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Characterisation of Toxicants in Waters from Port Phillip Bay: Metals

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EXECUTIVE SUMMARY

The primary objective of this investigation was to characterise the dispersion of dissolved and suspended particulate concentration of toxic substances from the major point source inputs (the Yarra River system and the Western Treatment Plant) into Port Phillip Bay. Additionally, the data obtained would be used to identify any concerns posed by elevated concentrations of specific toxicants in Bay waters as well as providing information for modelling toxicant dispersion and fate within the Bay. This report details the investigation of metal toxicants (cadmium, copper, chromium, iron, nickel, lead, zinc, arsenic, selenium and mercury) and is complimented by an investigation of organic toxicants to be reported elsewhere.

The study consisted of two component investigations - a Bay-wide survey and a rain event survey. For the Bay-wide study sampling was undertaken at twenty five sites throughout the Bay including a concentration of sites near the Western Treatment Plant (Geelong Arm) and the Yarra River (Hobsons Bay) regions. The rain event study involved the taking of samples at distances of approximately 0, 2, 4, 6 and 8 km south of the Westgate Bridge in the Yarra River plume at variable intervals for a period of two days following an increase in run-off and flow resulting from a significant rain event in the catchment.

Overall, the dissolved metal concentrations observed from the Bay-wide survey were within the range of concentrations that have been found for near-shore and estuarine environments in the northern hemisphere. The exception was the comparatively high arsenic concentrations that probably result from diagenic processes operating in the sediments rather than from surface inputs such as the Yarra and Western Treatment Plant. Although the highest metal concentrations were observed in samples from the Corio Bay and Hobsons Bay sites, the concentrations for most of the metals studied were lower than previously reported for these sites. Comparisons with other available data for the Bay suggest that metal concentrations in the waters of the Bay are now lower than was the case 20 years ago.

The concentrations of chromium, copper, iron, nickel and lead in river water were highest during the initial high flow period of the rain event. The metal loads that entered the Bay from the Yarra River system during this rain event ranged from 8 (zinc) to 25 (arsenic) times the loads that would have been carried into the Bay over the same period (30 hours) during normal (no rain) conditions. This survey demonstrated that rain events cause transient increases to the metal loads into the Bay and, depending on the frequency of such events, they are likely to contribute a considerable proportion of the annual metal load that is carried into the Bay by rivers and streams.

TABLE OF CONTENTS

List of Figures

Page

List of Figures (continued)

Page

List of Figures (continued)

Page

List of Tables

Page

1. INTRODUCTION

Toxic metals in near-shore marine environments are primarily transported from input sources either as dissolved complexes or in suspended matter (Salomons and Forstner 1984). Elevated concentrations of toxic metals in fish (Fabris and Gibbs 1985, Walker 1982) and shellfish (Hickman *et al.* 1984, Conron 1988, Conron 1994) from areas of Port Phillip Bay away from known inputs indicates that the transport of water borne contaminants within the Bay is a significant mechanism contributing to bioaccumulation of toxic metals in the Bay. Direct evidence of such a transport process has been reported for the export of cadmium from Corio Bay into Port Phillip Bay (Fabris *et al.* 1984). Therefore, in order to assess the ecological impacts of toxic metal inputs to the Bay it is necessary to determine the concentrations of the dissolved and particulate forms in the water column.

Currently the Victorian Environment Protection Authority (EPA) supports a continuing program that monitors total heavy metal and nutrient concentrations in waters at six fixed sites within Port Phillip Bay (EPA 1983, 1990 and Brown 1993; see Figure 1). The purpose of the EPA program is to detect and quantify long-term changes in water quality, but the program has a number of limitations which include:

- variable sampling design over time;
- current small sample size (six sites);
- heavy metals are the only toxicants which are monitored and
- the database has values for total concentrations only. Knowledge of the partitioning between dissolved and particulate fractions would help to determine the significance of concentrations in relation to transport and bioavailability of toxicants.

The present study was undertaken as part of the Port Phillip Bay Environmental Study (PPBES) in order to:

- characterise the dispersion of dissolved and suspended particulate concentrations of toxicants from major point source inputs in Port Phillip Bay;
- identify any concerns posed by elevated concentrations of specific toxicants in Bay waters;
- provide data for modelling of toxicant dispersion and fate.

This task, in addition to providing information which can be used in modelling toxicant dispersion and fates within the Bay, will complement the objectives of the continuing Fixed Sites Monitoring program.

The task had two components. The first involved a Bay-wide survey of metal concentrations in the water column. A study of metal fluxes into the Bay from the Yarra/Maribyrnong River system during a major rain event formed the second part. Toxicant inputs from the Yarra River system are believed to constitute the major percentage of total stream-borne toxicant inputs into Port Phillip Bay. It has been suggested (G. Batley, CSIRO, pers. comm.) that about 80% of the contaminants that enter the Bay do so immediately following storm events. The Yarra River system constitutes about 60% of total run-off inputs to the Bay. Therefore, measurement of toxicant concentrations in the freshwater plume of the Yarra River system following a storm event would provide an estimate of the importance of storm events on the toxicant load into the Bay.

2. METHODS

Sampling and analysis were carried out in accordance with procedures essential for determination of metals at trace levels (Florence and Batley 1980, Ashton and Chan 1987). The dissolved and particulate component metal species were determined because these are crucial to the understanding of the dispersion and fate of metals in the Bay, as well as their bioavailability and toxicity (Millward 1995).

2.1 Sampling Design

Bay-wide survey

The two areas within the Bay which have been identified as key areas for modelling the dispersion and fate of toxicants (and nutrients) are the regions close to the Western Treatment Plant (WTP) and the Yarra/Maribyrnong River (HOB) systems (CSIRO PPBES modelling workshop November 1992). To satisfy the needs of the modelling tasks, sampling was to be carried out along salinity gradients at these regions. As a starting point, sites were initially selected on the basis of a grid sampling design. Because of the low rainfall and high wind conditions that predominated prior to and during the sampling period, the Bay waters were well mixed and no salinity gradients were observed. Therefore, samples were collected at the pre-selected sites.

Sampling was undertaken between 22 June and 25 June 1993. Twenty five sites were sampled (Figure 1). There were no major sampling difficulties experienced during the cruise, although the first day had to be cut short due to rough weather conditions. The geographic co-ordinates of each sampling site (sites 1 to 25) are listed in Appendix 1.

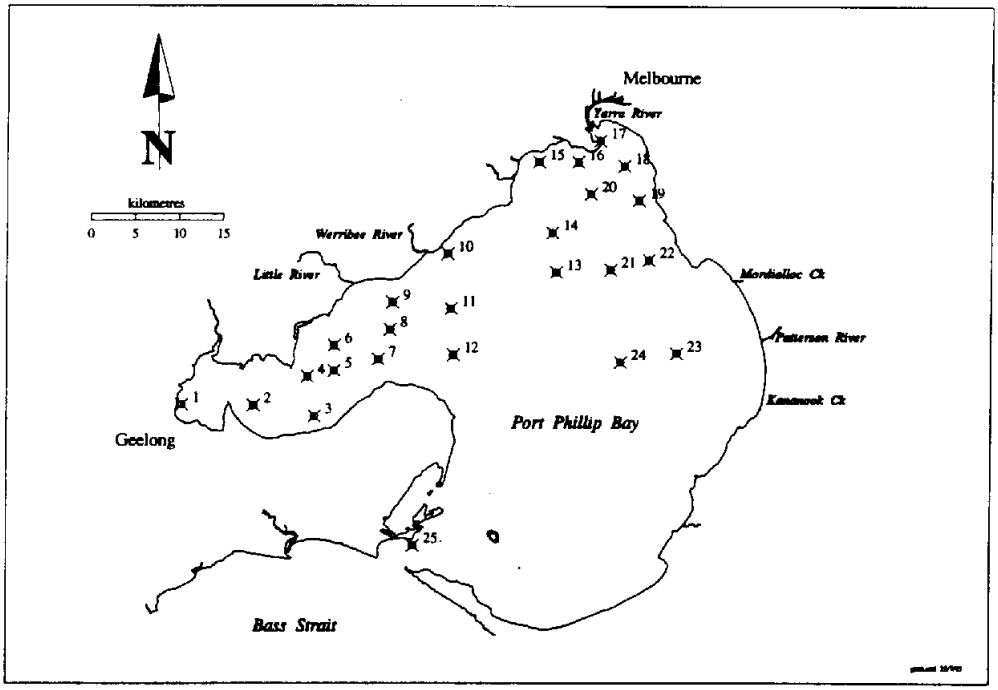


Figure 1. Map of Port Phillip Bay showing the 25 sites sampled during 22 to 25 June 1993. Co-ordinate locations for each site are listed in Appendix 1. Sites 2, 17 and 24 are the EPA fixed sites in Corio Bay, Hobsons Bay and the Bay centre.

Sampling was based on the assumption that the Bay was well mixed vertically and therefore surface (0.5-1m depth) samples only were collected. Salinity measurements during the cruise indicated that there was no vertical stratification of the water column at all but two of the sampling sites. At site 25 stratification was observed at 8m from the surface and deeper and at site 17 stratification was observed throughout the vertical column (Longmore, VFRI, pers. comm.)

Rain Event Survey

The major part of the metal inputs from the river systems is likely to originate in run-off from Melbourne's urban areas. The metal concentrations from these sources would be expected to peak within a few hours of the first heavy rains. In anticipation of this, the commencement of sampling for a rain event was based on the following criteria:

a) there should be no significant rainfall for a period of several weeks prior to a significant rain event;
b) approximately 15 mm (or more) of rain should have fallen in the preceding hour;
c) there was a high probability that more rain would fall over the following few hours, and;
d) the flow rate of the Yarra River 10 km upstream from the Bay was more than 50 m^3/s (mean base flow rate for the Yarra River is between 5 and 10 m^3/s).

These conditions were met during the early hours of 8 March 1995. Originally it was proposed to sample the freshwater plume daily for five days at distances approximately 0, 2, 4, 6 and 8 km south of the Westgate Bridge (Figure 2). The plume was to be located at each distance by taking salinity measurements at the surface. Samples were to be collected at 12, 24, 48, 72 and 96 hr following the initial sampling. However, in this case it was decided to reduce the sampling period and increase the frequency because:

(a) rainfall ceased within a few hours of the event;
(b) the Yarra River flow decreased to near pre-event rates within 36 hr, and;
(c) the rain event was accompanied by strong southerly winds which, due to the 1-1.5 m waves that were generated, accelerated the mixing of the freshwater plume with saline Bay water.

The revised sampling scheme used for this rain event is listed with the results in Appendices 3, 4 and 5. Site locations were fixed by GPS navigation. The geographic co-ordinates for each sampling site (26 to 30) are listed in Appendix 1.

2.2 Sample Collection:

Pre-cleaned polyfluorethylene (PTFE) hose and a peristaltic pump were used to collect water from a depth of 0.5-1 m below the surface. All sampling operations were performed whilst wearing lint-free coveralls and polyethylene gloves. Sampling was carried out from the bow of the vessel which was traveling into the wind at 1-2 knots while samples were being taken. Samples for metals other than arsenic, selenium and mercury were collected into polycarbonate bottles. Samples for arsenic and selenium were collected into polyethylene bottles and preserved with 3 ml ultra-pure HCl per litre of sample. Samples for mercury were collected into borosilicate glass bottles and preserved with 3 ml ultra-pure HNO_3 per litre of sample. All sample containers were pre-cleaned in a laminar flow cabinet and individually stored in polyethylene bags.

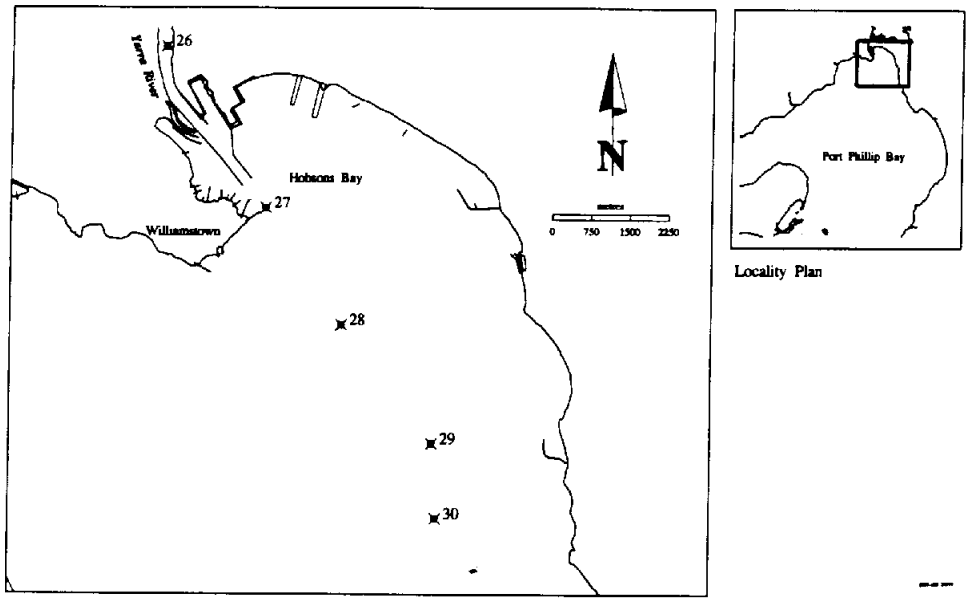


Figure 2. Map of Hobsons Bay and Yarra River showing the five sites sampled during 8 to 10 March 1995. Latitude and longitude co-ordinates for the sites are given in Appendix 1.

2.3 Sample Analysis

Partitioning between dissolved and particulate metal species was achieved by low pressure (<25 kpa) filtration (Florence and Batley 1980) through acid washed 0.45 µm polycarbonate membrane filters using polycarbonate filtration vessels and filtered (0.2 µm) nitrogen. Filtrations were performed inside a clean room (containing a class 100 laminar flow cabinet). The dissolved and particulate metals species were determined as follows:

- cadmium, lead, copper, zinc, chromium, iron and nickel (stored in the dark at 4^{o}C for less than 4 days). The filtrates were analysed for dissolved metals; the residues on the filters for particulate metals;
- mercury, arsenic and selenium: by difference between dissolved and total metal species.

Cadmium, lead, copper, zinc, chromium, iron and nickel.

Dissolved species were determined by chelation/solvent extraction/back extraction followed by furnace or flame atomisation atomic absorption spectrometry (Danielsson *et al*. 1978). The detection limits achievable are listed in Table 1. No oxidation step was used, therefore only chromium (VI) was detected.

Particulate species of cadmium, lead, copper, zinc, chromium, iron and nickel were determined after digestion of the filters and particulate matter with nitric and hydrofluoric acids (10:1 v/v; Harris and Fabris 1979).

Table 1. Detection limits based on three times the standard deviation of the blank (pre-extracted seawater) unless otherwise stated. Data are in µg/L.

Element	Concentration ± standard deviation (n=7)	Detection limit [c]
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
As[b]	2.19±0.21	0.6
Se[b]	0.16±0.27	0.8

a. n=3
b. replicate determinations of a seawater sample by standard additions (n=7)
c. replicate (n=7) determinations of a sample of seawater from the eastern coast of Australia gave the following detection limits: Cd = 0.0045, Cr(VI) = 0.01, Cu = 0.08, Pb = 0.04, Ni = 0.03 and Zn = 0.27.

Mercury, arsenic and selenium:

Dissolved species were determined on filtered water samples oxidised by UV irradiation followed by hydride generation/atomic absorption spectrometry (arsenic and selenium) and cold vapour atomic absorption spectrometry (mercury).

Total mercury, arsenic and selenium concentrations were determined by analysis of unfiltered water samples after oxidation using UV irradiation.

Fluoride

Determinations were performed by ion selective electrode (APHA 1992).

3. RESULTS

3.1 Quality Control

The detection limits (three times the standard deviation of the mean metal concentration) for cadmium, chromium, copper, iron, nickel lead and zinc (Table 1) were determined from the extracted seawater samples used as the blanks during the analyses. Detection limits for arsenic, selenium and mercury were determined from replicate determinations of a seawater sample. The detection limits for all metals except selenium were adequate for detecting the respective metal concentrations in the samples. Selenium concentrations were lower than the detection limits attainable by the method used here.

