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Impact of Shipping and Dredging on Toxicants in Port Phillip Bay.

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EXECUTIVE SUMMARY

In the course of their passage across Port Phillip Bay and whilst in port, ships can contaminate the waters of the Bay through discharge of bilge water, spillage of oil and other hydrocarbons and release of antifouling paint toxins from their hulls. The effects of these potential sources of contaminants to the Bay have not previously been investigated. Maintenance and capital works dredging is periodically carried out in dock areas and along shipping channels of the Bay. Often these dredged sediments contain elevated concentrations of toxic metals, hydrocarbons and toxic constituents from antifouling paints. As well as redistributing toxic substances to different parts of the Bay, the dredging processes can potentially remobilise toxic substances into the water column. These processes can be regarded as creating additional inputs of toxicants into the Bay. The present task was designed to determine the extent and possible impacts that shipping and dredging have on toxicants entering the Bay.

Sediments in the Port of Melbourne contain elevated concentrations of copper, nickel, lead, zinc, mercury and petroleum hydrocarbons compared to both Bay-wide sediments and to sediment quality guidelines published in the scientific literature. Concentrations of butyltin compounds are generally low, however some sediment samples contained very high concentrations. Dumping of these sediments on the spoil ground located in the northern part of the Bay has resulted in elevated concentrations of metals and petroleum hydrocarbons in the spoil ground sediments. The concentrations of nickel and mercury in parts of the spoil ground are such that they could cause adverse biological effects to biota inhabiting the sediments. It is unlikely that leaching of dissolved toxicants from the sediments into the water column during dredging operations is significant. The annual load of metals such as cadmium, copper, lead and mercury transported from the Port of Melbourne to the spoil ground is less than the annual load that enters the Bay from rivers, streams and drains.

Sediments from the shipping channels of the Port of Geelong contain lower concentrations of toxicants than those of the Port of Melbourne. However, because the volume of material that is proposed to be dredged for the Port of Geelong is greater, the loads of metals and petroleum hydrocarbons that will be translocated during dredging are comparable to those from the Port of Melbourne.

The toxicant concentrations in the waters of the Port areas are influenced primarily by historical factors (e.g. Cd in the Inner Harbour of the Port of Geelong) or catchment inputs (e.g. Pb and Zn in the Port of Melbourne). Direct contamination of the water column by normal shipping operations (i.e. excluding spills and discharges) was not detected during the course of this study.

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1. INTRODUCTION

1.1 Shipping

Each week approximately 50 commercial ships cross the Bay to the Port of Melbourne and a further seven, on average, service the Port of Geelong. Total shipping in the Bay amounts to 35 million gross registered tonnes annually, with an average size of 10,000 tonnes (Batley 1992).

During the course of their passage across the Bay and whilst docked in port, ships invariably discharge bilge water, release antifouling paint toxins from their hulls and also contribute oil and other hydrocarbons to the water column. Tributyltin (TBT) from antifouling paints is extremely toxic to marine life at very low concentrations and the adverse effects of this compound has been of particular concern worldwide. Ships longer than 25 m are exempt from the ban on the use of TBT, but prior approval for the use of TBT must be obtained. On average, individual ships release about 2.5 g of TBT to the water column each day. The release rate for freshly painted ships can be an order of magnitude greater than this (Batley 1992).

The impacts of shipping have not yet been satisfactorily assessed in Port Phillip Bay although some monitoring of TBT has been carried out (Daly and Fabris 1993, Foale 1993). Few data are available for oil and other hydrocarbons in dock areas or shipping lanes.

1.2 Dredging

Maintenance dredging to remove accumulated sediments is periodically carried out in dock areas and along shipping channels in Port Phillip Bay. Maintenance dredging by the Port of Melbourne and Port of Geelong authorities involves the dredging and subsequent dumping of more than 500,000 m^3 of material annually (Batley 1992). Capital works dredging programs create additional volumes of sediment that are translocated from one part of the Bay and deposited on spoil grounds in another part of the Bay. Dredged sediments - particularly those from Port areas - may contain elevated concentrations of heavy metals, petroleum hydrocarbons, polynuclear aromatic hydrocarbons (PAH) and antifouling paint constituents. During dredging and dumping operations there is the potential for a proportion of these contaminants to be remobilised into the water column. Transport of substances released into the water column can adversely affect biota located in areas away from the dredging and spoil ground sites.

Assessment of the impact of dredging on toxicant inputs to the Bay is listed as a specific objective of the Port Phillip Bay Study. Any process that potentially remobilises toxic substances is effectively creating an additional input and as such should be considered in any model of the Bay.

1.3 Objectives

The objectives of this task were:

- to determine the impact of shipping and dredging activities on toxicants entering Port Phillip Bay;
- to estimate toxicant loading to the Bay from these sources and assess the environmental significance of these inputs, and;
- to provide data for use in the Port Phillip Bay Environmental Study predictive toxicant model.

1.4 Previous Work

1.4.1 Port of Melbourne

During 1991 the Port of Melbourne Authority (PMA) undertook a study to determine the environmental impact of its shipping channel maintenance dredging operations in the Port of Melbourne (PMA 1991). The study design was based on guidelines outlined in the Victorian Environment Protection Authority's Trial Dredge Protocol (EPA 1992). The Protocol was developed to provide guidelines for achieving maximum environmental protection when planning and conducting dredging operations, but it is not mandatory for agencies to comply with the recommendations.

Sediment cores from the area to be dredged as well as from the spoil ground site were analysed for a range of physico-chemical variables specified in the Protocol, including:

- particle size, specific gravity, total solids, total organic carbon;
- metals (Cd, Cr, Cu, Pb, Zn, Hg and As);
- tributyltin;
- chlorinated organic compounds (pesticides and polychlorinated biphenyls);
- volatile organic compounds;
- petroleum hydrocarbons;
- phenols;
- polynuclear aromatic hydrocarbons (16 US EPA priority pollutant compounds).

The sediments were also subjected to an elutriation test according to procedures outlined in the Protocol.

This 1991 study was one of the first to use the Protocol and some anomalies became apparent. For example, metal determinations were carried out on sediments that had already been subjected to the elutriation test, the analytical method used to determine tributyltin was not specific for tributyltin and was not capable of detecting tributyltin at environmentally significant concentrations and the analytical method used for petroleum hydrocarbon determinations returned very low results compared with previously published data for this region (Burns and Smith 1982, PMA 1989). Additional work was carried out during 1993 that confirmed that the metal data obtained for sediments analysed in the 1991 study were valid (PMA 1993). However, the results obtained for petroleum hydrocarbons, as in the 1991 work, were much lower than would have been expected from historical data.

Given the uncertainties in some of the existing data and the time elapsed since those studies, additional field studies were carried out as part of the present study.

1.4.2 Port of Geelong

Improvements to the existing shipping channels in the Port of Geelong are proposed that will involve the dredging and disposal of approximately 5 million m^3 of material. Before the proposed works could commence an Environment Effects Statement (EES) was required by the Victorian State Government. The EES commissioned by the Port of Geelong Authority (PGA) was completed during 1993 and included studies of physical processes, sediment chemistry, water quality and marine ecology (PGA 1993a). A set of toxicant data were obtained for the material to be dredged as well as for the proposed spoil grounds. These data, contained in the EES and supplementary documents (PGA 1993b), were used for toxicant load calculations in the present study.

2. METHODS

2.1 Sampling Design

2.1.1 Sediment

Sediment sampling for the current study was carried out on 12/12/1994. Within the Port of Melbourne six sediment cores (10 cm internal diameter) were collected to a depth of 50 cm where possible as described previously (Fabris *et al*. 1994). One core was collected at random within each of the following dock areas (Figure 1):

1. North Wharf;
2. Victoria Dock;
3. Appleton Dock;
4. Swanson Dock;
5. Yarraville Wharves, and;
6. Holden Dock.

The core from the Appleton Dock site penetrated only to a depth of 10 cm. The substrate below this depth was very hard and it was not possible by hand to push the core liner any deeper.

Six cores (10 cm internal diameter) were also collected within the spoil ground site in Port Phillip Bay used by the PMA to dispose of spoil dredged from these dock areas. The spoil ground was arbitrarily divided into two approximately equal areas by the 38^0 S parallel. Three cores were collected at random within each of the two areas (sites 7 to 12; Figure 2). The coordinates for the sediment sampling sites are listed in Appendix 1.

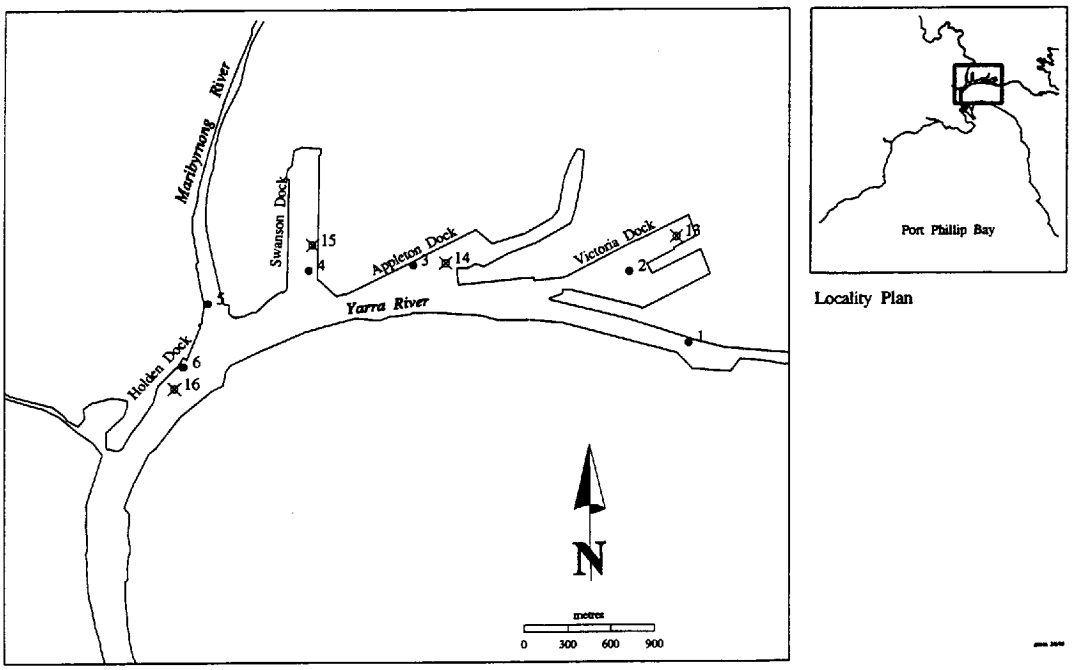

Figure 1. Sites used for the sediment (sampled 12/12/1994) and water (sampled 23/01/1995) study of the Port of Melbourne.

