Stormwater Heavy Metal Loadings to Port Jackson Estuary, NSW, Australia

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Declaration

The field and analytical work discussed in this Masters Thesis was undertaken by Stephen Barry, a former student of the University of Sydney. All other work undertaken for this Masters Thesis, including the analysis of data, modelling and written component, is my own work, unless otherwise referenced. This document is less than 80,000 words and is in compliance with the University's academic honesty requirements.

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Louisa Rochford	Date

Abstract

Investigations of fluvial and estuarine sediments have indicated stormwater is an important source of heavy metals to Port Jackson estuary and high concentrations of these sedimentary contaminants are a threat to the healthy functioning of the estuarine ecosystem. Stormwater remediation devices have been installed in stormwater channels entering the estuary, however these devices are mainly for removing gross pollutants and are ineffective in removing heavy metals from stormwater.

A thorough characterisation of heavy metal inputs and behaviour has been undertaken by sampling, analysing and modelling heavy metals in stormwater entering Port Jackson estuary to provide a rigorous data base for future remediation efforts. A conceptual model of transport and fate of heavy metals in stormwater entering Port Jackson estuary has also been developed to identify heavy metals, subcatchments and flow regimes requiring remediation, and to assist in designing remediation devices for optimum removal of heavy metals from stormwater.

Modelling of stormwater using the Model for Urban Stormwater Improvement Conceptualisation (MUSIC) indicated that the average annual discharge of stormwater from the Port Jackson catchment was 215,307 ML. Average annual loadings of arsenic, cadmium, chromium, copper, nickel, lead and zinc in stormwater discharging to Port Jackson estuary were 0.8, 0.5, 1.7, 3.2, 1.1, 3.6 and 17.7 tonnes per year, although comparison to other studies in the catchment suggests these values may be underestimations of actual loadings by 1.3 to 10 times. The proportion of heavy metals discharged under low-flow conditions (<5mm of rainfall in 24 hours), medium-flow conditions (between 5 and 50mm in 24 hours), and high-flow conditions (>50 mm of rainfall in 24 hours) was 6.5%, 62.5% and 31%, respectively.

The conceptual model indicates stormwater loadings of copper, lead and zinc pose a risk to the health of riverine and estuarine ecosystems in the catchment and these metals should be targeted for remediation. Stormwater channels which should be prioritised for remediation include the channels entering southern embayments west of Darling Harbour; Duck, Parramatta and Lane Cove Rivers; and the channels and rivers entering Neutral, Long and Sugarloaf Bays. Stormwater loadings of lead are predominantly associated with suspended particulates, whereas loadings of copper and zinc are equally partitioned between dissolved and particulate phases. Stormwater remediation strategies should target both dissolved and particulate phases to ensure effective removal of copper, lead and zinc.

Research suggests heavy metals in stormwater discharged to the estuary under high-flow conditions

are rapidly exported seaward and bypass the estuary. Preliminary research also suggests that under medium-flow conditions, particulate heavy metals bypass the embayments of Port Jackson and are deposited in the main channel. Once deposited in the main channel, particulate heavy metals are likely to be remobilised and removed from the estuary through multiple phases of resuspension. Although further research is required in this area, this preliminary research suggests remediation should target low-flow conditions.

The findings of the current research could be used to identify appropriate remediation strategies for dissolved and particulate phase heavy metals in stormwater discharging to Port Jackson estuary. However, in designing stormwater remediation devices, consideration should also be given to the range of contaminants that may be present in stormwater entering Port Jackson estuary (including suspended solids, nutrients, pesticides and organics).

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1. Introduction

1.1 Background

Research undertaken over the last 15 years has shown extensive areas of sediment in the Port Jackson estuary (Figure 1) to be contaminated by a range of toxicants including heavy metals (Birch 1996; Birch et. al., 1996; Birch and Taylor, 1999; 2000a), organochlorine compounds (Birch and Taylor, 2000b) and polycyclic aromatic hydrocarbons (McCready et. al., 2000). Studies of the potential toxicity of these contaminants to biota in the estuary have demonstrated that heavy metals, and in particular copper, lead and zinc, are of concern for the health of the aquatic ecosystem (Irvine and Birch, 1998; Birch and Taylor, 2000a,b; Hatje et. al., 2001a).

Industrial and commercial activities in the catchment have resulted in contamination of Port Jackson estuary over a long period (Birch and Taylor, 1999). Recent research has identified urban stormwater as the largest contemporary source of heavy metals to Port Jackson (Birch et. al., 1996; Birch & Taylor, 1999; Barry et. al., 2000). A strong spatial relationship exists between the location of major stormwater outlets and distribution of heavy metals in estuarine sediment (Taylor, 2000). Concentrations of heavy metals are generally higher in fluvial sediment from stormwater canals compared to sediment in the adjacent estuary, indicating that stormwater canals continue to supply a substantial flux of heavy metals to the estuary (Birch et. al., 1996).

1.2 Urban Stormwater

Urbanisation has changed the natural movement of water in the Port Jackson catchment. Vegetated areas have been replaced with impervious surfaces, such as roofing and paving, and the topography has been altered through land levelling and grading. Natural water courses have been replaced with stormwater drainage systems comprising gutters, pipes and channels, which rapidly convey stormwater runoff to receiving waters and minimise risk of flooding in urban areas (ARMCANZ/ANZECC, 2000a).

Stormwater includes major flows generated by rainfall (wet weather flows), as well as dry weather flows. Dry weather flows generally originate from groundwater (baseflows), permitted and illegal discharges, excess irrigation, automobile washing and other residential and commercial activities (McPherson et al., 2005; ARMCANZ/ANZECC, 2000a). Overflows from sewerage systems may also become part of stormwater flows during wet weather (ARMCANZ/ANZECC, 2000a).

Urban stormwater is recognised as a major source of pollutants and is estimated to contribute between 50 and 90% of the annual contaminant load in most Australian waterways (Water Board, 1993b). Contaminants washed from surfaces in the urban environment by rainfall are transported to receiving waters by stormwater. Urban stormwater generated by dry weather sources may also contain contaminants.

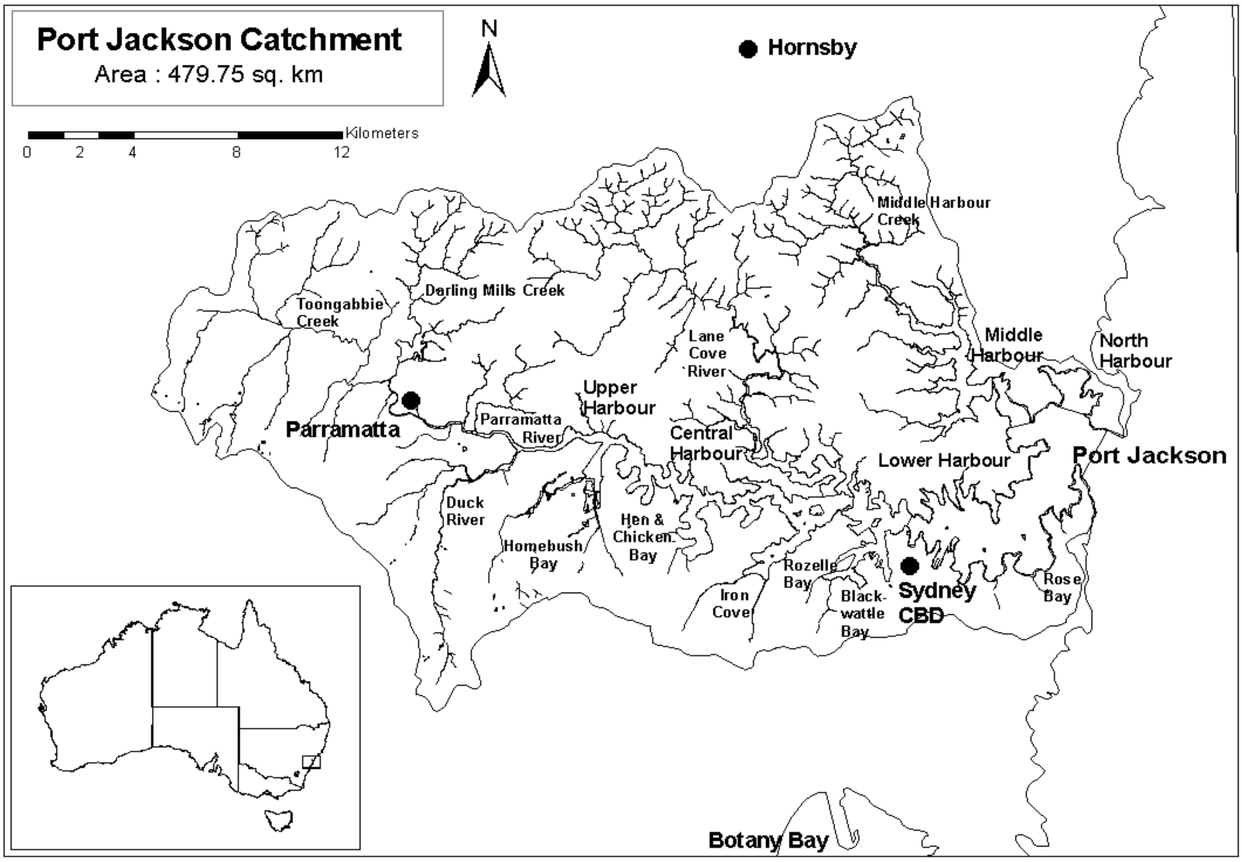


Figure 1: The Port Jackson estuary and catchment

1.3 Sources of Heavy Metals

Major sources of heavy metals in urbanised catchments include road surfaces, atmospheric deposition, roof runoff, industrial activities, soil erosion, contaminated sites, sewer overflows and illegal discharges (Water Board, 1993a; Birch et. al., 1999; McPherson et al., 2005).

Investigations of road surfaces and adjacent gully pots in Port Jackson catchment found that road dust is highly enriched in heavy metals (Scollens, 1998, Birch et al., 1999) and that there is a direct relationship between concentration of trace metals in road dust and traffic volumes (Scollens, 1998). Contaminant fingerprinting undertaken by Brown and Peake (2006) indicated that road dust was a significant source of particulate heavy metals in stormwater collected from urban catchments in New Zealand. These findings are supported by a study by Kayhanian et al. (2007), which found higher traffic volumes resulted in higher concentrations of heavy metals in stormwater.

Road dust and associated particulate metals are the result of wear on brakes, tyres and wheel balances and the degradation of asphalt road surfaces (Peterson and Batley, 1992). In the study conducted by Davis et al. (2001), vehicle brake emissions were found to be an important source of copper, and tyre wear was found to be an important source of zinc. Leakage of engine oil and the corrosion of parts and bodywork are other potential sources of road dust (Revitt et al., 1990).

Atmospheric deposition, both wet and dry, is a significant source of heavy metals in stormwater. Hamilton et al. (1987) found the mass of heavy metals deposited from the atmosphere greatly exceeded the mass removed by stormwater runoff, with a fifteen-fold difference for zinc, decreasing to a four-fold difference for copper. Davis et al. (2001) also found atmospheric deposition to be a significant source of heavy metals in urban stormwater runoff. Heavy metals in the atmosphere are probably derived from vehicle emissions, industrial emissions, and resuspension of particulates from roads and exposed soils (Revitt et al., 1990).

Building structures and industrial land uses have also been identified as important sources of heavy metals in stormwater. Davis et al. (2001) found building structures to be an important source of lead, copper, cadmium and zinc in stormwater. Brown and Peake (2006) found high concentrations of zinc in stormwater were linked to extensive use of zinc galvanised roofing for houses in the catchment and elevated concentrations of copper and lead were linked to industrial land uses.

Source of heavy metals, as reported in the AWT EnSight (1993) investigation, are provided in Table 1 below.

Heavy Metal	Sources
Arsenic	Soils, insecticides, fungicides
Cadmium	Tyre wear, insecticides, combustion
Chromium	Metal plating, moving parts, brake lining wear, cement pathways
Copper	Metal plating, insecticides, fungicides, leaching from copper pipes, roofing, brake lining wear
Nickel	Diesel fuel exhaust, petrol exhaust, lubricating oils, metal plating, asphalt paving
Lead	Tyre wear, lubricating oils, grease, leaded petrol
Zinc	Galvanised roofs, tyre wear, motor oil, grease

Table 1: Sources of heavy metals in urban stormwater

1.4 Stormwater Quality Modelling

The New South Wales (NSW) government has recognised that pollution of urban stormwater is a significant problem. The Urban Stormwater Program was implemented in 2001 to encourage and support improved urban stormwater quality management practices and improve the condition of urban waterways across the State. As part of this program, local councils were required to prepare and implement stormwater management plans for urban areas (Stormwater Trust, 2001).

One of the tools used in management of urban stormwater is water quality modelling. Water quality models have the ability to predict loadings of various types of stormwater pollutants from catchments (Atlanta Regional Commission, 2001). Interest in water quality models has grown due to the expense involved in obtaining monitoring data. Predictive models can aid in management of unmonitored catchments.

Most water quality models available within Australia and internationally are for prediction of nutrient and sediment generation at the catchment scale. The Model for Urban Stormwater

Improvement Conceptualisation (MUSIC) is one of the more commonly used models in Australia for simulation of nitrogen, phosphorous and suspended sediment loadings in urban stormwater.

Modelling generation of metals from the urban environment is an emerging science and there is still considerable research being undertaken in this area. Cycling and transportation of metals in the urban environment is complex and influenced by metal characteristics, availability of metals in the urban contributing area and urban hydrological conditions (Yuan et al., 2001). Rainfall volume and intensity, catchment size and slope, and antecedent dry period length have also been identified as factors influencing the load of metals in stormwater from urban areas (Brezonik and Stadelmann, 2002) adding to the potential complexity of modelling approaches.

Internationally, there have been a number of metal generation models developed using a range of approaches. The capabilities and complexity of these metal generation models vary, as do the application for which they were designed.

Yuan et al. (2001) developed a model, which assumed that transport of metals was correlated to transport of suspended sediment from urban impervious surfaces. Cycling of total suspended sediment and associated heavy metals in the urban area was depicted with pollutant accumulation and wash-off processes. The model was developed and verified using monitoring data for lead from a highway in Perth. As a result, there are limitations to the applicability of the model to other urban catchments, particularly those where there may be significant areas of parkland or agricultural land.

Revitt et al. (1990) developed a simple predictive model, which related atmospheric heavy metal concentrations to heavy metal concentrations in urban stormwater. Mass balance studies investigated heavy metal deposition rates from the atmosphere through wet (precipitation) and dry deposition and identified processes that prevented metals from being washed off by stormwater (e.g. street sweeping, resuspension and binding to sediments retained in gully pots). The model closely predicted heavy metal concentrations for two stormwater events, however reproduction of a third event was poor. The poor performance of this model is probably related to the lack of specificity of hydrological characteristics of the catchment.

Solo-Gabriele and Perkins (1997) developed a catchment-specific model that quantified streamflow, suspended sediment and metals transport. The streamflow hydrograph was examined and separated into three components: quick-storm flow, slow-storm flow and long-term baseflow. Sediment inputs associated with each of the streamflow components were also defined. The model was developed using monitoring data which defined dissolved and particulate metals concentrations for each streamflow and sediment component. This approach to modelling the generation of metals from the urban environment removed the complexity associated with the investigation of catchment areas, including analyses of stormwater infrastructure, impervious areas and groundwater system.

Brezonik and Stadelmann (2002) compiled lead and other pollutant data collected in 15 studies and used it to develop predictive models which related runoff volumes, loads and concentrations to physical, land use and climatic characteristics of small catchments. Lead loadings were found to be more closely correlated with total precipitation, rainfall intensity and antecedent dry period, rather than drainage area. The models that were developed were found to be suitable for prediction of lead concentrations in small unmonitored catchments.

A widely used model for simulation of heavy metal loads during storm events is the United States Environment Protection Agency (USEPA) Storm Water Management Model (SWMM) (Huber and Dickenson, 1988). This model is relatively sophisticated and runs hydrologic, hydraulic and water quality simulations. The hydrologic simulation considers how the processes of rainfall, evaporation, infiltration, groundwater discharge and overland flow in the catchment generate runoff. Runoff is then routed using the hydraulic capabilities of the model which diverts the flow through the drainage system network of pipes, channels, storage/treatment units and diversion structures.

McPherson et al. (2005) used the SWMM to simulate the wet-weather load of heavy metals in a southern Californian catchment. The pollutant loads associated with runoff were generated by attributing flow weighted event mean concentrations to each land use in the catchment. This approach was used because it was considered that total load estimated with event-mean concentrations for a long-term simulation may be as accurate as that obtained using more complex models, e.g. build up wash off models (Charbeneau and Barrett, 1998).

1.4.1 Model for Urban Stormwater Improvement Conceptualisation

MUSIC was developed by the Cooperative Research Centre (CRC) for Catchment Hydrology in 2001. The model simulates quantity and quality of runoff from catchments and predicts effectiveness of a wide range of stormwater remediation approaches. MUSIC was primarily designed to simulate generation of total nitrogen, total phosphorous and total suspended solids from Australian urban catchments ranging from 0.01 km^2 to 100 km^2 (MUSIC Development Team, 2005). In the current investigation, MUSIC has been used to generate stormwater concentrations of heavy metals for the Port Jackson catchment.

The hydrologic simulation in MUSIC uses a 6 minute rainfall file from the Bureau of Meteorology and a rainfall-runoff algorithm adapted from Chiew and McMahon (1999) to derive runoff. The majority of runoff is generated on impervious surfaces. Rain falling on pervious surfaces infiltrates and percolates to groundwater, of which a proportion becomes baseflow. Once the modelled pervious store is full, rain falling on pervious areas becomes runoff.

1.5 Study Site

The Port Jackson estuary (Sydney Harbour) is located in the Sydney metropolitan area, on the south- eastern coastal plain of New South Wales (NSW), Australia. It comprises Middle Harbour, North Harbour, Duck River and Lane Cove River (Figure 1).

The Port Jackson estuary is a drowned river valley with an approximate area of 50 km^2, a maximum width of 3 km, and an axial length of 30 km. The estuary is well-mixed and saline to the tidal limit at the Parramatta River weir. It has a narrow, winding channel and irregular bathymetry, varying from 3 to 45 m depth.

The estuary drains a catchment of approximately 480 km^2, of which 86 % is urbanised and industrialised. Significant areas of parkland and bushland are located in Lane Cove, Homebush and Middle Harbour (Australian Bureau of Statistics, 2005).

Stormwater channels draining the Port Jackson catchment include concrete lined channels (e.g. Dobroyd, Hawthorne, Cintra Park and Massey Park Canals and Powells and Haslams Creeks) and natural channels (e.g. Duck, Parramatta and Lane Cove Rivers).

1.6 Objectives

Concentrations of heavy metals in sediments in Port Jackson estuary are a threat to the healthy functioning of the estuarine ecosystem (Taylor, 2000; Birch and Taylor, 2002a, b). Investigations of fluvial and estuarine sediments have suggested stormwater is a source of heavy metals to Port Jackson estuary (Taylor, 2000; Birch and Taylor, 1999). In the current study, extensive sampling, analysis and modelling of stormwater entering Port Jackson estuary has been undertaken to better understand the nature and magnitude of continued flux of heavy metals to the estuary via stormwater.

Increased awareness of the significant problems associated with stormwater pollution has led to the installation of stormwater remediation devices in the Port Jackson estuary catchment. However, the remediation devices currently in use are mostly gross pollutant traps, which are ineffective in removing heavy metals, and other contaminants, from stormwater. To target future remediation efforts and ensure optimum efficiency of new or retrofitted remediation devices in removing heavy metals, a thorough characterisation of heavy metal inputs and behaviour will be undertaken. A conceptual model of the transport and fate of heavy metals in stormwater entering Port Jackson estuary will be developed to assist in identifying heavy metals, subcatchment locations and flow regimes to be targeted for future remediation works.

The current research provides important quantitative information for stormwater management. It will establish a baseline for stormwater quality in Port Jackson against which long-term trends may be assessed, and provides information that may be used to design stormwater remediation works to protect the aquatic ecosystem in Port Jackson estuary.

The results of the present study are currently being used in the development of a numerical model to predict the transport and fate of contaminants in Port Jackson estuary.

2. Methodology

2.1 Fieldwork

Fieldwork was conducted by Stephen Barry, a former student of the University of Sydney, in the period August 1999 to May 2002. A total of 866 stormwater samples were collected from nine stormwater channels discharging to the Port Jackson estuary under low- and high-flow conditions.

2.1.1 Sampling Sites

The nine stormwater channels selected for this investigation were: Hawthorne Canal and Dobroyd Canal which drain into Iron Cove, Cintra Park Canal and Massey Park Canal which drain into Hen and Chicken Bay, Powells Creek and Haslams Creek which drain into Homebush Bay, Duck River and Parramatta River which drain into the upper section of the main channel and Lane Cove River which drains into the lower section of the main channel.

Sampling sites for each stormwater channel were selected on the basis of ease of access, and position downstream but above the salt-fresh water interface during low-flow conditions. The same sampling site was used for low- and medium/high-flow sampling events. The locations of the sampling sites for each of the stormwater channels are provided in Table 2.