Analytical accuracy was estimated from analytical determinations on a pre-extracted seawater sample spiked with the metals at the µg/L level and also a US EPA quality assurance sample which was diluted to give metal levels in the µg/L level, both of which were analysed along with the samples. The mercury analyses were checked with a diluted sample of US NIST standard reference material 1643c. The recoveries for most of the metals ranged between 99% and 113%, while the mean recovery for cadmium was 83% (Table 2).

Methods are available to estimate summary statistics that include data falling below the detection limit (Helsel 1990). All such methods have limitations, and commonly used substitution methods can bias the data towards high values. To avoid such problems we included the measured values that fell below the calculated detection limit (Table 1) in estimating the summary statistics presented in this report. All measured results are included in the appendices, so that alternative statistical treatment of the data can be applied at some later stage if necessary.

Table 2. Results for the determination of metals in two quality control samples analysed with the Bay samples. All data µg/L

Element	In-house spiked sample		Diluted US EPA quality control sample		% Recovery (range)
	Nominal value	Mean value obtained (n=3)	Nominal value	Mean value obtained (n=4)	
Cd	0.13	0.095	0.25	0.23	83 (73-92)
Cu	1.05	1.16	1.0	1.16	113 (110-119)
Fe	105.9	92.2	1.0	1.11	102 (87-113)
Ni	2.01	2.05	1.0	1.16	109 (99-135)
Pb	1.05	0.93	1.0	1.20	105 (75-131)
Zn	5.2	5.1	1.0	1.00	99 (84-109)
As	2.99	3.02	1.0	1.13	107(96-113)
Se	2.08	2.07			99
Hg[a]			14.7±0.4	15.4	109(95-126)

a. A diluted sample of NIST SRM 1643c. Result is ng/L.
Chromium recoveries were poor because the quality control samples were prepared with Cr (III), but the procedure detects Cr (VI) only.

3.2 Metal Distributions in Bay Waters

All data are reported as µg/L (ng/L for mercury). All selenium results were below the detection limit and will not be discussed further. Except for arsenic and mercury, data for total metal (T) were obtained by adding the results for the soluble and particulate forms. The data for particulate forms (P) of mercury and arsenic were obtained by subtracting the soluble forms from the total forms. Statistical comparisons of untransformed means were performed using the approximated t-test (assumes unequal variances).

Anomalous results were obtained for some samples and these may have been contaminated rather than representing actual concentrations in the water or suspended matter. The suspect results are:

- Particulate cadmium for sites 7 and 25 appear unusually high since for all other samples the particulate form of cadmium was lower than the soluble form and, in the case of site 25, we would expect cadmium to be low since this site is away from any major stream inputs. This site was previously sampled during a test cruise (on 25 May 1993) and we obtained a value of 0.01 μg/L for soluble cadmium and no particulate cadmium was detected.
- Particulate lead at site 5 was relatively high compared to all other sites and the concentrations of the other metals from this sample were not unusually high.
- Dissolved mercury for site 18 and site 24 were greater than the mercury results for unfiltered samples.

The complete data set for this Bay-wide survey is listed in Appendix 2. Summary statistics for dissolved and particulate metal concentrations are listed in Table 3. The metals could be divided into three broad groups on the basis of their proportions in the dissolved and particulate forms:

- cadmium (Figure 3), copper (Figure 4), nickel (Figure 5), zinc (Figure 6), and arsenic (Figure 7) occur primarily as dissolved species;
- chromium (Figure 9), iron (Figure 10) and lead (Figure 11) occur primarily as particulate species, and;
- mercury (Figure 12) species were not dominated by either dissolved or particulate forms.

Table 3. Summary statistics for metal concentrations found in the 25 sites in Port Phillip Bay sampled during cruise 1. Data are μg/L (mercury is in ng/L). diss. = dissolved, part. = particulate, tot. = total metal forms.

Element[a]	Mean diss. ± s.d.	Mean part. ± s.d.	Mean tot. ± s.d.	Min diss.	Max diss.	Min part.	Max part.	Min tot.	Max tot.
Cd	0.026±0.014	0.011±0.013	0.037±0.024	0.000	0.070	0.000	0.110	0.015	0.120
Cr	0.04±0.02	0.09±0.06	0.13±0.07	0.01	0.09	0.01	0.29	0.04	0.32
Cu	0.47±0.05	0.03±0.02	0.50±0.06	0.40	0.63	0.00	0.11	0.42	0.68
Fe	0.76±0.44	28.98±18.60	29.74±18.63	0.17	1.8	5.96	83.05	7.76	84.77
Ni	0.70±0.14	0.05±0.05	0.76±0.15	0.54	1.10	0.00	0.19	0.58	1.23
Pb	0.06±0.02	0.13±0.14	0.19±0.14	0.02	0.13	0.00	0.70	0.05	0.74
Zn	0.47±0.21	0.11±0.08	0.57±0.26	0.25	1.05	0.00	0.26	0.25	1.26
As	2.75±0.27	-0.09±0.26	2.66±0.23	2.24	3.16	-0.49	0.52	2.28	3.16
Hg	1.7±0.73	1.32±1.30	2.90±1.29	0.82	4.92	-0.22	5.74	1.30	7.52

a. Selenium data were all below the detection limit (<0.8 μg/L)

Cadmium

Nineteen (76%) of the samples had a dissolved cadmium concentration between 0.01 and 0.03 µg/L (Figure 3). The highest concentration (0.07 µg/L) was found in the Corio Bay sample (site 1, Figure 1). Overall, the dissolved cadmium concentrations observed for this study are comparable to the concentrations reported for near-shore and estuarine environments elsewhere in the world (Table 4).

With the exception of sites 7 and 25 (for which contamination is suspected) particulate cadmium concentrations were comparatively low and overall accounted for about 25% of the total cadmium concentration in the water. Total cadmium concentrations (Appendix 2) were lower ($P<0.001$) than had been previously recorded for the Bay, and much lower than the concentrations recorded from Corio Bay (Table 5).

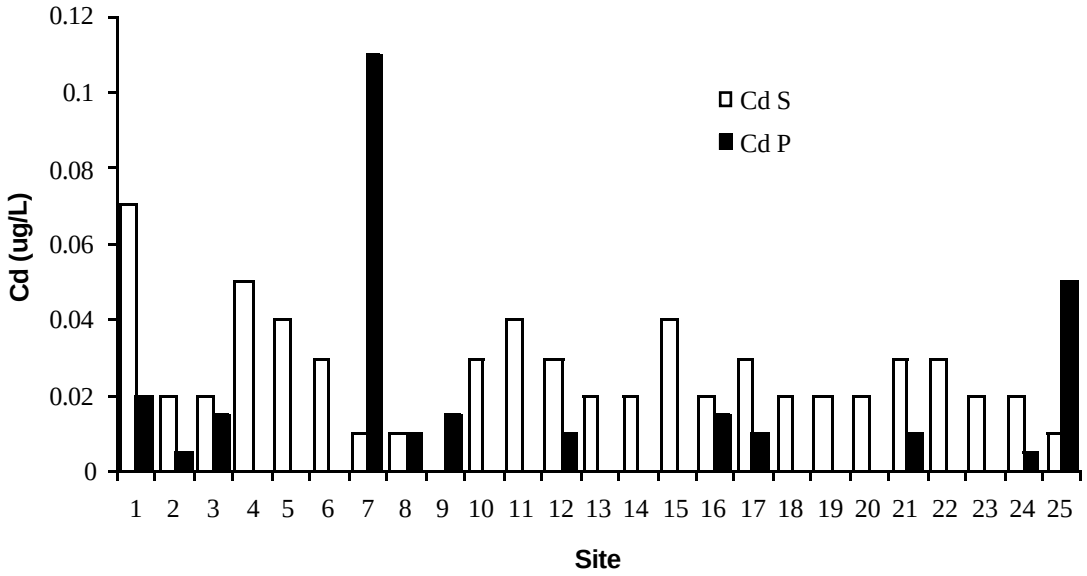


Figure 3. Dissolved and particulate cadmium in water from 25 sites sampled during 22 to 25 June 1993 in Port Phillip Bay. S = dissolved, P = particulate.

Table 4. Comparison of dissolved metal concentrations in marine waters from various regions. Concentrations in µg/L unless otherwise indicated.

Element	Nearshore & estuarine range	This study mean (range)
Cd	0.02-0.1[a,b]	0.026 (0.015-0.070)
Cr		0.04 (0.01-0.09)
Cu	0.06-1.3[a,b]	0.47 (0.40-0.63)
Fe		0.76 (0.17-1.8)
Ni	0.2-0.9[b]	0.70 (0.54-1.10)
Pb	0.02-0.06[a]	0.06 (0.02-0.13)
Zn	0.01-3.3[a,b]	0.47 (0.25-1.05)
As	1.0-3.3[c,d]	2.8 (2.2-3.2)
Hg (ng/L)	0.7-3.0 [a,e,f,g]	1.7 (0.8-4.9)

a. Balls et al. (1993), *b*. van Geen and Luoma (1993), *c*. Reidel (1993), *d.* Seyler and Martin (1990), *e*. Cossa et al. (1988), *f*. Dalziel (1992), *g*. Regnier and Wollast (1993).

Table 5. Mean total metal concentrations in waters from Port Phillip Bay. Units are µg/L unless otherwise stated.

Element	1975[a]	1989[b]	1989-1994[c] (n=36)	This study[d] (n=25)	
Cd		0.07-0.23	0.05±0.03	0.037±0.024	
			0.05±0.02		
	0.11-5.6		0.13±0.05		**
Cu			0.81±0.30	0.50±0.06	**
			1.25±0.61		**
	1.5-25		0.92±0.17		**
Fe			21.9±16.3	29.7±18.6	
			67.3±35.3		**
	24-300		32.0±17.4		
Ni			0.88±0.12	0.76±0.15	*
			1.15±0.27		**
			1.35±0.21		**
Pb		0.68-1.47	0.18±0.22	0.19±0.14	
			0.51±0.29		**
	<0.4-11		0.26±0.19		
Zn			1.16±0.37	0.57±0.26	**
			4.09±2.30		**
	3.9-67		1.32±0.51		**
As			2.24±0.46	2.7±0.3	
			2.36±0.48		
			2.94±0.64		
Hg (ng/L)			4.7±6.9	2.9±1.3	
			4.3±5.6		
			3.9±5.8		
Se				<0.5	

a. Corio Bay: Smith *et al.* (1981)
b. Eastern Port Phillip Bay. Talbot (1989) - date of sampling unknown.
c. EPA fixed sites monitoring data June 1989 to June 1994. Mean ± standard deviation. Top line = Bay centre, middle line = Hobsons Bay, bottom line = Corio Bay.
d. Mean and standard deviation for whole Bay. Comparisons with the 1989 to 1994 fixed sites data were based on the approximate T-test. ** $P<0.001$; * $P<0.05$.

Copper

Dissolved copper concentrations were relatively uniform throughout the Bay (Figure 4) with a mean concentration of 0.47 µg/L. Samples from site 1 (Corio Bay) and site 17 (Hobsons Bay) recorded the highest dissolved copper concentrations (0.63 µg/L and 0.57 µg/L respectively). The dissolved copper concentrations observed in this study were within the range of concentrations found in near-shore and estuarine environments elsewhere (Table 4). Less than 10% of the copper was present as particulate species. The mean total copper concentration observed in this study (0.50 µg/L) was lower ($P<0.001$) than the mean concentrations observed for the central Bay, Hobsons Bay and Corio Bay fixed sites over the past four years and much lower than was previously recorded in Corio Bay (Table 5).

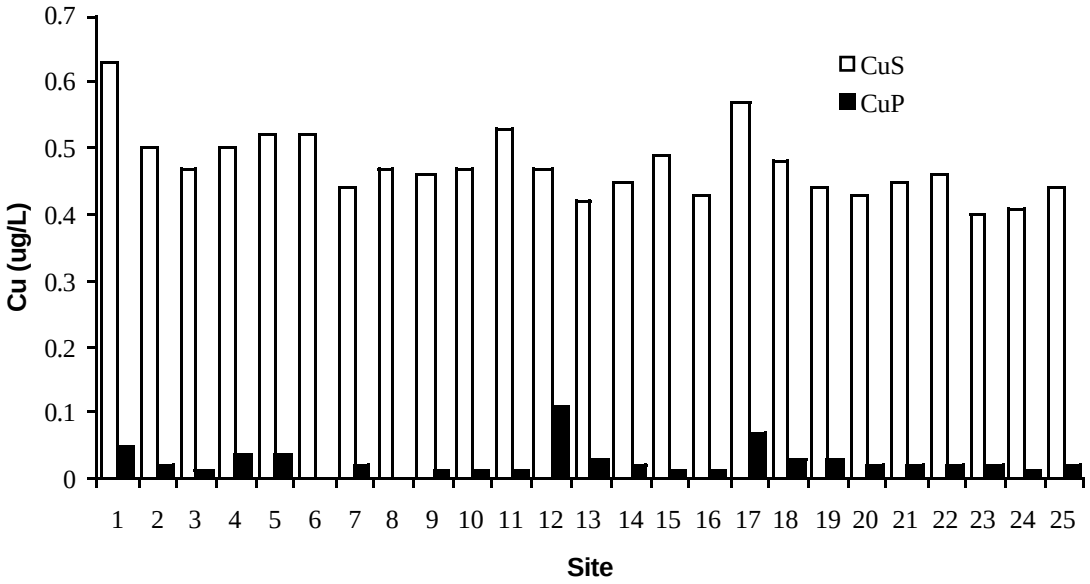


Figure 4. Dissolved and particulate copper in water from 25 sites sampled during 22 to 25 June 1993 in Port Phillip Bay. S = dissolved, P = particulate.

Nickel

The mean dissolved nickel concentration observed for this study (0.7 µg/L) was at the high end of the range observed for near-shore and estuarine environments elsewhere (Table 4). Dissolved nickel concentrations were relatively evenly distributed throughout the Bay (Figure 5), although levels in Corio Bay and the Geelong Arm tend to be slightly higher than in other parts of the Bay. The highest concentration (1.1 µg/L) was observed for the Corio Bay site. Less than 10% of the nickel was present as particulate species. The total nickel concentrations observed for this study were lower ($P<0.05$) than those observed for the three EPA fixed sites over the past four years (Table 5).

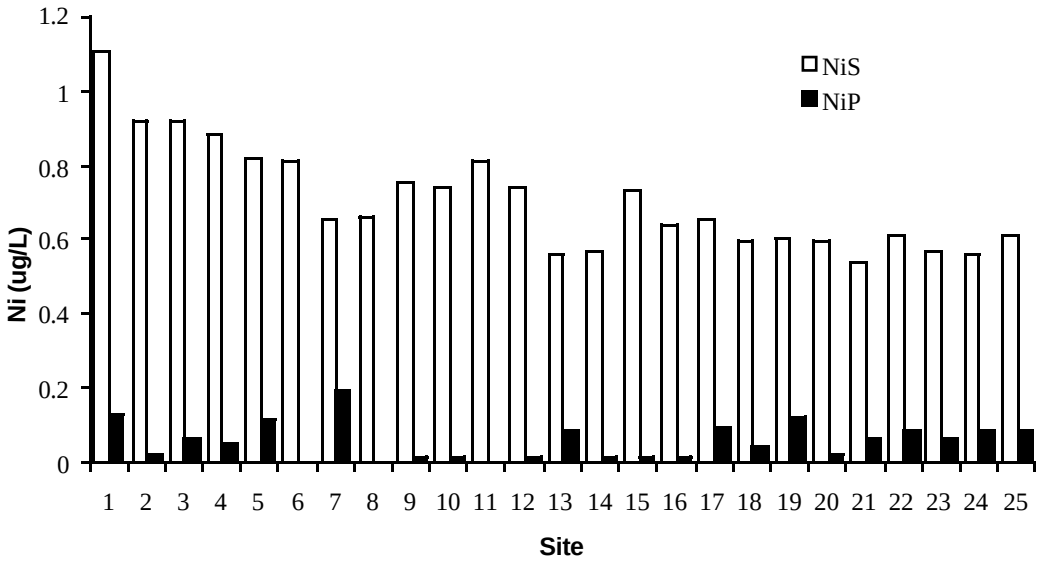


Figure 5. Dissolved and particulate nickel in water from 25 sites sampled during 22 to 25 June 1993 in Port Phillip Bay. S = dissolved, P = particulate.