2.1.2 Water

Surface (0 - 0.5 m) water samples were collected from the Port of Melbourne during 23/01/1995 and from the Port of Geelong during 23/01/1995 and 25/01/1995. At each site two and one half litres of water was collected for the metals and butyltin determinations and a further four litres for petroleum hydrocarbon determinations.

In the Port of Melbourne single samples were collected at random from the Victoria Dock, Swanson Dock, Appleton Dock, and Holden Dock areas (sites 13 to 16 respectively; Figure 1). In the Port of Geelong single samples were collected at random from the following locations: Refinery Pier, Corio Quay, Bulk Grain Pier and Point Henry Pier (sites 17 to 20 respectively; Figure 3).

In addition single samples were collected on each of three occasions within the Hopetoun Channel (Port of Geelong) immediately following the passage of bulk carrier ships. Control samples for this exercise were collected from the same sites in the shipping channel prior to the passage of the ships (sites 21 to 23; Figure 3).

All samples were collected according to the clean sampling procedures described in Fabris and Monahan (1995). The coordinates for the sediment sampling sites are listed in Appendix 1.

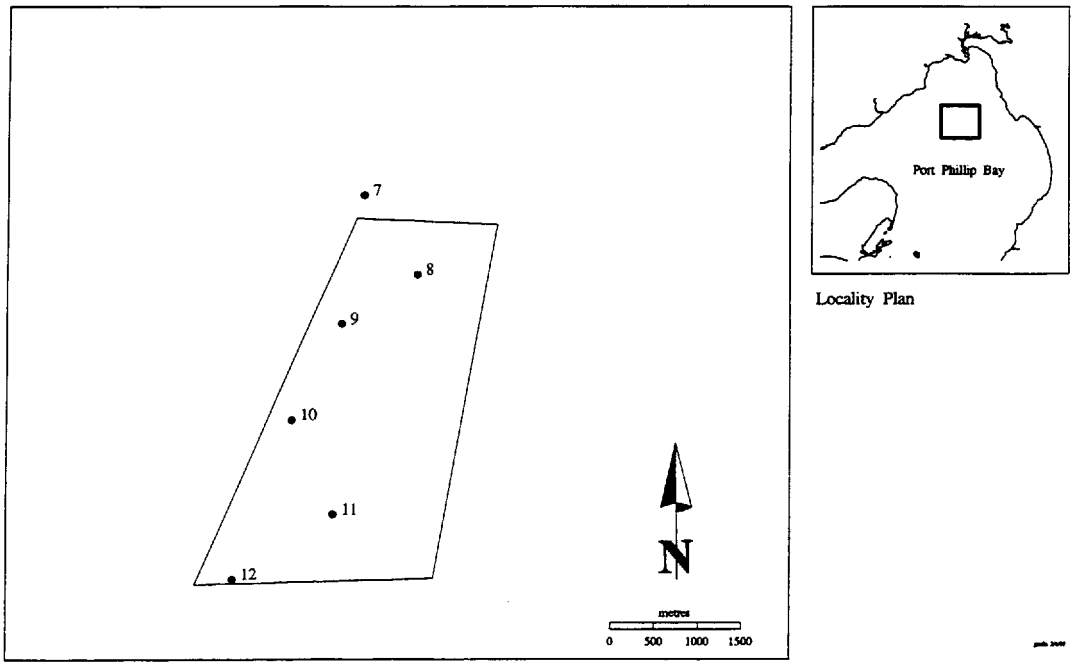

Figure 2. Sites used for the sediment study of the Port of Melbourne spoil ground (sampled 12/12/1994).

2.2 Sample Analysis

2.2.1 Sediment

The sediment samples were extruded from the core liners while in a semi-frozen state. Sections (nominally 10 cm long, but shorter sections as listed in Appendices 2 and 3 were also taken depending on the overall length of the core sample) were transferred into pre-cleaned glass jars and mixed using a glass rod. Subsamples for metals and TBT determinations (300 g and 30 g respectively) were transferred from the glass jar to labelled polyethylene bags. All samples were re-frozen (-20 ^{0} C) until analysis.

Metal determinations were performed on freeze dried samples that had been sieved through 200 µm mesh nylon. The fraction of material passing through the sieve was analysed for cadmium, lead, copper, zinc, iron, manganese, nickel, chromium and mercury by atomic absorption spectrometry (AAS) after extraction from the sediment with hot nitric acid (USEPA method 3050A but excluding the hydrogen peroxide).

Because it is suspected that drying and sieving causes losses of TBT and organic components, determinations of TBT and organic components were performed on whole wet sediment.

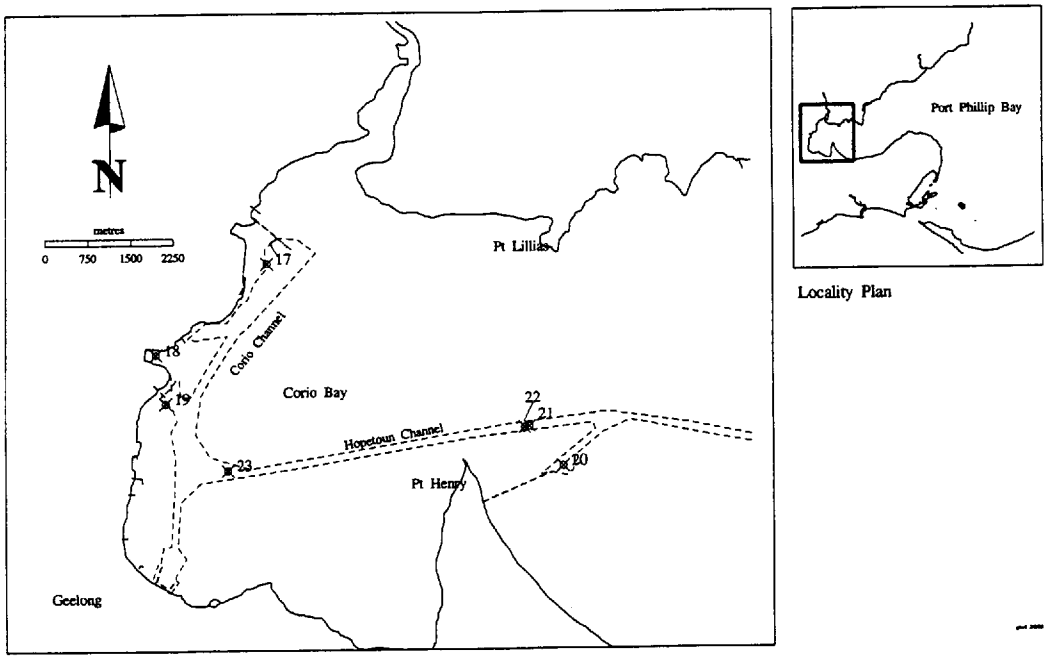

Figure 3. Sites used for the water and ship track (sampled on 23 & 25 /1/1995) study in Corio Bay.

TBT determinations were conducted at the CSIRO Centre for Advanced Analytical Chemistry (Lucas Heights, NSW). TBT was extracted from the sediment with a methanol/hydrochloric acid mixture and determined using atomic absorption spectrometry after derivatisation to hydrides.

Organic components were extracted from sediments by solvent extraction, followed by alumina/silica chromatography cleanup. PAH were determined by reverse phase high performance liquid chromatography (HPLC) with fluorescence detection. The compounds measured were the high molecular weight compounds benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene.

Total petroleum hydrocarbons were determined by gas chromatography (GC) using flame ionisation detection. Compounds eluting in the boiling point range of the C_{12} and C_{32} n-alkanes were measured on the basis of the unresolved complex mixture (UCM). External standards for quantitative calibration consisting of a mixture of equal concentrations of C_{12} to C_{32} even-numbered n-alkanes. N-decylbenzene and n-nonadecylbenzene were used as internal standards to determine recoveries. Owing to an average 79% recovery rate the results have not been corrected for recoveries. One reagent blank sample was analysed with every batch of eleven samples. The detection limit for total petroleum hydrocarbons in the sediment samples was 5 $\mu g\ g^{-1}$ dry weight. The detection limits for individual PAH compounds was 0.001 $\mu g\ g^{-1}$. Single samples were analysed and replication to determine precision was carried out using reference sediment samples.
The surface (0-10 cm) core section from the most contaminated sample from the dock sites (Swanson Dock; site 4, Figure 1) and spoil ground (site 7, Figure 2) were subjected to a standard elutriation test, as set out in the Victorian Trial Dredge Protocol (EPA 1992), in order to determine the potential for mobilisation of each of the key contaminants listed above.

The elutriate samples contained fine suspended particles that remained in suspension after the one hour waiting period had elapsed. The elutriate waters were therefore filtered through a 1 μm pore size glass fiber filter prior to analysis in order to reduce the contribution of toxicants associated with the fine suspended particulate matter.

2.2.2 Water

Partitioning between "dissolved" and "particulate" metal species was achieved by low pressure (<25 kpa) filtration of the water samples through 0.45 μm membrane filters using polycarbonate filtration vessels (Florence and Batley, 1980). Filtrations were performed inside a "clean" room (Fabris and Monahan 1995). Samples were filtered as soon as possible after return to the laboratory and within four days of collection. All untreated samples were stored in the dark at 4^0C.