Channel	Discharge Point	Sampling Site
Dobroyd Canal	Iron Cove	West Street, Ashfield
Hawthorne Canal	Iron Cove	Grosvenor Crescent, Summer Hill
Cintra Park Canal	Hen and Chicken Bay	St Lukes Park, Renown Street, Canada Bay
Massey Park Canal	Hen and Chicken Bay	Tripod Street, Concord
Powells Creek	Homebush Bay	Lemnos Street, North Strathfield
Haslams Creek	Homebush Bay	Cnr Great Western Highway and Nyrang Street, Lidcombe
Duck River	Upper Main Channel	Railway Bridge, Granville
Parramatta River	Upper Main Channel	Cumberland Hospital, Parramatta
Lane Cove River	Lower Main Channel	Lane Cove National Park, Upstream of Fullers Bridge, Millwood Avenue, Chatswood West

Table 2: Location of sampling sites

2.1.2 Sampling Design

Stormwater samples were collected under low- and medium/high-flow conditions at intervals considered appropriate to account for the temporal scales at which variability in water composition occurs (Hatje et. al., 2001a; Hatje et. al., 2001b).

Low-Flow

For the purposes of this study, low-flow events were defined as sampling events conducted when less than 5 mm of rainfall was measured at the nearest Bureau of Meteorology (BOM) rainfall station in the preceding 24 hours.

A nested sampling design was employed for the characterisation of low-flow events which incorporated six temporal scales: seasons (Summer and Winter), months (1st and 2nd months of each season), weeks (1st and 2nd weeks of each month), days (Monday and Tuesday of each week), hours (two random hours for each day) and minutes (one sample split into two or three sample bottles). The sampling design used to follow this temporal hierarchy is presented in Table 3 (only one season is shown).

Medium/High-Flow

For the purposes of the present study, medium/high-flow events were defined as sampling events conducted when greater than 5 mm of rainfall was measured at the nearest BOM rainfall station in the preceding 24 hours.

Sampling of medium/high-flow events was conducted using approximate logarithmic time intervals to achieve high sampling density at the start of the event and thereby characterise any potential first flush effects. The sampling intervals employed for medium/high-flow events are presented in Table 4.

Season	Month	Week	Day	Hour	Minute	Sample
Season 1	Month 1	Week 1	Day 1	Hour 1	Minute 1	1
					Minute 2	2
				Hour 2	Minute 1	3
					Minute 2	4
			Day 2	Hour 1	Minute 1	5
					Minute 2	6
				Hour 2	Minute 1	7
					Minute 2	8
		Week 2	Day 1	Hour 1	Minute 1	9
					Minute 2	10
				Hour 2	Minute 1	11
					Minute 2	12
			Day 2	Hour 1	Minute 1	13
					Minute 2	14
				Hour 2	Minute 1	15
					Minute 2	16
	Month 2	Week 1	Day 1	Hour 1	Minute 1	17
					Minute 2	18
				Hour 2	Minute 1	19
					Minute 2	20
			Day 2	Hour 1	Minute 1	21
					Minute 2	22
				Hour 2	Minute 1	23
					Minute 2	24
		Week 2	Day 1	Hour 1	Minute 1	25
					Minute 2	26
				Hour 2	Minute 1	27
					Minute 2	28
			Day 2	Hour 1	Minute 1	29
					Minute 2	30
				Hour 2	Minute 1	31
					Minute 2	32

Table 3: Low-flow sampling design

Time Elapsed from Trigger (hours)	Sample Number (n)	Time Elapsed from Trigger (hours)	Sample Number (n)	Time Elapsed from Trigger (hours)	Sample Number (n)
0:01	1	0:25	9	4:30	17
0:02	2	0:30	10	5:30	18
0:03	3	0:45	11	6:30	19
0:04	4	1:00	12	7:30	20
0:05	5	1:15	13	8:30	21
0:10	6	1:30	14	9:30	22
0:15	7	2:30	15	10:30	23
0:20	8	3:30	16	11:30	24

Table 4: Medium/high-flow sampling design

2.1.3 Sampling Regime

The total number of samples collected, and the dates on which samples were collected, varied for each of the stormwater channels. Details of the sampling regimes employed for each of the stormwater channels under baseflow and stormflow conditions are provided below.

Low-Flow

A total of 468 stormwater samples were collected under low-flow conditions in the period from December 1999 to May 2002. The number of samples collected from each of the stormwater channels, and the months of collection, are presented in Table 5.

Channel	**Summer 2000**		**Autumn/Winter 2000**			**Spring/Sum 2000**		**Autumn 2002**			**Total**
	Dec 1999	Jan 2000	Mar 2000	May 2000	June 2000	Nov 2000	Dec 2000	Mar 2002	Apr 2002	May 2002	
Dobroyd Canal	36	36	6	16	36						130
Hawthorne Canal	36	36	6	16	36						130
Cintra Park Canal			6	14	2						22
Massey Park Canal			6	14	2						22
Powells Creek				8	8	8	8				32
Haslams Creek				8	8	8	8				32
Duck River								16	8	8	32
Parramatta River								16	8	8	32
Lane Cove River								16	8	8	32

Table 5: Low-flow sampling regime

Medium/High-Flow

A total of 398 stormwater samples were collected under medium/high-flow conditions in the period from December 1999 to May 2002. The number of medium/high-flow events sampled at each stormwater channel are between zero and three (Table 6).

Channel	**Number of Events Sampled**	**Total Number of Samples**
Dobroyd Canal	3	71
Hawthorne Canal	3	72
Cintra Park Canal	0	0
Massey Park Canal	0	0
Powells Creek	3	70
Haslams Creek	3	70
Duck River	3	66
Parramatta River	2	50
Lane Cove River	0	0

Table 6: Medium/high-flow sampling regime

2.1.4 Sampling Methods

In general, sampling of low-flow events was undertaken manually and sampling of medium/high-flow events was undertaken using an automatic sampler.

Bottle Cleaning

Stormwater samples were collected in pre-cleaned 1 L polyethylene bottles. The bottles and caps were cleaned by soaking for 24 h in a detergent solution (Pyroneg) in a covered tank. They were then rinsed with deionised water (DI; 18MΩ cm^{-1} resistivity) and soaked in a 10 % nitric acid (HNO_3) bath for at least 48 h. Finally, the bottles were rinsed three times with DI water and stored in two polyethylene bags. All cleaning operations were carried out in a laminar flow cabinet and powderless gloves were worn during all procedures.

Manual Grab Sampling

In the field, sample bottles were removed from the protective bags and rinsed twice with ambient water. Samples obtained from open drains were collected by hand dipping bottles beneath the water surface. Samples obtained from closed drains required removal of the surface plate and lowering of the sample bottles into the drain using an extendable sampling arm. Following collection of the water samples, the bottles were capped immediately, sealed inside two polyethylene bags and transported to the laboratory.

Automatic Samplers

Sigma 900 Max automatic samplers were deployed to collect stormwater samples during medium/high-flow events. The installation of automatic samplers enabled representative first flush samples to be obtained at any time during the day or night.

Automatic samplers were located in fibreglass housing adjacent to the drain, with a 9.5 mm (inner diameter) Teflon^{TM} coated sampling tube and an acoustic flow meter running from the housing down into the drain. The sampling tube and flow meter were fixed into the stormwater drain and the flow meter was calibrated.

Activation of the automatic samplers was triggered by the acoustic flow meter when the water level exceeded a predetermined height. The automatic samplers were set to be triggered by changes in water level (i.e. pressure), rather than flow, due to difficulties quantifying flow in sampling pits where access to the inflow pipe was limited. The trigger level for the commencement of sampling was dependent on the site characteristics and the pipe geometry, but in general was set at a water height of 20 mm. At all sampling locations, the trigger level was set to ensure that sampling commenced within a few minutes of the commencement of rainfall, so that the first flush of stormwater runoff was captured.

Once the automatic sampler was triggered, stormwater samples were collected at intervals specified in Section 4.1.2. A total of 24 sample bottles were placed inside each automatic sampler. Stormwater was pumped up the sampling tube and delivered directly to the sample bottles to minimise contamination. Routine maintenance of equipment, downloading of data. and battery-recharging was undertaken regularly. Stormwater samplers were transferred to the laboratory immediately following rainfall events.

Field Parameters

In addition to the collection of stormwater samples for laboratory analysis, field measurement of temperature, salinity, turbidity, dissolved oxygen and pH was undertaken for selected sampling events using a field water quality analyser (Yeo-Kal, model 611). Field measurement of water quality parameters was undertaken manually. Sensors were calibrated before each survey.

2.2 Analytical

The stormwater samples collected were analysed by Stephen Barry, a former student of the University of Sydney. Samples were analysed for dissolved phase concentrations and suspended particulate matter concentrations of metals. Quality assurance and quality control methods were employed to enable the accuracy and precision of the data to be assessed. The following dissolved and particulate trace metals were analysed: arsenic (As); cadmium (Cd); chromium (Cr); copper (Cu); nickel (Ni); lead (Pb); and zinc (Zn). The stormwater samples analysed for trace metals are summarised in Table 7.

Channel	Flow Regime	Dissolved	Particulate
Dobroyd Canal	Low	129	129
	Medium/High	70	70
Hawthorne Canal	Low	130	130
	Medium/High	72	72
Cintra Park Canal	Low	22	22
	Medium/High	0	0
Massey Park Canal	Low	22	22
	Medium/High	0	0
Powells Creek	Low	32	32
	Medium/High	0	68
Haslams Creek	Low	32	32
	Medium/High	0	44
Duck River	Low	24	24
	Medium/High	65	65
Parramatta River	Low	24	24
	Medium/High	40	40
Lane Cove River	Low	24	24
	Medium/High	0	0

Table 7: Samples analysed for heavy metals

2.2.1 Dissolved Phase

Stormwater samples were filtered through pre-weighed 0.45 µm Millipore (cellulose) membranes to separate the operationally defined dissolved and particulate fractions.

Filters were cleaned by soaking in a teflon jar filled with 10 % HNO_3 for 5 days, then rinsed with DI water. Filters were dried to a constant weight at room temperature in a laminar flow hood, weighed and stored wet in DI water until being loaded onto filter holders. The filters for suspended particulate matter (SPM) determinations were rinsed with 20 mL of DI water to remove salt, dried and subsequently reweighed to obtain the mass of SPM.

Filtered water samples were stored in acid cleaned polyethylene bottles and acidified with concentrated nitric acid (1-2 mL L-1 Merck Suprapur).

2.2.2 Suspended Particulate Matter

The membranes for suspended matter analysis were dried in a laminar fume hood and sealed in petri dishes until analysis. After re-weighing, the sample membranes and blanks were placed in 50 mL test tubes and digested with a strong acid solution (1:1, concentrated nitric : hydrochloric acid) to dryness at 120°C, using a hotplate (USEPA Method 200.8). This strong digestion does not extract the total detrital metal content. Arsenic, cadmium, chromium, copper, nickel, lead and zinc were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) Spectro Flame-EOP).

2.2.3 Validation of Analytical Results

Field analytical results were validated by comparison to the results of other studies in Port Jackson. The data collected for Dobroyd and Hawthorne Canals were compared to the data reported in Barry et al. (1999) and Water Board (1993b), and the data collected for Powells and Haslams Creeks were compared to the data reported in Chambers (2000).

2.2.4 Quality Control

The quality of the data collected in this study was ensured through the use of appropriate: field sampling and analytical procedures; preservation and storage of samples upon collection and during transport to the laboratory; sample holding times; limits of reporting; and frequency of conducting quality control measurements, such as duplicates and blanks.

The accuracy and precision of analytical data were assessed for each batch of samples using a range of quality control measurements, generated through the field and analytical programs. Specific elements that were assessed in this study include: laboratory duplicates and triplicates; field, filtration and digest blanks; internal standards; and reference materials.

Replicates

Stormwater samples collected under low-flow conditions were analysed in duplicate and triplicate to assess the precision of the analytical techniques used. Average 1σ relative standard deviations (percentage variation) are presented in Table 8.

Replicates	As	Cd	Cr	Cu	Ni	Pb	Zn
RSD (%)	2.6	1.6	9.3	9.3	4.3	8.9	8.6

Table 8: Average relative standard deviations for replicate analyses of total metals

Blanks

Field blanks were collected to assess potential contamination of samples during the fieldwork. Filtration and digest blanks were collected assess potential contamination of samples during the laboratory work. The results of field, filtration and digest blank analyses indicate that average concentrations of dissolved metals were below laboratory limit of reporting. Average concentrations of particulate arsenic, cadmum, chromium, copper, nickel, lead and zinc were less than 0.03, 0.03, 0.01, 0.01, 0.02, 0.03 and 0.05 μg/L, respectively.

Internal Standards

Internal laboratory standard ILS-3 from the University of Sydney was included in each batch of samples to verify the accuracy of total particulate metals analyses. The average percent recoveries of in-house values are presented in Table 9.

Standard	As	Cd	Cr	Cu	Ni	Pb	Zn
ILS-3	-	79	91	90	94	82	83

Table 9: Average percent recoveries of in-house values for particulate metal internal standards

Certified Reference Materials

Certified reference materials from the United States Geological Survey (marine sediment MAG-1) and the Australian Government Analytical Laboratories (estuarine sediment AGAL-10) were included in each batch of samples to verify the accuracy of total particulate metals analyses. The average percent recoveries of international certified values are presented in Table 10.

CRM	As	Cd	Cr	Cu	Ni	Pb	Zn
MAG-1	136	49	52	81	71	70	81
AGAL-10	-	73	98	103	133	75	123

Table 10: Average percent recoveries of international certified values for particulate metal reference materials

Certified reference material (river water) from the National Research Council of Canada (SLRS-4) was included in each batch to verify the accuracy of dissolved metals analyses. Average percent recoveries of international certified values are presented in Table 11.

CRM	As	Cd	Cr	Cu	Ni	Pb	Zn
SLRS-4	125	146	387	75	111	88	168

Table 11: Average percent recoveries of international certified values for dissolved metal reference materials

2.3 Metal Export Modelling

Loadings of heavy metals in stormwater discharged to Port Jackson under low-flow, medium-flow and high-flow conditions were calculated using the Model for Urban Stormwater Improvement Conceptualisation (MUSIC). MUSIC was developed by the Cooperative Research Centre for Catchment Hydrology in 2001 to simulate stormwater discharges of nutrients and suspended solids from urban catchments in Australia (MUSIC Development Team, 2005). In the current study, MUSIC was used to simulate stormwater discharge of heavy metals. Field concentrations of heavy metals were entered into the total suspended solids field in MUSIC.

2.3.1 Model Input Parameters

Delineation of Subcatchments

The subcatchments used in this study are derived from Cruickshank (2006) and are presented in Figure 2. Cruickshank (2006) delineated the subcatchments of Port Jackson using 1:25,000 topographic maps produced by the Department of Lands in 2001. Subcatchments were defined on the basis of elevation (ridge lines) rather than drainage infrastructure.

For the purposes of the present study, the subcatchments of the stormwater channels that have been sampled and modelled in detail are referred to as the ‘sampled subcatchments’ (shown in colour in Figure 2). The subcatchments that have not been sampled in this investigation and have been modelled using typical metals concentrations have been referred to as the ‘modelled subcatchments’ (Figure 2). A list of the 70 subcatchments is provided in Table 12.

Subcatchment Areas

Subcatchment areas were calculated in ArcGIS using the subcatchment boundaries delineated by Cruickshank (2006). Subcatchment areas are summarised in Table 12.

Land Use

Land use data were derived from Cruickshank (2006). Cruickshank (2006) entered land use data from the Australian Bureau of Statistics Draft Mesh Blocks (2005) into ArcGIS and then used the program to calculate the land use of each subcatchment. Road and rail areas for the major subcatchments were calculated by hand using Google Earth images.

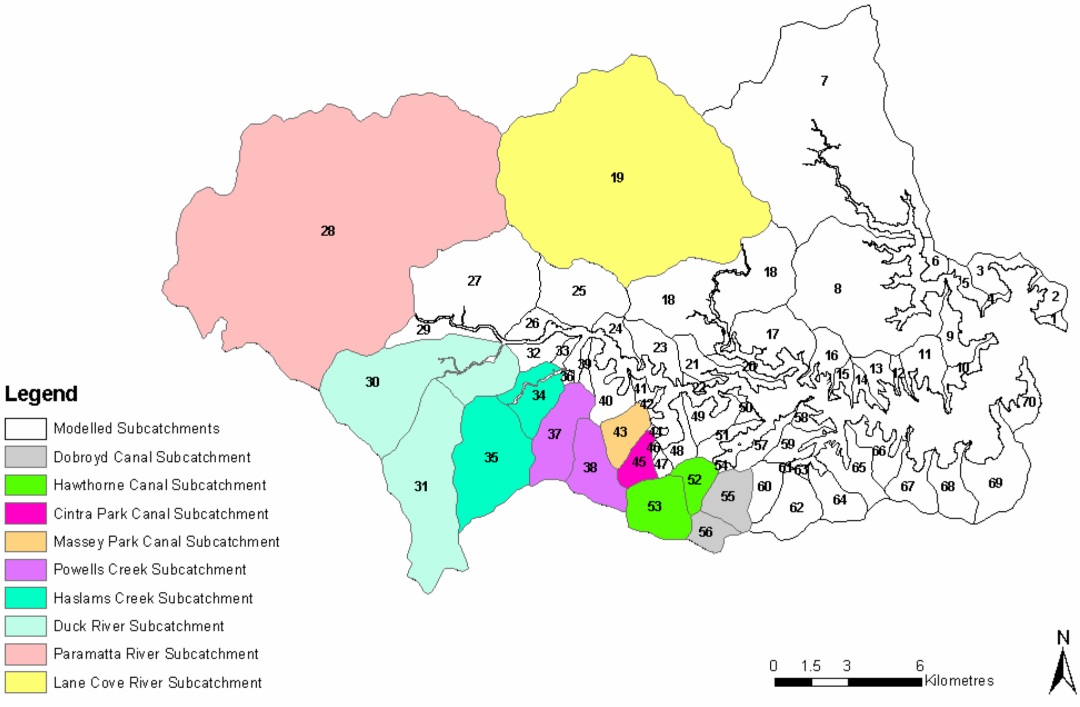
ID	Subcatchment	Type	Area (ha)	Impervious Area (%)	Rainfall Scaling Factor
1	North Harbour ESE	Modelled	53.28	0.000	1.01
2	North Harbour E	Modelled	155.29	0.391	1.01
3	North Harbour N	Modelled	257.43	0.421	0.99
4	North Harbour WSW	Modelled	38.59	0.150	1.00
5	Middle Harbour ENE	Modelled	128.47	0.380	0.99
6	Middle Harbour NE	Modelled	128.13	0.392	0.99
7	Upper Middle Harbour	Modelled	5169.21	0.410	0.95
8	Middle Harbour SW	Modelled	2271.74	0.467	0.97
9	Middle Harbour SSW	Modelled	252.24	0.454	0.99
10	Lower Harbour N5	Modelled	147.41	0.321	1.00
11	Lower Harbour N4	Modelled	329.14	0.464	1.00
12	Lower Harbour N3	Modelled	65.44	0.442	0.99
13	Lower Harbour N2	Modelled	212.44	0.468	0.99
14	Lower Harbour N1	Modelled	88.87	0.501	0.99
15	Central Harbour N4	Modelled	97.51	0.465	0.98
16	Central Harbour N3	Modelled	256.86	0.457	0.97
17	Lower Lane Cove N	Modelled	604.33	0.438	0.95
18	Central Lane Cove	Modelled	1932.68	0.431	0.93
19	Upper Lane Cove River	Sampled	6840.84	0.401	0.91
20	Lower Lane Cove S	Modelled	109.74	0.448	0.94
21	Central Harbour N2	Modelled	303.67	0.425	0.92
22	Central Harbour N1	Modelled	61.01	0.417	093
23	Upper Harbour N3	Modelled	333.21	0.441	0.92
24	Upper Harbour N2	Modelled	160.40	0.464	0.89
25	Archer Creek Diffuse Source	Modelled	783.56	0.451	0.81
26	Lower Parramatta River N	Modelled	179.94	0.409	0.79
27	Central Parramatta River N	Modelled	1676.35	0.428	0.77
28	Upper Parramatta River	Sampled	10677.48	0.489	0.77
29	Central Parramatta River S	Modelled	266.34	0.487	0.77
30	Lower Duck River	Sampled	2219.10	0.503	0.77
31	Upper Duck River	Sampled	1790.67	0.503	0.78
32	Lower Parramatta River S	Modelled	201.87	0.376	0.84
33	Homebush Bay W	Modelled	60.42	0.327	0.86
34	Lower Haslams Creek	Sampled	443.38	0.484	0.84
35	Upper Haslams Creek	Sampled	1251.91	0.484	0.81
36	Homebush Bay S	Modelled	24.62	0.000	0.86

Table 12: Subcatchment area, proportion impervious and rainfall scaling factor

ID	Subcatchment	Type	Area (ha)	Impervious Area (%)	Rainfall Scaling Factor
37	Lower Powells Creek	Sampled	624.13	0.638	0.86
38	Upper Powells Creek	Sampled	547.42	0.638	0.86
39	Homebush Bay E	Modelled	78.83	0.524	0.87
40	Upper Harbour S1	Modelled	346.45	0.437	0.88
41	Upper Harbour S2	Modelled	73.57	0.409	0.90
42	Hen and Chicken Bay NNW	Modelled	49.58	0.382	0.90
43	Massey Park Canal	Sampled	316.72	0.466	0.89
44	Hen and Chicken Bay W	Modelled	25.21	0.386	0.90
45	Cintra Park Canal	Sampled	226.73	0.493	0.89
46	Hen and Chicken Bay SW	Modelled	16.85	0.453	0.90
47	Kings Bay Canal	Modelled	61.15	0.588	0.90
48	Hen and Chicken Bay E	Modelled	174.40	0.454	0.91
49	Central Harbour S1	Modelled	283.82	0.433	0.92
50	Central Harbour S2	Modelled	81.55	0.472	0.94
51	Iron Cove W	Modelled	154.13	0.435	0.93
52	Lower Dobroyd Canal	Sampled	251.33	0.527	0.90
53	Upper Dobroyd Canal	Sampled	573.86	0.527	0.90
54	Iron Cove S	Modelled	23.52	0.368	0.93
55	Lower Hawthorne Canal	Sampled	391.09	0.550	0.92
56	Upper Hawthorne Canal	Sampled	211.90	0.550	0.92
57	Iron Cove E	Modelled	191.11	0.432	0.95
58	Central Harbour S3	Modelled	114.34	0.408	0.97
59	Johnstons Bay	Modelled	223.22	0.470	0.95
60	Whites Creek	Modelled	260.37	0.622	0.94
61	Rozelle Bay SW	Modelled	7.15	0.411	0.96
62	Johnstons Creek	Modelled	457.11	0.568	0.96
63	Rozelle Bay SE	Modelled	25.66	0.381	0.96
64	Blackwattle Bay S	Modelled	316.06	0.504	0.97
65	Darling Harbour	Modelled	415.10	0.736	0.98
66	Lower Harbour S1	Modelled	291.71	0.515	1.00
67	Lower Harbour S2	Modelled	330.00	0.468	0.99
68	Lower Harbour S7	Modelled	365.51	0.483	0.99
69	Lower Harbour S4	Modelled	665.62	0.451	0.99
70	Lower Harbour S5	Modelled	226.61	0.408	1.01

Table 12: Subcatchment area, proportion impervious and rainfall scaling factor

Figure 2: Subcatchments of Port Jackson (sampled and modelled)



Impervious Areas

Impervious areas were calculated on the basis of catchment land use. Typical impervious fractions for various landuses were taken from those recommended by the NSW Department of Local Government (2006) as presented in Cruickshank (2006). The proportion impervious area calculated for each of the subcatchments is presented in Table 12. Dominantly natural subcatchments comprising less than 1 % impervious area (subcatchments 1, 36 and 61) were assumed to have 1 % impervious area for the purposes of this investigation. The hydrologic simulation in MUSIC for total suspended solids does not generate loadings from pervious areas, so no discharge of heavy metals would be reported for subcatchments with 0 % impervious area.