Zinc

Dissolved zinc concentrations were within the range reported for near-shore and estuarine environments elsewhere (Table 4). The highest concentrations were found for sites in Corio Bay (site 1; 1.03 µg/L) and Hobsons Bay (sites 17 and 18; 1.05 µg/L and 0.84 µg/L respectively) (Figure 6). These concentrations were about two times greater than the concentrations from any of the other sites. Particulate species of zinc accounted for about 20% of the total zinc in the water. The mean total zinc concentration was lower ($P<0.001$) than the mean concentration observed at each of the three EPA fixed sites over the past four years, and much lower than previously reported for Corio Bay (Table 5).

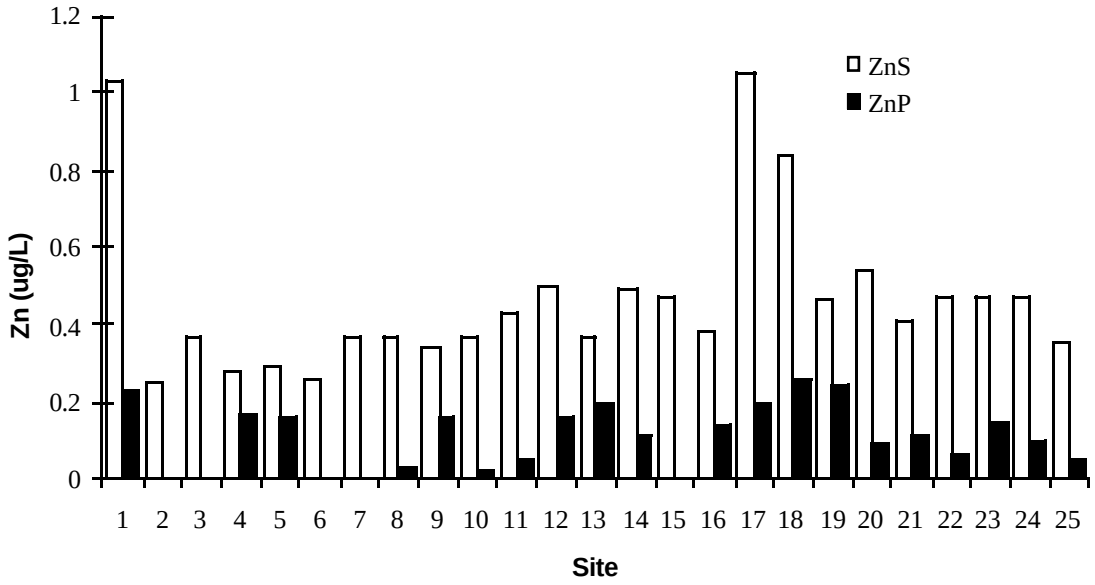


Figure 6. Dissolved and particulate zinc in water from 25 sites sampled during 22 to 25 June 1993 in Port Phillip Bay. S = dissolved, P = particulate.

Arsenic

Virtually all of the arsenic was found in dissolved species and arsenic concentrations were relatively evenly distributed throughout the Bay (Figure 7). The concentrations were similar ($P<0.05$) to those reported for the three EPA fixed sites over the past four years (Table 5). The mean concentration and range were at the higher end of the range reported for near-shore and estuarine environments elsewhere (Table 4). Indeed, the arsenic concentrations from Port Phillip Bay waters appear to be consistently higher than those from other Victorian Bays and inlets (Figure 8).

Chromium

Most of the chromium (70%) occurs in particulate species (Table 9). Dissolved chromium (i.e. Cr VI) concentrations were mostly close to the detection limit (Figure 9). The mean particulate chromium concentration is skewed toward the higher concentration due to the high concentrations at sites 1 (0.29 µg/L), 17 (0.20 µg/L) and 19 (0.17 µg/L). The remaining 22 sites had concentrations below 0.15 µg/L.

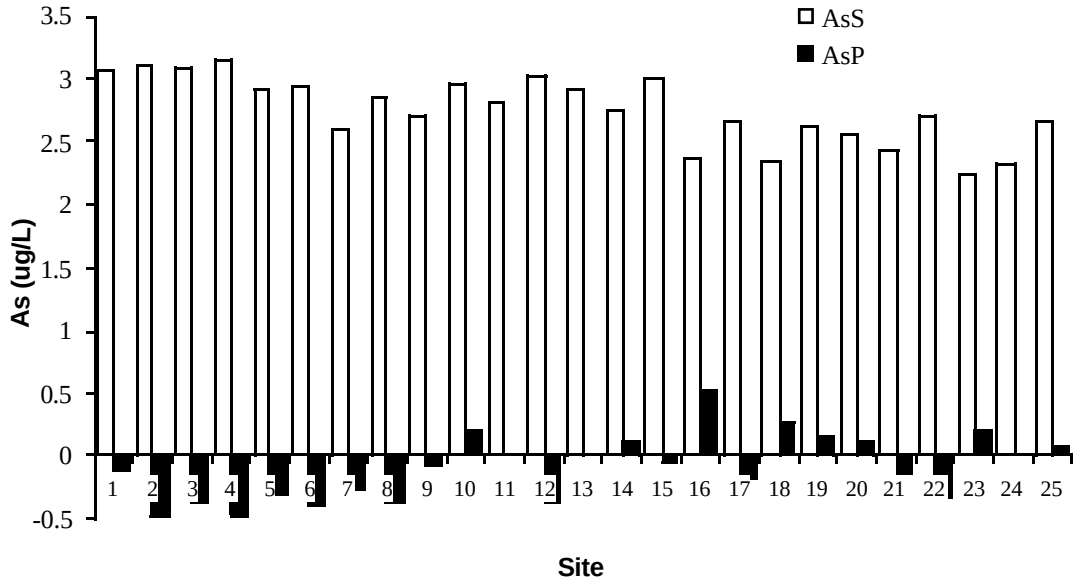


Figure 7. Dissolved and particulate arsenic in water from 25 sites sampled during 22 to 25 June 1993 in Port Phillip Bay. S = dissolved, P = particulate.

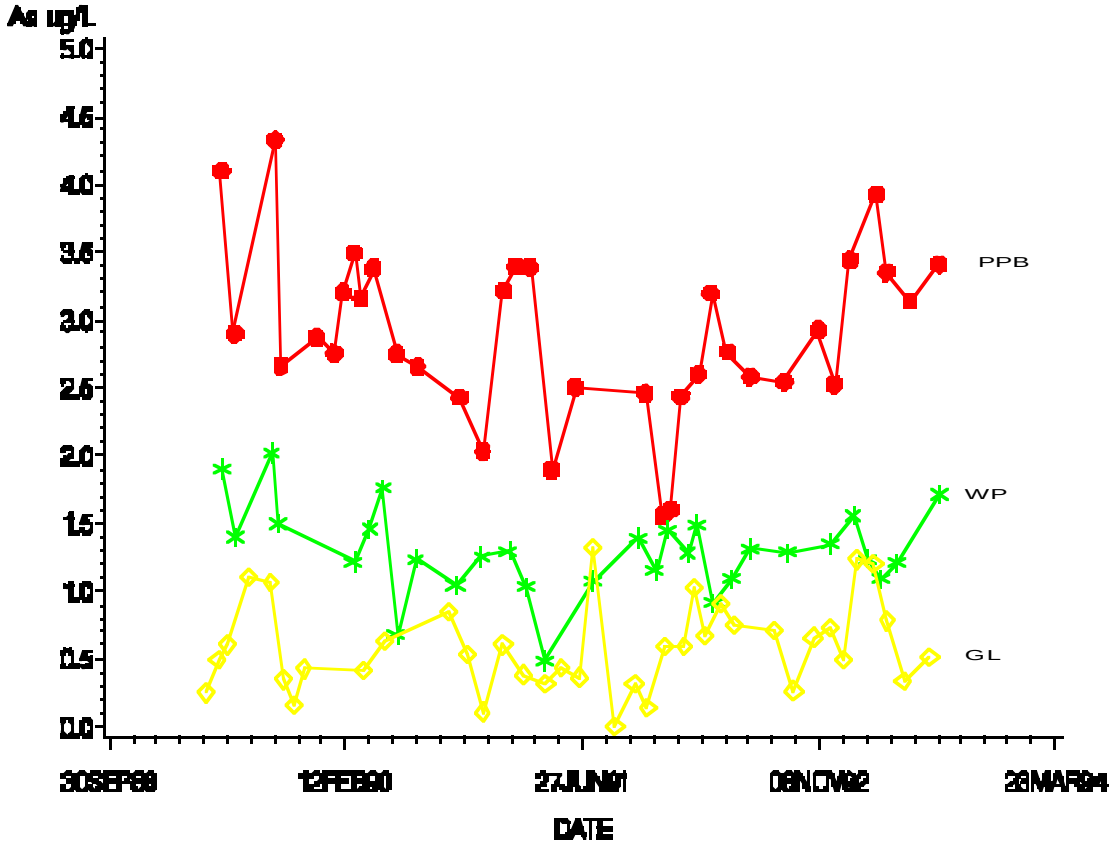


Figure 8. Arsenic concentrations in Victorian Bays and inlets with time between September 1988 and March 1994. PPB = Port Phillip Bay; WP = Western Port; GL = Gippsland Lakes

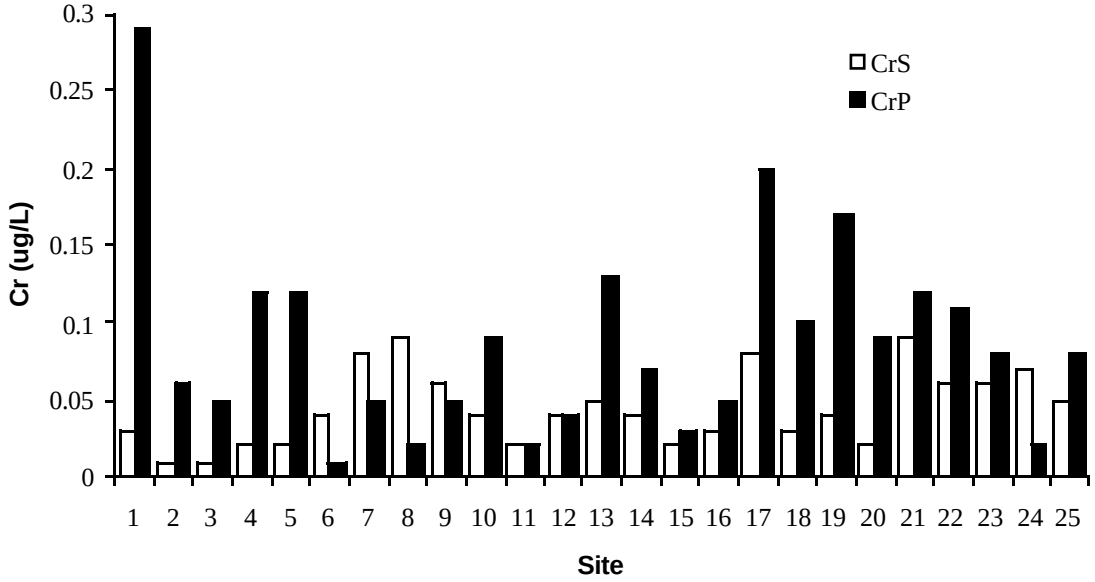


Figure 9. Dissolved and particulate chromium in water from 25 sites sampled during 22 to 25 June 1993 in Port Phillip Bay. S = dissolved, P = particulate.

Iron

Most of the iron (97%) was present as particulate species (Figure 10, Table 9). The highest concentrations of total iron were observed at sites 1 (85 µg/L) and 17 (68 µg/L). The remaining 23 sites had total iron concentrations below 50 µg/L. The mean total iron concentration was similar to that recently recorded from the EPA fixed sites in Corio Bay and Central Bay, but significantly lower ($P<0.001$) than that for the Hobsons Bay site (Table 5).

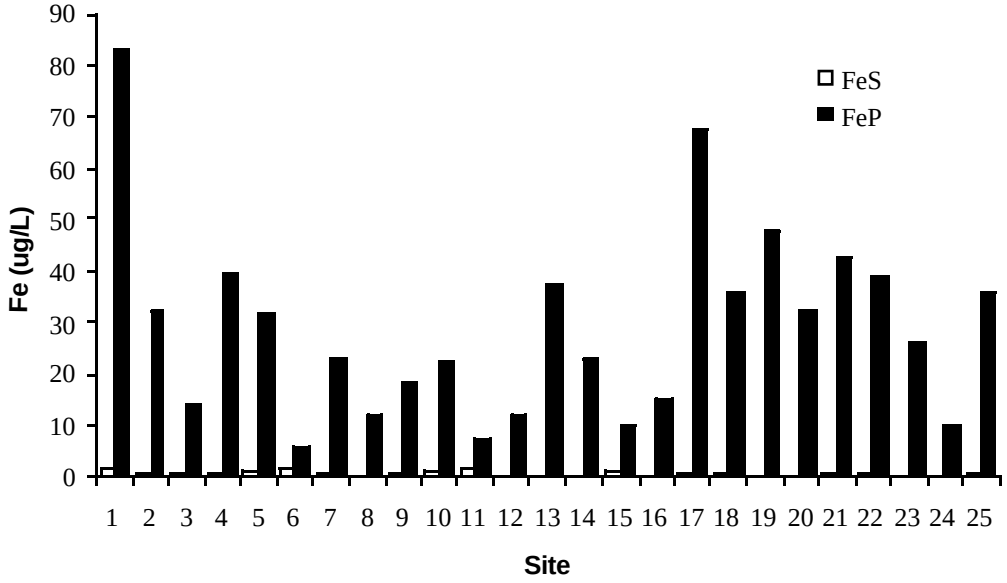


Figure 10. Dissolved and particulate iron in water from 25 sites sampled during 22 to 25 June 1993 in Port Phillip Bay. S = dissolved, P = particulate.

Lead

Dissolved lead concentrations (Figure 11) were in the upper range of concentrations observed for near-shore and estuarine waters elsewhere (Table 4). The mean total lead concentration was similar (P>0.5) to that found for the fixed sites in the middle of the Bay and in Corio Bay over the past four years, but lower (P<0.001) than the concentration from the Hobsons Bay site (Table 5).

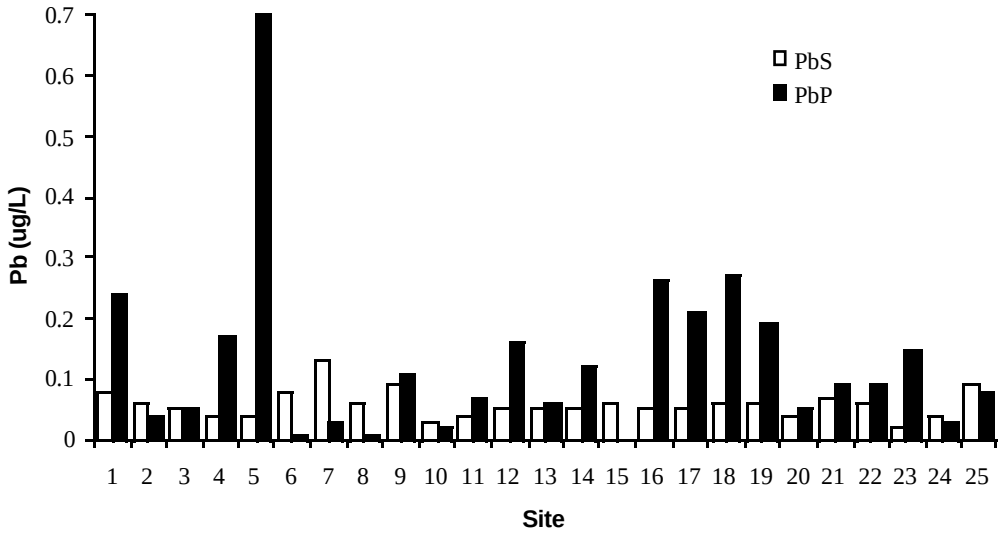


Figure 11. Dissolved and particulate lead in water from 25 sites sampled during 22 to 25 June 1993 in Port Phillip Bay. S = dissolved, P = particulate.