With the exception of mercury, dissolved metal species (cadmium, chromium, copper, iron, nickel, lead and zinc) were determined by chelation/solvent extraction/back extraction and furnace or flame atomisation atomic absorption spectrometry (Danielsson *et. al*. 1978). No oxidation step was used, therefore only the Cr(VI) form of chromium could be reported. With the exception of mercury, particulate metal species were determined after digestion of the filters and particulate matter with HNO_3/HF (10:1 v/v; Harris and Fabris 1979). Mercury was determined by cold vapour atomic absorption spectrometry (APHA 1992) after samples were oxidised using UV irradiation. The concentration of particulate mercury species was determined by subtracting the mercury concentration in filtered samples from that of unfiltered samples.

TBT determinations were conducted at the CSIRO Centre for Advanced Analytical Chemistry (Lucas Heights, NSW). TBT was extracted from the water with dichloromethane in the presence of tropolone. The TBT was determined by atomic absorption spectrometry after derivatisation to the hydride.

Determinations of petroleum hydrocarbons were carried out on whole (unfiltered) samples. The petroleum hydrocarbons were extracted from four-litre samples with hexane. Total petroleum hydrocarbons (sum of aliphatic and aromatic species) were analysed by GC with flame ionisation detection (GC/FID) using the hexane extract after column chromatography (silica/alumina) cleanup. Compounds eluting in the boiling point range of the C_{12} and C_{32} n-alkanes were determined. External standards for quantitative calibration consisted of a mixture of equal concentrations of C_{12} to C_{32} even numbered n-alkanes. N-decylbenzene and n-nonadecylbenzene were used as internal standards to determine recoveries. Recoveries averaged 79%, therefore, the results were not corrected for the recoveries. One reagent blank was analysed with each batch of ten samples. The detection limit for total petroleum hydrocarbons in these samples was 1 μg L^{-1} (PAH were not determined in the aqueous samples).

3. RESULTS AND DISCUSSION

3.1 Sediment

3.1.1 Quality Control

National Research Council of Canada marine sediment standard reference material BCSS-1 (metals other than mercury), PACS-1 (mercury), an in-house marine sediment CSS-2 (metals) were used to determine the precision of the analytical procedures for sediments (Table 1). The concentrated acid digestion procedure used for this work does not necessarily recover the total metal content in the sediments, therefore the results obtained for different components may be lower than the certified values depending on how those components were incorporated in the sediment matrix. Percent recovery of metals was determined by spiking in-house sediment with known concentrations of metals. The coefficient of variation obtained from replicate determinations of the CSS-2 sample varied between 4% (Zn) and 14% (Hg). The coefficient of variation in the alkane response factor for 13 daily runs of the n-alkane standard was 9.5 %. The coefficient of variation for peak retention times of the C_{32} alkane peak was 0.6 %. The mean recovery of the internal standards was 79 ± 13 % (n = 20). The coefficient of variation in the fluorescence response factor for benzo(a)pyrene over the course of sample analyses was 11 % (n = 14). In general, the accuracy (where applicable), spike recovery (Table 1) and repeatability data indicate that the analytical procedure used for this work produced valid results.

3.1.2 Metals and Organics Results

The results of the metal determinations of the sediment samples from the Port of Melbourne and spoil ground are listed in Appendix 2 and the organics data, including the butyltins, are listed in Appendix 3. In all cases most of the material in the samples (>95%) passed through the 200 μm mesh sieve. Visual observations of the material together with its high water content (30 to 65%), indicate that most of the samples could be classed as mixtures of fine sands, silts and clays. The material retained by the sieves consisted mainly of shell grit.

In the Port of Melbourne cores the concentrations of cadmium, chromium, copper, nickel, lead, zinc and mercury are consistently higher than the concentrations of the corresponding elements in cores collected from relatively uncontaminated areas of the Bay during 1993 (Fabris *et al.* 1994). Additionally, unlike the Bay core samples in which concentrations of copper, lead and zinc decreased with increasing depth, the metal and organics concentrations within the Port of Melbourne core segments did not change appreciably or consistently with depth. Dredging in the Port of Melbourne is carried out using a cutter-suction dredge that typically removes a 30 cm thick layer of material. Therefore the material that is deposited at the spoil ground would consist mostly of material contaminated with metals and organics having concentrations greater than those that occur in Bay sediments generally.

Table 1. Results of metals determinations in quality control sediment samples analysed with the Port samples. Units μg g^{-1} dry weight (Fe is in %)[a].

Variable	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Hg
BCSS-1									
Mean (n = 2)	0.25	54.6	16.9	3.28	115.4	49.4	19.5	125	
Certified value (National Research Council of Canada)									
	0.25	123	18.5	3.37	229	55.3	22.7	119	
±95% confidence limit	0.04	14	2.7	0.10	15	3.6	3.4	12	
CSS-2 (In-house sediment quality control sample)									
Mean (n = 18)	<0.1	27.8	12.2	1.53	68	14.7	15.2	71	0.07
SD		1.9	0.9	0.13	7	0.7	1.4	3	0.01
% CV		7	7	9	10	5	9	4	14
% Recovery of spike	119	116	101			96	98	97	
PACS-1									
Mean (n=6)									4.95
SD									0.44
Certified value (National Research Council of Canada)									4.57
±95% confidence limit									0.16

a. the concentrated acid digestion procedure does not necessarily extract all metals in the sediment matrix, hence the results obtained by this procedure are likely to be lower than the certified values, depending on how the metals are incorporated into the sediment matrix.

Preliminary statistical comparisons of means (Waller-Duncan K-ratio t-test using natural logarithm transformed data) of each site (excluding the Appleton Dock sample) in which the data from the core sections were treated as replicate samples indicated that the samples could be grouped into three areas based on their toxicant concentrations as follows:

- Port of Melbourne area based on the five Port of Melbourne samples;
- spoil ground north based on the three samples from the northern half of the spoil ground; and,
- spoil ground south based on the three samples from the southern half of the spoil ground.

On this basis, the concentrations of toxic substances in sediments from the Port of Melbourne, the northern and the southern spoil ground areas were collectively compared to each other. A general linear model (GLM, SAS Institute Inc, Cary, NC USA) analysis was used in which the core section data from each site were nested within each area (i.e. the core sections were treated as repeated measures). For each variable (Cd, Cu, TPH etc.) the core section nested within area term in the model [model = area + core-section(area) + error] was used as the error term to test the null hypothesis of no difference between the means of the areas. The analyses were carried out using natural logarithm transformed data. For each variable Duncan's multiple range test was used to assess differences between means for the three areas.

The results of the statistical analysis (Table 2) indicate that the sediment samples from the spoil ground south area have significantly lower concentrations of cadmium, chromium, copper, manganese, nickel, lead, zinc, TPH and TBT than sediment samples from the Port of Melbourne area. The comparatively high TBT mean for the Port of Melbourne area was the result of the high concentrations in two samples from the Swanson Dock core (Site 4, Figure 1) which contained two segments at 11-20 cm and 21-30 cm with concentrations of 12.0 and 0.650 $\mu g\ g^{-1}$ TBT as tin respectively (Appendix 3). These concentrations are orders of magnitude greater than those found in the other sediment samples, most of which had concentrations below 10 $ng\ g^{-1}$ TBT as tin. (Appendix 3). The high TBT concentrations in the two core segments from Swanson Dock are comparable to the elevated concentrations that were found in sediments from some Victorian marinas prior to the introduction of restrictions on the use of TBT in antifouling formulations (Daly and Fabris 1993). The occurrence of elevated TBT concentrations in the middle sections of the Swanson Dock core indicates that while TBT concentrations in the sediments from the Port are likely to be low, there may be localised areas with very high concentrations. The extent of such localised contamination and assessment of potential adverse effects could only be determined by a more comprehensive sampling scheme than was used in the present study. If these two high values are excluded, the mean for the Port of Melbourne areas becomes 0.032 $\mu g\ g^{-1}$. In this case the differences between means are not significant. Iron, dibutyltin (DBT), monobutyltin (MBT) and total PAH concentrations were similar for all three areas. Mercury concentrations in the spoil ground south area were intermediate between the Port of Melbourne (higher) and spoil ground north (lower) areas.

The comparison with the spoil ground north area is more complex. Mean cadmium, lead and zinc concentrations were similar to the concentrations of these variables in the Port of Melbourne area, but higher than those for the spoil ground south area. The TPH concentration was higher than that of the spoil ground south area, but lower than that of the Port of Melbourne area. The concentrations of copper, manganese, nickel, and TBT were similar to those of the spoil ground south area. Mercury concentrations were higher in the spoil ground south area. Chromium concentrations were intermediate between those from the other two areas. The mean cadmium, copper, lead, zinc, mercury and TPH concentrations from the Port of Melbourne, spoil ground north and spoil ground south (except perhaps for zinc) are higher than the corresponding mean Bay-wide concentrations (Table 3). The mean chromium, iron and manganese concentrations in Bay-wide sediments are higher than the respective concentrations in the Port of Melbourne and spoil ground sediments. The concentrations of cadmium, lead, zinc and petroleum hydrocarbons in sediments from the spoil ground south area were lower than the respective concentrations in sediments from the spoil ground north area. These results suggest that:

- spoil from Port of Melbourne dredging operations has been dumped predominantly in the northern half of the spoil ground, and;
- The surface (0 - 40 cm) sediments of the spoil ground as a whole have progressively become more contaminated with cadmium, copper, lead, zinc and petroleum hydrocarbons compared to the surrounding Bay-wide sediments.

Table 2. Comparison of toxicant concentrations in sediments from Port of Melbourne, spoil ground north and spoil ground south using Duncan's multiple range test (alpha = 0.05 and confidence = 0.95). The Type III SS general linear model significance level *P* is indicated. Tests were performed on natural logarithm transformed data. Values in the Table are arithmetic least squares means. Data are μg g^{-1} dry weight (Fe is %).

