36		30	
Spencer G.																				
PtB	17	7			7	4600	1612			106	44	21			10	43	6			18
WRbeach	3	1			4	1200	120			76	87	40			26	113	8			28
WRpipe	10	4		13		14580	5074		121		170	84		52		378	125	not measured		
PtA.E	53	24		17		23950	5820		197		89	49		33		320	196		16	
PtA.W	7	6			6	7600	1731			182	25	11			21	51	12			45
B1Pt	0	0			7	1100	90			106	10	7.5			35	20	16			26
F2HW	9	-	4			30340	13530	106			1390	1091	27			540	210	49		
W1-W2C	18	10			7	69200	35300			197	2280	1740			24	981	424			70
W3 $\genfrac{}{}{0pt}{}{A}{C}$	27	6	10		6	50000	31000	915		615	8280	5065	114		29	1200	1100	168		117
W3S $\genfrac{}{}{0pt}{}{A}{D}$	31	6	6		4	34140	23530	677		215	3620	3170	100		48	1075	590	136		99
W7	50	37	9			60800	9030	369			492	422	7			1473	1450	63		
W11B	3	3	0		4	1670	210	154		123	30	12	22		42	70	<5	49		36
W12C	10	5	3		4	11960	4660	185		185	103	52	11		29	90	17	42		88
8MC1C	12	5	3		4	27090	1020	169		154	35	9	14		23			30		33

TABLE A5

Metal concentration in intertidal organisms (in ppm of dry weight)

Area	Sample	Date	Cd	Cr	Cu	Fe	Mn	Pb	Zn	Note
W2	Mussels	1.79	3	0	9	588	40	94	162	Clump, small. *Mytilis hirsutus*
W2	Mussels	5.79	1	0	6	590	41	180	200	Clump, poor condition. *Mytilis hirsutus*
W2	Barnacles	1.79	2	0	5	-	225	34	-	Whole, small, *Elimnius modestus*
W2	Snails	1.79	1	0	14	186	318	88	436	Few, small, whole. *Salinator fragilis*
W3	Snails	1.79	0	16	10	320	667	195	928	Few, small, whole. *S. Fragilis*
W3S	Snails	1.79	1	23	13	108	531	125	474	Few, small, whole. *S. Fragilis*
W5	Mussels	1.79	3	0	14	-	195	397	376	Clump, hairy. *M. hirsutus*
W6	Mussles	1.79	1	0	10	-	-	0	85	Full. *M. hirsutus*
W6	Mussels	5.79	2	0	10	710	30	10	77	Full. *M. hirsutus*
W6	Barnacles	1.79	4	0	82	-	-	0	>500	1 cm, *Balanus amphitrite*
W6	Barnacles	5.79	1	0	150	1110	73	13	5300	Larger, *B. amphitrite*
W9	Mussels	5.79	2	0	3	180	10	<5	64	Beacon, 2 only 5 cm, *Mytilis planulatus*
W9	Mussels	5.79	1	0	3	220	9	<5	65	Beacon, *M. hirsutus*
W9	Mussels	5.79	1	0	3	210	9	<5	62	Full, *M. hirsutus*

..continued

Area	Sample	Date	Cd	Cr	Cu	Fe	Mn	Pb	Zn	Note
W11	Mussels	1.79	1	0	10	-	16	0	80	Small. *Austromytilis erosus*
	Snails	1.79	0	4	11	-	39	3	57	Whole, many. 1 cm *S. fragilis*
8MC	Cockles	5.79	2	0	4	470	7	0	52	Small. *Katelysia sp.*
PtG1	Cockles	2.79	1	4	17	-	8	0	50	Small. *Katelysia sp.*
PtG3	Snails	1.79	0	4	24	-	89	0	76	Whole, larger, many. *S. fragilis*
	Snails	6.79	1	0	25	860	79	13	91	Whole, larger, many. *S. fragilis*
PtG5	Snails	5.79	1	0	19	630	76	0	64	Whole, larger, many *S. fragilis*

TABLE A6

'Industrial' and available metals in sediments

1 = 'Industrial' metal (strong oxidizing leach - hot HNO_3/H_2O_2), (ppm)
2 = Available metal (reducing leach - Ammonium oxalate and oxalic acid at pH 3), (ppm)
3 = Mobile fraction - available proportion of 'Industrial' metal (%)
(M) = Mangroves