Mercury

Dissolved mercury concentrations (Figure 12) were within the range observed for near-shore and estuarine environments elsewhere (Table 4). The values obtained in this survey are not significantly different (P>0.5) from those observed for the three EPA fixed sites over the past four years (Table 5).

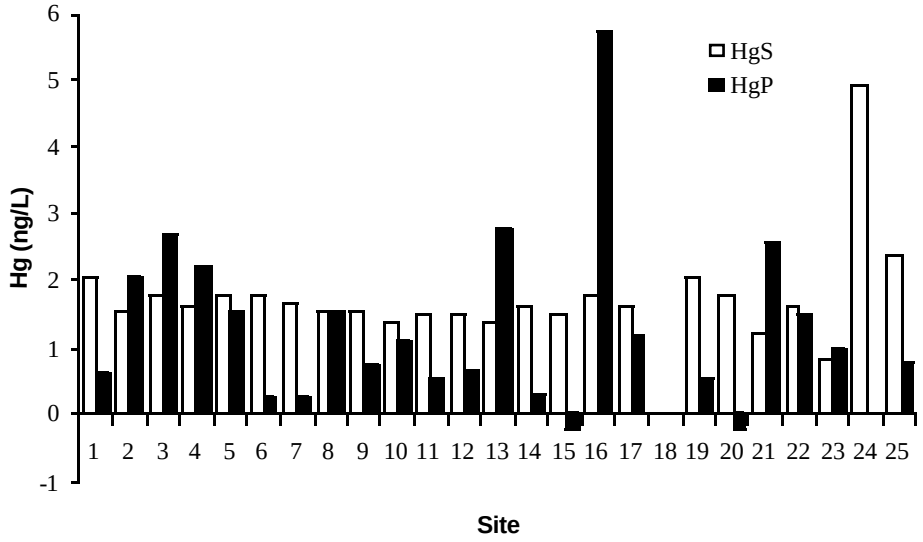


Figure 12. Dissolved and particulate mercury in water from 25 sites sampled during 22 to 25 June 1993 in Port Phillip Bay. S = dissolved, P = particulate.

3.2.1 Interelement Correlations

Significant (P<0.05) interelement correlations were observed between dissolved nickel and arsenic, iron, copper, cadmium and chromium (Table 6). Examples of the scatter diagrams for these correlations are shown in Figures 13 to 17. Significant correlations were also observed between copper and cadmium, iron, nickel zinc and arsenic. Arsenic also correlated with chromium. The correlations with chromium were negative, all other significant correlations were positive. No significant interelement correlations were observed with either lead or mercury.

Table 6. Pearson Correlation Coefficients for soluble forms of metals in Port Phillip Bay waters. (Cruise No.1: June 22-25, 1993. Prob > |R| under Ho: Rho=0 / Number of Observations = 25).

	Cd	Cr	Cu	Fe	Ni	Pb	Zn	Hg	As
Cd	1.00000	-0.37546	0.69380	0.50800	0.63039	-0.16625	0.33373	-0.02732	0.45469
P	0.0	0.0644	**0.0001**	**0.0095**	**0.0007**	0.4271	0.1030	0.8992	0.0224
Cr		1.00000	-0.23241	-0.21373	-0.57447	0.27334	0.18166	0.08989	-0.51665
P		0.0	0.2636	0.3050	**0.0027**	0.1861	0.3848	0.6762	**0.0082**
Cu			1.00000	0.74072	0.74259	0.22594	0.51013	-0.13892	0.55654
P			0.0	**0.0001**	**0.0001**	0.2775	**0.0092**	0.5174	**0.0039**
Fe				1.00000	0.66452	0.28762	0.17024	-0.06674	0.4128
P				0.0	**0.0003**	0.1633	0.4159	0.7567	0.0403
Ni					1.00000	0.13061	0.04178	-0.09822	0.7503
P					0.0	0.5338	0.8428	0.6480	**0.0001**
Pb						1.00000	0.11040	-0.08506	0.0225
P						0.0	0.5993	0.6927	0.9146
Zn							1.00000	0.07647	-0.1863
P							0.0	0.7225	0.3725
Hg								1.00000	0.2500
P								0.0	0.2387
As									1.0000
P									0.0

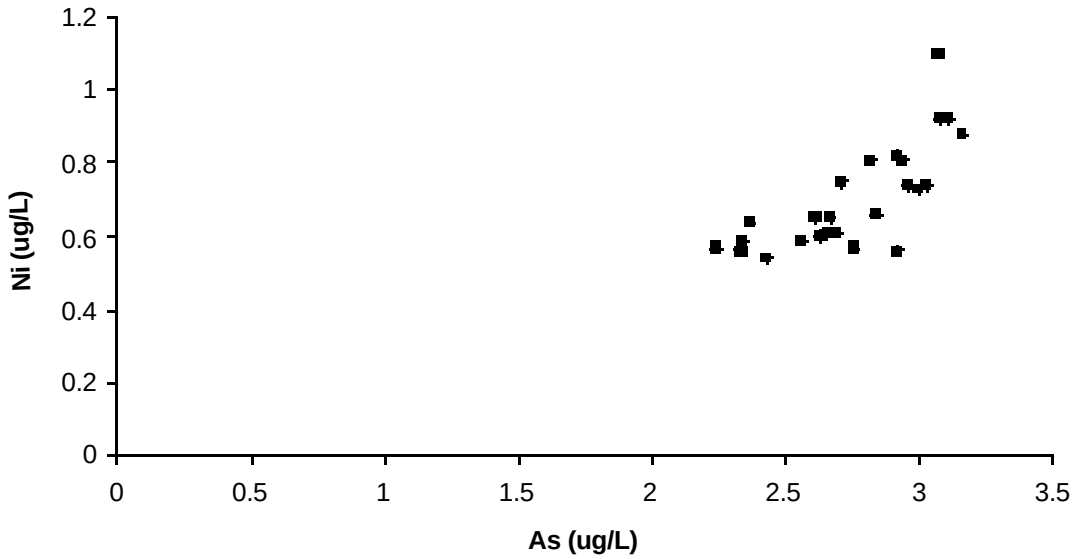


Figure 13. Scatter diagram showing the correlation between dissolved nickel and arsenic for the 25 samples collected in Port Phillip Bay during 22 to 25 June 1993.

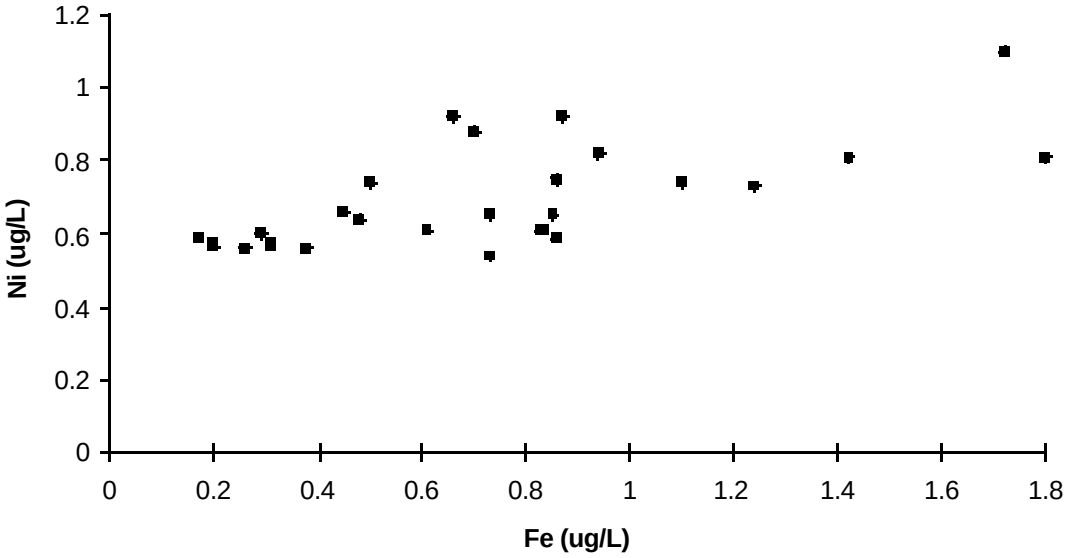


Figure 14. Scatter diagram showing the correlation between dissolved nickel and iron for the 25 samples collected in Port Phillip Bay during 22 to 25 June 1993.

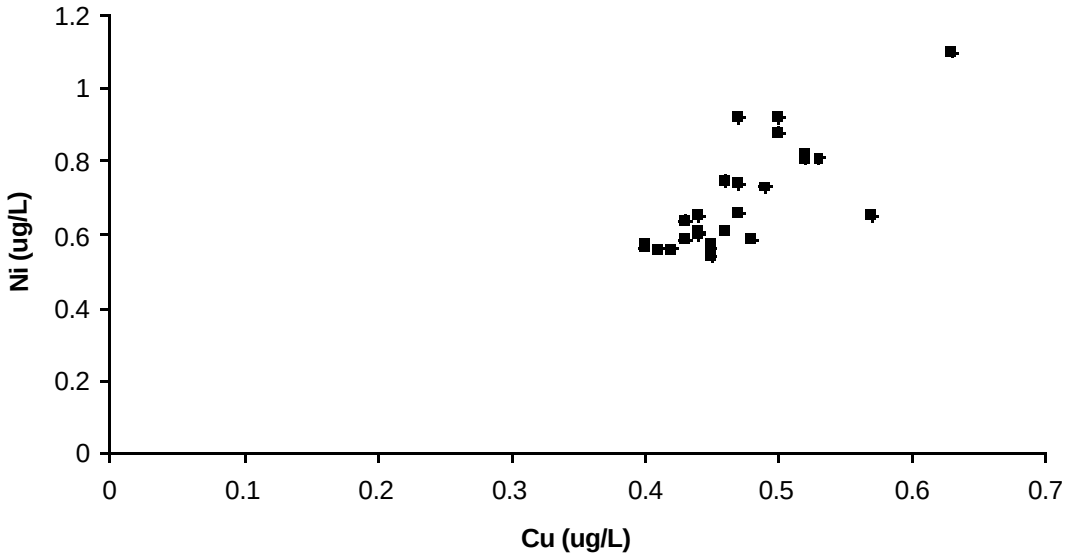


Figure 15. Scatter diagram showing the correlation between dissolved nickel and copper for the 25 samples collected in Port Phillip Bay during 22 to 25 June 1993.

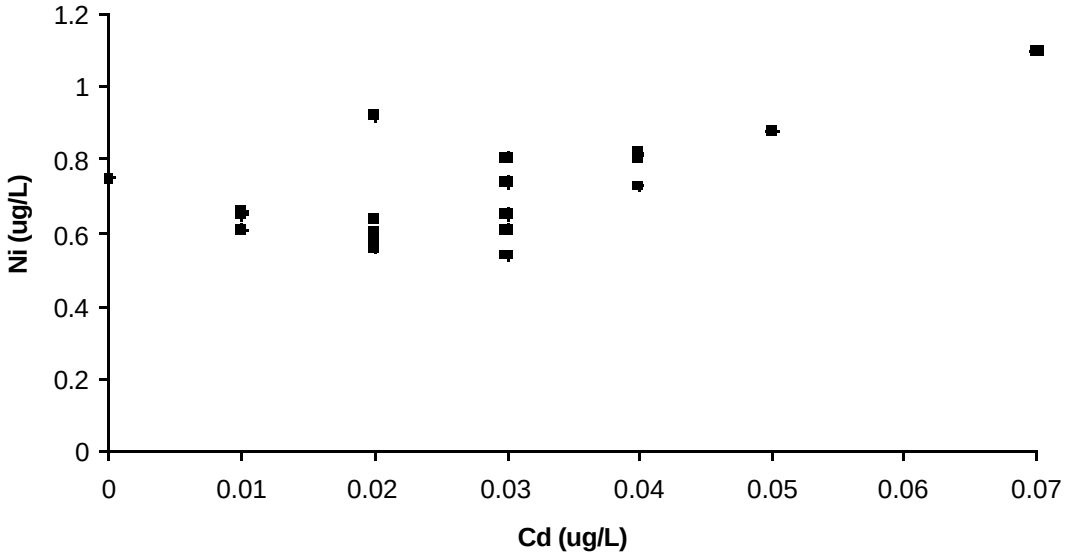


Figure 16. Scatter diagram showing the correlation between dissolved nickel and cadmium for the 25 samples collected in Port Phillip Bay during 22 to 25 June 1993.

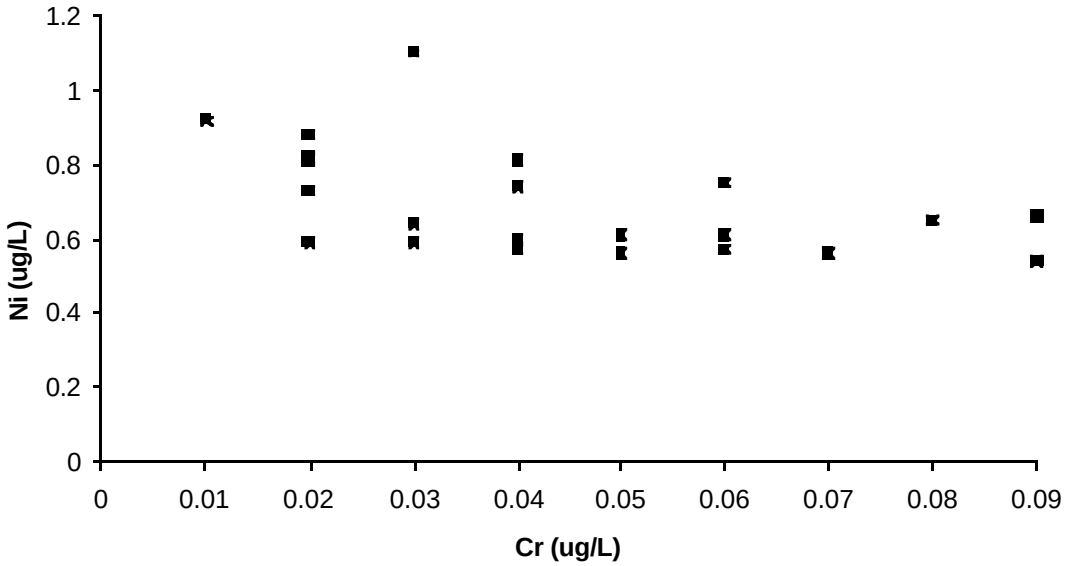


Figure 17. Scatter diagram showing the correlation between dissolved nickel and chromium for the 25 samples collected in Port Phillip Bay during 22 to 25 June 1993.

Particulate iron correlated significantly ($P<0.05$) with chromium, copper, nickel and zinc (Table 7, Figures 18 to 21). Additional significant correlations were observed between chromium and nickel and zinc, lead with zinc and nickel with chromium.

Correlations between the dissolved and particulate forms of any given element were not significant.

Table 7. Pearson Correlation Coefficients for particulate forms of metals in Port Phillip Bay waters. (Cruise No.1: June 22-25, 1993). Prob > |R| under Ho: Rho = 0 / Number of Observations = 25).