Variable	Port of Melbourne[a]	Spoil ground north[a]	Spoil ground south[a]	*P* (d.f.=2)	Sediment Quality ERL[b]	Sediment Quality ERM[b]
Cd	0.57^{A}	0.44^{A}	0.20^{B}	0.0015	1.2	9.6
Cr	34.8^{A}	30.3^{AB}	28.1^{B}	0.032	81	370
Cu	48.5^{A}	34.3^{B}	26.1^{B}	0.0001	34	270
Fe	1.97^{A}	1.96^{A}	1.96^{A}	0.9840	nd	nd
Mn	73.8^{A}	59.3^{B}	51.8^{B}	0.0002	nd	nd
Ni	28.8^{A}	23.7^{B}	22.0^{B}	0.0067	20.9	51.6
Pb	89.7^{A}	74.2^{A}	43.2^{B}	0.0122	46.7	218
Zn	246^{A}	194^{A}	113^{B}	0.0005	150	410
Hg	0.46^{A}	0.24^{B}	0.32^{AB}	0.0574	0.15	0.71
TPH	546^{A}	282^{B}	150^{C}	0.0002	nd	nd
TBT[c]	0.647^{A}	0.0053^{B}	0.0043^{B}	0.0207	nd	nd
DBT	0.0257^{A}	0.0081^{A}	0.0043^{A}	0.1138	nd	nd
MBT	0.0103^{A}	0.0065^{A}	0.00103^{A}	0.7689	nd	nd
Total PAH	1.26^{A}	0.92^{A}	0.67^{A}	0.2432	1.70[d]	9.60[d]

a. for each variable, areas with the same superscript letters are not significantly different from each other. Common superscripts (e.g. AB) indicate that the mean at that area was not different to the means of either of the other two areas.
b. Long *et al*. (1995). ERL - Effects Range Low designated by the lower 10^{th} percentile of biological effects data. ERM - Effects Range Median designated by the 50^{th} percentile of effects of biological effects data.
c. mean TBT for Port of Melbourne is 0.032 μg g^{-1} if two high values from Swanson Dock core (Appendix 3) are excluded
d. high molecular weight PAH (as determined in this study).
nd. no data.

The sediments from the Port of Melbourne area contained concentrations of copper, nickel, lead, zinc and mercury that exceed the 10^{th} percentile of biological effects data (ERL, Table 2). The sites from the northern half of the spoil ground contained levels of nickel, lead, zinc and mercury that exceed ERL data. Nickel and mercury from all three areas exceed the ERL data. However, none of the areas exceed the 50^{th} percentile of biological effects data (ERM, Table 2). ERL and ERM data for butyltin compounds and TPH are not available.

The PAH concentrations within each of the three areas (i.e. Port of Melbourne, spoil ground north and spoil ground south; Appendix 3) varied widely and there were no significant differences between means of total (i.e. sum of concentrations of the eight individual compounds) PAH (Table 2). PAH in Bay-wide sediments vary, but sediments from a site north of the Port of Melbourne spoil ground had some of the highest PAH concentrations [total PAH at site 18 = 4.11 μg g^{-1} (Good and Gibbs 1995)] found in Bay-wide sediments (excluding inputs sites).

Sediments from the Port of Geelong shipping channels had comparably lower concentrations of cadmium, copper, lead, zinc, mercury, TPH, PAH and TBT than those from the Port of Melbourne (Table 3). The mean total PAH concentrations reported for the shipping channels within the Inner Harbour (Table 3) were lower than previously reported (e.g. 0.17 to 1.29 μg g^{-1}; Fabris *et al.* 1992). Nickel in the Inner Harbour channel, the Inner Harbour spoil ground, and the Outer Harbour channel exceeds the ERL value listed in Table 2. Lead in the Inner Harbour spoil ground would also exceed the ERL if the mean is calculated after including one sample with a high lead concentration (Table 3)

Table 3. Mean toxicant concentrations in sediments from the Port of Melbourne and Port of Geelong shipping channels and spoil grounds, and in Bay-wide sediments. Units μg g^{-1} dry weight, unless otherwise stated.

Variable	PMA[a] (Port)	PGA[b] (Inner Harbour)		PGA[b] (Outer Harbour)		Bay-wide[d]
		channel	spoil grnd	channel	spoil grnd	
Cd	0.57	0.13	0.36	0.05	0.05	0.14
Cr	34.8	45.3	31.6	25.7	21.8	41.5
Cu	48.5	9.7	3.7	8.8	2.6	7.4
Fe %	1.97	3.29	2.58	2.7	1.66	3.1
Mn	73.8	232	84.7	153	63.1	86.9
Ni	28.8	51.9	39.3	25.8	15	23.3
Pb	89.7	30.5	40.8[c]	14.6	11.9	16
Zn	246	37.9	39.9	22.5	22.2	106.7
Hg	0.42	0.1	0.08	0.04	0.02	0.09
TPH	546	50	1.1	12.4	2.6	25.8[e]
TBT	0.032[f]	0.0004	0.0001	0.002	0.0001	nd
Total PAH	1.26	0.11	0.18	0.05	0.04	0.77[e]

nd = no data.

a. mean toxicant concentrations based on data obtained during this work.
b. mean toxicant concentrations based on data from PGA (1993b).
c. one sample with a lead concentration of 177 μg g^{-1} was omitted. If this high sample is included the mean concentration is 73.6 μg g^{-1}.
d. mean of data in Appendix 6 of Fabris *et al.* (1994), but excluding the nine shoreline locations.
e. Good and Gibbs (1995). PAH value is the mean of 33 Bay-wide sites and includes low molecular weight PAH.
f. the two high values from the Swanson Dock core (Appendix 3) were omitted, otherwise the mean value would be 0.647 μg g^{-1}.

Table 4 shows summary data from previous studies of toxicant concentrations in sediments from the Port of Melbourne and spoil ground areas. Generally the metals data are comparable to those obtained during the current study. However, widely different results have been found for TPH. The data obtained during the present study are in general agreement with those obtained by Burns and Smith (1982), and PMA (1989). These results are much higher than data reported in PMA (1991) and PMA (1993). The Port of Melbourne area previously has and continues to support frequent shipping traffic, crude oil transfer and bunkering. Spillages during these operations have been reported (D. Palmer 1995, Victorian Marine Pollution Committee, *pers. comm.*). Therefore it would be expected that the sediments would contain at least detectable levels of petroleum hydrocarbons. Similarly, the TBT concentrations from PMA (1993) appear to be low compared to the data obtained during the present study.

Table 4. Concentrations of toxicants in sediments from Port of Melbourne and near the spoil ground obtained from previous studies. Units are μg g^{-1} dry wt (Fe is %).

Site	Cd	Cr	Cu	Fe	Ni	Pb	Zn	Hg	TPH	PAH	TBT
Victoria Dock area											
1976[a]									955		
1991[b]	0.43	63	42			104	283	0.12	22.4		
1993[b]	0.32	40	26		11	68	280	0.01	<2		<0.01
Near Swanson Dock											
1976[a]									505		
Holden Dock area											
1989[c]	1.1	32		1.5		42	81	0.42	245(<4)	<1	
1991[b]	0.56	89	54			87	212	0.31	28.6		
1993[b]	0.32	48	30		14	44	180	0.1	<2		<0.01
Adjacent to Spoil ground											
1991[b]	1.8	66	54			24	66	0.22	<5		
1993[b]	0.16	44	19		11	26	95	0.21	<2		<0.01
Spoil ground region											
1993[d]	0.12	59	13	4.9	39	27	158	0.13			
1993[e]									27	2.1	
Current Study[f]											
Port of Melbourne	0.57	34.8	48.5	1.97	28.8	89.7	246	0.46	546	1.26	0.032
spoil ground north	0.44	30.3	34.3	1.96	23.7	74.2	194	0.24	282	0.92	0.005
spoil ground south	0.20	28.1	26.1	1.96	22.0	43.2	113	0.32	150	0.67	0.004

a. Burns and Smith (1982) sites 16 and 17.
b. PMA work carried out during 1991 and 1993.
c. PMA work carried out during 1989. The TPH result is a mean of 4 samples, a fifth sample had a result below the detection limit indicated in parentheses.
d. Fabris *et al*. (1994). The data are means of values from sites 15, 16 and 17 listed in Appendix 6 of the report.
e. Good and Gibbs (1995). The data are means of values from sites 15, 16 and 17 listed in Appendix 2 of the report.
f. from Table 2.

The top 20 cm of sediment from the Swanson Dock (Site 4, Figure 1) and from the spoil ground (Site 7, Figure 2) were among the most contaminated in terms of metals, petroleum hydrocarbons and butyltin compounds (Appendices 2 and 3). To assess whether any of the contaminants present in these sediments could be readily leached into the water column during dredging and disposal operations the sediments were subjected to an elutriation test as specified in the Victorian Trial Dredge Protocol (EPA 1992, Schedule A). The weight to weight ratio of water to sediment specified by the Protocol is 4:1. The metals results for the Swanson Dock sample (Table 5) were comparable to Bay-wide concentrations of dissolved metal species (Fabris and Monahan 1995). The butyltin data were also very low, and the TBT concentration was below the detection limit. The elutriate from the spoil ground site had higher concentrations of most of the metals, TPH and butyltin compounds than the Swanson Dock sample. The high iron concentration in this sample suggests that the elevated concentrations in this elutriate sample might be associated with fine suspended matter that passed through the 1 μm pore size glass fiber filters used to filter the samples.

Overall, the results of the elutriation test carried out during this study were lower than previously reported for samples from the Port of Melbourne area (Table 5). On the basis of the results from the present study (and taking into account the dilution factors that are involved) it is unlikely that any dissolved metal, TPH and TBT species that might be released into the water column during dredging or disposal of the sediments at the spoil ground will significantly alter existing concentrations of dissolved species of these substances in the water column.

However, since the sediments dredged from the Port of Melbourne consist primarily of fine material, it is likely that contaminated suspended matter resulting from the dredging and spoil dumping operations could remain in the water column (as evidenced by the results of the elutriation test of the spoil ground sediment) long enough to be transported further afield than the immediate dredging or dumping area.