False Bay

Sample	Depth cm	Cd			Cr			Cu			Fe			Mn			Pb			Zn		
		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
(M)BLPtRed	0-10	-	-	-	-	-	-	-	-	-	1100	90	8	20	16	80	-	-	-	10	8	80
BLPtGrey	0-20	-	-	-	-	-	-	-	-	-	790	120	15	25	5	20	-	-	-	30	17	57
FB33A	0-2	-	-	-	8	4	50	-	5	100	850	126	15	75	9	12	28	-	-	128	40	31
B	2-16	-	-	-	8	4	50	-	5	100	1120	168	15	75	7	9	20	-	-	128	50	39
C	16-45	-	-	-	4	4	100	-	5	100	450	42	9	24	<5	<20	-	-	-	ND	<1	<1
F3A	0-2	-	-	-	12	-	-	-	-	-	850	126	15	74	10	14	-	-	-	127	67	53
B	2-20	-	-	-	8	-	-	-	3	100	710	126	18	65	8	12	8	-	-	140	79	56
C	20-40	-	-	-	4	-	-	-	3	100	580	84	14	27	<5	<18	-	-	-	1	2	
FB3	0-10	-	-	-	8	4	50	-	-	-	1030	320	31	100	13	13	8	-	-	130	46	35
FB2	0-10	2	-	-	-	-	-	6	-	-	4170	1250	30	67	22	33	96	8	8	675	480	71
(M)F2HWA	0-12	1	-	-	20	9	45	9	-	-	30340	13530	45	540	210	39	200	15	8	1390	1091	78
B	12-30	-	-	-	12	9	75	-	-	-	1830	42	2	55	7	13	-	-	-	3	2	67
C	30-45	-	-	-	16	4	25	-	-	-	4330	290	7	85	16	19	-	-	-	4	1	25

..continued

TABLE A6 (continued)

Sample	Depth cm	Cd			Cr			Cu			Fe			Mn			Pb			Zn		
		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
FBCrA	0-5	-	-	-	-	-	-	3	-	-	1700	500	29	30	11	37	12	8	67	110	74	67
B	5-17	-	-	-	8	-	-	3	-	-	3880	1600	41	69	19	28	36	-	-	240	202	84
C	17-30	-	-	-	8	-	-	-	-	-	1380	210	15	19	<5	<26	-	-	-	9	6	67
D	30-40	-	-	-	12	-	-	-	-	-	670	42	6	25	<5	<20	-	-	-	1	4	100
SAB1A	0-10	-	-	-	20	-	-	4	-	-	5360	880	16	69	7	10	-	-	-	22	6	27
B	10-25	-	-	-	32	-	-	4	-	-	19260	2500	13	27	9	33	-	-	-	7	6	86
C	25-50	-	-	-	16	-	-	2	-	-	3880	220	6	25	4	16	-	-	-	2	2	100
(M)F1A	0-10	3	-	-	27	9	33	13	-	-	41330	23400	57	810	360	44	448	8	2	2880	2175	76
B	10-22	-	-	-	13	-	-	-	-	-	3080	420	14	47	9	19	-	-	-	65	51	78
C	22-45	-	-	-	17	-	-	-	-	-	5040	378	8	43	5	12	-	-	-	5	3	60
FB1	0-10	3	-	-	13	8	62	13	-	-	11200	5080	45	340	100	29	240	8	3	1210	860	71