	Cd	Cr	Cu	Fe	Ni	Pb	Zn
Cd	1.00000	-0.05687	-0.01875	0.02311	0.56939	-0.16511	-0.30358
P	0.0	0.7872	0.9291	0.9127	**0.0030**	0.4407	0.1401
Cr		1.00000	0.47682	0.96977	0.57578	0.41949	0.63079
P		0.0	0.0160	**0.0001**	**0.0026**	0.0413	**0.0007**
Cu			1.00000	0.45860	0.22463	0.40318	0.56274
P			0.0	0.0211	0.2803	0.0508	**0.0034**
Fe				1.00000	0.56975	0.34201	0.57609
P				0.0	**0.0029**	0.1019	**0.0026**
Ni					1.00000	0.29162	0.22351
P					0.0	0.1668	0.2828
Pb						1.00000	0.56544
P						0.0	**0.0040**
Zn							1.00000
P							0.0

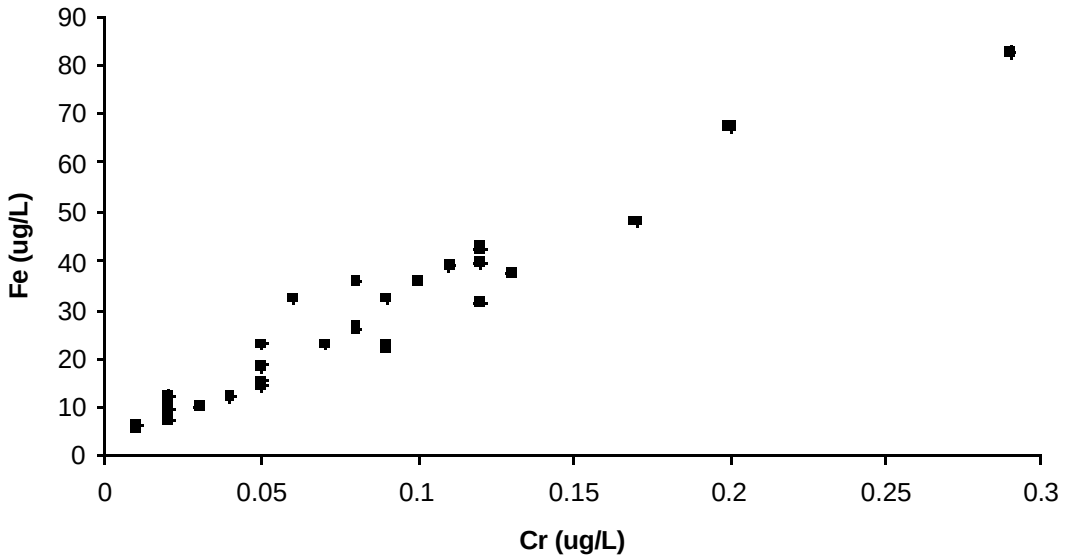


Figure 18. Scatter diagram showing the correlation between particulate iron and chromium for the 25 samples collected in Port Phillip Bay during 22 to 25 June 1993.

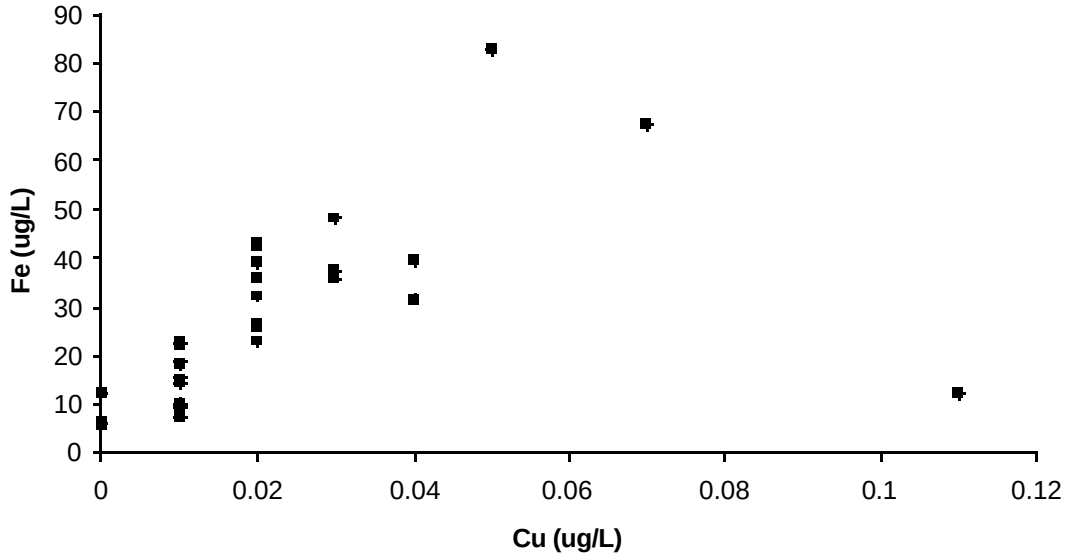


Figure 19. Scatter diagram showing the correlation between particulate iron and copper for the 25 samples collected in Port Phillip Bay during 22 to 25 June 1993.

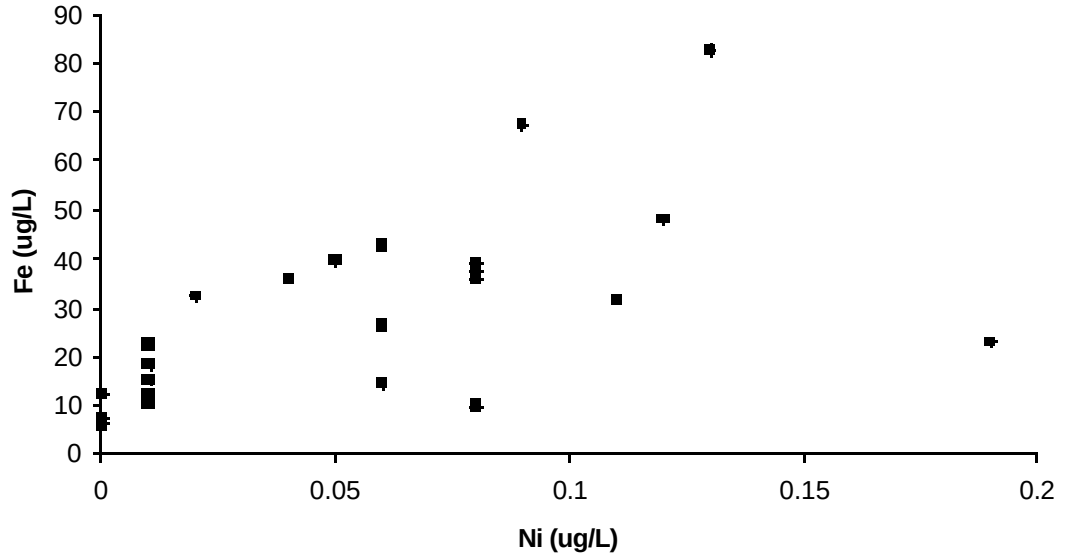


Figure 20. Scatter diagram showing the correlation between particulate iron and nickel for the 25 samples collected in Port Phillip Bay during 22 to 25 June 1993.

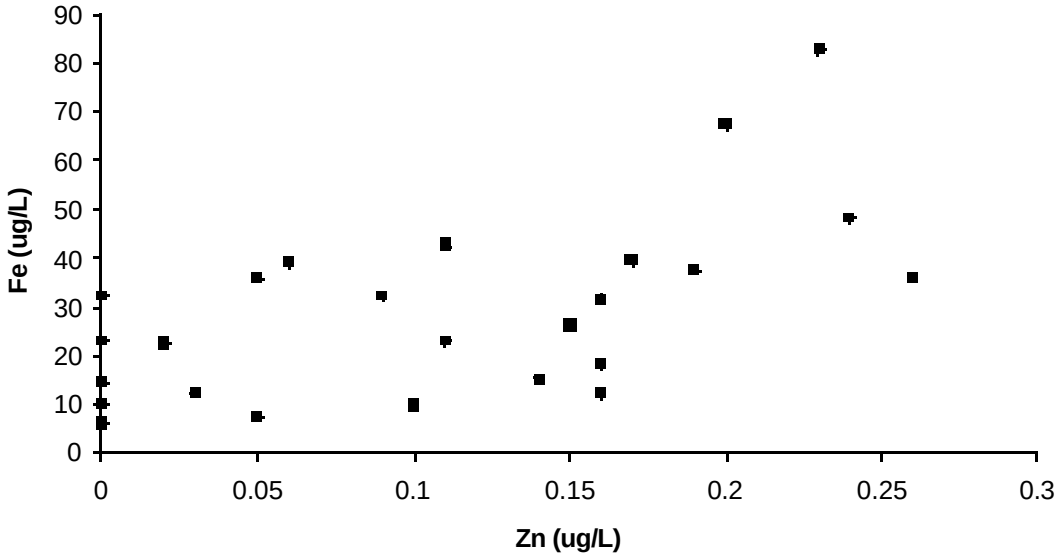


Figure 21. Scatter diagram showing the correlation between particulate iron and zinc for the 25 samples collected in Port Phillip Bay during 22 to 25 June 1993.

3.2.2 Fluoride distributions

Fluoride concentrations varied between 1.15 and 1.91 mg/L (Table 8) with a mean concentration of 1.59 $\pm$ 0.21 mg/L. This is slightly higher than the mean fluoride concentration of the open oceans of about 1.4 mg/L (Kullenberg and Sen-Gupta 1973). The lowest concentrations were observed for the three sites (17, 18 and 19) in the north of the Bay and the highest concentrations were observed for sites 8 and 9 in the Geelong Arm and site 23.

Table 8. Fluoride concentrations in seawater from Port Phillip Bay.

Site	F (mg/L)
1	1.63
8	1.77
9	1.91
10	1.65
17	1.52
18	1.15
19	1.42
22	1.59
23	1.78
25	1.54

3.3 Metal Distributions During the Rain Event

Selenium and fluoride were not determined since these variables were either very low or showed no regional variability in the Bay-wide study.

Rainfall and River Flows

Approximately 50 mm of rain fell in the Melbourne urban area between 02:00 hr and 07:00 hr on 8 March 1995 (MW, 1995). Rainfall levels in other parts of the catchment ranged from 10 to 50 mm during the same period. No further heavy rain was recorded in the Melbourne urban region after about 07:00 hr. Most of the precipitation occurred during a two hour period between 05:00 hr and 07:00 hr (Figure 22). During this period, the Yarra River flow into the Bay, based on composite flows from the Yarra measured at the Johnston Street Bridge (about 16 km upstream from the Bay), and Gardiners and Flemington Creeks which join the Yarra River further downstream, rose from about 5 m^3/s at 04:00 hr to about 200 m^3/s between 06:00 and 08:00 hr. The flow gradually decreased to about 15 m^3/s within 16 hr (Figure 22). The first samples were collected at 12:00 on that day, at least four hours after the river flow had peaked. This rain event was preceded by several weeks of dry weather. The prevailing dry conditions were reflected in the Yarra River flow which averaged 2.6 m^3/s (compared to the usual 5-7 m^3/s for March) for the four days prior to the rain event (G. Crapper, MW, pers. comm.).

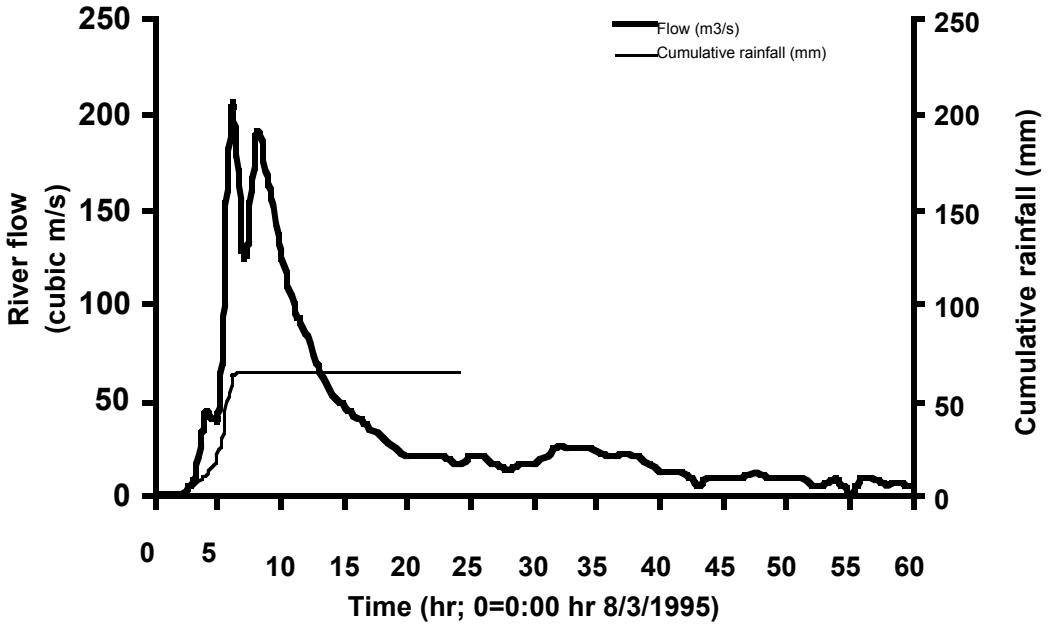


Figure 22. Cumulative rainfall (mm) at Bell Street, Coburg and Yarra River flow rates (cubic metres per second) at the Johnston Street Bridge during the rainfall event of 8 to 10 March 1995.

Surface salinity at the river site (site 26) was between 10 and 14 during the first day of sampling but increased to 22.5 during the next 24 hr. Salinity levels at all other sites were higher, ranging from 29.0 to 34.7. The surface salinity in Hobsons Bay during a mild rain period is about 33.5 (A. Longmore pers. comm.). Therefore, the influence of

the freshwater flow from the Yarra/Maribyrnong River system and the storm water drains situated along the north-eastern coast of the Bay was already evident at the start of the sampling. The salinity at site 30 returned to pre-rain values within 48 hr. This is attributed to:

(a) cessation of heavy rain within 4 hours of the rain event, and;
(b) mixing of the freshwater outflow with saline Bay waters by wave action.

Metal concentrations

The concentrations of the dissolved, particulate and total metal species for the rain event are listed in Appendices 3, 4 and 5 respectively. Temporal variations in the metal concentrations at each of the five sites were considerable, particularly for the river site (site 26). Samples from the river site had the highest overall concentrations for each of the metals, with the notable exceptions of cadmium and arsenic (Appendix 5, Table 9).

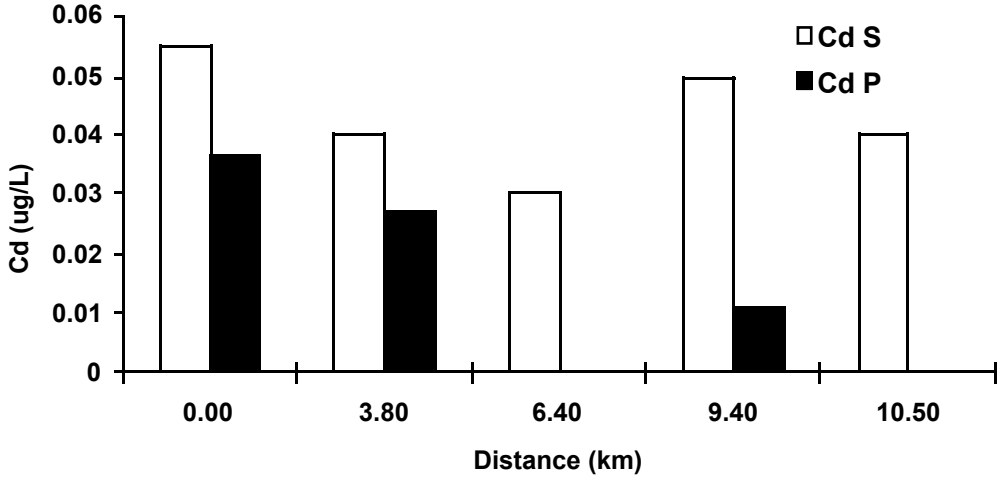
Table 9. Mean concentrations of the dissolved and particulate metal species for Bay-wide waters and rain event samples at sites 26 and 29/30 (combined). Data are μg/L (mercury is in ng/L).