Meteorological Data

The evapotranspiration data used were the default data for Sydney provided in MUSIC. These data are monthly potential evapotranspiration as reported by the Climatic Atlas of Australia (Bureau of Meteorology and Cooperative Research Centre for Catchment Hydrology, 2001).

The pluviograph data used were provided by the Bureau of Meteorology. These data are six minute rainfall data for Sydney’s Observatory Hill gauging station, number 66062, from January 1990 to July 2006. The rainfall data were split into three separate files to reflect days where there had been low-flow (less than 5 mm of rainfall in 24 hours), medium-flow (between 5 mm and 50 mm of rainfall in 24 hours), and high-flow (greater than 5 mm of rainfall in 24 hours).

To account for the spatial variability in precipitation across the Port Jackson catchment, subcatchment, areas were scaled to reflect the difference in local precipitation relative to Observatory Hill. For example, the area of the Upper Parramatta River subcatchment was scaled to 77 % to reflect that annual rainfall in this subcatchment is approximately 77% of that at Observatory Hill. The rainfall scaling factors used in this study are derived from Cruickshank (2006) and are presented in Table 12. Cruickshank (2006) plotted the average annual rainfall for several gauging stations across Port Jackson catchment and then interpolated between these fixed points to obtain rainfall scaling factors for each subcatchment.

Runoff

The algorithm used in MUSIC to generate urban runoff is based on the model developed by Chiew and McMahon (1999). The Chiew and McMahon (1999) model is a simplified description of the rainfall-runoff processes in catchments, which requires the definition of impervious area and two soil moisture storages. The Chiew and McMahon (1999) model was modified for MUSIC to enable disaggregation of the generated daily runoff into sub-daily temporal patterns.

Heavy Metal Concentrations

The analytical results for the stormwater samples collected in the present investigation were used to derive the input variables for the MUSIC simulations. Statistical analyses of raw analytical data were undertaken using Microsoft Excel™ to calculate event mean concentrations and standard deviations. Field event mean concentrations were calculated for low-flow events (less than 5 mm of rainfall in 24 hours) and medium/high-flow events (greater than 5 mm of rainfall in 24 hours) for each of the main subcatchments.

2.3.2 MUSIC Simulations

The MUSIC simulations were run using Version 3.0.1 on a Windows XP platform. Approximately 1500 deterministic simulations were run to calculate event mean concentrations and loadings of heavy metals for the 70 subcatchments.

Sampled Subcatchments

The MUSIC simulations for the sampled subcatchments were undertaken using the event mean concentrations and standard deviations calculated from field data for each subcatchment. Heavy metals were modelled by entering field event mean concentrations into the total suspended solids field in MUSIC.

Modelled Subcatchments

The MUSIC simulations for the modelled subcatchments were run using average concentrations calculated from the field data for the sampled subcatchments. These concentrations are presented in Table 13.

Flow	Statistic	As	Cd	Cr	Cu	Ni	Pb	Zn
Low-Flow	Mean	5.1	0.6	8.6	8.1	3.7	6.7	43.5
	SD	1.8	1.1	3.8	7.3	1.3	9.7	53.5
Medium/ High-Flow	Mean	4.5	2.5	9.0	15.9	5.1	18.1	83.5
	SD	5.1	4.8	11.9	12.3	1.9	25.5	55.5

Table 13: Heavy metal MUSIC input data for the modelled subcatchments

2.3.3 Validation of Model Outputs

MUSIC model outputs were validated by comparison of the loadings for Iron Cove to the loadings calculated by Barry and Birch (unpublished) and Birch et al. (1999).

3.1 Field Parameters

The results of field parameter measurements are summarised in Table 14. Mean, 95 % upper confidence limits and ranges of results are provided for each stormwater canal from the main subcatchments under low-flow and medium/high-flow conditions (where assessed). A discussion of the results of field parameter measurements is provided below. Graphs of the results are also provided (Figures 3A-D).

3.1.1 Temperature

Mean stormwater temperature ranged from 14.3 to 24.3 ºC (Figure 3A). The temperature of stormwater in concrete lined channels draining small catchments (Dobroyd, Hawthorne, Cintra Park and Massey Park Canals and Powells and Haslams Creeks) was lower than the temperature of stormwater in natural systems draining large catchments (Duck, Parramatta and Lane Cove Rivers) under both low- and medium/high-flow conditions. The temperature of stormwater in the concrete lined channels was higher under medium/high-flow conditions than under low-flow conditions. For the natural channels, the temperature of stormwater was lower under medium/high-flow conditions than under low-flow conditions.

3.1.2 Salinity

Stormwater entering Port Jackson ranged from fresh to brackish (Figure 3B). Stormwater in the natural channels was fresh. Stormwater in the concrete lined channels entering Iron Cove and Homebush Bay was fresh under low-flow conditions, and brackish under medium/high-flow conditions. Stormwater collected from Massey Park Canal under low-flow conditions had the highest salinity, suggesting the sampling location may have been below the salt-fresh water limit.

3.1.3 Dissolved Oxygen

Stormwater dissolved oxygen concentrations were generally around 9 to 10 mg/L (Figure 3C). These concentrations are typical for rainwater or a running stream. Powells Creek had higher dissolved oxygen concentrations than any other location under both low- and medium/high- flow conditions. This may be a result of more turbulent hydrologic conditions in the channel.

Site	Flow	Data	Temp	EC	TDS	Sal	DO	pH
Dobroyd Canal	**Low**	Mean	**15.6**	**0.70**	**0.55**	**0.42**	**11.6**	**8.5**
		95%UCL	17.7	0.83	0.64	0.49	13.4	8.8
		Range	(10.8-20.2)	(0.34-0.95)	(0.27-0.68)	(0.20-0.52)	(8.4-14.7)	(7.8-9.1)
	Med/High	Mean	**16.8**	**15.3**	**11.8**	**11.9**	**8.0**	**7.5**
		95%UCL	17.0	42.5	32.8	33.3	9.0	7.6
		Range	(16.4-17.9)	(0.60-50.1)	(0.46-39.5)	(0.34-40.8)	(5.3-11.6)	(6.6-8.0)
Hawthorne Canal	**Low**	Mean	**14.9**	**0.39**	**0.32**	**0.24**	**9.4**	**8.0**
		95%UCL	16.1	0.46	0.37	0.28	9.9	8.2
		Range	(12.6-17.5)	(0.22-0.49)	(0.18-0.38)	(0.13-0.29)	(8.6-11.0)	(7.7-8.5)
	Med/High	Mean	**17.2**	**4.0**	**3.0**	**2.9**	**10.9**	**7.6**
		95%UCL	17.3	16.0	12.2	12.0	12.3	7.7
		Range	(16.7-17.4)	(0.48-35.1)	(0.37-26.7)	(0.28-26.5)	(6.2-12.8)	(7.3-8.0)
Cintra Park Canal	**Low**	Mean	**16.3**	**6.2**	**5.0**	**4.3**	**9.3**	**8.1**
		95%UCL	18.3	8.2	6.4	7.9	11.4	8.4
		Range	(11.1-23.6)	(0.0-12.8)	(0.0-10.7)	(0.0-9.7)	(6.0-18.0)	(7.7-9.3)
	Med/High	Mean	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**
		95%UCL	nd	nd	nd	nd	nd	nd
		Range	(nd)	(nd)	(nd)	(nd)	(nd)	(nd)
Massy Park Canal	**Low**	Mean	**16.1**	**27.9**	**21.1**	**21.1**	**8.2**	**7.6**
		95%UCL	17.9	35.6	26.4	26.6	9.1	7.7
		Range	(8.9-20.7)	(0.0-49.1)	(0.0-34.9)	(0.0-35.5)	(5.8-12.0)	(6.7-7.9)
	Med/High	Mean	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**
		95%UCL	nd	nd	nd	nd	nd	nd
		Range	(nd)	(nd)	(nd)	(nd)	(nd)	(nd)

Table 14: Field Parameters

Site	Flow	Data	Temp	EC	TDS	Sal	DO	pH
Powells Creek	**Low**	Mean	**14.4**	**1.3**	**1.1**	**0.9**	**14.7**	**8.8**
		95%UCL	15.4	1.6	1.3	1.1	16.6	9.0
		Range	(10.6-18.6)	(0.6-2.6)	(0.5-2.3)	(0.4-1.9)	(7.5-28.5)	(7.8-9.7)
	Med/High	Mean	**18.6**	**6.6**	**4.7**	**4.5**	**18.6**	**7.2**
		95%UCL	19.2	17.0	12.1	11.8	28.8	7.5
		Range	(16.2-21.0)	(0.1-37.9)	(0.1-26.7)	(0.1-26.3)	(5.5-33.0)	(6.0-8.2)
Haslams Creek	**Low**	Mean	**14.3**	**0.9**	**0.7**	**0.6**	**11.6**	**8.8**
		95%UCL	15.3	1.0	0.8	0.6	12.4	9.1
		Range	(11-18)	(0.4-1.2)	(0.3-1.0)	(0.2-0.8)	(9.0-16.0)	(7.9-9.7)
	Med/High	Mean	**16.5**	**20.1**	**14.9**	**14.9**	**6.6**	**7.5**
		95%UCL	18.1	39.2	28.9	29.1	12.4	8.6
		Range	(11-21)	(0.3-48.8)	(0.2-34.4)	(0.2-34.9)	(2.3-14.2)	(6.8-8.7)
Duck River	**Low**	Mean	**22.8**	**0.49**	**0.34**	**0.25**	**9.3**	**nd**
		95%UCL	23.4	0.53	0.36	0.27	10.6	nd
		Range	(21-26)	(0.19-0.57)	(0.12-0.38)	(0.09-0.28)	(4.0-18.2)	nd
	Med/High	Mean	**18.6**	**0.41**	**0.31**	**0.22**	**10.7**	**7.7**
		95%UCL	19.5	0.66	0.52	0.36	11.1	7.9
		Range	(16-25)	(0.12-1.2)	(0.10-0.79)	(0.07-0.60)	(5.9-18.8)	(6.9-9.1)
Parramatta River	**Low**	Mean	**23.8**	**0.49**	**0.33**	**0.24**	**10.4**	**nd**
		95%UCL	24.1	0.54	0.36	0.27	11.0	nd
		Range	(22-26)	(0.17-0.65)	(0.11-0.44)	(0.08-0.33)	(7.1-12.4)	nd
	Med/High	Mean	**19.3**	**0.47**	**0.36**	**0.25**	**8.8**	**8.0**
		95%UCL	20.4	0.82	0.65	0.46	9.8	8.3
		Range	(17 -24)	(0.13-0.88)	(0.10-0.59)	(0.07-0.45)	(4.4-11.2)	(7.2-9.2)

Table 14: Field Parameters

Site	Flow	Data	Temp	EC	TDS	Sal	DO	pH
Lane Cove River	**Low**	Mean	**24.3**	**0.29**	**0.19**	**0.14**	**10.3**	**nd**
		95%UCL	24.9	0.33	0.21	0.16	11.5	nd
		Range	(21.8-26.6)	(0.17-0.57)	(0.11-0.38)	(0.08-0.28)	(6.4-16.3)	nd
	Med/High	Mean	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**
		95%UCL	nd	nd	nd	nd	nd	nd
		Range	(nd)	(nd)	(nd)	(nd)	(nd)	(nd)

Table 14: Field Parameters

LEGEND
Arithmetic means of available data reported
Temp – Temperature (^{o}C)
EC – Conductivity (mS/cm)
TDS – Total Dissolved Solids (g/L)
Sal – Salinity (ppt)
DO – Dissolved Oxygen (mg/L)
pH – pH units
nd – not determined

3.1.4 pH

Stormwater pH ranged from 7.2 to 8.8 and was consistently lower under medium/high-flow conditions than under low-flow conditions (Figure 3D). The highest pH reported was for stormwater entering Homebush Bay under low-flow conditions. The pH of these waters is slightly higher than the typical range for natural waters and may be indicative of contaminated groundwater discharging as baseflow to the stormwater channels, or other sources of high pH within the catchment.

3.2 Event Mean Metals Concentrations Calculated from Field Data

The analytical results for stormwater metal concentrations are presented in Table 15. Event mean concentrations, standard deviations and ranges for dissolved and particulate phase metals are provided for stormwater collected from stormwater canals draining the sampled subcatchments under low- and medium/high-flow conditions (where assessed). Event mean concentrations are also presented in Figures 4A-N.

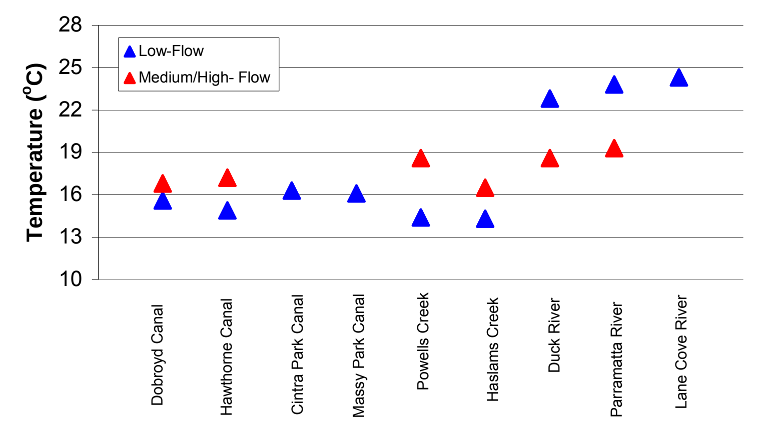


Figure 3A: Temperature

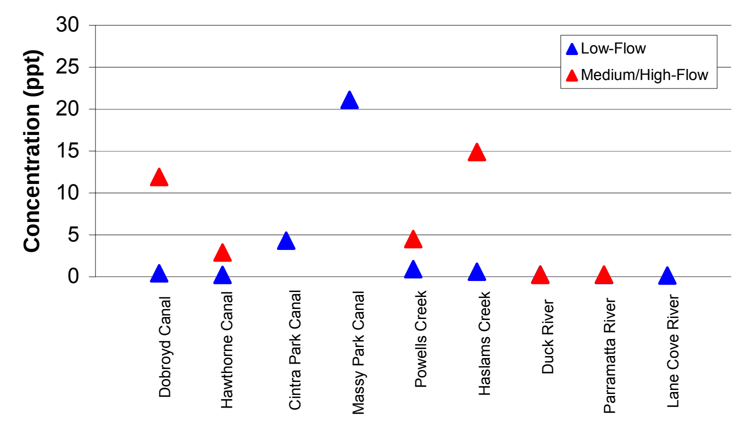


Figure 3B: Salinity

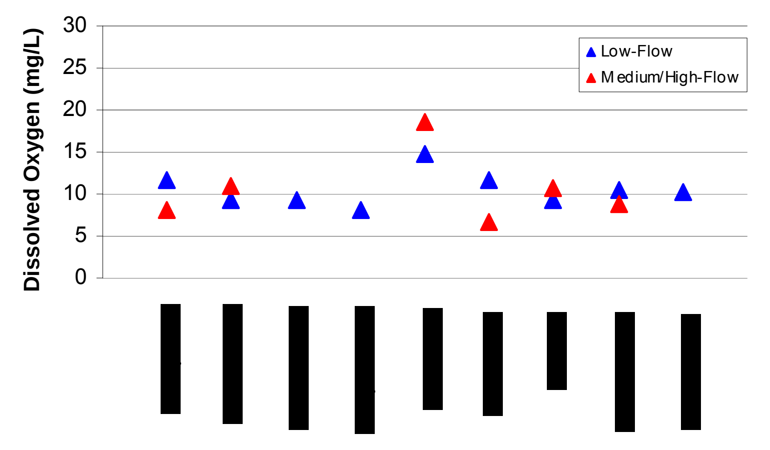


Figure 3C: Dissolved oxygen

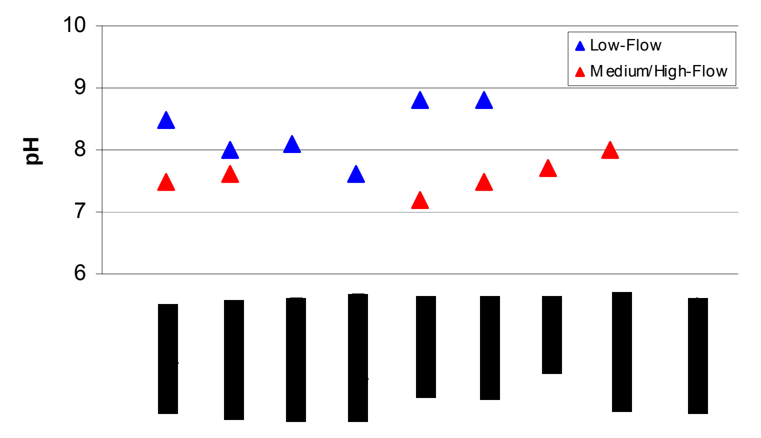


Figure 3D: pH

	LOW FLOW CONDITIONS										MEDIUM/HIGH FLOW CONDITIONS									
	Particulate					Dissolved					Particulate					Dissolved				
	Avg	Med	S.D.	Min	Max	Avg	Med	S.D.	Min	Max	Avg	Med	S.D.	Min	Max	Avg	Med	S.D.	Min	Max
Dobroyd Canal																				
Arsenic	1.1	1.3	0.4	0.0	3.2	2.1	2.1	0.9	<1.0	5.1	1.3	1.5	0.33	0.6	2.4	6.5	2.1	13	<1.0	46
Cadmium	0.13	0.14	0.09	0.0	0.62	0.5	0.5	0.0	<1.0	<1.0	0.16	0.15	0.10	0.07	2.1	3.8	0.50	6.1	<1.0	170
Chromium	1.2	0.7	1.5	0.2	9.4	2.7	1.7	2.4	<2.5	10.0	5.4	1.9	12	0.2	67	12	1.3	26	<2.5	88
Copper	4.6	2.4	6.9	0.8	38	6.6	6.1	3.7	1.9	20.0	11.9	8.6	17	0.2	390	6.5	4.9	4.1	2.4	15
Nickel	0.38	0.07	1.1	0.0	7.4	3.0	3.0	0.0	<6.0	<6.0	2.6	1.2	3.1	0.3	50	3.0	3.0	0.01	<6.0	8.0
Lead	8.9	2.4	25	0.0	170	0.7	0.3	1.3	<0.5	6.7	26	16	61	0.9	3000	2.0	1.4	3.0	<0.5	13
Zinc	20	18	31	4.4	180	22	19	16	<7.5	91	52	43	62	1.9	1100	49	54	19	17	100
Hawthorne Canal																				
Arsenic	1.1	0.85	0.41	0.0	3.2	1.5	1.4	0.58	<1.0	4.1	1.6	1.6	0.12	1.4	2.0	3.8	1.6	6.8	<1.0	37.0
Cadmium	0.12	0.14	0.04	0.0	3.2	0.5	0.50	0.00	<1.0	<1.0	0.2	0.16	0.01	0.1	0.20	2.2	0.50	3.9	<1.0	19.0
Chromium	0.9	0.73	0.63	0.2	3.0	1.3	1.3	1.0	<2.5	4.8	1.5	1.6	0.88	0.4	4.1	7.4	1.9	16	<2.5	82.0
Copper	5.9	3.7	6.3	1.9	37	6.6	5.5	4.1	1.6	22	7.3	7.6	4.8	1.4	20	3.8	3.6	1.4	1.7	7.8
Nickel	0.16	0.07	0.33	0.0	1.6	3.0	3.0	0.00	<6.0	<6.0	1.2	0.81	1.2	0.7	7.8	3.0	3.0	0.00	<6.0	<6.0
Lead	5.7	2.9	8.1	0.0	38	0.8	0.25	1.6	<0.5	10	10.3	5.6	13	1.5	53	0.7	0.25	0.71	<0.5	2.4
Zinc	28	21	24	7.8	120	30	25	16	14	93	31	30	24	7	100	43	26	33	18	190