TABLE A6

Steelworks area

Sample	Depth cm		Cd			Cr			Cu			Fe			Mn			Pb			Zn	
		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
W1A	0-6	1	-	-	8	-	-	5	3	60	6900	3150	46	270	110	41	111	15	14	726	552	76
B	6-20	<1	-	-	7	-	-	3	3	100	4200	2480	59	199	66	33	74	15	20	528	493	93
C	20-32	4	-	-	17	13	76	20	4	20	52000	26400	51	630	360	57	402	-	-	1584	1360	86
D	32-45	<1	-	-	17	-	-	15	8	53	10880	1130	10	103	25	24	19	-	-	73	89	100
(M)W2A	0-8	6	-	-	20	8	40	18	-	-	69200	35300	51	908	510	56	480	-	-	2280	1740	76
B	8-20	2	-	-	10	-	-	8	-	-	15540	6720	43	274	135	49	110	-	-	456	313	69
C	20-35	1	-	-	13	4	31	13	10	77	5320	250	5	72	17	24	3	-	-	19	9	47
D	35-40	1	-	-	18	4	22	15	13	87	6360	170	3	28	10	36	50	-	-	19	7	36
(M)W2MA	0-21	6	-	-	42	14	33	19	-	-	46990	29300	62	981	424	43	635	15	2	2800	2260	81
B	21-31	-	-	-	21	9	43	7	3	43	12460	2100	17	236	63	27	32	-	-	150	100	67
C	31-47	-	-	-	33	-	-	17	10	59	10040	420	4	76	16	21	-	-	-	16	4	25
(M)W3A	0-1	14	-	-	125	100	80	27	-	-	50000	31000	62	1200	760	63	1076	42	4	8280	5065	61
B	1-13	-	-	-	3	-	-	3	5	100	8220	2860	35	450	455	100	189	42	22	1674	1570	94
C	13-40	1	-	-	20	-	-	12	6	50	70000	48300	69	1065	1100	100	700	138	19	1850	1740	94
D	40-45	-	-	-	5	-	-	4	-	-	17080	12400	73	183	125	68	47	8	17	202	158	78
(M)W3SA	0-5	5	-	-	168	120	71	31	-	-	34140	23530	69	1075	590	55	345	-	-	2440	1830	75
B	5-20	9	-	-	181	110	61	23	-	-	46000	14200	31	560	190	34	603	16	3	3620	3170	88
C	20-38	3	-	-	20	9	45	16	-	-	50000	31100	62	495	280	57	215	8	4	1072	799	75
D	38-45	<1	-	-	30	-	-	9	6	67	12680	1510	12	55	17	31	7	-	-	31	23	74

..continued

TABLE A6 (continued)

Sample	Depth cm		Cd			Cr			Cu			Fe			Mn			Pb			Zn	
		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
W5A	0-16	1	–	–	30	13	43	3	–	–	166000	64200	39	3330	1600	48	607	270	44	3240	2560	79
B	16-24	5	–	–	26	14	54	17	2	12	36720	23950	65	675	330	49	482	–	–	2200	1750	80
C	24-32	2	–	–	13	9	69	8	2	25	18540	8400	45	420	170	40	150	–	–	634	487	77
(M)W7A	0-10	–	–	–	28	9	32	50	37	74	60800	9030	15	1473	1450	98	–	–	–	492	422	86
B	10-38	–	–	–	9	–	–	2	3	100	8960	130	1	4	<5	–	–	–	–	6	1	17
C	38-45	–	–	–	7	4	57	2	2	100	4410	210	5	4	<5	–	–	–	–	7	–	–

TABLE A6

Whyalla, south of steelworks

Sample	Depth	Cd			Cr			Cu			Fe			Mn			Pb			Zn		
	cm	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
TB1A	0-20	–	–	–	21	–	–	–	1	~100	1120	210	19	48	6	13	–	–	–	19	8	42
B	20-30	–	–	–	17	–	–	–	1	~100	1070	42	4	35	<5	~11	–	–	–	2	1	50
TB2A	0-1	–	–	–	21	–	–	3	5	~100	2190	590	27	65	17	26	–	–	–	38	18	47
B	1-15	–	–	–	17	–	–	–	1	~100	1470	378	26	50	8	16	–	–	–	36	17	47
C	15-20	–	–	–	17	–	–	–	3	~100	1610	250	16	48	8	17	–	–	–	33	17	52
W10A	0-2	–	–	–	9	–	–	3	3	100	1630	250	15	51	<5	<10	–	–	–	18	6	33
B	2-24	–	–	–	14	–	–	2	3	~100	2700	296	11	51	<5	<10	–	–	–	13	5	38
C	24-32	–	–	–	4	–	–	3	3	100	6000	380	6	70	<5	<7	–	–	–	5	1	20
(M)W11A	0-12	<.1	–	–	9	–	–	2	2	100	1670	210	13	60	<5	<8	5	–	–	30	12	40
B	12-24	<.1	–	–	–	–	–	3	3	100	4550	470	10	70	<5	<8	3	–	–	22	8	36
C	24-34	<.1	–	–	9	–	–	1	2	100	1000	85	9	55	<5	<10	–	–	–	2	–	–
(M)W12A	0-8	1	–	–	9	–	–	8	6	75	11010	1820	17	95	8	8	7	–	–	182	125	69
B	8-15	1	–	–	16	8	50	10	–	–	21800	9900	45	90	4	4	32	–	–	268	210	78
C	15-46	1	–	–	12	–	–	1	5	100	1560	85	5	60	<5	<8	3	–	–	2	1	50
(M)W12MA	0-1	–	–	–	31	–	–	10	2	20	11960	4660	39	90	17	19	32	–	–	103	52	50
B	1-12	–	–	–	17	–	–	6	1	17	2900	1270	44	65	7	11	9	–	–	130	81	62
C	12-35	–	–	–	13	–	–	–	–	–	1920	170	9	35	<5	<14	–	–	–	2	1	50
D	35-45	–	–	–	17	–	–	–	–	–	1290	130	10	35	<5	<14	–	–	–	–	1	–