Element	Bay-wide[a] Mean dissolved (n=25)	Rain event Mean dissolved at site 26 (n=6)	Rain event Mean dissolved at sites 29 & 30 (n=4)	Bay-wide[a] Mean particulate (n=25)	Rain event Mean particulate at site 26 (n=6)	Rain event Mean particulate at sites 29 & 30 (n=4)
Cd	0.026±0.014	0.03±0.011	0.04±0.005	0.011±0.013	0.02±0.01	0.01±0.01
Cr	0.04±0.02	0.21±0.21	0.03±0.01	0.09±0.06	1.61±0.90	0.23±0.08
Cu	0.47±0.05	1.72±0.43	0.61±0.06	0.03±0.02	1.02±0.72	0.13±0.04
Fe	0.76±0.44	74±72	2.1±0.7	28.98±18.60	252±102	41.3±13.4
Ni	0.70±0.14	1.83±0.16	0.76±0.03	0.05±0.05	1.35±1.28	0.11±0.06
Pb	0.06±0.02	1.09±0.79	0.19±0.01	0.13±0.14	3.53±1.51	0.48±0.20
Zn	0.47±0.21	19.79±5.01	1.72±1.04	0.11±0.08	4.24±1.91	0.49±0.25
As	2.75±0.27	0.21±0.22	1.04±0.03	-0.09±0.26	0.18±0.53	0.13±0.14
Hg	1.7±0.73	4.39±1.38	2.05±0.92	1.32±1.30	2.91±4.14	-0.78±1.04

a. From Table 3.

Although the concentration of total cadmium species in the first sample from site 26 was about two times greater than the overall mean concentration (0.05 ± 0.02 μg/L) at this site, the remaining samples had concentrations that were close to this mean (Appendix 5). The mean concentrations of dissolved and particulate cadmium species at sites 26 and 29/30 were comparable (< factor of 2 difference) to the respective Bay-wide concentrations (Table 9). No spatial or temporal trends were apparent for cadmium (Figure 23). Concentrations of dissolved and particulate arsenic species at site 26 were close to or below the detection limit (0.6 μg/L). The mean concentration of dissolved arsenic species at site 26 were more than ten times lower than the Bay-wide concentrations (Table 9). At sites 29/30 the margin had decreased to about three times. Concentrations of particulate arsenic species were below the detection limit in all cases.

a)



b)

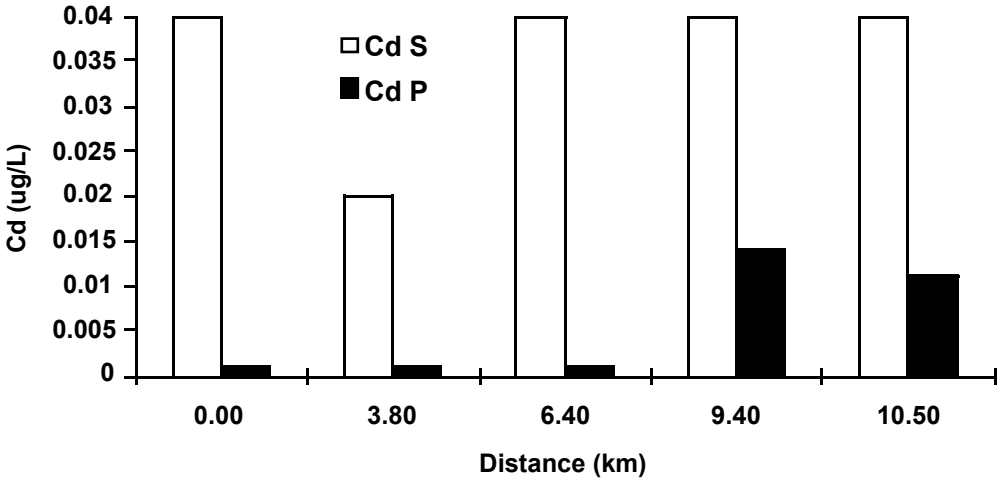
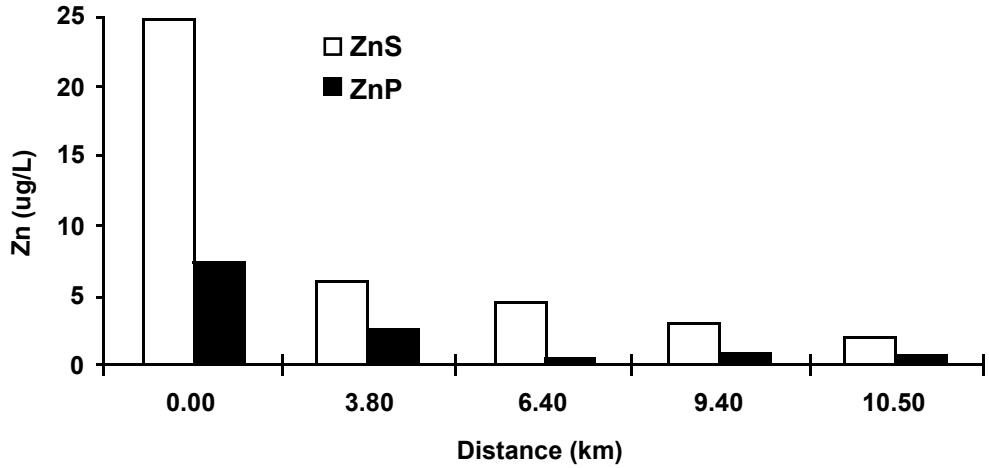


Figure 23. Concentrations of dissolved (S) and particulate (P) cadmium species with distance from site 26 at the start (a) and end (b) of the rain event.

The concentration of total mercury species in the second sample from site 26 was about two times greater that the overall mean concentration (8.2 $\pm$ 3.7 ng/L) at this site, but concentrations of all other samples were close to this mean (Appendix 5). Dissolved mercury species at site 26 had a mean concentration that was about three times the Bay-wide value, but at sites 29/30 the concentration was comparable to the Bay-wide value (Table 9). With the exception of four samples from site 26 (Appendix 4) the concentrations of particulate mercury species were below the detection limit (1 ng/L).

The concentrations of total zinc species at site 26 on each occasion were comparable to the mean concentration (24 ± 5 μg/L) at this site. The highest concentrations were observed in the first (32 μg/L) and last (30.8 μg/L) samples collected at this site. The mean concentration of dissolved species from site 26 was about 42 times the Bay-wide mean, and the concentration of the particulate species was about 38 times the Bay-wide mean (Table 9). At sites 29/30 these differences were much lower (Table 9). Figure 24 indicates that zinc concentrations decreased with distance in moving from site 26 towards site 30. At site 26 the concentration of dissolved zinc species decreased during the first 6.7 hr but then increased again until after 45.6 hr the concentration was comparable to that at 0 hr (Figure 25). The concentration of the particulate zinc species progressively decreased during the initial 22.1 hr of sampling (Figure 25).

a)



b)

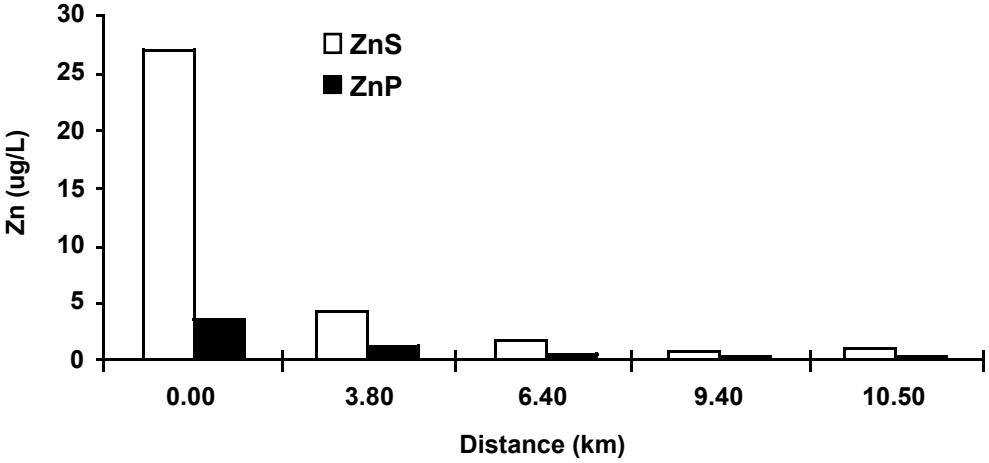


Figure 24. Concentrations of dissolved and particulate zinc species with distance from site 26 at the start (a) and at the end (b) of the rain event.

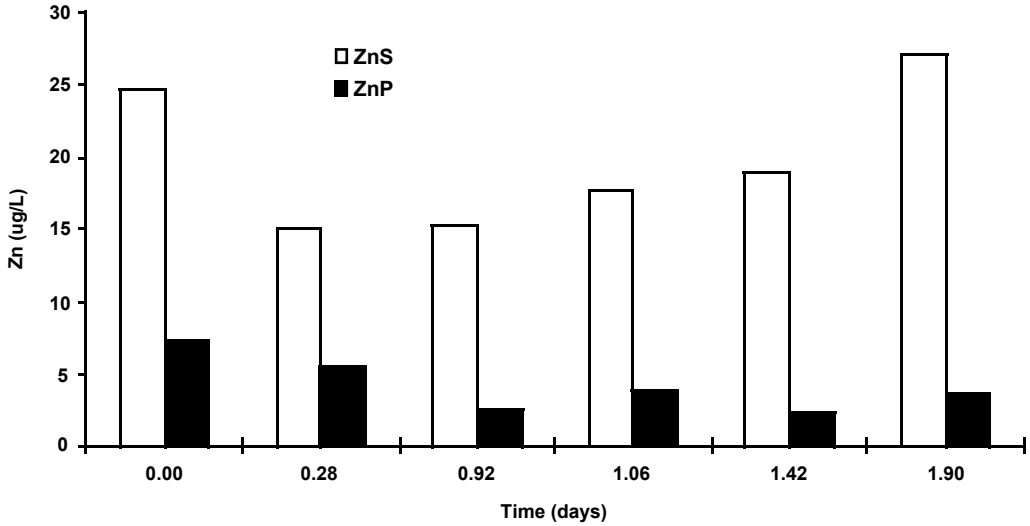
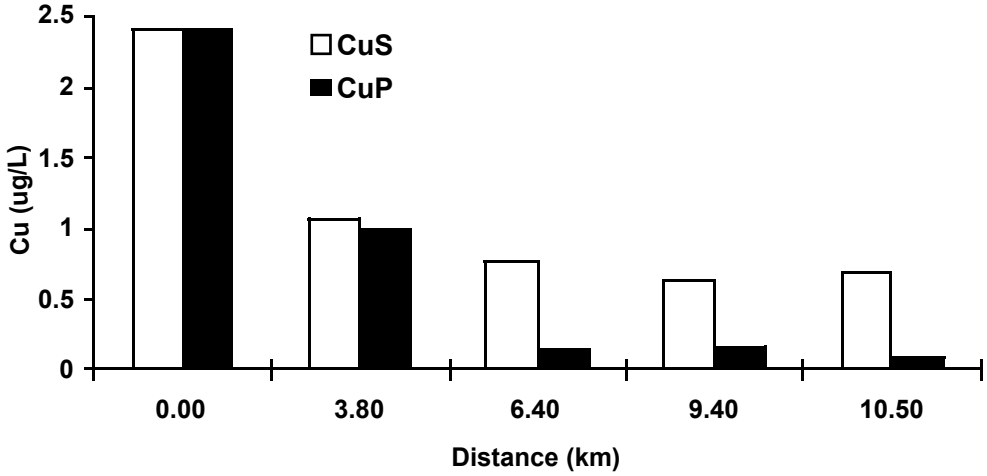


Figure 25. Concentrations of dissolved and particulate forms of zinc at site 26 following a rain event.

The concentrations of total chromium, copper, iron, nickel and lead species were highest in the first sample collected at site 26 (Appendix 5). At this site mean concentrations of particulate species of chromium, copper, nickel and lead were about 18, 34, 27 and 27 times greater than the corresponding Bay-wide means (Table 9). Mean concentrations of the respective dissolved species were about 5, 4, 3 and 18 times the Bay-wide means (Table 9). Figures 26 to 30 illustrate that the concentrations of the particulate and dissolved species of some of these metals decreased both with distance from site 26, and with elapsed time following the rain event.

Iron differed from the other metals only in that the proportion of the dissolved species at site 26 was greater (about 97 times) than the proportion of the particulate species (about 9 times) compared to the respective Bay-wide values (Table 9). However, as with the other metals, the corresponding differences for the dissolved and particulate species were much smaller at sites 29/30 (Table 9). Iron exhibited the most obvious temporal and spatial concentration trends of all the metals. At site 26, concentrations of particulate iron species decreased from 427 to 326 µg/L within 6.7 hr of the start of sampling, and for the following 38.9 hr the concentrations remained between 175 and 207 µg/L. Dissolved iron species decreased from 216 to 32.7 µg/L within 6.7 hr, after which the concentrations hovered between 23.7 and 78.2 µg/L (Figure 29). Similar patterns, where the highest concentrations were encountered in the early samples, were observed for chromium, copper, nickel and lead (Appendices 3 and 4). Figure 29 shows that the concentration of particulate iron species increased slightly 25.4 hr after the start of sampling. This increase corresponds to the slight increase in river flow that followed the main event (Figure 22). A similar pattern can be seen for particulate lead species (Figure 30).

a)



b)

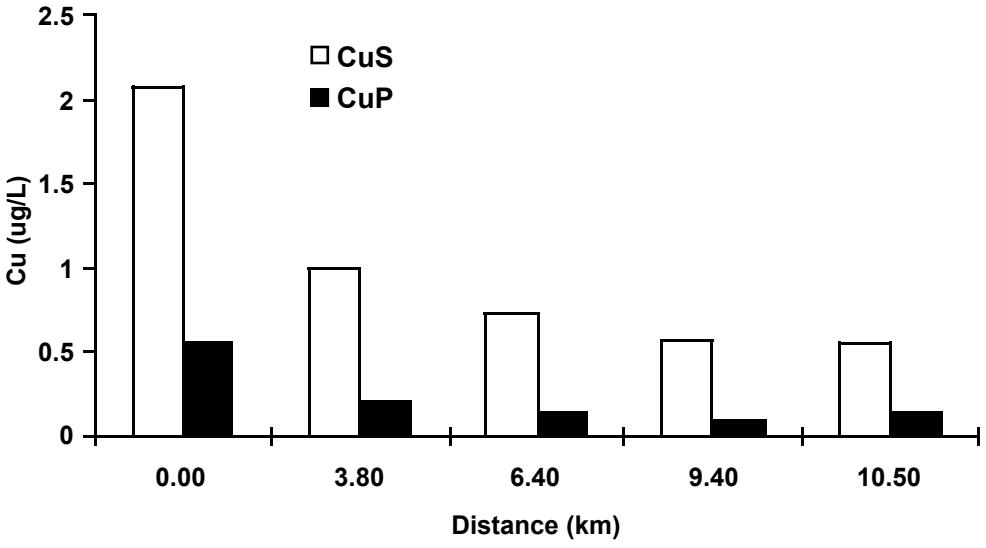
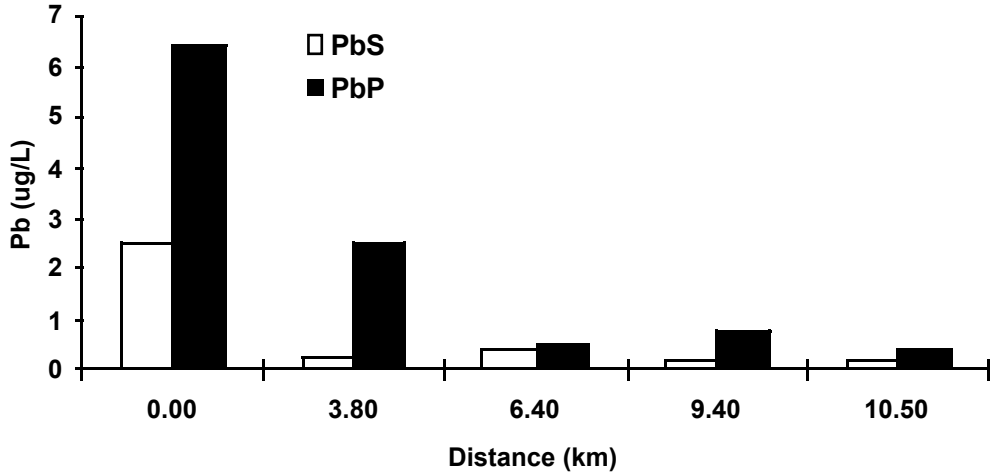