Table 5. Toxicant concentrations in waters obtained from elutriate tests using sediments from the Port of Melbourne and spoil ground. Units are μg L^{-1} (butyltin compounds are in ng L^{-1} as tin)

Site (number; Figures 1 and 2)	Toxicant concentration in elutriate solution											
	Cd	Cr	Cu	Fe	Ni	Pb	Zn	Hg	TPH	TBT	DBT	MBT
This study												
Swanson Dock (4)	0.01	0.1	0.6	2.0	2.5	0.3	1.6	0.003	12	<0.3	1.7	2.5
Spoil ground (7)	0.06	0.1	3.8	1624	3.8	4.2	13.2	0.02	32	8.7	4.5	17
Previous work												
Holden Dock[a]	<10	<10		220		<10	<10	<1				
(0-50cm)		10		9100			450	2				
Victoria Dock[b]												
1991	<0.1	2.5	4			13	25	0.1	<10			
1993	<0.3	<1	6		<2	1	<2	<0.01	0.9	<0.02		
Near Holden Dock[b]												
1991	<0.1	17	8			3	21	0.2	55			
1993	<0.3	<1	4.4		<2	<1	5	<0.01	0.9	<0.02		
Adjacent to Spoil ground[b]												
1991	0.15	33	16			2	71	0.25	<10			
1993	<0.3	1	1.5		<2	<1	140	<0.01	0.5	<0.02		

a. PMA, work carried out during 1989
b. PMA, work carried out during 1991 and 1993.

3.1.3 Toxicant Loads in Dredged Material

3.1.3.1 Port of Melbourne

On average, maintenance dredging in the Port of Melbourne removes about 200,000 m^3 to 250,000 m^3 of material annually. Additional material may be occasionally dredged because of capital works programs (Captain Tim Muir, PMA, *pers. comm.*). Table 6 shows that between 1987 and 1994 an annual average of 335,063 m^3 of material was dredged from the Port of Melbourne. All of this material was deposited in the Port Phillip Bay spoil ground (Figure 2).

Most of the dredging (78%) during this period was carried out in the areas north of the Westgate Bridge. All of the sediment samples for the Port of Melbourne study were collected north of the Westgate Bridge.

Table 6. Summary data for dredging operations in the Yarra River area of the Port of Melbourne for the period September 1987 to November 1994[a]

Year	Volume dredged m^3 (whole port)	Volume dredged m^3 (north of Westgate Bridge)	Volume dredged m^3 (south of Westgate Bridge)
1987	131470	44621	86849
1988	757777	569073	188704
1989	394722	323967	70755
1990	445500	397200	48300
1991	475633	464083	11550
1992	143400	130300	13100
1993	24900	23300	1600
1994	307104	150055	157049
Annual mean	335063	262825	72238
% of total		78	22

a. summary of data supplied by PMA.

Measurements on three sediment samples indicated that the sediments from the Port of Melbourne contain 540 kg of dry material per cubic metre of wet sediment. This value, together with the data from Tables 3 and 6, was used to calculate the annual loads of toxic substances that are transported from the port to the spoil ground as a result of dredging activities (Table 7).

Comparison of the mean annual metal loads contained in sediments dredged from the Port of Melbourne with loads contained in an equivalent volume of Bay-wide sediments shows that cadmium, copper, lead and mercury loads in the Port of Melbourne sediments exceed those in Bay-wide sediments by a factor of three or more (Table 7). TPH loads in the Port of Melbourne sediments are about 21 times greater than the load in comparable volumes of Bay-wide sediments (Table 7). To place these results in perspective, available data indicates that the mean annual metal loads contained in the dredged sediments from the Port of Melbourne (excepting manganese) are lower than the annual loads of metals that enter the Bay from streams, drains and the Western Treatment Plant (Table 7). Input streams loads for petroleum hydrocarbons are not available at the time of writing, but reported spills (from ships) in the whole of Port Phillip Bay amount to approximately 15 tonnes of oil annually (D. Palmer 1995, Victorian Marine Pollution Committee; *pers. comm*.).

3.1.3.2 Port of Geelong

Maintenance dredging of the shipping channels within the Inner Harbour (Corio Bay) and Outer Harbour (Geelong Arm) has been carried out periodically since the shipping channels were created *circa* 1854. Cutting of the channels and their maintenance since then has involved the dredging and disposal of about 20 million m^3 of material (PGA 1993a).

Additional proposed works to increase the depth of the shipping channels from 11m to 12m will involve the dredging and disposal of about 2.1 million m^3 of material from the Inner Harbour and about 3 million m^3 of material from the Outer Harbour (Table 8). It is intended that sediments dredged from the Inner Harbour will be disposed of at a new spoil ground within the Inner Harbour and spoil from the Outer Harbour will be disposed of at a new spoil ground located in the Outer Harbour.

Table 7. Estimates of toxicant loads contained in sediments that are dredged or proposed to be dredged from the Ports of Melbourne (annual mean) and Geelong (channel improvement) compared to toxicant loads in equivalent volumes of Bay sediments and estimated annual loads entering the Bay from streams. Units in tonnes.

Toxicant	PMA[a]	Bay-wide[a] (PMA volume)	PGA[b]				Load from stream inputs (incl. WTP)[c]
			PGA (inner channel)	PGA (inner spoil)	PGA (outer channel)	PGA (outer spoil)	
Cd	0.1	0.03	0.15	0.41	0.08	0.08	0.33
Cr	6.3	7.5	51.1	35.7	42.0	35.6	16.5
Cu	8.8	1.3	10.9	4.2	14.3	4.2	17.3
Fe	3564	5609	37095	29090	44105	27116	3788
Mn	13.4	15.7	261.4	95.4	249.2	103.1	nd
Ni	5.2	4.2	58.5	44.3	42.1	24.5	14.1
Pb	16.2	2.9	34.4	46.0[d]	23.9	19.4	31.1
Zn	44.5	19.3	42.8	45.0	36.8	36.2	126.8
Hg	0.08	0.02	0.1	0.09	0.07	0.03	0.1
TPH	95	4.7	56.5	1.2	20.3	4.2	nd
PAH	0.23	0.14	0.13	0.20	0.08	0.07	nd
TBT	0.006	nd	0.0005	0.0001	0.003	0.0002	nd

nd = no data.

a. calculated from data in Tables 3 and 6 and assuming 540 kg of dry material per m^3 of wet sediment.

b. calculated from data in Tables 3 and 8 and assuming 540 kg of dry material per m^3 of wet sediment.

c. from Table 12 in Fabris and Monahan (1995).

d. 83 tonnes if the high lead concentration (note d, Table 3) is used.

Table 8. Summary data for the proposed dredging operations for the channel improvement in the Port of Geelong[a].

Volume dredged m^3 (whole Port)	Volume dredged m^3 (Inner Harbour)	Volume dredged m^3 (Outer Harbour)
5113000	2088000	3025000

a. PGA (1993a)

The mean concentrations of toxic substances in the sediments of the Inner Harbour channels are generally higher than their respective concentrations in sediments from the Outer Harbour channels (Table 3). Industrial contamination of the Inner Harbour (Phillips *et al*. 1992) accounts for this difference. Similarly, the spoil ground sediments from the Inner Harbour are more contaminated than spoil ground sediments from the Outer Harbour for all variables measured except TPH and TBT (Table 3). TPH concentrations in the channel sediments are greater than those of the respective spoil grounds (45 times in the case of the Inner Harbour and 5 times in the case of the Outer Harbour; Table 3). The respective loads of metals and petroleum hydrocarbons are affected similarly. The petroleum hydrocarbon loads transported to the spoil grounds will therefore increase the concentrations of petroleum hydrocarbons in the spoil grounds, with the Inner Harbour spoil ground being more affected than the Outer Harbour spoil ground.

Sediment samples from the Port of Geelong were subjected to elutriate tests as part of the EES program (PGA 1993b). The analytical methods used to determine the toxic components in the elutriate samples were not sensitive enough to detect components at naturally occurring concentrations. The results of these elutriate tests cannot be considered conclusive since most of the toxic substances were found to be below the detection limits. The issue was highlighted for cadmium (PGA 1993b), which has been a problem metal in both the Inner and Outer Harbours during the past 20 years (Phillips *et al.* 1992). The overall conclusion reached in the EES document was that dredging of channel sediments was unlikely to cause adverse environmental effects (PGA 1993b). However, in order to ensure that any adverse effects can be detected, a monitoring program will be implemented before, during and after dredging. This program is designed to provide interactive information so that the Environment Protection Authority can recommend that ameliorative measures be taken if necessary during the implementation of the proposal (PGA 1993a).

3.2 Water

3.2.1 Quality Control

Detection limits for the metal determinations are listed in Table 9. Analytical accuracy was estimated from determinations of:

- a pre-extracted seawater sample spiked with the metals at the $\mu g\ L^{-1}$ level;
- a US EPA quality assurance sample which was diluted in pre-extracted seawater to give metal concentrations in the $\mu g\ L^{-1}$ range;
- US National Institute of Standards and Technology standard reference water samples (1641c - diluted for Hg and 1643c - diluted in pre-extracted seawater); and;
- a National Research Council of Canada nearshore seawater standard reference material (CASS-3).

The mean recoveries of the metals in these determinations ranged between 97% and 117% (Table 10). The coefficient of variation in the alkane response factor for 13 daily runs of the n-alkane standard was 9.5%. The coefficient of variation for peak retention times of the C_{32} alkane peak was 0.6%. The mean recovery of the internal standards was 79 ± 13% (n=20).

Table 9. Detection limits for water samples are based on three times the standard deviation of the blank (n=7; pre-extracted seawater) unless otherwise stated. Data are in μg L^{-1}.