Table 15: Event mean concentrations calculated from field data

	LOW FLOW CONDITIONS										MEDIUM/HIGH FLOW CONDITIONS									
	Particulate					Dissolved					Particulate					Dissolved				
	Avg	Med	S.D.	Min	Max	Avg	Med	S.D.	Min	Max	Avg	Med	S.D.	Min	Max	Avg	Med	S.D.	Min	Max
Cintra Park Canal																				
Arsenic	1.4	1.4	0.02	1.4	1.5	6.9	7.1	2.2	3.1	10	-	-	-	-	-	-	-	-	-	-
Cadmium	0.19	0.14	0.17	0.14	0.70	0.50	0.50	0.00	<1.0	<1.0	-	-	-	-	-	-	-	-	-	-
Chromium	3.1	0.99	6.7	0.38	23	18	19	6.2	6.9	27	-	-	-	-	-	-	-	-	-	-
Copper	11	6.2	15	2.1	54	5.1	3.5	5.5	1.7	21	-	-	-	-	-	-	-	-	-	-
Nickel	2.0	0.07	6.4	0.07	21	3.0	3.0	0.00	<6.0	<6.0	-	-	-	-	-	-	-	-	-	-
Lead	13	5.0	26	1.4	92	0.28	0.25	0.11	0.25	0.61	-	-	-	-	-	-	-	-	-	-
Zinc	46	21	80	7.7	280	17	16	8.2	8.7	38	-	-	-	-	-	-	-	-	-	-
Massey Park Canal																				
Arsenic	1.4	1.4	0.09	1.1	1.5	16	13	10	4.3	29	-	-	-	-	-	-	-	-	-	-
Cadmium	0.14	0.14	0.01	0.11	0.15	0.50	0.50	0.00	<1.0	<1.0	-	-	-	-	-	-	-	-	-	-
Chromium	1.0	0.9	0.74	0.4	2.9	36	33	18	14	60	-	-	-	-	-	-	-	-	-	-
Copper	3.9	2.6	4.0	1.2	12	2.6	2.6	1.5	0.8	5.5	-	-	-	-	-	-	-	-	-	-
Nickel	0.17	0.07	0.33	0.06	1.2	3.0	3.0	0.00	<6.0	<6.0	-	-	-	-	-	-	-	-	-	-
Lead	7.2	1.5	12	1.4	40	0.58	0.25	0.75	0.3	2.4	-	-	-	-	-	-	-	-	-	-
Zinc	30	20	25	11	84	34	31	11	23	58	-	-	-	-	-	-	-	-	-	-

Table 15: Event mean concentrations calculated from field data

	LOW FLOW CONDITIONS										MEDIUM/HIGH FLOW CONDITIONS									
	Particulate					Dissolved					Particulate					Dissolved				
	Avg	Med	S.D.	Min	Max	Avg	Med	S.D.	Min	Max	Avg	Med	S.D.	Min	Max	Avg	Med	S.D.	Min	Max
Powells Creek																				
Arsenic	1.4	1.4	0.06	0.00	3.1	2.7	2.5	0.55	1.2	3.9	1.7	1.6	0.65	1.5	4.2	-	-	-	-	-
Cadmium	0.14	0.14	0.01	0.00	0.31	0.50	0.50	0.00	<1.0	<1.0	0.20	0.16	0.10	0.15	0.45	-	-	-	-	-
Chromium	0.9	0.60	0.81	0.00	3.9	3.8	2.8	2.0	<2.5	7.5	2.5	1.1	2.3	0.34	7.1	-	-	-	-	-
Copper	7.4	4.4	7.8	0.90	28	4.7	5.4	2.6	1.8	12	13.6	7.4	15.8	1.1	76.0	-	-	-	-	-
Nickel	0.9	0.71	0.62	0.00	3.5	3.0	3.0	0.91	<6.0	8.1	1.9	0.82	1.7	0.77	6.3	-	-	-	-	-
Lead	5.60	3.9	10	0.00	48	0.40	0.25	0.97	<0.5	3.6	20	5.9	25	1.5	130	-	-	-	-	-
Zinc	40	31	44	9.0	190	20	20	73	<7.5	310	64	23	77	8.1	360	-	-	-	-	-
Haslams Creek																				
Arsenic	1.4	1.4	0.06	0.00	3.0	2.1	1.4	1.8	<1.0	8.9	2.5	1.6	2.8	1.4	15	-	-	-	-	-
Cadmium	0.15	0.14	0.03	0.00	0.30	0.50	0.50	0.00	<1.0	<1.0	0.25	0.16	0.28	0.14	1.5	-	-	-	-	-
Chromium	0.39	0.38	0.62	0.00	2.9	2.0	1.3	1.1	<2.5	5.8	1.5	0.98	1.4	0.46	13	-	-	-	-	-
Copper	1.8	1.4	5.0	0.30	22	2.7	2.4	2.3	<1.5	11	7.3	3.0	14	0.37	130	-	-	-	-	-
Nickel	0.78	0.71	0.38	0.00	2.3	3.0	3.0	0.70	<6.0	7.0	1.2	0.81	1.4	0.71	7.5	-	-	-	-	-
Lead	1.8	1.4	11	0.00	51	0.25	0.25	0.74	<0.5	3.3	12	6.3	21	1.4	190	-	-	-	-	-
Zinc	29	19	70	6.0	310	13	12	56	<7.5	260	56	29	102	3.7	980	-	-	-	-	-

Table 15: Event mean concentrations calculated from field data

	LOW FLOW CONDITIONS										MEDIUM/HIGH FLOW CONDITIONS									
	Particulate					Dissolved					Particulate					Dissolved				
	Avg	Med	S.D.	Min	Max	Avg	Med	S.D.	Min	Max	Avg	Med	S.D.	Min	Max	Avg	Med	S.D.	Min	Max
Duck River																				
Arsenic	1.5	1.4	0.38	1.4	3.3	0.50	0.50	0.33	<1.0	1.3	1.8	1.8	0.03	1.6	1.9	1.11	0.50	0.34	<1.0	1.5
Cadmium	0.14	0.14	0.00	0.14	0.14	0.50	0.50	0.00	<1.0	<1.0	0.24	0.18	0.10	0.16	0.72	0.50	0.50	0.00	<1.0	<1.0
Chromium	0.76	0.71	0.23	0.71	1.9	1.3	1.3	0.00	<2.5	<2.5	2.4	2.6	1.5	0.80	8.0	3.3	1.3	1.8	<2.5	8.1
Copper	0.9	0.69	0.37	0.4	1.6	1.8	1.0	1.4	<1.5	5.0	10	8.6	9.5	1.7	36	7.2	4.4	8.6	1.9	33
Nickel	0.72	0.71	0.00	0.71	0.72	3.0	3.0	0.00	<6.0	<6.0	2.2	2.0	1.1	0.80	5.1	3.4	3.0	0.16	<6.0	<6.0
Lead	9.0	8.9	2.7	5.2	15	2.5	1.9	1.3	1.4	5.9	23	17	15	10	76	0.27	0.62	0.49	<0.50	1.8
Zinc	11	11	1.7	6.8	13	23	19	7.5	15	38	53	43	21	27	120	14	24	12	<7.5	54
Parramatta River																				
Arsenic	1.4	1.4	0.00	1.4	1.4	0.50	0.50	0.00	<1.0	<1.0	1.7	1.7	0.03	1.7	1.9	0.50	0.50	0.00	<1.0	<1.0
Cadmium	0.14	0.14	0.00	0.14	0.14	0.50	0.50	0.00	<1.0	<1.0	2.7	0.17	9.6	0.17	150	0.50	0.50	0.00	<1.0	<1.0
Chromium	1.0	0.71	0.60	0.7	3.0	1.3	1.3	0.00	<2.5	<2.5	3.8	3.9	3.2	0.83	10	1.3	1.3	0.42	<2.5	2.8
Copper	1.5	0.8	1.8	0.35	7.1	2.8	1.7	2.8	<1.5	11	7.6	7.8	6.6	1.3	24	2.8	2.7	0.41	2.0	3.8
Nickel	0.78	0.71	0.24	0.71	1.70	3.0	3.0	0.00	<6.0	<6.0	2.9	3.1	2.3	0.83	8.0	3.0	3.0	0.00	<6.0	<6.0
Lead	1.8	1.4	0.8	1.4	3.7	0.25	0.59	0.36	<0.50	0.97	11	11	10	1.7	36	0.25	0.03	0.34	<0.50	0.81
Zinc	10	8.0	5.4	3.9	21	9.0	5.7	6.2	3.8	20	72	68	64	13	250	18	18	11	3.8	34

Table 15: Event mean concentrations calculated from field data

	LOW FLOW CONDITIONS										MEDIUM/HIGH FLOW CONDITIONS									
	Particulate					Dissolved					Particulate					Dissolved				
	Avg	Med	S.D.	Min	Max	Avg	Med	S.D.	Min	Max	Avg	Med	S.D.	Min	Max	Avg	Med	S.D.	Min	Max
Lane Cove River																				
Arsenic	1.4	1.4	0.00	1.4	1.4	0.50	0.50	0.00	<1.0	<1.0	-	-	-	-	-	-	-	-	-	-
Cadmium	0.14	0.14	0.00	0.14	0.14	0.50	0.50	0.00	<1.0	<1.0	-	-	-	-	-	-	-	-	-	-
Chromium	0.81	0.71	0.47	0.71	3.0	1.3	1.3	0.00	<2.5	<2.5	-	-	-	-	-	-	-	-	-	-
Copper	1.1	0.38	1.5	0.14	7.3	2.4	1.6	1.9	<1.5	7.2	-	-	-	-	-	-	-	-	-	-
Nickel	0.71	0.71	0.00	0.71	0.72	3.0	3.0	0.00	<6.0	<6.0	-	-	-	-	-	-	-	-	-	-
Lead	1.4	1.4	0.00	1.4	1.4	0.31	0.03	0.42	<0.5	1.0	-	-	-	-	-	-	-	-	-	-
Zinc	3.4	2.5	1.7	1.8	6.5	3.8	3.8	4.3	<7.5	18	-	-	-	-	-	-	-	-	-	-

Table 15: Event mean concentrations calculated from field data

LEGEND
Avg – Average (arithmetic mean)
Med – Median
S.D. – Standard deviation
Min – Minimum
Max – Maximum
- Not measured

Event mean concentrations of metals in the natural channels draining large catchments (Duck River, Parramatta River and Lane Cove River) were generally lower than concentrations in concrete-lined channels draining small catchments (Dobroyd Canal, Hawthorne Canal, Cintra Park Canal, Massey Park Canal, Powells Creek and Haslams Creek) under low-flow conditions. However, there was generally no discernible difference in concentrations under medium/high-flow conditions. Event mean concentrations of metals were generally higher under medium/high-flow conditions than under low-flow conditions for all stormwater channels where samples were collected under both medium/high- and low-flow conditions. A summary of results for each metal analysed is provided below.

Arsenic

The average concentrations of arsenic in stormwater ranged from 1.9 to 17.6 µg/L. The highest concentrations of arsenic were reported in Massey Park Canal and Cintra Park Canal under low-flow conditions and the lowest concentrations were reported in natural channels under low-and medium/high-flow conditions. Results indicate that arsenic was predominantly in the particulate phase in the natural stormwater channels and predominantly in the dissolved phase in the concrete-lined stormwater channels under low- and medium/high-flow conditions. Dissolved phase concentrations of arsenic were particularly high relative to particulate phase concentrations in Cintra Park Canal and Massey Park Canal under low-flow conditions, and Dobroyd Canal and Hawthorne Canal under medium/high-flow conditions.

Cadmium

Average concentrations of cadmium in stormwater ranged from less than 1 µg/L to greater than 4 µg/L. Under low-flow conditions, event mean concentrations of cadmium were less than 1 µg/L for all stormwater channels sampled. Under medium/high-flow conditions, elevated concentrations of cadmium were reported for the stormwater channels discharging to Iron Cove and for Parramatta River. Cadmium concentrations in Duck Creek were less than 1 µg/L under medium/high-flow conditions. Cadmium was predominantly in the dissolved phase under low- and medium/high-flow conditions, except in Parramatta River under medium/high-flow conditions, where cadmium was predominantly in the particulate phase.

Chromium

Event mean concentrations of chromium in stormwater ranged from 2 µg/L to 36.5 µg/L. Low-flow concentrations of chromium were less than 5 µg/L for all stormwater channels sampled, with the exception of Massey Park and Cintra Park Canals, which had average concentrations of 36.5 µg/L and 21.1 µg/L, respectively. Results indicate chromium was predominantly in particulate phase in the natural stormwater channels and predominantly in dissolved phase in concrete-lined stormwater channels under low- and medium/high-flow conditions. Dissolved phase concentrations of chromium were particularly high relative to particulate phase concentrations in Cintra Park Canal and Massey Park Canal under low-flow conditions, and Dobroyd Canal and Hawthorne Canal under medium/high-flow conditions.

Copper

Average stormwater concentrations of copper ranged from 2.7 µg/L to 24.0 µg/L. Low-flow concentrations of copper were less than 5 µg/L in natural channels, whereas low-flow concentrations of copper ranged from 4.7 µg/L to 15.6 µg/L in concrete-lined channels. Similar concentrations of copper were reported for channels sampled under medium/high-flow conditions. In general, the proportion of copper in particulate phase was slightly higher than the proportion in dissolved phase under low-flow and medium/high-flow conditions for all the channels sampled.

Nickel

Event mean concentrations of nickel ranged from 3.2 µg/L to 5.9 µg/L. Low-flow concentrations of nickel were 3.2 µg/L to 3.9 µg/L, with the exception of Cintra Park Canal, which had an average concentration of 5 µg/L under low-flow conditions. Event mean concentrations of nickel under medium/high-flow conditions were greater than under low-flow conditions and within the range 4.9 µg/L to 5.9 µg/L. Nickel was predominantly in the dissolved phase under both low- and medium/high-flow conditions.

Lead

Low-flow concentrations of lead ranged from 1.7 µg/L to 13.4 µg/L, and medium/high-flow concentrations ranged from 11 µg/L to 28.1 µg/L. The lowest concentrations of lead were in stormwater collected from Haslams Creek, Parramatta River and Lane Cove River under low-flow conditions and the highest concentrations were in stormwater collected from Dobroyd Canal and Duck River under mediumh/high-flow conditions. Results indicate lead has a strong association with particulates under both low- and medium/high-flow conditions.

Zinc

Event mean concentrations of zinc ranged from 7.1 µg/L to 100.8 µg/L. Medium/high-flow concentrations (73.5 µg/L to 100.8 µg/L) were consistently higher than low-flow concentrations (7.1 µg/L to 64.2 µg/L). The proportions of zinc in dissolved and particulate phases varied, however concentrations were generally similar.