Figure 26. Concentrations of dissolved and particulate copper species with distance from site 26 at the start (a) and at the end (b) of the rain event.

a)



b)

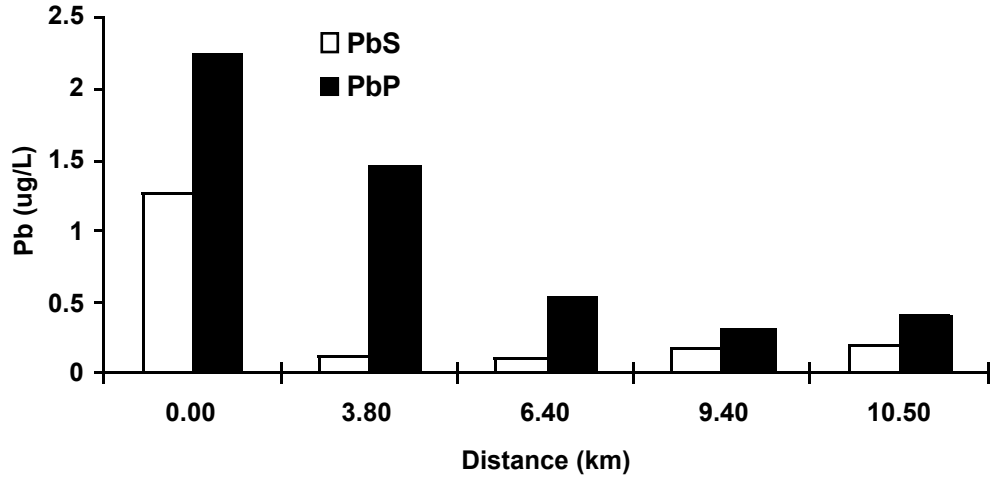
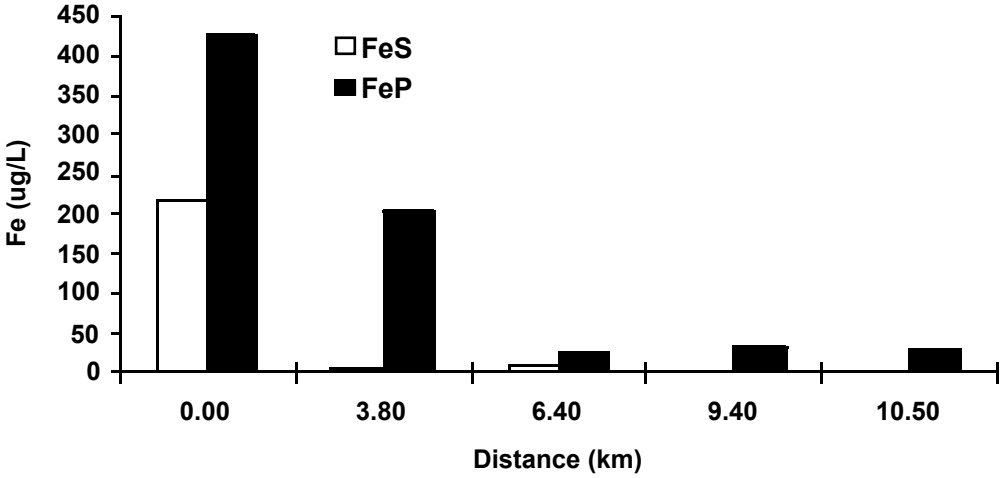


Figure 27. Concentrations of dissolved and particulate lead species with distance from site 26 at the start (a) and at the end (b) of the rain event.

a)



b)

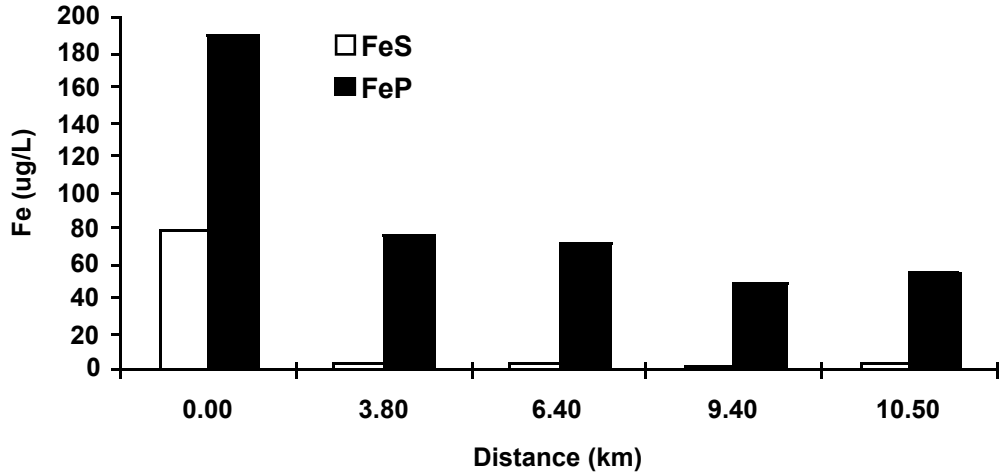


Figure 28. Concentrations of dissolved and particulate iron species with distance from site 26 at the start (a) and at the end (b) of the rain event.

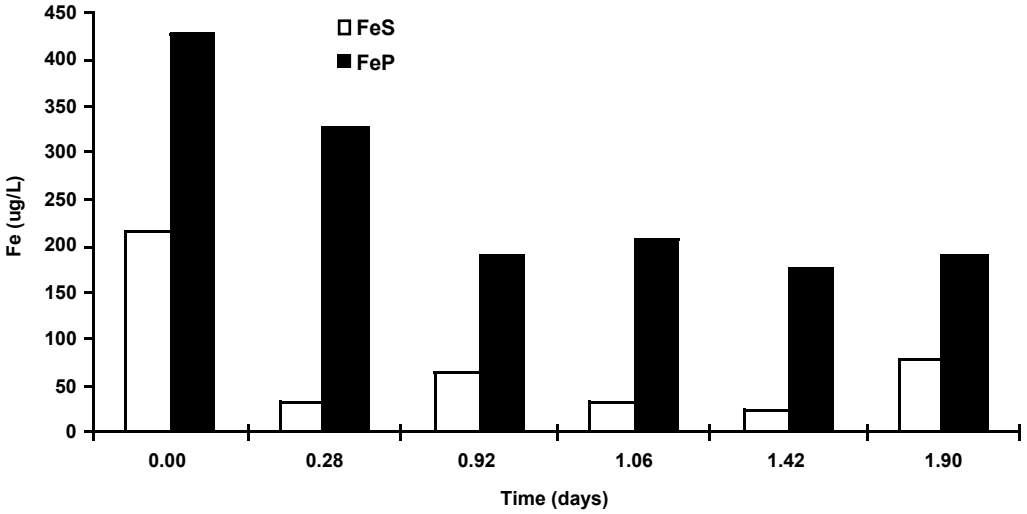


Figure 29. Concentrations of dissolved (s) and particulate (p) forms of iron at site 26 following a rain event.

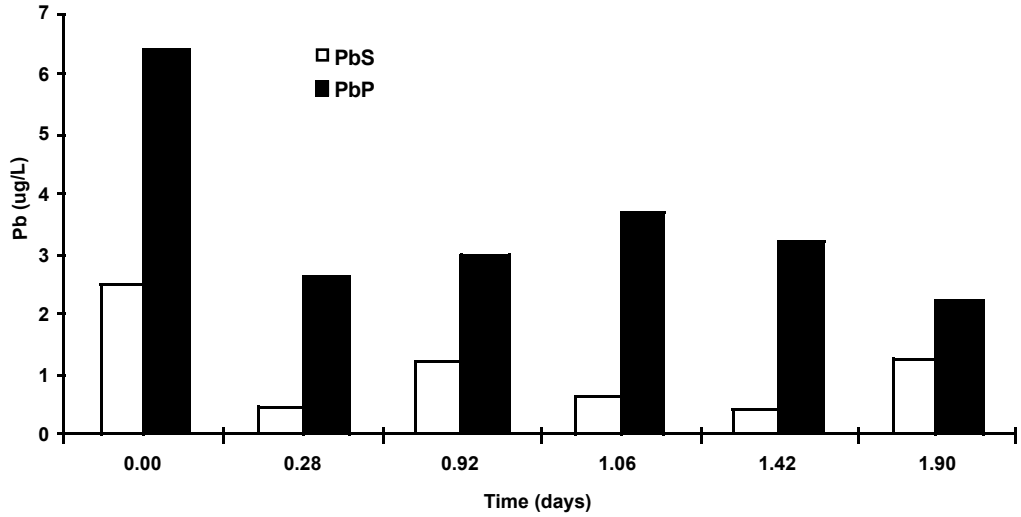


Figure 30. Concentrations of dissolved (s) and particulate (p) forms of lead at site 26 following a rain event.

Significant ($P<0.001$) positive interelement correlations were found for the dissolved and particulate metal species (Tables 11 & 12, and Figures 31, 32, 33 & 34). Significant ($P<0.001$) negative correlations were found between dissolved arsenic and chromium, copper, iron, nickel, lead and zinc (Table 11 and Figure 35). In the case of the particulate metal species, this suggests that there may be a common source of the metals involved. The negative correlation between arsenic and the other metals is a consequence of the saline waters having a higher arsenic concentration than the river water.

Table 10. Pearson Correlation Coefficients for dissolved metal species for the rain event waters (8-10 March 1995). Number of Observations = 19.

	Cd	Cr	Cu	Fe	Ni	Pb	Zn	As	Hg
Cd	1.0000								
P	0.0								
Cr	0.4392	1.0000							
P	0.0599	0.0							
Cu	0.1512	0.8585	1.0000						
P	0.5365	**0.0001**	0.0						
Fe	0.3889	0.9848	0.8582	1.0000					
P	0.0998	**0.0001**	**0.0001**	0.0					
Ni	0.0430	0.7128	0.9491	0.7300	1.0000				
P	0.8611	**0.0006**	**0.0001**	**0.0004**	0.0				
Pb	0.3406	0.9610	0.8834	0.9799	0.7774	1.0000			
P	0.1535	**0.0001**	**0.0001**	**0.0001**	**0.0001**	0.0			
Zn	0.1160	0.7672	0.9669	0.7633	0.9823	0.8136	1.0000		
P	0.6361	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.0001**	0.0		
As	0.0195	-0.704	-0.900	-0.736	-0.951	-0.765	-0.9185	1.0000	
P	0.9366	**0.0008**	**0.0001**	**0.0003**	**0.0001**	**0.0.001**	**0.0001**	0.00	
Hg	0.1521	0.3370	0.3463	0.3555	0.3075	0.2869	0.2981	-0.2918	1.0000
P	0.5340	0.1582	0.1463	0.1352	0.2003	0.2336	0.2150	0.2254	0.0

Table 11. Pearson Correlation Coefficients for particulate metal species for the rain event waters (8-10 March 1995). Number of Observations = 19.

	Cd	Cr	Cu	Fe	Ni	Pb	Zn	As	Hg
Cd	1.0000								
P	0.0								
Cr	0.7315	1.0000							
P	**0.0004**	0.							
Cu	0.7779	0.9256	1.0000						
P	**0.0001**	**0.0001**	0.						
Fe	0.6841	0.9654	0.9234	1.0000					
P	**0.0012**	**0.0001**	**0.0001**	0.0					
Ni	0.5978	0.8744	0.9191	0.8989	1.0000				
P	0.0069	**0.0001**	**0.0001**	**0.0001**	0.				
Pb	0.8506	0.8818	0.9185	0.8834	0.7970	1.0000			
P	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.0001**	0.0			
Zn	0.67097	0.8673	0.9366	0.9361	0.8912	0.9192	1.0000		
P	**0.0017**	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.0001**	0.0		
As	0.0648	0.1567	0.2141	0.2862	0.4191	0.0721	0.3027	1.0000	
P	0.7919	0.5217	0.3786	0.2348	0.0741	0.7692	0.2078	0.0	
Hg	0.2217	0.3946	0.4435	0.5722	0.5649	0.2869	0.2981	0.2916	1.000
P	0.3616	0.0945	0.0571	**0.0105**	0.0117	0.2336	0.2150	0.2254	0.0

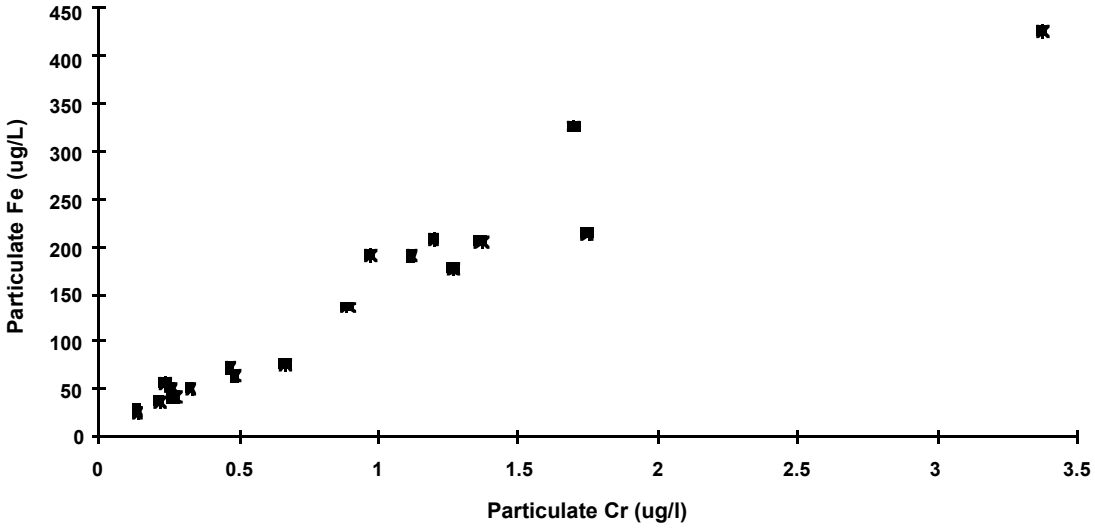


Figure 31. Scatter diagram showing the correlation between particulate iron and chromium for the rain event samples collected during 8 to 10 March 1995.

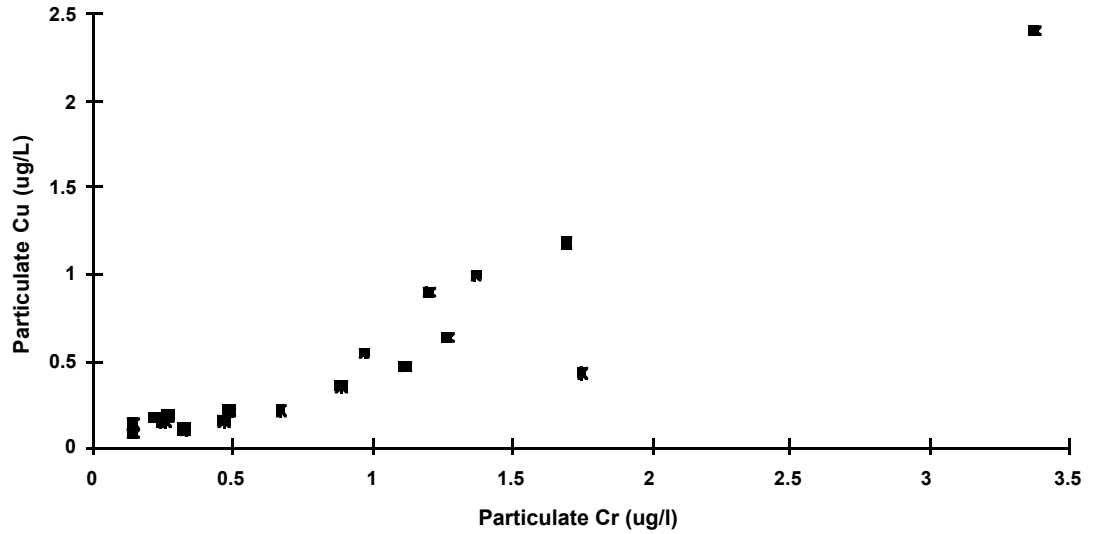


Figure 32. Scatter diagram showing the correlation between particulate copper and chromium for the rain event samples collected during 8 to 10 March 1995.