Variable	Concentration ± standard deviation (n=7)	Detection limit
Hg	0.00091±0.00033	0.001
Cd	0.0012±0.0011	0.005
Cr(VI)[a]	0.03±0.0086	0.03
Cu	0.04±0.01	0.03
Fe	0.25±0.02	0.1
Ni	0.024±0.008	0.02
Pb	0.03±0.02	0.1
Zn	0.04±0.04	0.2

a. n=3

Table 10. Results for duplicate determinations of metals in quality control water samples analysed with the Port samples. Units μg L^{-1} (Hg is ng L^{-1})

Sample	Cd	Cu	Fe	Ni	Pb	Zn	Hg
In-house QC: found	0.09	1.19	92.5	2.0	1.08	5.27	
In-house QC: expected	0.13	1.05	105.9	2.01	1.05	5.23	
EPA WP287: found	0.34	1.04	1.25	0.98	1.21	1.01	
EPA WP287: expected	0.25	1.0	1.0	1.0	1.0	1.0	
NIST 1643c: found	0.277	0.85	3.9	2.32	1.405		
NIST 1643c: expected	0.488	0.89	4.28	2.42	1.41		
CASS-3: found	0.042	0.52	2.1	0.37	<0.1	1.16	
CASS-3: expected	0.03	0.517	1.26	0.386	0.012	1.24	
NIST 1641c: found							16.2
NIST 1641c: expected							14.7
Mean % recovery (range)	101 (57-140)	103 (96-113)	117 (87-167)	97 (96-99)	108 (100-121)	98 (94-101)	110

3.2.2 Metals and Organics Results

The results for the metals determinations in waters are listed in Tables 11 to 13. The concentrations of the dissolved and particulate species of each metal in the four Port of Melbourne samples were compared to those of the four samples from the Port of Geelong. Computations were based on the approximate t-test which assumes unequal variances (Sokal and Rohlf 1969).

The concentrations of dissolved cadmium species in the Port of Geelong samples (mean 0.055 μg L^{-1}) were significantly ($P<0.02$) higher than in the Port of Melbourne samples (mean 0.032 μg L^{-1}). The cadmium concentrations in both areas were greater than the Bay-wide mean (0.026 μg L^{-1}, Fabris and Monahan 1995). Dissolved chromium species were not detectable in the waters of either Ports. The elevated cadmium levels in the Port of Geelong is mostly the result of historical inputs (Fabris 1983) and it is unlikely that the contribution from shipping activities is significant. Similarly, the higher mean cadmium concentration from the Port of Melbourne samples compared to the Bay-wide mean concentration is most likely to be the result of catchment inputs *via* the Yarra River as opposed to shipping activities.

Catchment inputs would also be the source of the elevated copper and zinc concentrations in the Port of Melbourne samples compared to both the Port of Geelong and Bay-wide values for these metals. Concentrations of dissolved species of iron, nickel, lead and mercury were similar in the samples from both ports, and apart from lead, not very different from the Bay-wide means for these metals. The mean lead concentration from the Port of Melbourne samples was about one order of magnitude greater than the Bay-wide mean, but individual concentrations within the port varied considerably (Table 11).

Table 11. Comparison of soluble metal species concentrations in waters from the Port of Melbourne and Port of Geelong. Units are μg L^{-1} (ng L^{-1} for Hg).

Site (number; Figs 1 or 3)	Cd	Cu	Fe	Ni	Pb	Zn	Hg
Victoria Dock (13)	0.035	1.74	1.5	1.45	0.26	4.39	1.71
Appleton Dock (14)	0.035	1.14	2.9	0.94	0.41	4.43	1.65
Swanson Dock (15)	0.028	1.48	0.75	1.16	1.48	4.04	5.81
Holden Dock (16)	0.03	1.27	2.4	1.1	0.07	4.62	0.46
Mean	0.032	1.408	1.888	1.163	0.555	4.370	2.408
SD	0.004	0.262	0.954	0.213	0.632	0.242	2.340
Refinery Wharf (17)	0.065	0.77	11.3	1.02	0.23	0.81	2.28
Corio Quay (18)	0.058	0.58	0.5	0.93	0.08	0.55	0.57
Wheat Wharf (18)	0.058	0.66	5.8	0.98	0.26	0.56	1.25
Alcoa Wharf (20)	0.037	0.52	4	0.99	0.07	1.46	3.91
Mean	0.055	0.633	5.400	0.980	0.160	0.845	2.003
SD	0.012	0.108	4.507	0.037	0.099	0.427	1.453
Approximate t-test (n=4) P[a]	<0.02	<0.005	>0.1	>0.1	>0.2	<0.001	>0.5
Outer Harbour: control (21)	0.052	0.62	3.5	0.97	0.16	1.33	1.32
Inner Harbour: control (22)	0.051	0.60	0.8	0.87	0.22	0.31	2.07
Outer Harbour: Ship (22)	0.040	0.54	3.6	1.01	0.16	0.16	1.61
Outer Harbour: Ship (22)	0.058	0.57	0.4	1.01	0.32	0.33	1.61
Inner Harbour: Ship (23)	0.063	0.58	0.8	0.87	0.37	0.37	1.27
Bay-wide mean[b]	0.026	0.47	0.76	0.70	0.06	0.47	1.7
SD	0.014	0.05	0.44	0.14	0.02	0.21	0.7

SD = Standard Deviation

a. assumes that the variances of the two groups are unequal.

b. Fabris and Monahan (1995). Data from Appendix 3 of the report.

The concentrations of particulate species of chromium, copper, iron and zinc in the Port of Melbourne samples were significantly greater than those from the Port of Geelong samples (Table 12). Catchment input *via* the Yarra River would account for most of the load of these metals in the port of Melbourne. Particulate cadmium species were not detectable in any of the samples. Table 13 shows the concentrations of total metal species (sum of data from Tables 11 and 12) for the water samples taken in the current study.

Table 12. Comparison of particulate metal species concentrations in waters from the Port of Melbourne and Port of Geelong. Units are μg L^{-1} (ng L^{-1} for Hg). Cadmium was not detected in the particulate matter.

Site (number; Figures 1 and 3)	Cr	Cu	Fe	Ni	Pb[a]	Zn	Hg
Victoria Dock (13)	0.27	0.20	54	0.27	<1	6.47	0.20
Appleton Dock (14)	0.25	0.20	65	0.32	<1	2.79	1.19
Swanson Dock (15)	0.32	0.22	97	0.16	<1	5.60	0.20
Holden Dock (16)	0.33	0.19	91	0.24	<1	2.74	2.67
Mean	0.29	0.20	76.8	0.25		4.40	1.07
SD	0.04	0.01	20.6	0.07		1.92	1.17
Refinery Wharf (17)	0.15	0.05	28	0.03	<1	0.15	9.62
Corio Quay (18)	0.06	0.08	28	0.05	<1	0.19	1.31
Wheat Wharf (18)	0.21	0.07	72	0.18	<1	0.30	1.82
Alcoa Wharf (20)	0.15	0.03	18	0.31	<1	0.16	0.20
Mean	0.14	0.06	36.5	0.14		0.20	3.24
SD	0.06	0.02	24.1	0.13		0.07	4.31
Approximate t-test (n=4) P[b]	<0.01	<0.001	<0.05	>0.2		<0.005	>0.5
Outer Harbour: control (21)	0.24	0.01	15	0.27	<1	0.12	<1
Inner Harbour: control (23)	0.23	0.02	36	0.31	<1	0.19	<1
Outer Harbour: Ship (22)	0.65	0.10	159	0.38	<1	0.34	<1
Outer Harbour: Ship (22)	0.31	0.04	43	0.39	<1	0.20	<1
Inner Harbour: Ship (23)	0.37	0.03	36	0.38	<1	0.21	<1
Bay-wide mean[c]	0.09	0.03	29	0.05	0.13	0.11	1.32
SD	0.06	0.02	19	0.05	0.14	0.08	1.30

SD = Standard Deviation

a. blanks were high and variable, these samples were probably contaminated.
b. assumes that the variances of the two groups are unequal.
c. Fabris and Monahan (1995). Data from Appendix 3 of that report.

The concentrations of butyltin compounds and total petroleum hydrocarbons were similar in samples from both ports (taking into account the variability of individual results at each area), and within the range of concentrations previously found in the Bay (Table 14).

Table 13. Comparison of total metal species concentrations in waters from the Port of Melbourne and Port of Geelong. Units are μg L^{-1} (ng L^{-1} for Hg). Lead was not included because of contamination of particulate lead data.

Site (number; Figures 1 and 3)	Cd	Cr	Cu	Fe	Ni	Zn	Hg
Victoria Dock (13)	0.04	0.27	1.94	55.5	1.72	10.9	1.65
Appleton Dock (14)	0.04	0.25	1.34	67.9	1.26	7.22	2.84
Swanson Dock (15)	0.03	0.32	1.7	97.8	1.32	9.64	2.73
Holden Dock (16)	0.03	0.33	1.46	93.4	1.34	7.36	3.13
Mean	0.032	0.29	1.61	78.7	1.41	8.8	2.59
SD	0.004	0.04	0.27	20.3	0.21	1.8	0.65
Refinery Wharf (17)	0.06	0.06	0.66	28.5	0.98	0.74	1.88
Corio Quay (18)	0.06	0.21	0.73	77.8	1.16	0.86	3.07
Wheat Wharf (19)	0.04	0.15	0.55	22.0	1.30	1.62	0.69
Alcoa Wharf (20)	0.06	0.14	0.69	41.9	1.12	1.05	4.39
Mean	0.06	0.14	0.66	42.6	1.14	1.07	2.51
SD	0.01	0.06	0.08	24.9	0.13	0.39	1.59
Outer Harbour: control (21)	0.05	0.24	0.63	18.5	1.24	1.45	1.43
Inner Harbour: control (23)	0.05	0.25	0.62	36.8	1.18	0.50	1.49
Outer Harbour: Ship (22)	0.04	0.65	0.64	163	1.39	0.50	1.04
Outer Harbour: Ship (22)	0.06	0.31	0.61	43.4	1.40	0.53	1.55
Inner Harbour: Ship (23)	0.06	0.37	0.61	36.8	1.25	0.58	1.38
Bay-wide mean[a]	0.04	0.13	0.50	30	0.76	0.57	2.90
SD	0.02	0.07	0.06	19	0.15	0.26	1.29

SD = Standard Deviation

a. Fabris and Monahan (1995). Data from Appendix 3 of that report.