...continued

TABLE A6 (continued)

Sample	Depth cm	Cd			Cr			Cu			Fe			Mn			Pb			Zn		
		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
(M) 8MC1A	0-15	-	-	-	0	-	-	3	-	-	1600	170	11	31	<5	<16	-	-	-	3	1	33
B	15-20	-	-	-	4	-	-	2	-	-	2840	210	7	33	14	42	-	-	-	1	2	50
C	20-30	-	-	-	33	-	-	12	5	42	27090	1020	4	55	<5	<9	-	-	-	35	9	26
D	30-45	-	-	-	46	-	-	24	10	42	21300	170	1	81	<5	<6	-	-	-	48	3	6
(M) 8MC2A	0-15	-	-	-	17	-	-	-	-	-	1600	170	11	30	<5	<17	-	-	-	4	4	100
B	15-25	-	-	-	8	-	-	-	-	-	1600	130	8	29	<5	<17	-	-	-	1	1	100
C	25-40	-	-	-	24	-	-	4	3	75	13110	1060	8	240	49	20	-	-	-	14	3	21
8MC3A	0-12	-	-	-	24	-	-	-	-	-	6130	1990	32	34	8	24	-	-	-	7	4	57
B	12-30	-	-	-	20	-	-	-	-	-	2490	250	10	10	<5	<50	-	-	-	2	1	50
C	30-40	-	-	-	32	-	-	-	-	-	1510	170	11	33	<5	<15	-	-	-	1	1	100

TABLE A6

Other areas

Spencer Gulf

Sample	Depth cm	Cd			Cr			Cu			Fe			Mn			Pb			Zn		
		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
(M)PtAe	0-20	-	-	-	41	8	20	42	24	45	23950	5820	24	320	196	61	38	-	-	89	49	55
(M)PtAW	0-20	-	-	-	15	-	-	7	6	86	7600	1731	23	51	12	24	-	-	-	25	11	44
ChCkBchA	0-20	-	-	-	20	-	-	7	3	43	16560	2750	17	99	24	24	-	-	-	21	3	14
B	2-45	-	-	-	32	-	-	10	2	20	43370	2330	5	149	19	13	-	-	-	35	3	9
(M)ChCkStA	0-10	-	-	-	20	4	20	6	3	50	11470	3260	28	128	39	30	29	-	-	57	31	54
B	10-20	-	-	-	8	4	50	-	3	~100	1480	127	9	57	<5	<9	-	-	-	2	1	50
C	20-45	-	-	-	8	-	-	-	3	~100	930	170	18	14	<5	<36	-	-	-	1	-	-
WR1A	0-15	-	-	-	12	-	-	1	2	~100	2510	680	27	57	12	21	17	-	-	36	10	28
B	15-40	-	-	-	20	-	-	6	2	33	10130	470	5	50	13	26	-	-	-	12	2	17
WR2A	0-20	23	-	-	20	-	-	13	2	15	8160	1530	19	148	26	18	335	-	-	1090	682	63
B	20-35	4	-	-	12	-	-	4	3	75	4480	420	9	129	16	12	50	-	-	77	68	88
(M)WR3A	0-15	3	-	-	16	-	-	7	3	43	7000	1690	24	950	48	5	208	-	-	196	154	79
B	15-30	2	-	-	24	-	-	7	3	43	7310	680	9	62	19	31	188	-	-	80	53	60
(M)WRBchS	0-20	2	-	-	7	-	-	3	1	33	1200	120	10	113	8	7	113	-	-	87	40	46
(M)WRpipe	0-20	-	-	-	26	12	46	10	4	40	14580	5074	35	378	125	33	329	-	-	170	84	49
(M)PtBr	0-20	-	-	-	7	-	-	17	7	41	4600	1612	35	43	6	14	21	-	-	44	21	48

..continued

TABLE A6 (continued)