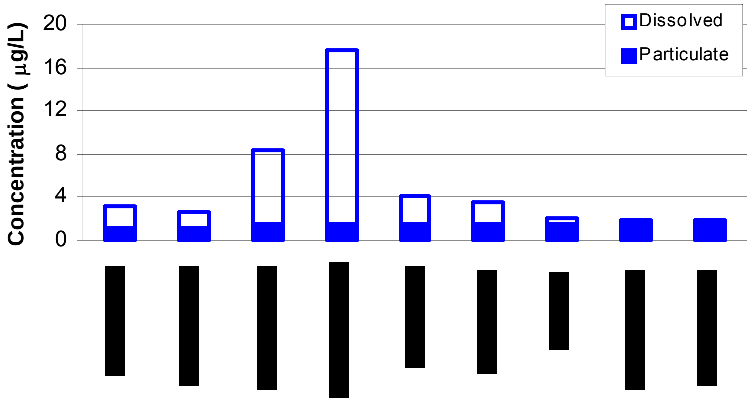


Figure 4A: Event mean arsenic concentrations
Low-flow

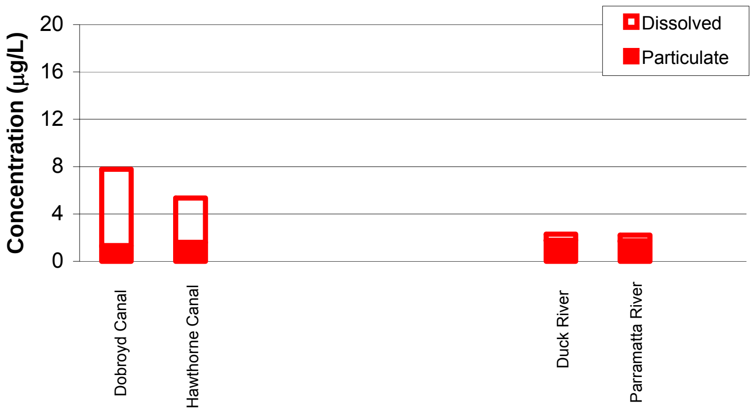


Figure 4B: Event mean arsenic concentrations
Medium/high-flow

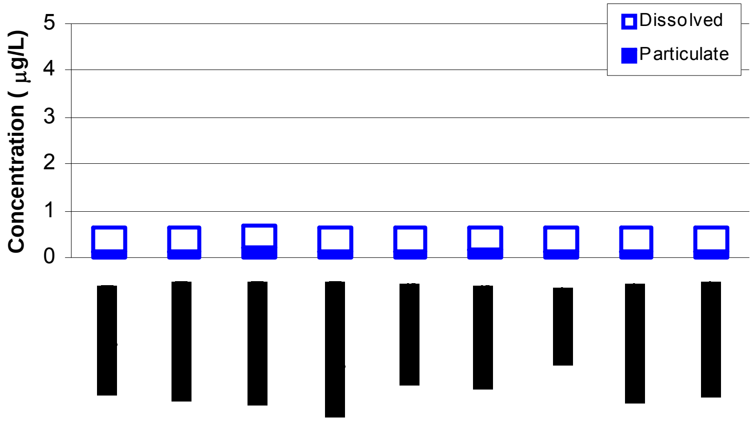


Figure 4C: Event mean cadmium concentrations
Low-flow

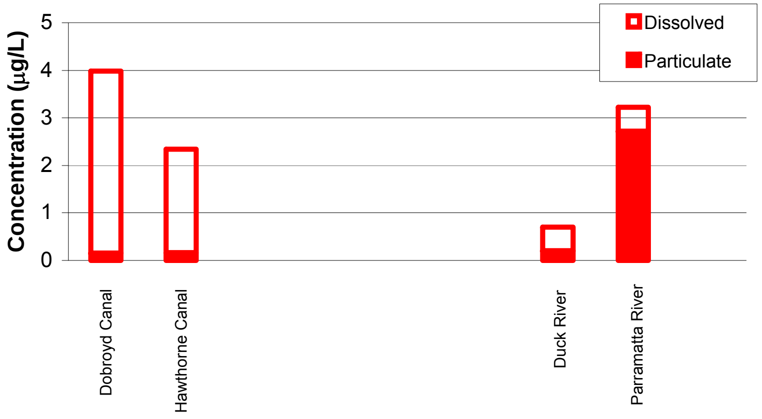


Figure 4D: Event mean cadmium concentrations
Medium/high-flow

Figure 4E: Event Mean chromium concentrations
Low-flow

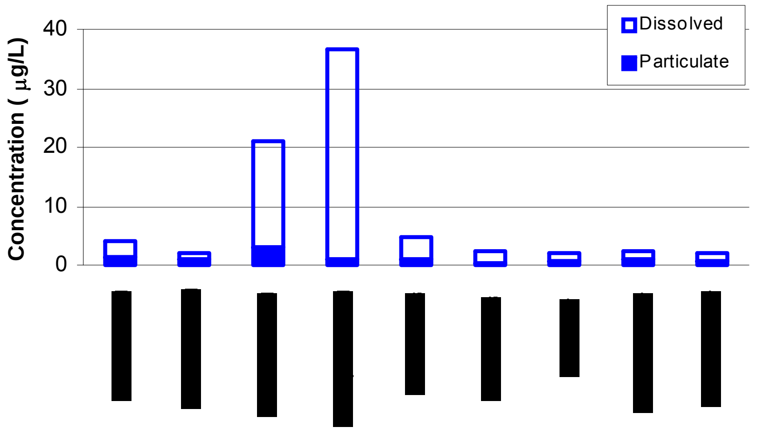


Figure 4F: Event mean chromium concentrations
Medium/high-flow

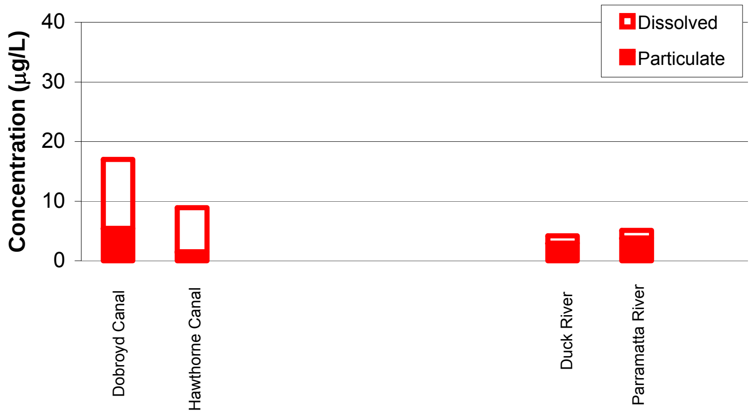


Figure 4G: Event mean copper concentrations
Low-flow

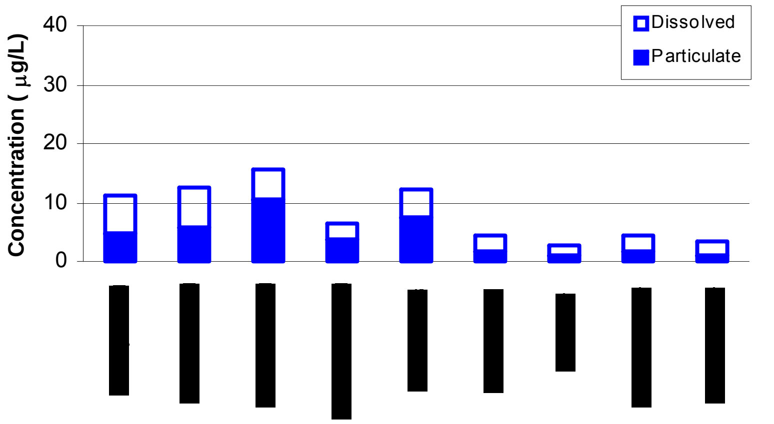


Figure 4H: Event mean copper concentrations
Medium/high-flow

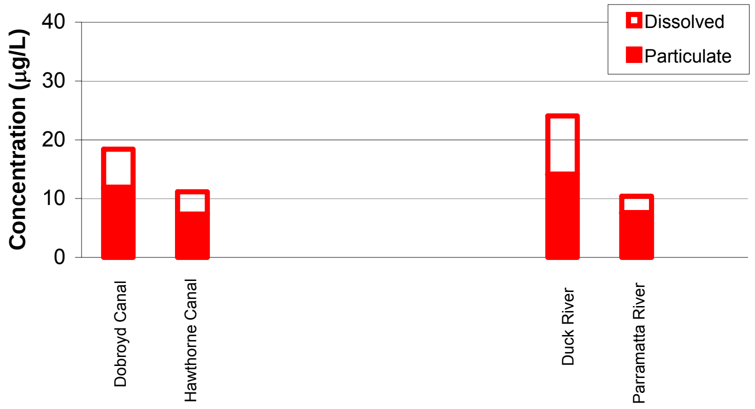


Figure 4I: Event mean nickel concentrations
Low-flow

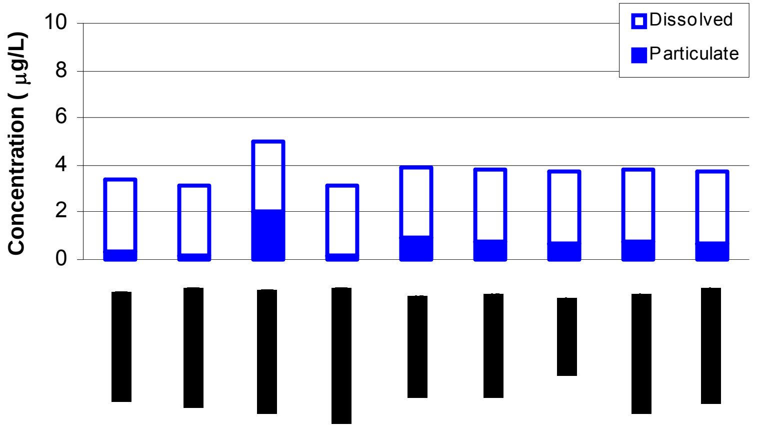


Figure 4J: Event mean nickel concentrations
Medium/high-flow

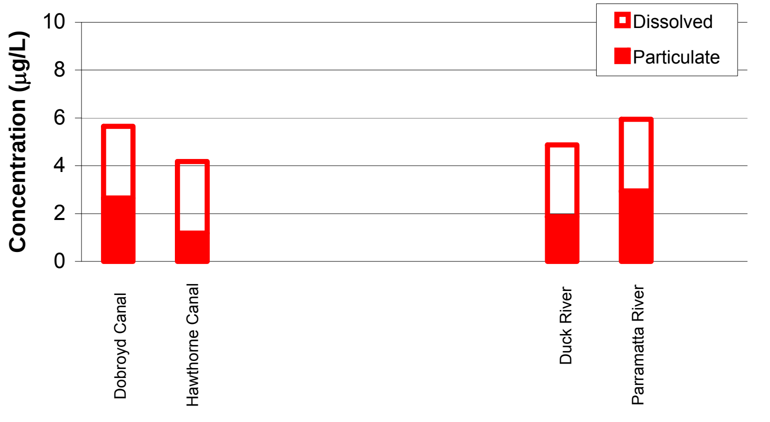


Figure 4K: Event mean lead concentrations
Low-flow

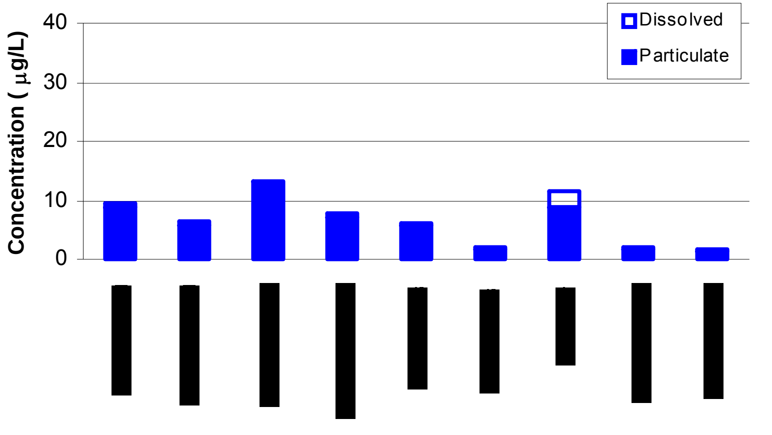
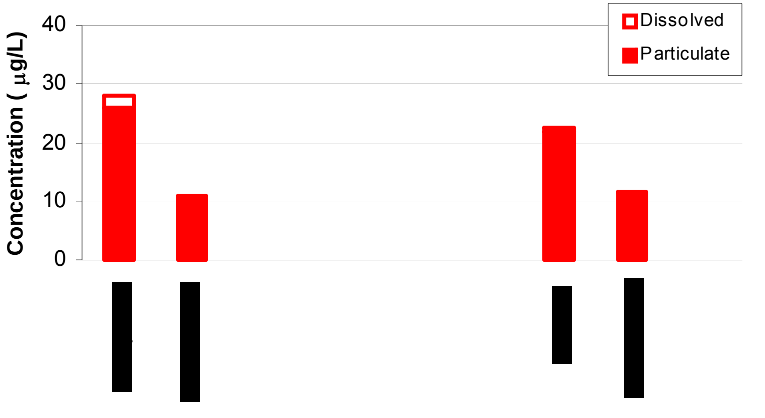


Figure 4L: Event mean lead concentrations
High/very high-flow



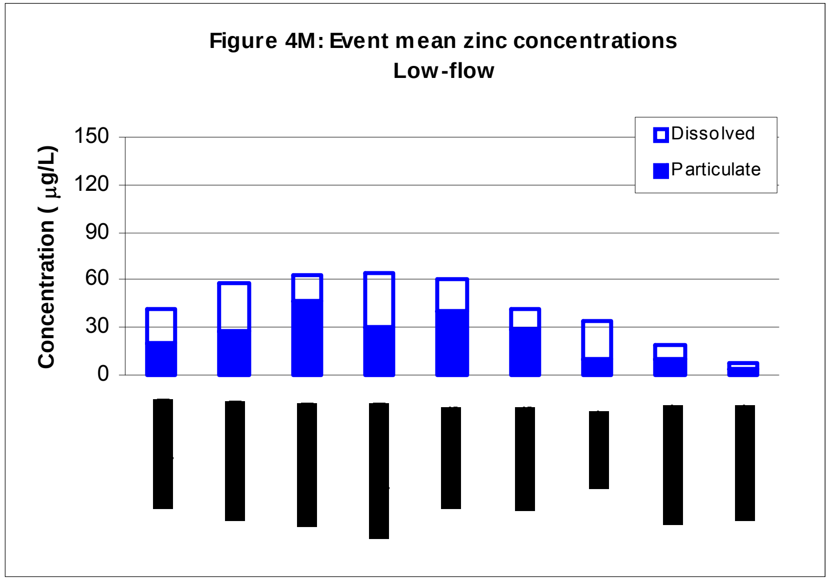


Figure 4M: Event mean zinc concentrations Low-flow

[redacted]

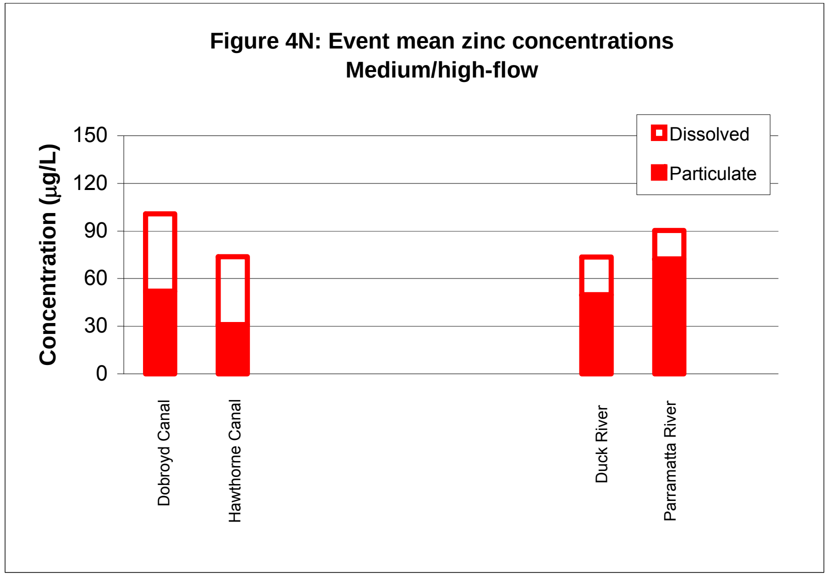


Figure 4N: Event mean zinc concentrations Medium/high-flow

3.3 Model Outputs

3.3.1 Stormwater Discharge

For the simulation period from 1990 to 2006, average annual discharge of stormwater from the Port Jackson catchment was 215,307 ML. The proportion of stormwater discharge attributed to precipitation events less than 5mm, between 5mm and 50mm, and greater than 50mm was 6.5%, 62.5% and 31%, respectively. Stormwater discharge volumes for each of the 70 subcatchments of Port Jackson under low-flow, medium-flow and high-flow conditions, are presented in Table 16.

3.3.2 Metal Loadings

Modelled loadings of heavy metals for the 70 subcatchments of Port Jackson are presented in Appendix A. Average annual loadings of heavy metals for stormwater discharge attributed to precipitation events less than 5mm, between 5mm and 50mm, and greater than 50mm are provided (Appendix A). Average annual loadings of heavy metals per hectare and proportion as dissolved and particulate phases are provided in Appendix B.

Sampled Subcatchments

Average annual loadings of heavy metals from sampled stormwater channels entering Port Jackson, as calculated using MUSIC, are presented in Figures 5A-G. Of the nine stormwater channels assessed, the highest annual loadings of metals in stormwater were from Parramatta and Lane Cove Rivers. High annual loadings of copper and lead were also reported in stormwater from Duck River. The lowest contributions of metals to Port Jackson were from Cintra Park Canal and Massey Park Canal.

The high annual loadings of metals from Parramatta and Lane Cove Rivers relative to other subcatchments is related to the large catchment areas of these streams. The Parramatta River subcatchment is 16,803 ha, and the Lane Cove River is 15,513 ha, compared with 404 ha for Cintra Park Canal and 591 ha for Massey Park Canal. In MUSIC, the larger the subcatchment area, the more rainfall and runoff, and therefore the higher the pollutant load. It is for this reason

Subcatchment	Flow attributed to precipitation events (ML/year)			Total Flow (ML/year)
	<5mm*	>5mm, <50mm*	>50mm*	
1	0	0	0	0
2	45	432	382	858
3	78	751	382	1210
4	4	44	31	80
5	0	0	0	0
6	36	350	180	566
7	1473	14160	7190	22823
8	757	7253	3564	11574
9	82	788	391	1262
10	34	337	183	555
11	111	1060	523	1694
12	21	200	100	321
13	72	691	341	1103
14	32	307	149	488
15	33	314	155	501
16	84	801	397	1282
17	185	1772	886	2843
18	564	5550	2725	8840
19	1820	17534	8956	28310
20	37	353	172	562
21	88	842	423	1353
22	17	167	85	269
23	99	946	473	1518
24	48	460	227	735
25	209	1999	993	3202
26	43	410	208	661
27	407	3910	1958	6276
28	2945	28130	13718	44794
29	73	703	341	1117
30	624	5960	2892	9477
31	511	4888	2362	7761
32	47	454	236	737
33	13	122	66	201
34	131	1249	612	1991
35	356	3406	1665	5427
36	0	0	0	0

Table 16: Stormwater discharge from Port Jackson subcatchments

Subcatchment	Flow attributed to precipitation events (ML/year)			Total Flow (ML/year)
	<5mm*	>5mm, <50mm*	>50mm*	
37	251	2378	1097	3727
38	220	2085	962	3267
39	26	249	120	394
40	98	940	470	1508
41	20	191	97	308
42	12	120	62	194
43	97	927	457	1481
44	6	62	32	101
45	72	691	337	1100
46	5	48	24	77
47	24	225	106	355
48	52	501	249	802
49	82	788	397	1268
50	26	252	124	402
51	46	442	221	709
52	88	773	401	1261
53	200	1766	911	2878
54	6	57	30	93
55	145	1375	653	2173
56	79	744	353	1176
57	57	549	275	881
58	33	319	163	514
59	73	697	344	1114
60	111	1050	489	1650
61	0	0	0	0
62	183	1738	820	2740
63	7	66	34	107
64	112	1069	517	1698
65	220	2075	933	3229
66	111	1056	508	1675
67	112	1075	527	1714
68	127	1214	593	1934
69	217	2078	1031	3326
70	69	659	334	1062
Port Jackson Total	**14068**	**134604**	**66636**	**215307**

Table 16: Stormwater discharge from Port Jackson subcatchments

* – Rainfall in 24 hours

Figure 5A: Annual arsenic loading for sampled subcatchments (kg/year)

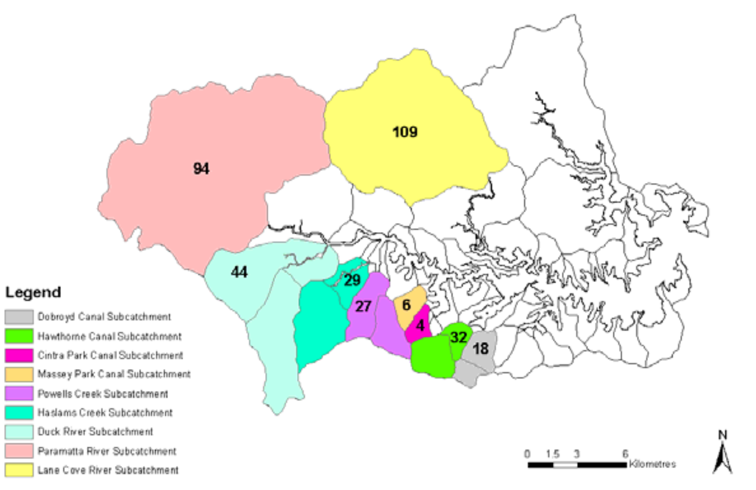


Figure 5B: Annual cadmium loading for sampled subcatchments (kg/year)

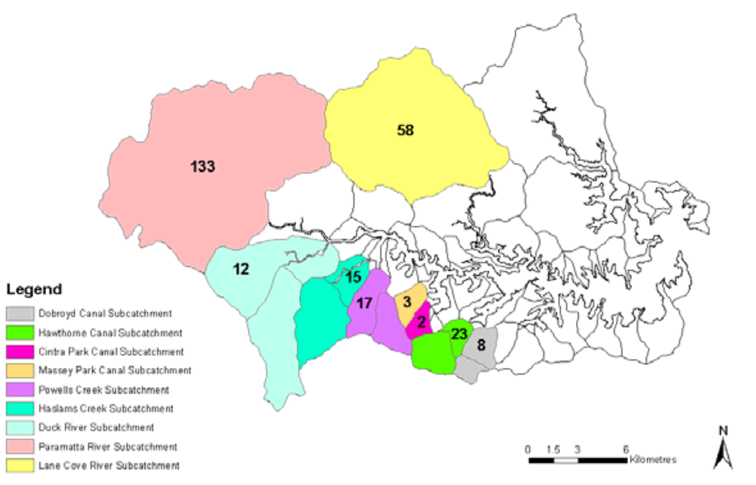


Figure 5C: Annual chromium loading for sampled subcatchments (kg/year)

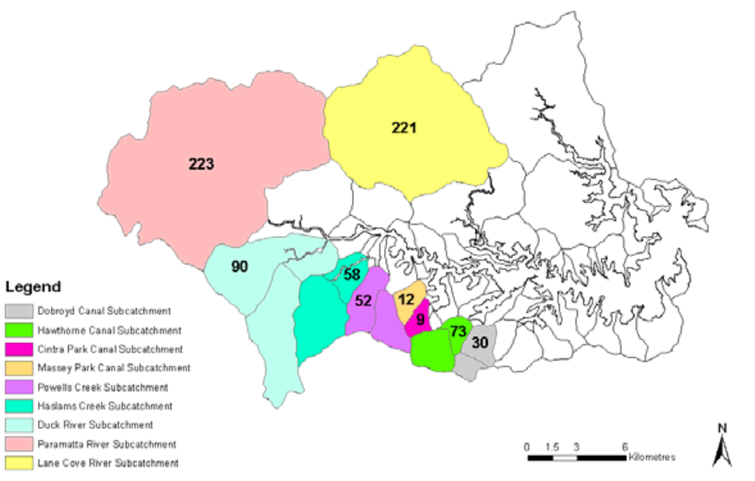


Figure 5D: Annual copper loading for sampled subcatchments (kg/year)

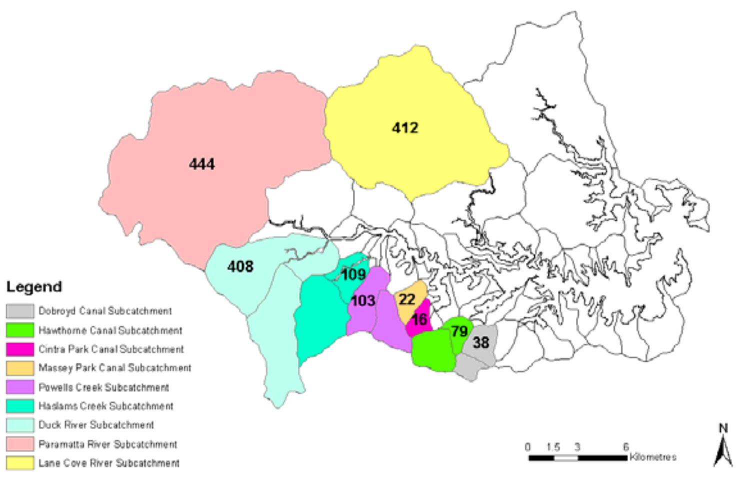


Figure 5E: Annual nickel loading for sampled subcatchments (kg/year)

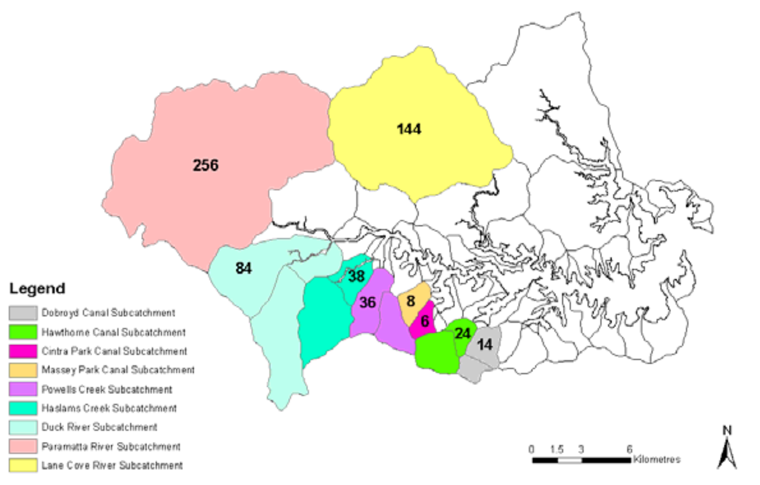


Figure 5F: Annual lead loading for sampled subcatchments (kg/year)

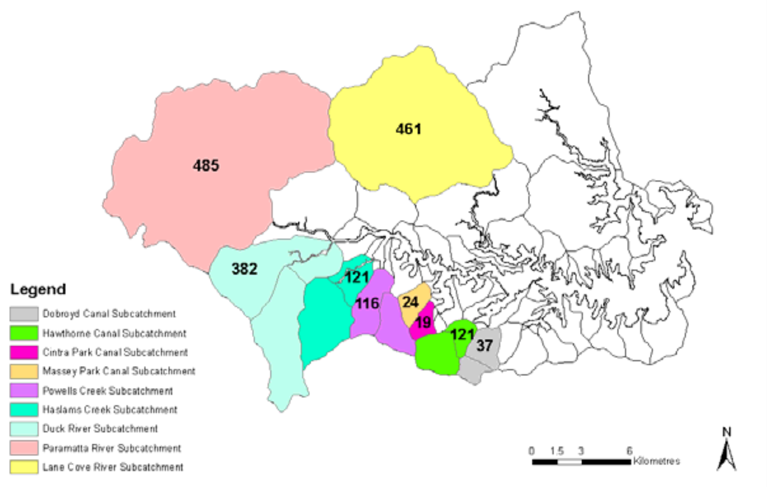
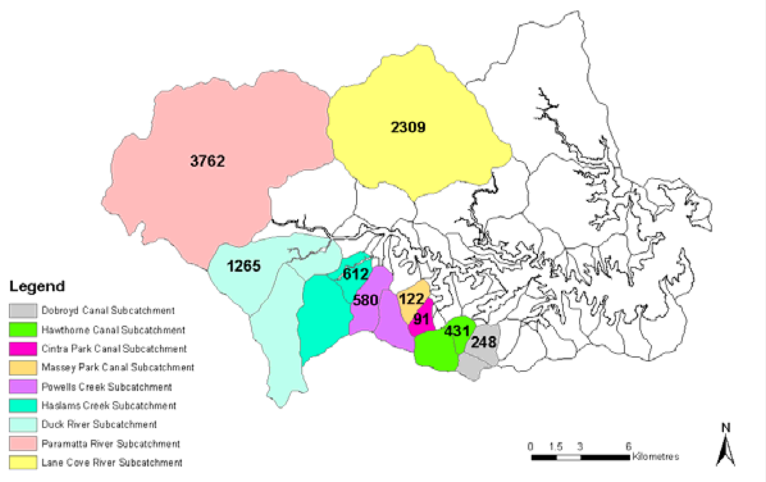


Figure 5G: Annual zinc loading for sampled subcatchments (kg/year)



that the larger subcatchments have consistently higher loadings than the smaller subcatchments for all metals sampled.