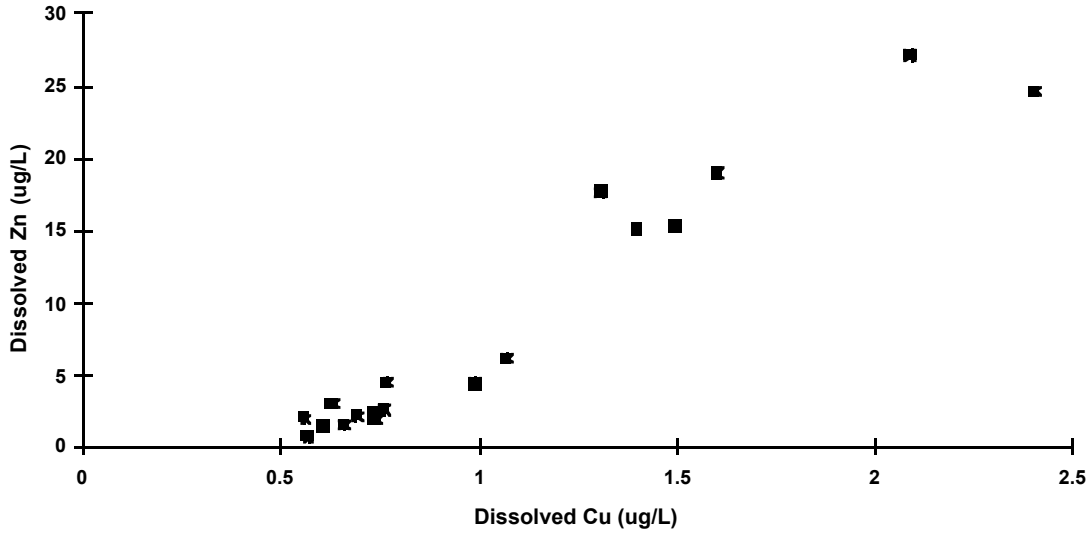


Figure 33. Scatter diagram showing the correlation between dissolved zinc and copper for the rain event samples collected during 8 to 10 March 1995.

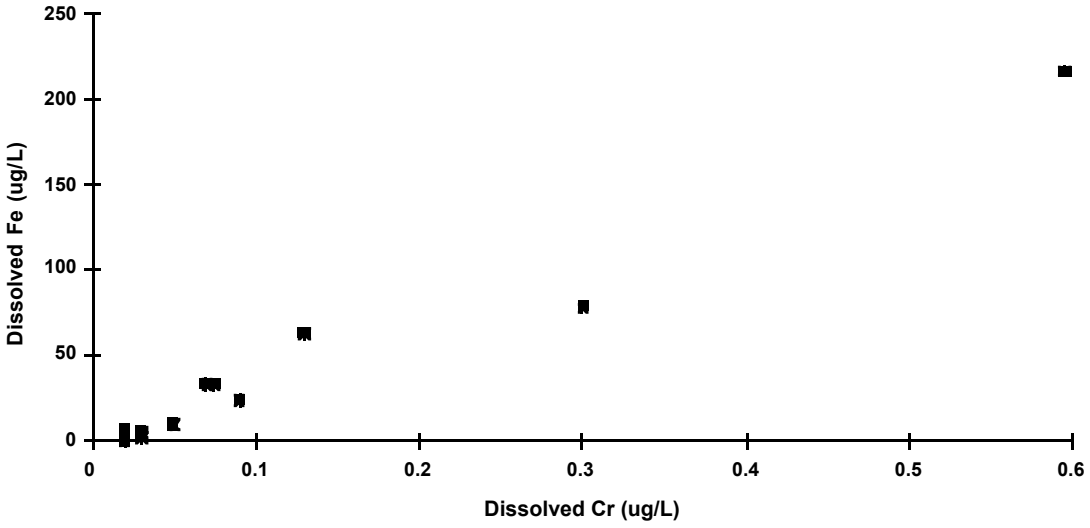


Figure 34. Scatter diagram showing the correlation between dissolved iron and chromium for the rain event samples collected during 8 to 10 March 1995.

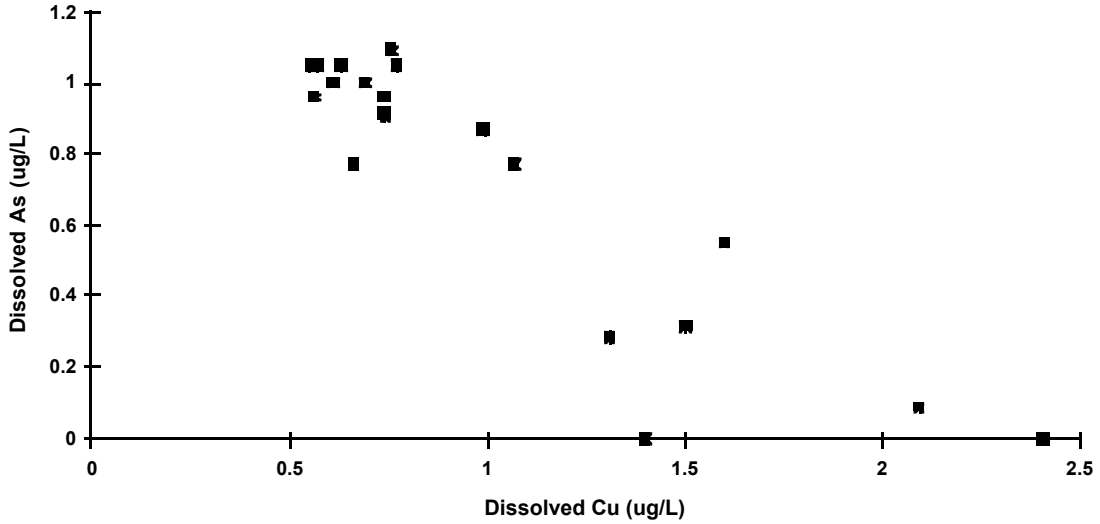


Figure 35. Scatter diagram showing the correlation between dissolved arsenic and copper for the rain event samples collected during 8 to 10 March 1995.

4. DISCUSSION

Bay-wide Survey

Overall, the dissolved metal concentrations observed in this Bay-wide survey fell within the range of concentrations reported for near-shore and estuarine environments in the northern hemisphere. Concentrations of total copper, nickel and zinc were lower than those obtained within the previous four years from the EPA fixed site in the centre of the Bay, while no differences were observed for cadmium, iron, lead, arsenic and mercury. Although the highest metal concentrations were observed in the samples from the Corio Bay and Hobsons Bay sites, the concentrations for most of the metals were lower than previously reported for these sites. The exceptions were arsenic and mercury where no significant differences were observed. Comparisons with other available data suggest that metal concentrations in the waters of the Bay are now lower than was the case 20 years ago. However, it is not possible to determine whether these differences are genuine or partly due to the application, in more recent times, of sampling and analytical procedures that reduce contamination.

Sand flathead, regarded as a biological indicator of mercury contamination, collected from the Bay during the late 1970s contained mercury concentrations above the food standards maximum permitted concentration (MPC). Although data for mercury in Bay water are not available for that period, it is assumed that anthropogenic mercury inputs were responsible for the elevated mercury concentrations in the fish (Walker 1982). Mercury concentrations in sand flathead from the Bay are now below the MPC (Fabris *et al.* 1992) and the mercury concentrations, determined in the present study and from the recent data for the fixed sites monitoring program, are correspondingly low by international standards. Occasional episodes of elevated mercury concentrations in the waters of the Bay still occur (Gibbs 1987). Continued monitoring is essential to detect fugitive discharges of mercury (and other elements) in order to ensure the continuing improvement of the water quality of the Bay.

The contamination of Corio Bay by cadmium is mostly historic and goes back at least 20 years (Phillips *et al.* 1992). However, the data from the present study, together with observations from the EPA fixed sites monitoring program, indicate that cadmium concentrations in the waters of Corio Bay are now lower than in the past. Indeed, the concentrations over the past four years have generally been below 0.2 µg/L. Cossa (1988) showed that mussels exposed to cadmium concentrations above 0.2 µg/L will accumulate cadmium to levels that exceed the MPC for cadmium in shellfish. Recent data for cadmium in mussels from Corio Bay confirm that cadmium concentrations in mussels have decreased (Nicholson *et al.* 1991). Although cadmium concentrations in the Bay are relatively low, data on the bioaccumulation of cadmium by oysters in the Bay suggest that further improvement is needed in order for conditions to be comparable with other Victorian coastal environments (Conron 1994 unpublished).

Table 12 shows data comparing the metal loads in the waters of the Bay with the estimated annual loads to the Bay from the major input streams and drains (assuming a residence time of one year). The data indicate that for chromium, iron, lead and zinc the annual loads from inputs exceed those of the standing loads in the Bay. Most of the chromium, iron and lead occur in the particulate fraction, therefore sedimentation probably accounts for the difference. The zinc discrepancy is not so readily explained since only 20% of the zinc occurs in the particulate fraction.

Table 12. Comparison of total metals loads from inputs with load in Port Phillip Bay calculated using data from this study.

Variable	Load from inputs tonne/yr		Load in Bay tonne[b]	Conc. from input µg/L[c]	Conc. in Bay µg/L[d]
	Excluding WTC[a]	WTC[e]			
Cd	0.31	0.02[f]	0.92	0.013	0.037*
Cr	12.6	3.9	3.2	0.67	0.13**
Cu	14.6	2.7	12.4	0.70	0.50*
Fe	3608	180	737	153	29.7**
Ni	9.2	4.9	18.8	0.57	0.76*
Pb	30	1.1	4.6	1.26	0.19**
Zn	121	5.8	14.2	5.12	0.57**
As	2.3		66	0.09	2.66*
Hg	0.08	0.02[f]	0.07	0.004	0.0029
Se					<0.8

a. NSR 1993

b. calculated from cruise 1 data and using a volume of 24785 x 10^9 L as the Bay volume (Cowdell *et al.* 1985).

c. calculated from input loads and Bay volume.

d. mean data for total concentration from cruise 1.

e. Murray (1994)

f. Melbourne Water unpublished data.

*. Concentration in Bay exceeds concentration calculated from input - additional source from elsewhere?

**. Concentration in Bay is less than calculated from input - removal by sedimentation?

Arsenic concentrations in the Bay are at the high end of those reported internationally for near-shore and estuarine embayments. In particular, they are high in comparison with arsenic concentrations observed from Victoria's other coastal environments. Available data for arsenic inputs into the Bay indicated that these are not the current source of the elevated arsenic in the water column (Table 12). Data for arsenic input from the WTP are unavailable, but it is unlikely to explain the difference since the input from this source would have to be massively high compared to all other inputs. Alternatively, the excessive arsenic load in the Bay could be explained if some diagenic process in the sediments was acting to release arsenic into the water column. Arsenic concentrations in surface sediments of the Bay are depleted relative to deeper sections and this suggests that arsenic is being released to the water column (Fabris *et al.* 1994). The process leading to elevated arsenic concentrations in Port Phillip Bay needs further investigation before the issue can be resolved.

Rain event

Yarra River flow rates 24 to 36 hr after the rain event were close to average river flows for March (MW, 1995). Therefore, it may be assumed that the metal concentrations in samples collected after 24 hr approximated those during normal flow conditions in March. The mean concentrations of the dissolved and particulate species of cadmium, arsenic and mercury in river water were comparable to those found within the Bay (Table 9). Mean concentrations for the particulate species of chromium, copper, iron, nickel, lead and zinc in the river water (Site 26) ranged from about 8 (Fe) to 39 (Zn) times their Bay-wide concentrations. The corresponding concentrations for the dissolved species ranged from about 4 (Cu) to 42 (Zn). The metal loads entering the Bay from the Yarra River system during a rain event of the magnitude that occurred on 8 March 1995 range from about 8 to 25 times the loads that are carried into the Bay during normal (March average) flow conditions over the same time interval (Table 13). In all probability, these values are underestimates since:

- the actual concentrations at peak flow were probably higher than the concentrations used in the calculations since the sampling missed the pre-peak and peak flows. Additionally the concentrations during actual low flow are probably lower than those used here (Appendix 6), and;
- the load calculations exclude flows from the more than 300 other streams and storm water drains that discharge directly into the Bay.

5. CONCLUSIONS

On the basis of the data obtained both from this survey, the longer term fixed sites monitoring program and the rain event exercise we conclude that:

- Heavy metal concentrations in the Bay, with the exception of arsenic, are within the range of concentrations found in near-shore environments elsewhere in developed regions of the world.
- Generally, heavy metal concentrations in the Bay are now lower than in the past.

Table 13. Approximate metal loads entering the Bay from the Yarra River system during the rain event of 8 March 1995 compared with estimated low flow loads. Data are in kg (mercury load is grams)[a].

Element	Load from the rain event during peak flow (0:00 hr 8/3/95 to 6:00 hr 9/3/95)	Load from low flow conditions over the same time (30 hr)	Proportion of load from the rain event as a % of low flow load.
Cd	0.45	0.038	1184
Cr	19.7	0.95	2074
Cu	24.5	1.8	1361
Fe	3278	178	1842
Ni	27.9	1.8	1550
Pb	44.1	2.9	1251
Zn	154	18.6	828
As	6.8	0.28	2429
Hg	58.6	4.8	1221

a. Estimated from concentrations of total metal species at site 26 (Appendix 5) and River flow data supplied by Melbourne Water. The calculation procedure is outlined in appendix 6.

- The highest metal concentrations occur in Corio and Hobsons Bays.
- Arsenic concentrations are elevated compared to other Victorian coastal environments, but it appears that inputs to the Bay are not the source of the arsenic.
- Rain events cause transient increases in the metal load to the Bay, and it is likely (depending on the frequency of such events) that they contribute a considerable proportion of the annual metal load that is carried into the Bay by rivers and streams. Additionally, the transient increases in metal loads from rain events may have other direct adverse effects on the Bay including:
  (a) the increased flow could act to transport suspended matter and associated metals further into the Bay than would otherwise be the case, and;
  (b) the sudden increase in metal concentrations in the water column may exert adverse effects on biota either by causing direct toxic effects or through bioaccumulation.

6. ACKNOWLEDGEMENTS

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Appendix 1. Decimal latitudes and longitudes for sampling sites used during theBay-wide sampling cruise (22 - 25 June 1993) and the Rain event (8-10 March 1995).

Bay-wide Survey			Rain Event		
Station	Lat. South	Long. East	Station	Lat. South	Long. East
1	38.128	144.363	26	37.8358	144.8977
2	38.1309	144.456	27	37.8648	144.9183
3	38.1439	144.535	28	37.8857	144.9345
4	38.1022	144.527	29	37.9068	144.9540
5	38.0967	144.562	30	37.9199	144.9546
6	38.0702	144.563			
7	38.086	144.62			
8	38.0552	144.636			
9	38.0267	144.64			
10	37.9778	144.713			
11	38.035	144.716			
12	38.0834	144.718			
13	37.9997	144.854			
14	37.9585	144.85			
15	37.8836	144.834			
16	37.8846	144.885			
17	37.863	144.914			
18	37.89	144.945			
19	37.9265	144.963			
20	37.9185	144.901			
21	37.9984	144.925			
22	37.9891	144.975			
23	38.087	145.009			
24	38.095	144.936			
25	38.2812	144.6599			