Gulf St. Vincent

Sample	Depth cm	Cd			Cr			Cu			Fe			Mn			Pb			Zn		
		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
(M)PtG1A	0-10	-	-	-	24	-	-	12	6	50	10840	1910	18	85	20	24	5	-	-	28	10	36
B	10-35	-	-	-	7	-	-	-	3	~100	1850	170	9	129	18	14	-	-	-	1	-	-
C	35-45	-	-	-	9	-	-	1	-	-	6750	300	4	115	28	24	-	-	-	3	-	-
PtG2A	0-8	-	-	-	5	-	-	-	5	~100	2480	510	21	70	11	16	3	-	-	8	3	38
B	8-26	-	-	-	4	-	-	-	5	~100	1560	127	8	60	<5	8	-	-	-	1	1	100
(M)PtG3A	0-3	<.1	-	-	28	-	-	14	8	57	16700	3620	22	98	16	16	12	-	-	47	17	36
B	3-19	<.1	-	-	21	-	-	8	5	63	6700	890	13	102	13	13	7	-	-	28	11	39
C	19-35	-	-	-	7	-	-	1	2	~100	3110	210	7	95	10	11	-	-	-	3	1	33
(M)PtG3S	0-10	<1	-	-	26	8	31	15	4	27	12500	1900	15	110	16	15	10	-	-	39	16	41
(M)PtG4Feb	0-10	<.1	-	-	27	-	-	14	11	79	20400	1270	6	90	11	12	7	-	-	28	11	39
(M)PtG4S	0-10	1	-	-	37	4	11	12	-	-	9930	1540	16	86	10	12	7	-	-	27	14	52
(M)PtG4MA	0-6	-	-	-	44	-	-	21	11	52	20230	2330	12	105	13	12	8	-	-	43	17	40
B	6-30	-	-	-	40	-	-	20	11	55	18420	1100	6	117	12	10	-	-	-	30	9	30
C	30-60	-	-	-	20	-	-	4	3	75	4220	470	11	950	12	1	-	-	-	1	1	100
PtG6	0-10	-	-	-	8	-	-	4	-	-	1800	880	49	74	10	14	-	-	-	15	9	60
PtG9A	0-6	-	-	-	8	-	-	4	-	-	1930	380	20	53	7	13	-	-	-	2	2	100
B	6-20	-	-	-	8	-	-	3	-	-	1520	250	16	57	<5	<9	-	-	-	2	2	100
PtGSA	0-10	-	-	-	20	-	-	6	-	-	5910	1530	26	100	42	42	-	-	-	13	7	54
B	10-45	-	-	-	8	-	-	1	-	-	1820	340	19	40	12	30	-	-	-	2	3	100
(M)PtWCr	0-20	-	-	-	35	-	-	13	6	46	19580	4000	20	197	72	37	-	-	-	24	4	17
(M)PtWHb	0-20	-	-	-	31	-	-	13	9	69	14900	5300	36	123	36	29	4	-	-	34	15	44

TABLE A7 APPENDIX

Metals removed from surface sediments by alkaline leach at pH 9.5, compared with 'Industrial' metal content of sediments.

1 = 'Industrial' metal (HNO_3/H_2O_2), (ppm)

2 = Alkaline leach (pH 9.5),(ppm)

3 = Mobile fraction (fraction of 'Industrial' metal removed by alkaline leach),(%)

	Zn			Fe			Mn		
Sample	1	2	3	1	2	3	1	2	3
F1A	2880	22	.8	41330	71	.2	810	5	.6
F2HWA	1390	14	1.0	30340	43	.1	540	3	.6
FB3	130	1	.8	1030	14	1.4	100	0	0
W1A	726	12	1.7	6900	43	.62	270	6	2.2
W2A	2280	17	.7	69200	80	.1	908	8	.9
W2MA	2800	12	.4	46990	28	.1	981	5	.5
W3SA	2440	21	.9	34140	28	.1	1075	10	.9
W7A	492	4	.8	60800	14	.02	1473	9	.6
TB1A	19	0.3	1.6	1120	0	0	48	0	0
TB2A	38	1	2.6	2190	43	2	65	2	3.0
W12MA	103	1	1	11960	71	.6	90	0	0
8MC2A	4	0	0	1600	0	0	30	0	0
WR2A	1090	10	.9	8160	14	.2	148	0	0
PtG1A	36	0	0	10840	28	.3	85	2	2.3
PtG3	39	1	2.6	12500	28	.2	110	0	0
PtG4S	27	0	0	9930	43	.4	86	0	0
PtG6	15	2	13	1800	57	.03	74	2	3.0

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