Figures 6A-G present annual loadings of metals per hectare for each main stormwater channel entering Port Jackson. The proportion impervious area in each of the subcatchments is also shown. Dobroyd Canal had the highest average annual loadings of metals per hectare for all metals except copper and nickel. Powells Creek had the highest average annual loading of nickel and was generally second to Dobroyd Canal for most other heavy metals. Duck River had the highest average annual loading of copper per hectare.

As shown in Figures 6A-G, there is some relationship between loading and proportion impervious area in the subcatchment. Generally, the higher the proportion impervious area, the higher the loading of metals. This relationship is evident for Powells Creek, which has the highest proportion impervious area of the sampled subcatchments and comparatively high loadings of heavy metals.

Figure 6A: Annual arsenic loading per hectare

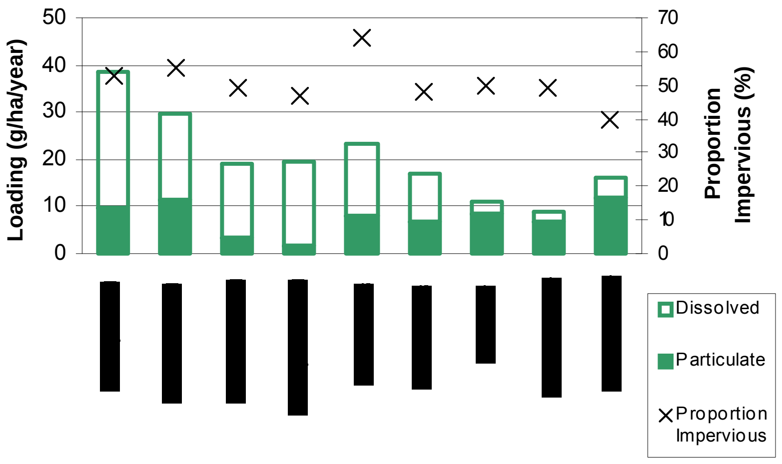


Figure 6B: Annual cadmium loading per hectare

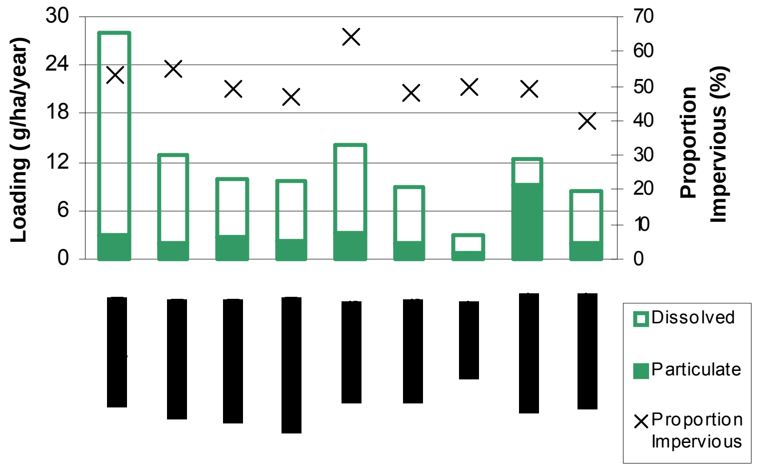


Figure 6C: Annual chromium loading per hectare

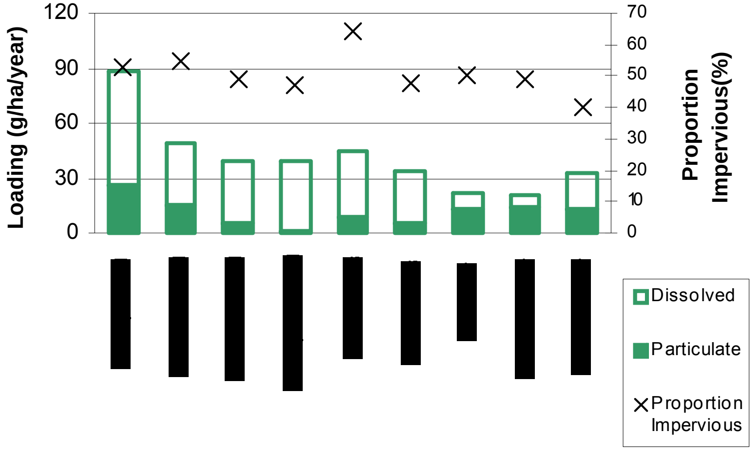


Figure 6D: Annual copper loading per hectare

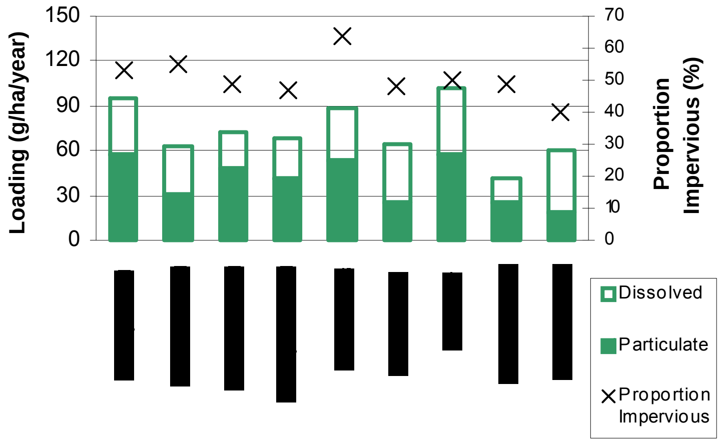


Figure 6E: Annual nickel loading per hectare

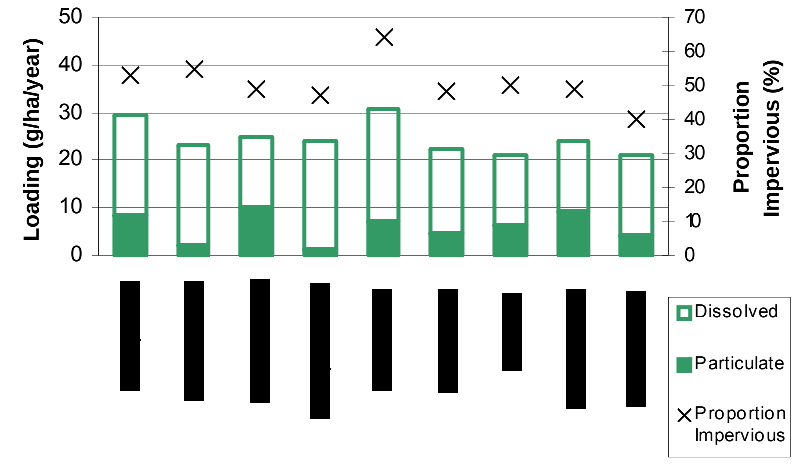


Figure 6F: Annual lead loading per hectare

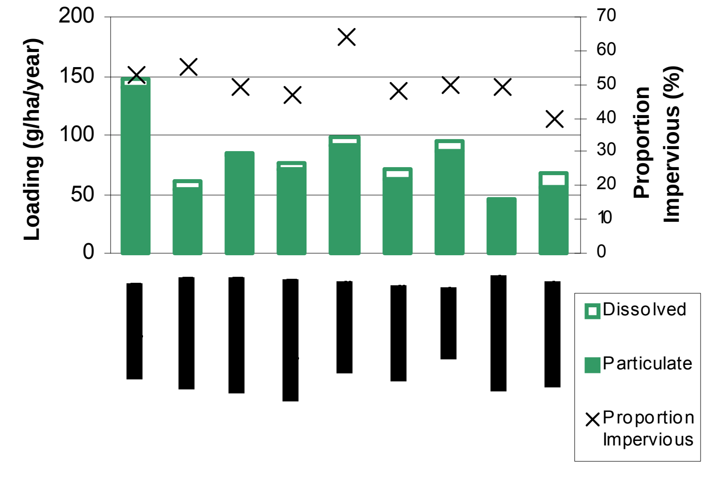
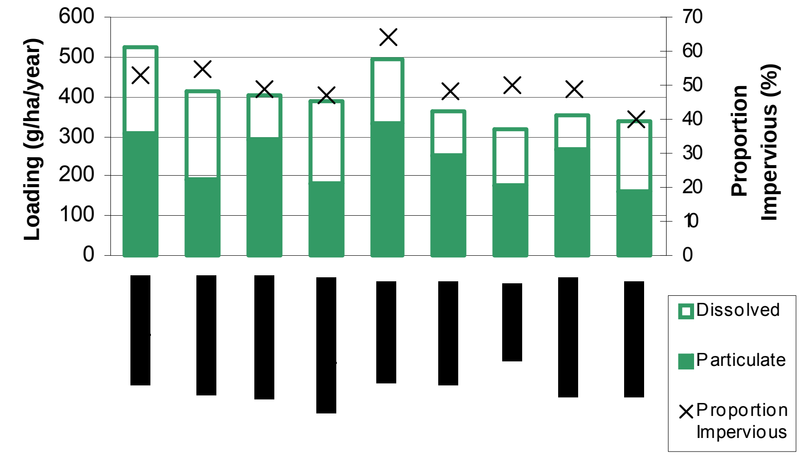


Figure 6G: Annual zinc loading per hectare



Modelled Subcatchments

Average annual loadings of heavy metals from Port Jackson's catchment for the simulation period from 1990 to 2006 are shown in Table 17.

Port Jackson	As	Cd	Cr	Cu	Ni	Pb	Zn
Average Annual Loading (tonnes)	0.8	0.5	1.7	3.2	1.1	3.6	17.7

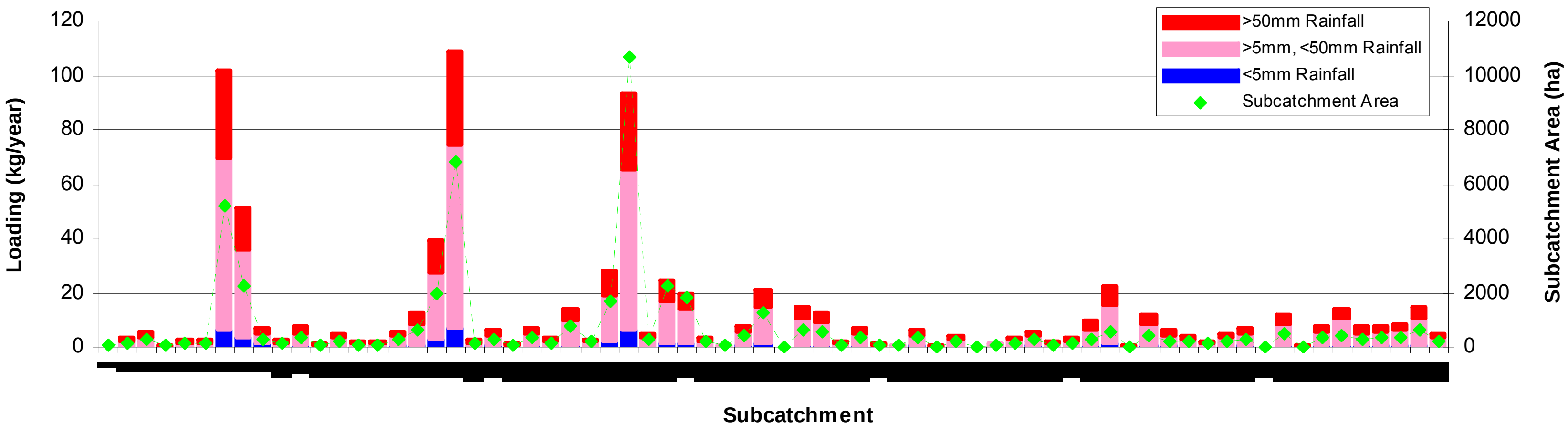
Table 17: Average annual loadings of heavy metals from the Port Jackson catchment

Figures 7A-G present average annual loadings of heavy metals for the 70 subcatchments of Port Jackson. The proportion of heavy metal loadings attributed to precipitation events less than 5mm (in 24 hours), between 5mm and 50mm (in 24 hours), and greater than 50mm (in 24 hours) are shown.

The largest subcatchment, Upper Parramatta River (subcatchment 28), had the highest annual discharge of cadmium, chromium, copper, nickel, lead and zinc to Port Jackson. The second largest subcatchment, Upper Lane Cove River (subcatchment 19), had the highest annual discharge of arsenic, and the second highest annual discharge of other heavy metals. The third largest subcatchment, Upper Middle Harbour (subcatchment 7), had the second highest annual discharge of arsenic and the third highest discharge of other heavy metals. These results indicate there is a relationship between heavy metal loading and subcatchment area, with the largest subcatchments having the highest loadings of heavy metals.

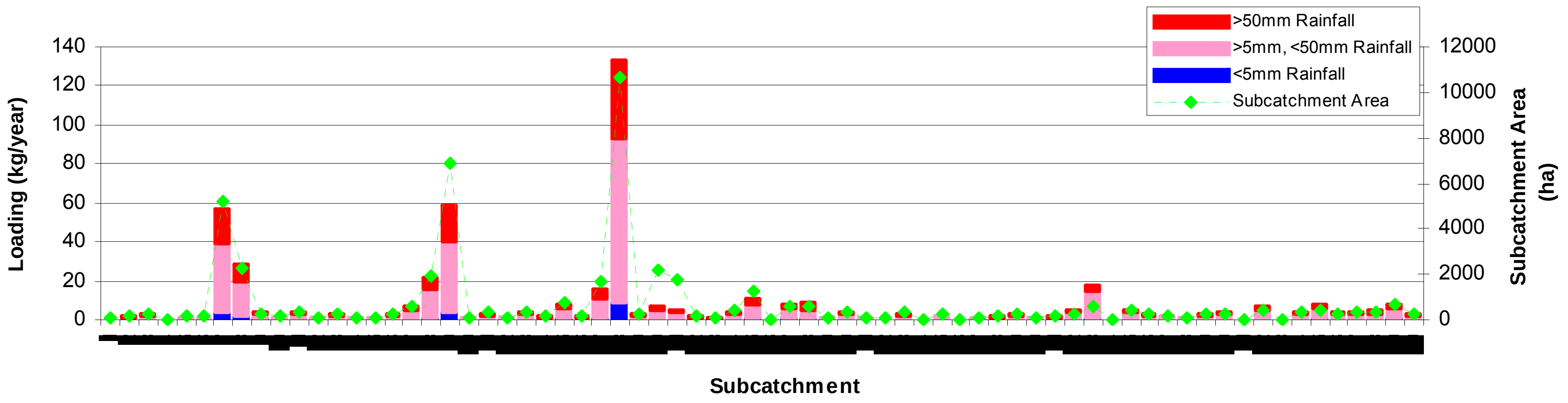
The lowest annual discharge of heavy metals was from Homebush Bay S (subcatchment 36), which is the fourth smallest subcatchment in Port Jackson and has less than 1 % impervious area. The second lowest annual discharge of heavy metals was from North Harbour ESE (subcatchment 1), which is the ninth smallest subcatchment in Port Jackson and also has less than 1 % impervious area. These results indicate that impervious area is an important factor in determining heavy metal loading.

Figure 7A: Stormwater arsenic loadings



[redacted]

Figure 7B: Stormwater cadmium loadings



[redacted]