The concentrations of metals (Tables 11, 12 & 13), tributyltin and total petroleum hydrocarbons (Table 14) in water samples collected from behind moving freighters were similar to control samples. The concentration of particulate iron species was higher than the control samples on one of the three occasions. This was, in all probability, the result of an increase in suspended matter that had been stirred from the bottom sediments as the ship moved along the channel. The results indicate that any toxicants that may be released by ships as they move through the Bay are not detectable by the methods used in this work.

5. CONCLUSIONS

5.1 Sediment

Sediments in the Port of Melbourne contain elevated concentrations of metals (copper, nickel, lead, zinc and mercury) and petroleum hydrocarbons compared to Bay-wide sediments and to sediment quality guidelines published in the scientific literature. Concentrations of butyltin compounds are generally low, but some sediments contain very high concentrations suggesting that the contamination is not widely or evenly distributed within the Port. Dumping of sediments dredged from the Port of Melbourne in the spoil ground located in the northern part of the Bay has resulted in elevated concentrations of metals and petroleum hydrocarbons and to a lesser extent butyltin compounds in the spoil ground sediments.

Table 14. Comparisons of tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT) and total petroleum hydrocarbons (TPH) in waters from the Port of Melbourne and Port of Geelong. Units ng L^{-1} as tin for organotin species and µg L^{-1} for TPH.

Site (site number Figures 1 and 3)	TBT	DBT	MBT	TPH
Victoria Dock (13)	<0.3	6.6	30	0.53
Appleton Dock (14)	<0.3	2.6	6.4	0.51
Swanson Dock (15)	1.1	2.9	8.0	0.62
Holden Dock (16)	1.4	14	34	0.37
Mean[a]	0.7	6.5	19.6	0.51
SD	0.6	5.3	14.4	0.10
Refinery Wharf (17)	11	6.0	4.3	0.55
Corio Quay (18)	9.3	5.4	13	0.69
Wheat Wharf (19)	<0.3	2.6	3.3	0.63
Alcoa Wharf (20)	7.6	5.4	17	0.29
Mean[a]	7.0	4.9	9.4	0.54
SD	4.8	1.5	6.7	0.18
Outer Harbour: control (21)	6.9	3.3	7.8	0.05
Inner Harbour: control (23)	4.0	2.9	15	0.88
Outer Harbour: Ship (22)	<0.3	1.7	2.4	0.93
Outer Harbour: Ship (22)	7.5	0.4	2.2	0.44
Inner Harbour: Ship (23)	0.3	0.3	3.0	0.72
Central Bay (1988)[b]	1	6	9	
Central Bay (1990-91)[b]	2-9	2.6-6.1	3-8.3	
Hobsons Bay (1990-91)[b]	<0.2-11	3.4-6.1	3-8.3	
Bay-wide[c]				0.02 - 2.1

SD = Standard Deviation

a values below the detection limit were arbitrarily assigned a value of one half of the detection limit. This approach tends to positively skew the summary data (Helsel 1990)

b. Daly and Fabris (1993)

c. Good (1994)

The northern half of the spoil ground is more adversely affected than the southern half. The concentrations of nickel and mercury in the sediments of the spoil ground are such that they could cause adverse biological effects to biota inhabiting the sediments.

It is unlikely that leaching of dissolved toxicants from the sediments into the water column during dredging operations is a problem. However, the suspension of fine material during dredging and dumping operations could be spreading contaminated sediments further afield than the immediate area of the port and spoil ground.

The concentrations of most metals and also petroleum hydrocarbon and butyltin compounds in the sediments from the shipping channels of the Port of Geelong are low in comparison to those in the Port of Melbourne (Table 3). However, because the volume of material to be dredged from the Port of Geelong is approximately 15 times greater, the total loads of metals and petroleum hydrocarbons are comparable to those of the Port of Melbourne (Table 7).

In relative terms, the loads, with the exception of petroleum hydrocarbons, are comparable to the loads contained in equivalent volumes of respective spoil ground sediments (Table 15). The petroleum hydrocarbon loads transported to the Inner Harbour and Outer Harbour spoil grounds will be 47 and 4.8 times greater respectively (Table 15). Early warning of any unforeseen adverse effects of toxicants should be obtained from the monitoring program that will be implemented before, during and after the dredging proposal.

The annual load of metals such as cadmium, copper, lead and mercury and petroleum hydrocarbons transported from the Port of Melbourne to the spoil ground is greater than the load contained in an equivalent volume of Bay sediments (Table 15), but less than the annual load that enters the Bay from rivers, streams, and drains and the Western Treatment Plant (Table 7).

Table 15. Ratio of toxicant load in dredged sediment compared with the load contained in an equivalent volume of Bay-wide sediment (Port of Melbourne) or spoil ground sediment (Port of Geelong)[a].

Variable	Melbourne Port	Geelong Inner Harbour	Geelong Outer Harbour
Cd	3.3	<1	1
Cr	<1	1.4	1.2
Cu	6.5	2.6	3.4
Fe	<1	1.3	1.6
Mn	<1	2.7	2.4
Ni	1.2	1.3	1.7
Pb	5.6	<1	1.2
Zn	2.2	<1	1.0
Hg	4	1.1	2.3
TPH	20.2	47	4.8

a. derived from Table 7.

5.2 Water

The toxicant concentrations in the waters of the port areas are influenced primarily by historical factors (e.g. Cd in the Inner Harbour of the Port of Geelong) or catchment inputs (Pb and Zn in the Port of Melbourne). Direct contamination of the water column by normal shipping operations (i.e. excluding spills and discharges) was not detected during the course of this study.

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APPENDIX 1. Decimal latitude and longitude coordinates for the sediment and water sampling sites used in this study.

Site number (Figures 1, 2 and 3)	Date sampled	Sample type	Latitude south	Longitude east
1	12/12/94	sediment	144.942398	-37.823837
2	12/12/94	sediment	144.937866	-37.819221
3	12/12/94	sediment	144.920853	-37.818504
4	12/12/94	sediment	144.912689	-37.818687
5	12/12/94	sediment	144.904724	-37.820625
6	12/12/94	sediment	144.902740	-37.824589
7	12/12/94	sediment	144.883301	-37.983299
8	12/12/94	sediment	144.889999	-37.991695
9	12/12/94	sediment	144.880005	-37.996700
10	12/12/94	sediment	144.873306	-38.006699
11	12/12/94	sediment	144.878296	-38.016701
12	12/12/94	sediment	144.865005	-38.023300
13	23/01/95	water	144.941589	-37.817112
14	23/01/95	water	144.923447	-37.818424
15	23/01/95	water	144.912994	-37.817101
16	23/01/95	water	144.902039	-37.825951
17	23/01/95	water	144.384995	-38.093601
18	23/01/95	water	1144.36399	-38.115700
19	23/01/95	water	144.362350	-38.107758
20	25/01/95	water	144.443466	-38.127811
21	25/01/95	water (ship)	144.436859	-38.121342
22	25/01/95	water (ship)	144.435867	-38.121445
23	25/01/95	water (ship)	144.375900	-38.126793

APPENDIX 2. Metal concentrations in sediment cores from the Port of Melbourne (Figure 1) and spoil ground (Figure 2). Units are µg g^{-1} dry weight of whole sediment (Fe is in %).

Site name (number, Figure 1)	Core Section (cm)	Water content %	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Hg
North Wharf	0-10	65.1	0.39	29	41	1.64	53	21	102	351	0.21
(1)	11-20	59.1	0.61	24	45	1.47	65	20	148	427	0.2
	21-30	56.8	0.74	25	58	1.67	65	22	187	516	0.29
	31-40	60.8	0.34	24	38	1.72	78	19	116	345	0.19
Victoria Dock	0-10	52.8	0.36	37	43	1.92	101	29	76	190	0.45
(2)	11-15	39.1	0.31	28	26	1.89	81	29	28	107	0.19
	16-20	30.9	0.05	27	23	1.79	86	29	13	73	0.11
	21-25	34.6	0.42	34	35	1.86	88	29	48	133	0.36
Appleton Dock	0-10	44	0.08	27	22	2.6	52	21	28	97	0.26
(3)											
Swanson Dock	0-10	52.2	0.41	31	49	2.06	55	24	77	224	0.34
(4)	11-20	58.7	0.5	35	50	2	53	24	76	229	0.44
	21-30	55.9	0.47	29	46	2.3	59	22	69	219	0.31
	31-40	61.9	0.37	32	44	2.08	53	23	82	223	0.26
Yarraville Dock	0-10	59	1.13	45	62	2.14	94	34	115	236	0.99
(5)	11-19	55.7	1.05	51	65	2.12	84	39	113	281	0.43
	20-24	52.5	1.45	51	78	1.97	78	38	132	314	0.42
	25-30	47.5	1.27	48	70	1.9	75	34	138	261	2.23
Holden Dock	0-10	60.5	0.31	35	45	2.09	71	25	62	180	0.4
(6)	11-19	57.5	0.47	39	53	2.23	67	28	82	206	0.71
	20-24	54.9	0.44	38	54	2.19	77	58	74	223	0.5
	25-30	53.9	0.38	34	44	2.36	92	29	56	191	0.24

APPENDIX 2 (continued). Metal concentrations in sediment cores from the Port of Melbourne (Figure 1) and spoil ground (Figure 2). Units are μg g^{-1} dry weight of whole sediment (Fe is in %).