Figure 7C: Stormwater chromium loadings

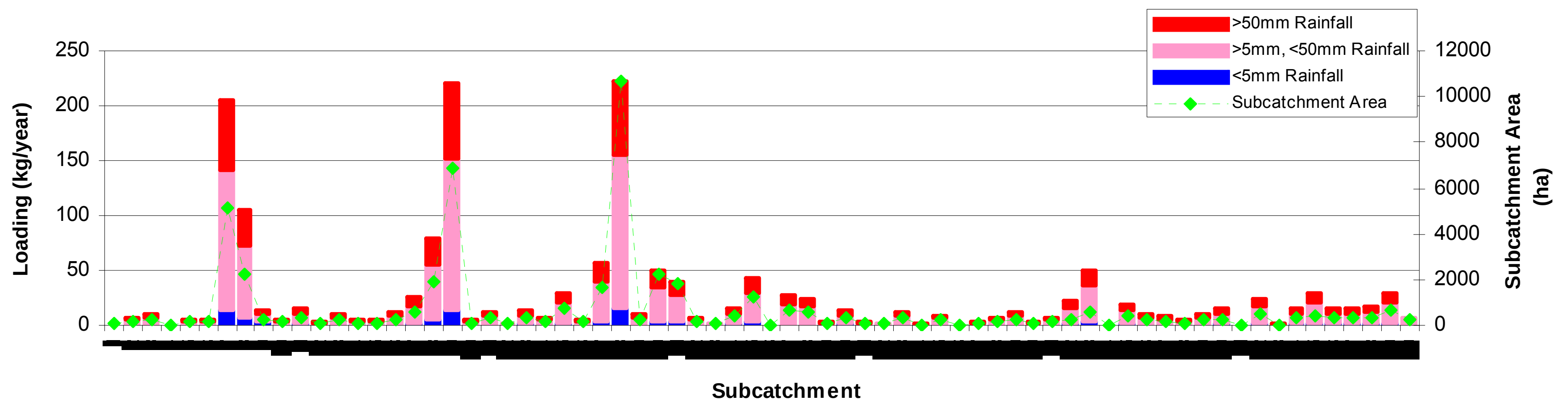


Figure 7D: Stormwater copper loadings

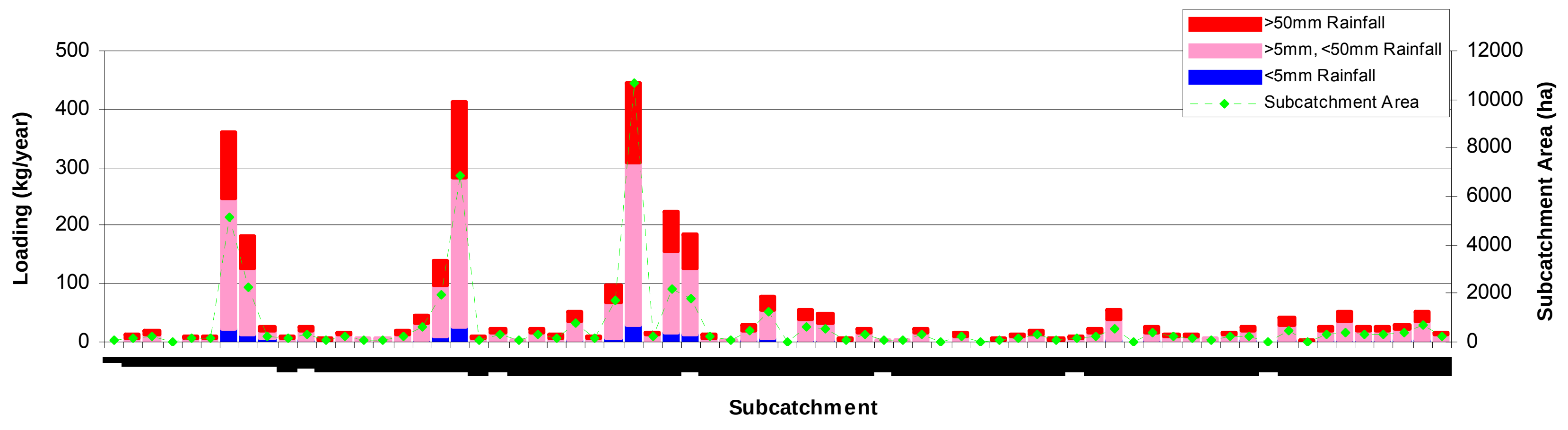


Figure 7E: Stormwater nickel loadings

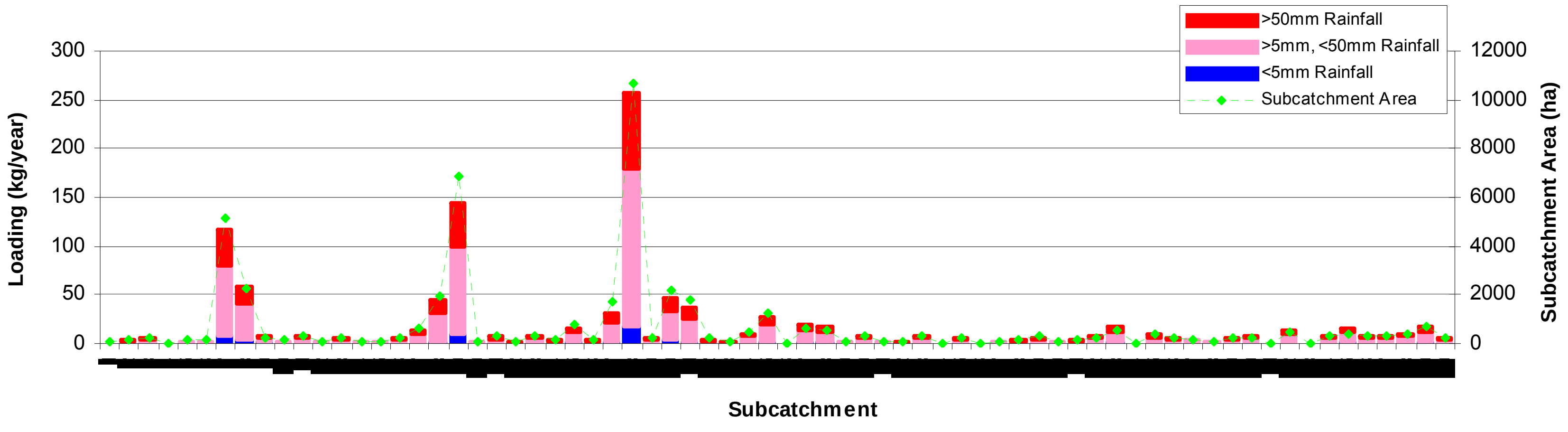
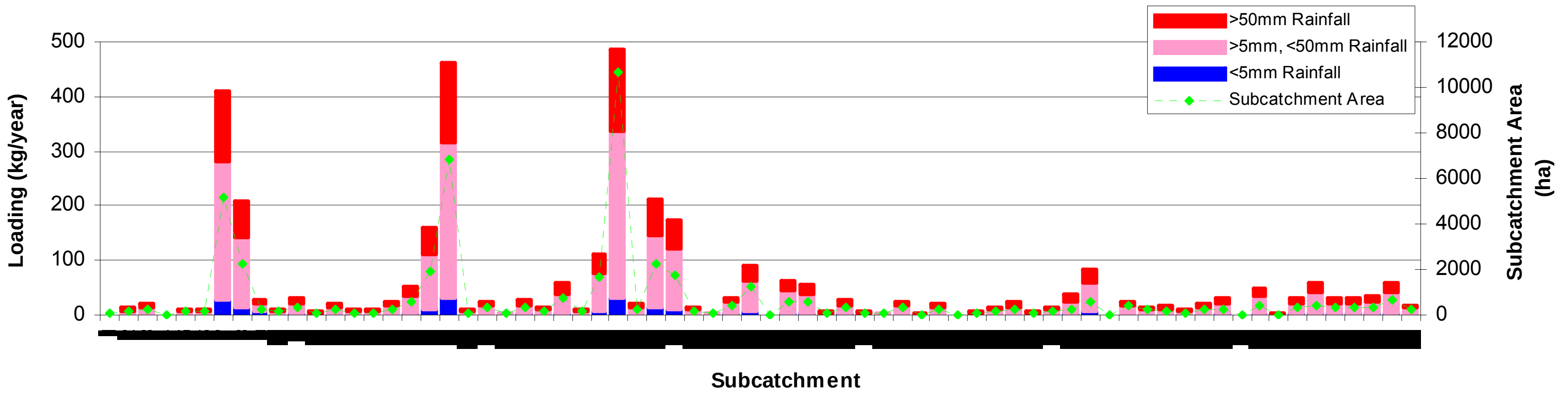


Figure 7F: Stormwater lead loadings



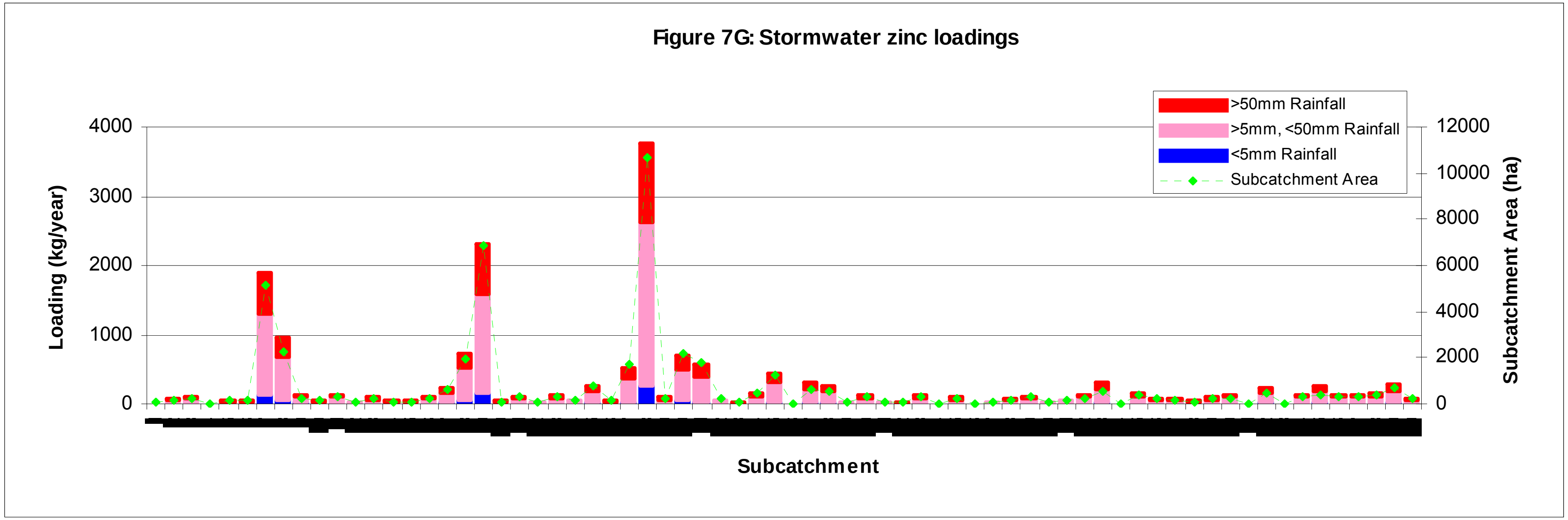


Figure 7G: Stormwater zinc loadings

The greatest contributor of heavy metals to Port Jackson was rainfall events between 5mm and 50mm (in 24 hours), followed by rainfall events greater than 50mm (in 24 hours). Rainfall events less than 5mm (in 24 hours) were the lowest contributor of heavy metals to Port Jackson. Rainfall events between 5mm and 50mm (in 24 hours) also contributed the greatest volume of stormwater discharge to Port Jackson. In MUSIC, the greater the volume of stormwater discharged, the greater the loading of heavy metals.

Figures 8A-G present subcatchments with significant per hectare loadings of heavy metals. The highest per hectare loadings of arsenic, cadmium, chromium and lead were from Upper Dobroyd Canal (subcatchment 53), followed by Lower Dobroyd Canal (subcatchment 52). These high per hectare loadings may be related to the highly residential nature of the Dobroyd Canal subcatchments. Of the sampled subcatchments, the Dobroyd Canal subcatchments have the highest proportion of residential landuse at 70 %.

The highest per hectare loadings of copper, nickel and zinc were from the Darling Harbour subcatchment (subcatchment 65). These high per hectare loadings are related to the high per hectare runoff volumes from this subcatchment. Darling Harbour is located in the eastern part of Port Jackson, near the coastline, where rainfall is high compared to the rest of the catchment, averaging 1200 mm per annum. Darling Harbour also has the highest proportion impervious area of the Port Jackson subcatchments. The combination of high rainfall and impervious area results in the highest runoff volumes per hectare in Port Jackson.

Other subcatchments with significant per hectare loadings of heavy metals include Whites Creek (subcatchment 60), Middle Harbour SSW (subcatchment 9), Johnstons Creek (subcatchment 62), Kings Bay Canal (subcatchment 47) and Lower Harbour S1 (subcatchment 66). These subcatchments all have greater than 50 % impervious area and are located in areas where rainfall averages more than 1100 mm per annum.

Figure 8A: Subcatchments with significant per hectare arsenic loadings

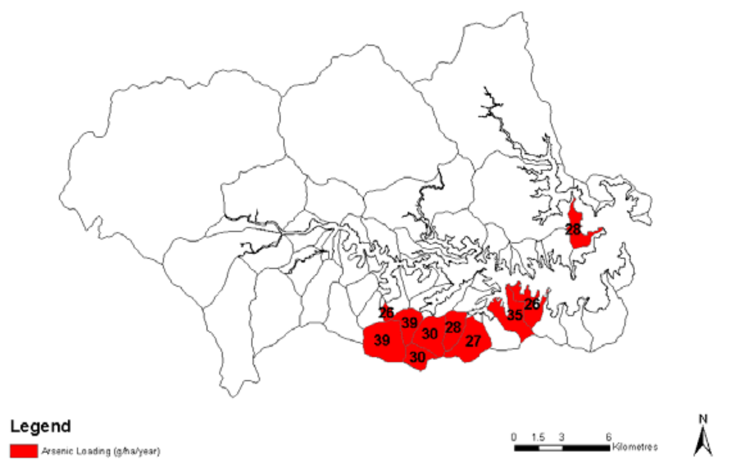


Figure 8B: Subcatchments with significant per hectare cadmium loadings

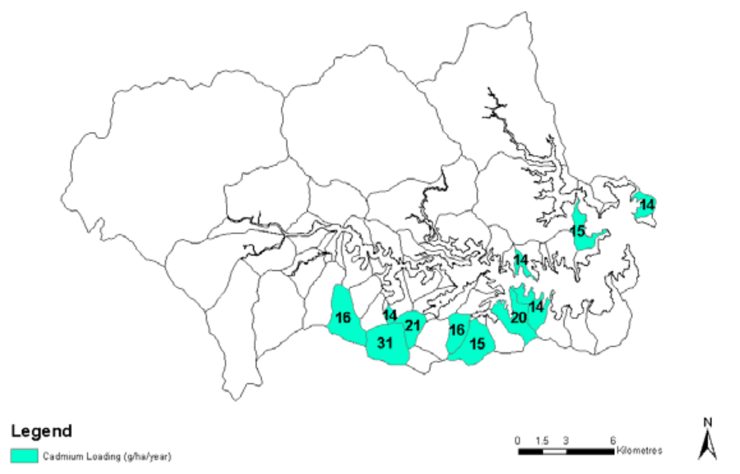


Figure 8C: Subcatchments with significant per hectare chromium loadings

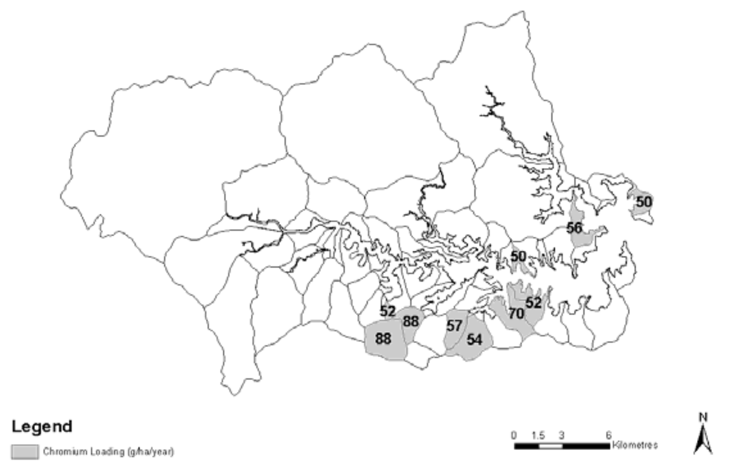


Figure 8D: Subcatchments with significant per hectare copper loadings

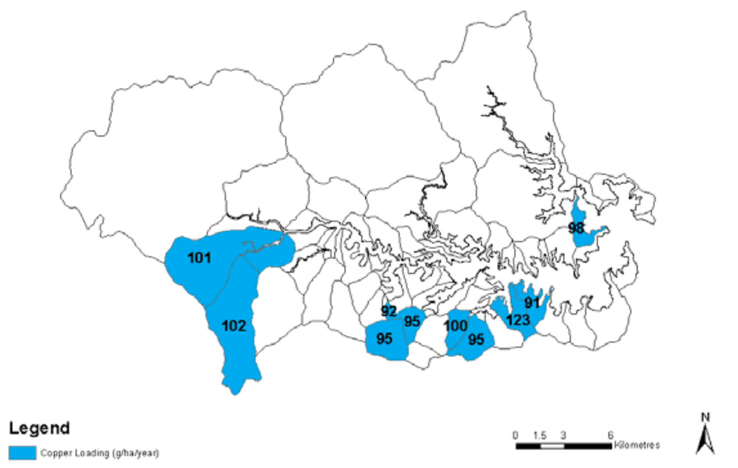


Figure 8E: Subcatchments with significant per hectare nickel loadings

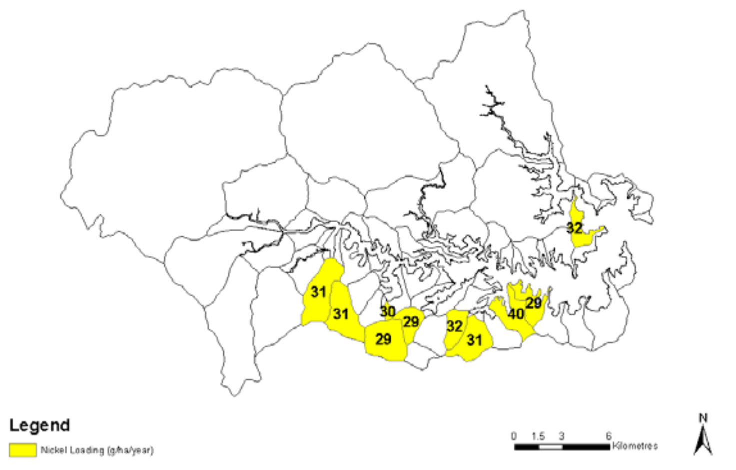


Figure 8F: Subcatchments with significant per hectare lead loadings

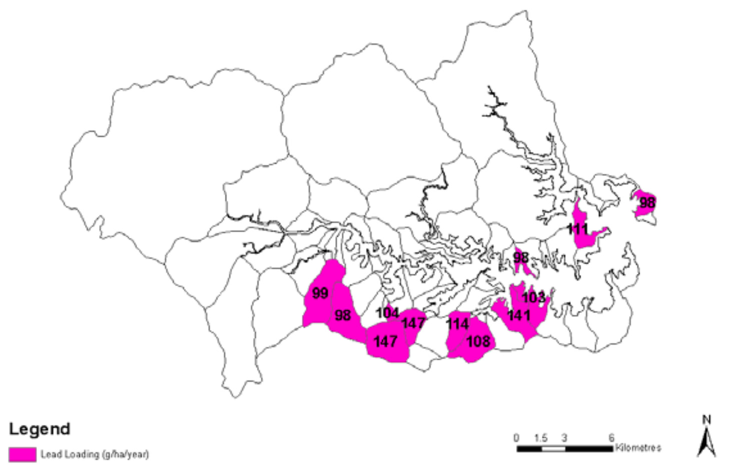
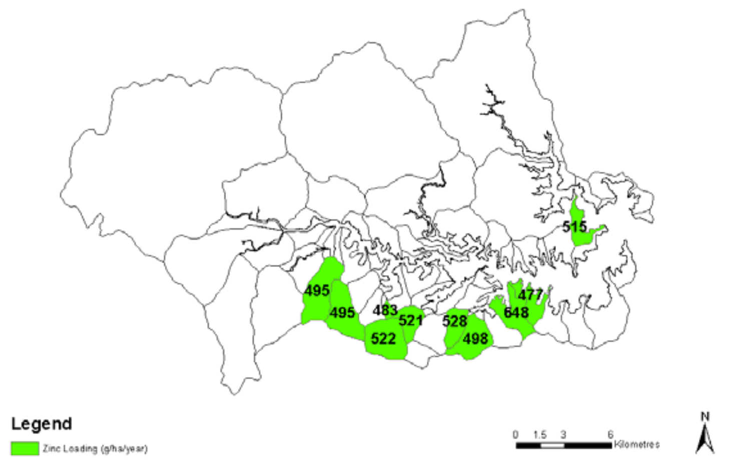


Figure 8G: Subcatchments with significant per hectare zinc loadings



4. Discussion

High concentrations of heavy metals in sediments in Port Jackson estuary are a threat to the healthy functioning of the estuarine ecosystem (Taylor, 2000; Birch and Taylor, 2002a, b). Investigations of fluvial and estuarine sediments have suggested stormwater is an important source of heavy metals to Port Jackson estuary (Taylor, 2000; Birch and Taylor, 1999). The current study supports stormwater discharge as a significant source of heavy metals to Port Jackson.

Stormwater remediation devices may reduce potential impacts of stormwater pollution on the estuarine ecosystem. However, the vast majority of remediation devices currently in use in the Port Jackson estuary catchment are gross pollutant traps, which are ineffective in removing heavy metals from stormwater. A thorough characterisation of heavy metal inputs is required to target remediation efforts and ensure optimum efficiency of new or retrofitted remediation devices in removing heavy metals from stormwater. A conceptual model of heavy metals in stormwater entering Port Jackson estuary has been developed in the current study to assist in the design of future remediation works.

4.1 Comparison to Other Catchments

Stormwater heavy metal loadings reported for urban catchments in Australia and overseas are presented in Table 18. Comparison to results of the current investigation indicate loadings of heavy metals in stormwater discharging to Port Jackson estuary are some of the highest in Australia and the world. Loadings of heavy metals in stormwater entering Port Jackson were greater than other urban catchments by 2 to 50 times for copper, 2 to 80 times for lead and 0 to 20 times for zinc.

Location	Reference	Cd	Cr	Cu	Ni	Pb	Zn
Port Jackson	Current study	**11**	**41**	**72**	**23**	**82**	**378**
Yarra River, Australia	Duncan (2000)	-	-	7.7 - 11	-	5.7 - 31	23 - 190
Los Angeles River, U.S.A.	Stein and Ackerman (2007)	-	-	6.3 - 21	-	0.0 – 0.9	19 - 78
Coyote Creek U.S.A.	Stein and Ackerman (2007)	-	-	1.3 - 1.5	-	0.4 – 1.0	13 - 59
San Gabriel River U.S.A.	Stein and Ackerman (2007)	-	-	0.4 - 4.2	-	0.1 – 1.4	268 - 398
San Jose Creek U.S.A.	Stein and Ackerman (2007)	-	-	5.5 - 7.2	-	1.0 – 1.5	144 - 313
Walnut Creek U.S.A.	Stein and Ackerman (2007)	-	-	1.2 - 5.6	-	0.8 – 1.3	9 - 19
Ballona Creek U.S.A.	Stein and Ackerman (2007)	-	-	4.6 - 6.2	-	1.5 – 3.5	18 - 21
Ballona Creek, U.S.A.	McPherson et al. (2005)	-	12	40	11	14	-

Loadings reported in g/ha/year

Table 18: Comparison to loadings in other catchments worldwide

4.2 Verification of Results

Results of field and analytical work and modelling in the present study were verified by comparison to published literature (Barry et al.1999; Water Board, 1993b; Birch et al., 1999) and unpublished data from Port Jackson (Barry and Birch, unpublished). Modelling results were further validated by manually calculating loadings for Dobroyd and Hawthorne Canals using the method in Barry and Birch (unpublished). Model inputs including rainfall, impervious area and subcatchment area were taken from published data and were not verified in the current study.

4.2.1 Verification of Field and Analytical Data

Comparison to Published Literature

Field and analytical data collected in the present study for Dobroyd and Hawthorne Canals were compared to results reported in Barry et al. (1999) and Water Board (1993b) (Table 19).

Barry et al. (1999) collected 7 stormwater samples from above the tidal limit in each of Dobroyd and Hawthorne Canals. Samples were collected under low-flow conditions and analysed for dissolved and particulate concentrations of copper, lead and zinc. Water Board (1993b) collected 30 stormwater samples from four locations on Hawthorne Canal under low- and medium/high-flow conditions. Samples were analysed for total concentrations of copper, lead and zinc.

Ranges of total metal concentrations measured in the present investigation under medium/high-flow conditions were similar to those measured in the Water Board (1993b) investigation. However, event mean concentrations measured in the present investigation under low-flow conditions were similar to (1.3 to 4.3 times lower) concentrations measured in the Barry et al. (1999) investigation for dissolved phase metals, but 3 to 20 times lower for particulate phase metals. Total metal concentrations measured in the present investigation under low-flow conditions were also lower than concentrations measured in the Water Board (1993b) investigation.

The comparatively low concentrations of heavy metals reported in the current study for low-flow conditions are unlikely to be due to sample collection or analytical methodologies as Barry conducted field and analytical work for both the current and Barry et al. (1999) studies. Also, results from the current investigation for Dobroyd and Hawthorne Canals were similar to those reported for other sampled subcatchments (Figures 4A-N). The current study involved the use of a hierarchical sampling design and collection of 260 samples over six months compared to 14 samples over 8 days in the Barry et al. (1999) study and 30 samples over six months in the Water Board (1993b) study. It is possible that higher concentrations of heavy metals were present during the Barry et al. (1999) and Water Board (1993b) studies. These results suggest heavy metal concentrations for particulates are temporally highly variable in Dobroyd and Hawthorne Canals.