Site (number, Figure 2)	Core Section (cm)	Water content %	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Hg
Spoil Ground North											
(7)	0-10	64.1	0.61	35	45	2.09	53	27	97	268	0.31
	11-20	57.2	0.83	34	48	1.99	51	23	117	297	0.3
	21-30	59.8	0.65	36	42	2.23	57	27	84	215	0.36
	31-40	50.6	0.13	27	27	2.1	48	22	54	127	0.27
(8)	0-10	62.4	0.54	33	42	2.11	56	26	78	208	0.31
	11-20	57.4	0.43	31	40	2.08	51	27	65	190	0.32
	21-30	54	0.87	29	54	1.75	43	24	180	413	0.29
	31-40	52.5	0.77	32	43	2.06	49	27	100	257	0.25
(9)	0-10	56	0.19	23	24	1.76	46	20	50	134	0.17
	11-20	45.6	0.05	21	18	1.87	44	20	24	80	0.14
	21-30	37.3	0.05	16	12	2.14	86	24	11	54	0.05
	31-40	37.1	0.21	21	17	1.35	37	18	30	86	0.11
Spoil Ground South											
(10)	0-10	58.9	0.05	26	25	2.11	64	22	44	103	0.26
	11-20	49.8	0.22	24	43	2.15	80	26	85	141	0.43
	21-30	43.5	0.32	30	30	1.83	39	22	33	107	0.54
	31-40	50.2	0.4	31	31	1.85	44	22	51	116	0.49
(11)	0-10	58.7	0.07	29	23	1.76	55	20	38	109	0.28
	11-20	48.8	0.26	28	27	1.53	43	19	47	120	0.29
	21-30	52.9	0.71	37	45	1.83	62	23	97	245	0.38
	31-40	50.5	0.21	30	22	1.46	55	17	39	97	0.33
(12)	0-10	62.4	0.06	33	18	2.25	71	24	26	88	0.26
	11-20	57.9	0.05	34	18	2.15	49	23	24	83	0.21
	21-30	57.2	0.05	29	16	2.55	65	24	15	80	0.15
	31-40	53.2	0.05	33	15	2.08	85	22	19	71	0.17

APPENDIX 3. Concentrations of total petroleum hydrocarbons (TPH), polynuclear aromatic compounds (PAH)*, tributyltin, dibutyltin and monobutyltin in sediments from the Port of Melbourne (Figure 1) and spoil ground (Figure 2). Units are ng g^{-1} dry weight (µg g^{-1} dry wt for TPH).

Site (number, Figure 1)	Core Section (cm)	TPH*	B[a]A	CHRY	B[b]F	B[k]F	B[a]P	DB[a,h]A	B[ghi]P	I[1,2,3,-cd]P	Total PAH	TBT	DBT	MBT
North Wharf	0-10	558	0.61	0.43	0.63	0.31	0.56	0.03	0.09	0.03	2.69	5.2	16	5.0
(1)	11-20	490	0.41	0.32	0.39	0.21	0.37	0.05	0.44	0.32	2.51	4.4	7.0	0.7
	21-30	689	0.53	0.4	0.39	0.17	0.41	0.04	0.45	0.24	2.63	15	10	4.0
	31-40	614	0.86	0.54	0.44	0.18	0.43	0.04	0.46	0.25	3.20	12	4.5	<0.3
Victoria Dock	0-10	237	0.27	0.19	0.66	0.33	0.78	0.12	0.84	0.48	3.67	7.0	9.5	<0.3
(2)	11-15	269	0.001	0.013	1.19	0.55	1.44	0.001	0.07	0.64	3.91	1.3	0.6	<0.3
	16-20	104	0.13	0.14	0.62	0.34	0.73	0.09	0.53	0.47	3.05	0.4	<0.3	<0.3
	21-25	155	0.49	0.49	3.16	1.81	3.52	0.94	0.51	0.17	11.09	2.0	<0.3	<0.3
Appleton Dock (3)	0-10	59	0.02	0.01	0.05	0.02	0.04	0.03	0.03	0.03	0.23	79	9.2	<0.3
Swanson Dock	0-10	331	0.01	0.002	0.007	0.001	0.001	0.01	0.02	0.03	0.08	68	10	<0.3
(4)	11-20	571	0.01	0.002	0.009	0.003	0.008	0.01	0.02	0.02	0.08	12000	315	130
	21-30	483	0.01	0.001	0.02	0.006	0.005	0.01	0.004	0.01	0.07	650	29	17
	31-40	437	0.005	0.002	0.02	0.004	0.004	0.02	0.03	0.04	0.13	8.1	10	7.9
Yarraville Dock	0-10	596	0.74	0.29	0.21	0.02	0.18	0.001	0.001	0.001	1.44	1.1	8.1	4.4
(5)	11-19	1202	0.001	0.004	0.1	0.04	0.04	0.05	0.08	0.19	0.51	4.3	13	6.4
	20-24	1007	0.05	0.004	0.04	0.01	0.002	0.08	0.101	0.2	0.49	64	37	27
	25-30	2009	0.09	0.003	0.01	0.003	0.004	0.03	0.03	0.05	0.22	<0.3	15	2.4
Holden Dock	0-10	315	0.03	0.001	0.003	0.001	0.01	0.008	0.001	0.02	0.07	16	13	<0.3
(6)	11-19	349	0.69	0.24	0.20	0.024	0.23	0.001	0.19	0.001	1.57	15	8.2	<0.3
	20-24	292	0.001	0.002	0.006	0.002	0.003	0.011	0.007	0.001	0.03	59	4.2	<0.3
	25-30	211	0.001	0.001	0.026	0.009	0.008	0.014	0.028	0.001	0.09	6.3	3.6	<0.3

Tot PAH = sum of 8 individual PAH. B[a]A = benz[a]anthracene, CHRY = chrysene, B[b]F = benzo[b]fluoranthene, B[k]F = benzo[k]fluoranthene, B[a]P = benzo[a]pyrene, DB[a,h]A = dibenzo[a,h]anthracene, B[ghi]P = benzo[ghi]perylene, I[1,2,3,-cd]P = indeno[1,2,3-cd]pyrene.

* the sum of aromatic and aliphatic hydrocarbons eluting within the range of C_{12} and C_{32} alkanes. Internal standard recovery =79 $\pm$13% (n = 20), results not corrected for recovery of internal standards.

APPENDIX 3 (continued). Concentrations of total petroleum hydrocarbons (TPH), polynuclear aromatic compounds (PAH)*, tributyltin, dibutyltin and monobutyltin in sediments from the Port of Melbourne (Figure 1) and spoil ground (Figure 2). Units are ng g^{-1} dry weight (µg g^{-1} dry wt for TPH).

Site (number, Figure 2)	Core Section (cm)	TPH*	B[a]A	CHRY	B[b]F	B[k]F	B[a]P	DB[a,h]A	B[ghi]P	I[1,2,3,-cd]P	Tot PAH	TBT	DBT	MBT
Spoil Ground North														
(7)	0-10	228	0.14	0.085	0.039	0.001	0.083	0.002	0.07	0.001	0.42	5.2	18	<0.3
	11-20	498	0.38	0.16	0.191	0.038	0.21	0.11	0.001	0.001	1.08	3.5	6.6	<0.3
	21-30	408	0.01	0.004	0.003	0.001	0.001	0.008	0.002	0.004	0.03	0.4	18	<0.3
	31-40	181	0.009	0.002	0.02	0.006	0.009	0.02	0.02	0.04	0.13	<0.3	7.5	0.6
(8)	0-10	396	0.11	0.11	1.57	0.09	0.07	0.04	0.43	0.27	2.69	2.2	1.0	6.1
	11-20	430	0.001	0.001	0.32	0.14	0.22	0.001	0.001	0.001	0.68	5.2	4.1	27
	21-30	492	0.43	0.16	0.15	0.019	0.15	0.001	0.124	0.008	1.04	22	15	2.4
	31-40	399	0.001	0.001	0.15	0.07	0.1	0.01	0.12	0.09	0.54	5.8	13	6.7
(9)	0-10	104	0.09	0.05	0.48	0.22	0.36	0.05	0.43	0.3	1.98	7.0	13	8.9
	11-20	26	0.03	0.02	0.15	0.67	0.12	0.1	0.04	0.11	1.24	3.5	<0.3	<0.3
	21-30	109	0.06	0.03	0.2	0.09	0.14	0.1	0.03	0.15	0.8	2.8	<0.3	<0.3
	31-40	107	0.001	0.01	0.14	0.06	0.12	0.01	0.12	0.08	0.54	5.3	<0.3	26
Spoil Ground South														
(10)	0-10	145	0.64	0.25	0.39	0.045	0.44	0.23	0.001	0.001	1.99	11	<0.3	<0.3
	11-20	117	0.18	0.12	0.5	0.23	0.47	0.04	0.41	0.3	2.25	<0.3	1.1	<0.3
	21-30	339	0.15	0.1	0.34	0.16	0.35	0.04	0.27	0.2	1.61	<0.3	3.3	6.1
	31-40	144	0.13	0.08	0.34	0.16	0.27	0.04	0.35	0.27	1.64	<0.3	<0.3	54
(11)	0-10	205	0.008	0.001	0.009	0.002	0.002	0.009	0.02	0.02	0.07	3.6	12	8
	11-20	236	0.02	0.001	0.02	0.005	0.004	0.02	0.04	0.04	0.15	10	8	<0.3
	21-30	381	0.01	0.002	0.03	0.01	0.01	0.02	0.05	0.05	0.18	6.2	15	4.3
	31-40	93	0.005	0.002	0.02	0.01	0.006	0.01	0.03	0.04	0.12	1.0	<0.3	<0.3
(12)	0-10	39	0.004	0.001	0.002	0.001	0.001	0.002	0.009	0.004	0.02	3.6	3.8	<0.3
	11-20	52	0.001	0.001	0.002	0.001	0.001	0.007	0.002	0.001	0.02	<0.3	5.2	<0.3
	21-30	26	0.001	0.001	0.001	0.001	0.001	0.008	0.004	0.001	0.02	<0.3	1.8	<0.3
	31-40	19	0.001	0.001	0.003	0.001	0.001	0.025	0.001	0.001	0.03	<0.3	1.3	0.7

Tot PAH = sum of 8 individual PAH. B[a]A = benz[a]anthracene, CHRY = chrysene, B[b]F = benzo[b]fluoranthene, B[k]F = benzo[k]fluoranthene, B[a]P = benzo[a]pyrene, DB[a,h]A = dibenzo[a,h]anthracene, B[ghi]P = benzo[ghi]perylene, I[1,2,3,-cd]P = indeno[1,2,3-cd]pyrene.

* the sum of aromatic and aliphatic hydrocarbons eluting within the range of C_{12} and C_{32} alkanes. Internal standard recovery =79 ±13% (n = 20), results not corrected for recovery of internal standards.