Location	Reference	Flow	Form	Units	Cu	Pb	Zn
Dobroyd Canal	Current study	Low	Diss	µg/L	6.6 (1.9-20)	0.7 (<0.5-6.7)	22 (<7.5-91)
			Part	µg/g	194 (27-455)	233 (0.0-894)	1358 (160-3114)
	Barry et al. (1999)*	Low	Diss	µg/L	26 (13-65)	3 (<0.5-11)	37 (4.0-162)
			Part	µg/g	1456 (437-5857)	1158 (365-4429)	4139 (2059-9000)
Hawthorne Canal	Current study	Low	Diss	µg/L	6.6 (1.6-22)	0.8 (<0.5-10)	30 (14-93)
			Part	µg/g	486 (69-1443)	361 (0.0-1754)	2408 (489-10308)
	Barry et al. (1999)*	Low	Diss	µg/L	18 (3-83)	1.0 (<0.5-3.0)	51 (2.0-303)
			Part	µg/g	9982 (439-51000)	3335 (585-7500)	14790 (1390-40000)
	Current study	Low	Total	µg/L	13 (3.5-59)	6.5 (<0.5-48)	38 (22-213)
		Medium/High	Total	µg/L	11 (3.1-28)	11 (1.5-55)	74 (25-290)
	Water Board (1993b)	Low	Total	µg/L	(5 –93)	(8-185)	(44-1480)
		Medium/High	Total	µg/L	(14-27)	<100	(164-182)

* Samples collected above the tidal limit
Diss – Dissolved phase
Part – Particulate phase

Table 19: Comparison of current field and analytical data to published literature

Comparison to Unpublished Literature

Field and analytical data collected in the present study for Powells and Haslams Creeks were compared to data reported in Chambers (2000) (Table 20).

Chambers (2000) collected 32 stormwater samples from each of Powells and Haslams Creeks under low- and medium/high-flow conditions. Samples were analysed for particulate heavy metals.

Location	Reference	Flow	Form	Units	Cd	Cr	Cu	Ni	Pb	Zn
Powells Creek	Current study	Low	Part	µg/L	0.14	0.90	7.4	0.90	5.6	40
		Medium/High	Part	µg/L	0.2	2.5	14	1.9	20	64
	Chambers (2000)	Low	Part	µg/L	0.01	0.07	0.50	0.05	0.66	2.6
		Medium/High	Part	µg/L	0.05	0.6	2.9	0.35	4.5	43
Haslams Creek	Current study	Low	Part	µg/L	0.15	0.39	1.8	0.78	1.8	29
		Medium/High	Part	µg/L	0.25	1.5	7.3	1.2	12	56
	Chambers (2000)	Low	Part	µg/L	0.05	0.56	2.9	0.35	4.5	43
		Medium/High	Part	µg/L	0.13	2.0	10	1.0	20	74

Part – Particulate phase

Table 20: Comparison of current event mean concentrations to other studies in Homebush Bay

Concentrations of particulate metals measured in Haslams Creek in the present investigation were similar to those measured by Chambers (2000) under low- and medium/high-flow conditions. However, concentrations of particulate metals measured in Powells Creek were 1.5 to 5.4 times higher in the present investigation than in the Chambers (2000) investigation under medium/high-flow conditions, and 8.5 to 18 times higher under low-flow conditions. These results also suggest that there is significant temporal variability in stormwater heavy metal concentrations.

Concentrations of heavy metals in stormwater vary as the result of a number of different factors (Warren and Zimmerman, 1994; Hall and Anderson, 1988) including activities within the catchment, the composition of groundwater discharging to canals (McPherson et al., 2005; ARMCANZ/ANZECC, 2000a), the availability of metals in the urban contributing area, antecedent dry period length, rainfall volume, duration and intensity, and catchment size and slope (Kayhanian et al., 2007; Yuan et al., 2001; Brezonik and Stadelmann, 2002).

4.2.2 Verification of the Model

Comparison of field and analytical data from the current study to results of other investigations in Iron Cove and Homebush Bay indicates heavy metal concentrations are highly variable and on the low side of a more comprehensive investigation. This variability flows through to loadings calculations and as a result, the loadings reported in the current study may be an underestimate of actual values.

Comparison to Published Literature

To verify the model, loadings calculated in the present study for Dobroyd and Hawthorne Canals were compared to loadings calculated in Birch et al. (1999) (Table 21).

Birch et al. (1999) determined loadings of copper, lead and zinc discharged to Iron Cove by doubling the loadings calculated for Hawthorne Canal by Peterson and Batley (1992) to account for the contribution of Dobroyd Canal, which had not be measured at this time.. Birch et al. (1999) also calculated loadings of copper, lead and zinc assuming that the total mass of heavy metals in sediment of Iron Cove (as calculated by Birch and Taylor, 1999) had been deposited over the last 100 years.

Loadings calculated in the current study are consistently lower than that estimated by Birch et al. (1999) (Table 21). This may be because average heavy metal concentrations used to calculate loadings in the current study are underestimated or that the methodologies used to calculate loadings by Birch et al. (1999) are incorrect.

Location	Reference	Units	Cu	Pb	Zn
Iron Cove	This study	kg/ha/yr	0.16	0.21	0.93
	Birch et al. (1999) using results from Peterson and Batley (1992)	kg/ha/yr	0.2	1.8	3.2
	Birch et al. (1999) using results from Birch and Taylor (1999)	kg/ha/yr	0.8	2.1	3.0

Table 21: Comparison of current loadings estimations to other studies in Iron Cove

Peterson and Batley (1992) calculated loadings for Hawthorne Canal using concentrations of heavy metals in stormwater runoff from road surfaces. Concentrations of heavy metals in road runoff are generally greater than concentrations in runoff from urban subcatchments (Fletcher et al. 2003). This may explain why loadings calculated by Birch et al. (1999) using the Peterson and Batley (1992) data were greater than loadings calculated in the current study.

Loadings calculated in Birch et al. (1999) using the sediment inventory data in Birch and Taylor (1999) include stormwater inputs of heavy metals to Iron Cove, as well as other sources of heavy metals such as leachates from backfilled areas adjoining the estuary, atmospheric deposition (Birch and Taylor, 1999) and remobilisation of deeper sediments contaminated by past industrial activities. The difference between loadings calculated in the present investigation and loadings calculated by Birch et al. (1999), may be due to loadings from sources other than Hawthorne and Dobroyd Canals.

Manual Calculation of Loadings

To evaluate the accuracy of MUSIC in calculating loadings, stormwater heavy metal loadings were calculated manually for Hawthorne Canal and Dobroyd Canal using the methodology in Barry and Birch (unpublished).

Precipitation, hydrological and contaminant concentration data were collected specifically for this investigation and precipitation results for four weather stations in the vicinity of Iron Cove were obtained from the Bureau of Meteorology (BOM) (Table 22).

Station Number	Location	Address
66070	Strathfield Golf Course	Majors Bay Road, Concord
66000	Ashfield Bowling Club	Queen Street, Ashfield
66017	Barnwell Park Golf Course	Lyons Road, Five Dock
66013	Concord Golf Course	Majors Bay Road, Concord

Table 22: BOM rainfall gauging stations

Flow data for Dobroyd and Hawthorne Canals were obtained from Australian Water Technologies (AWT) Environmental Management Services (Table 23).

Site	Station Number	Location Relative to Sampling Site	Address
Dobroyd Canal	213279	100 m upstream	Australia Street, Ashfield
Hawthorne Canal	213216	10 m downstream	Parramatta Road, Summer Hill

Table 23: AWT flow gauging stations

Precipitation recorded at Strathfield Golf Club correlated well with flow in Dobroyd Canal for the period 1 June 1999 to 20 February 2001 ($r^2 = 0.82$, $p<0.05$) (Figure 9A). A close correlation was also observed for precipitation at Ashfield Bowling Club and flow in Hawthorne Canal for the period 1 January 1993 to 31 December 1994 ($r^2 = 0.89$, $p<0.05$) (Figure 9B).

Low-flow conditions in Dobroyd and Hawthorne Canals were defined as days with less than 5 mm of rainfall in 24 hours. Medium/high-flow conditions were defined as days with greater than 5 mm of rainfall in 24 hours (Water Board, 1993b). Using the correlations to precipitation, flows in Dobroyd and Hawthorne Canals were divided into low- and medium/high-flows.

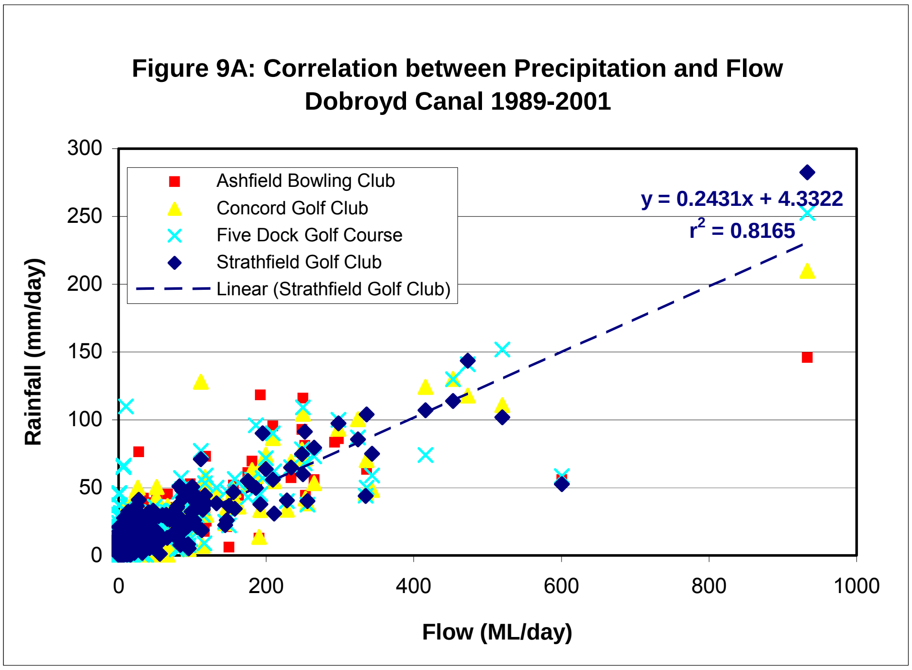
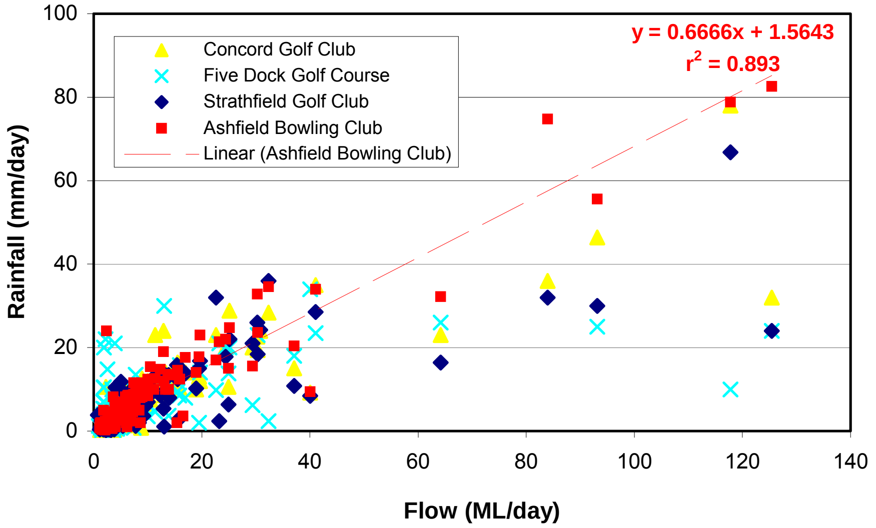
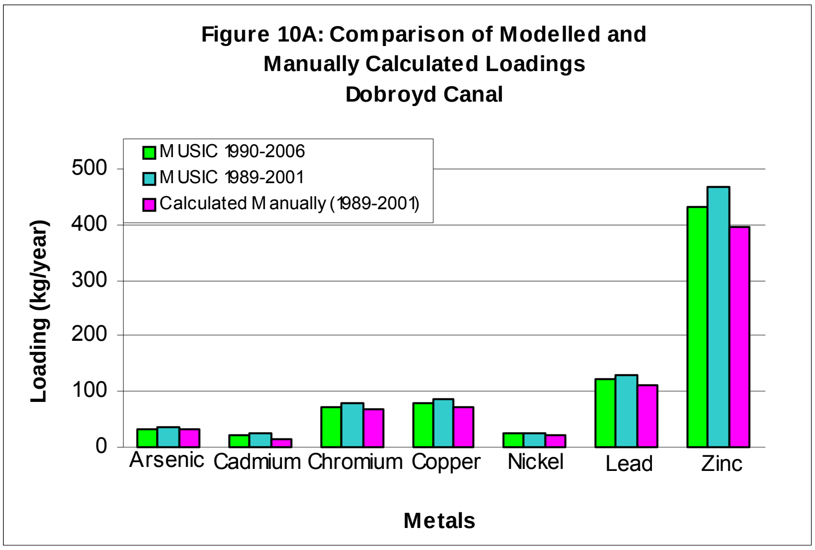


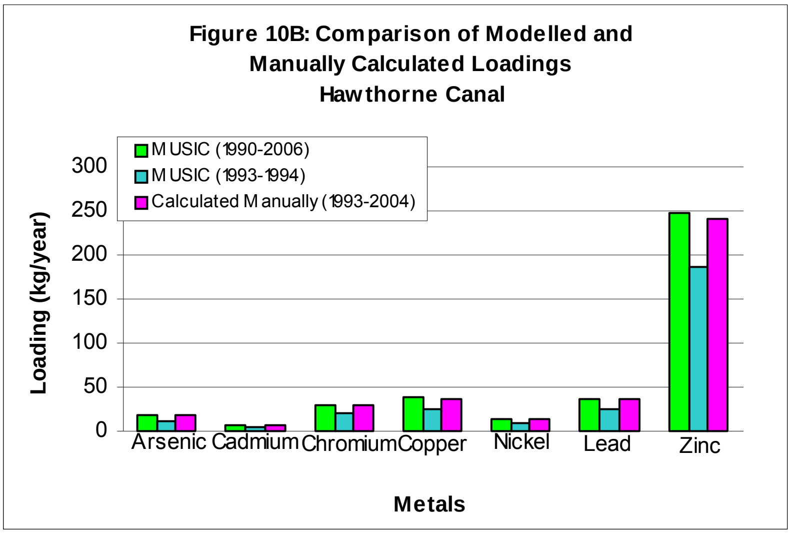
Figure 9B: Correlation between Precipitation and Flow
Hawthorne Canal 1993-1994



Stormwater samples were attributed to either low- or medium/high-flow conditions, based on precipitation in the preceding 24 hours of the sample being collected and average heavy metal concentrations were calculated for low- and medium/high-flow conditions. Loadings were calculated for the gauged catchment area, i.e. the catchment area upstream of the sample point, and the total catchment area using these average concentrations.

Manually calculated and modelled loadings of heavy metals for Dobroyd and Hawthorne Canals are presented in Figures 10A and 10B. Loadings were modelled for the same period as manual calculations (1989 to 2001 for Dobroyd Canal and 1993 to 1994 for Hawthorne Canal), as well as for a longer period (1990-2006). The modelled loadings presented in the current study are for the longer time.





Modelled loadings were similar to manually calculated loadings, particularly modelled loadings for the longer period (1990-2006). This indicates the TSS field in MUSIC is an appropriate tool for calculating heavy metal loadings where no flow data are available, as for the current study.

4.2.3 Sensitivity of Results and Suitability of Using MUSIC

The low concentrations of stormwater heavy metals reported in the current investigation compared to other investigations in Port Jackson may be due to the sampling design used. The hierarchical nested sampling design employed was appropriate for detecting small-scale temporal variation (hours and days), however variation at monthly and yearly scale was not assessed as the duration of the sampling program was limited to six months (Hatje et al., 2001a).

The annual cycle is a significant feature of water quality dynamics and sampling at monthly and seasonal scales should be included in monitoring programs to ensure representative results are obtained (Baldwin and Lall, 1999). The inability of the current study to assess the complete annual cycle may explain the low reported heavy metal concentrations compared to other studies. For example, the current sampling regime may not have accounted for variations in the length of the antecedent dry period or rainfall intensity, factors which vary seasonally and influence the load of heavy metals in stormwater from urban areas (Brezonik and Stadelmann, 2002).

The low reported concentrations in the current investigation compared to other investigations might also be due to shortcomings in using MUSIC to produce a heavy metal export model for Port Jackson. One limitation of using the total suspended solids simulation in MUSIC to model heavy metals is that loadings are not reported for pervious areas. MUSIC assumes that total suspended solids are filtered and captured by vegetated areas. Whilst this principle may be applicable to particulate bound heavy metals, it is not applicable to dissolved concentrations of heavy metals that may be present in stormwater runoff from pervious areas. Using MUSIC to calculate loadings of heavy metals to Port Jackson may therefore result in an underestimation of loadings.

A further shortcoming of using MUSIC to model heavy metals is that it does not account for irregular discharges. MUSIC models discharges of contaminants to the stormwater system as a function of rainfall and so irregular, unpredictable and sometimes illegal discharges are not included in the loadings calculated. Such discharges can contribute significant quantities of heavy metals to stormwater. Using MUSIC to calculate loadings of heavy metals to Port Jackson may therefore result in an underestimation of loadings.

Sensitivity of average heavy metal concentrations and loadings generated in the current study has been estimated using the results of other investigations (Table 24). These estimations suggest that average annual loadings of arsenic, cadmium, chromium, copper, nickel, lead and zinc in stormwater discharging to Port Jackson estuary may be underestimations of actual loadings by 1.3 to 10 times.

Result	Flow	Form	Cu		Pb		Zn	
			Lower	Upper	Lower	Upper	Lower	Upper
Average Concentrations	Low-Flow	Diss	2.7	3.9	1.3	4.3	1.7	1.7
		Part	0.07	20.5	0.06	9.2	0.07	6.1
	Medium/ High-Flow	Diss	-	-	-	-	-	-
		Part	0.21	1.4	0.18	0.83	0.67	1.3
Loadings	All	Total	1.3	5.0	8.6	10	3.2	3.4

Sensitivities are reported as lower and upper multiplication factors
- no results
Diss – Dissolved phase
Part – Particulate phase

Table 24: Sensitivity of current results based on other investigations

4.3 Conceptual Model

Before effective remediation strategies for stormwater heavy metals can be considered, thorough characterisation of heavy metal inputs and behaviour is required. A conceptual model of heavy metals discharged to Port Jackson estuary has been developed to assist in identifying the heavy metals, subcatchment locations and flow regimes to be targeted for future remediation works. Variability in stormwater heavy metal concentrations and partitioning of heavy metals between dissolved and particulate phases has been considered. The fate of stormwater heavy metals in the estuarine system and potential ecological risks associated with heavy metals has also been discussed.

4.3.1 Heavy Metal Signatures

Research undertaken over the last 15 years has shown sediment in extensive areas of Port Jackson estuary to be contaminated by heavy metals (Birch 1996, Birch et. al., 1996, Birch and Taylor, 1999, 2000a). Approximately 20% of the total mass of heavy metals in sediments in Port Jackson estuary is located in the four small southern embayments of Iron Cove, Hen and Chicken Bay, Rozelle/Blackwattle Bay and Homebush Bay. Strong declining trends in heavy metal concentrations away from canals discharging into the upper parts of harbour embayments, and elevated concentrations of heavy metals in fluvial sediments relative to adjacent estuarine sediments, suggest that stormwater is a major source of contamination to the estuary (Birch and Taylor, 1999).

Individual heavy metals have distinctive distributions in sediments in the estuary. Sediments in Hen and Chicken Bay have high copper concentrations, whereas sediments in Iron Cove are rich in cadmium and lead. The distinctive mixes of heavy metals in sediments in the estuary are matched by corresponding mixes of heavy metals in fluvial sediments entering the estuary via stormwater channels (Birch and Taylor, 2004). These distinctive and matching distributions of heavy metal concentrations in fluvial and estuarine environments support the view that stormwater is a major source of heavy metals to the estuary (Birch and Taylor, 1999).

Taylor (2000) analysed a limited number stormwater samples and concluded that high particulate heavy metal concentrations were further evidence that stormwater is a major source of heavy metals to Port Jackson estuary. In the current study, extensive analyses of stormwater and heavy metal loading calculations have been undertaken to further investigate the relationship between fluvial and estuarine environments to determine whether stormwater is a major source of heavy metals to Port Jackson.

Results of the present investigation indicate Lane Cove, Parramatta and Duck Rivers had high annual loadings of arsenic and chromium relative to other subcatchments. Dobroyd and Hawthorne Canals had the highest per hectare loadings of arsenic and chromium, followed by Powells Creek, Massey Park Canal and Cintra Park Canal. Massey Park and Cintra Park Canals discharged significantly higher concentrations of arsenic and chromium than other sampled stormwater channels under low-flow conditions. Elevated annual and per hectare loadings of chromium in stormwater were generally matched by elevated concentrations of chromium in estuarine sediments. Estuarine sediments in the upper reaches of Parramatta River, Duck River, Iron Cove, Homebush Bay and Hen and Chicken Bay contained high concentrations of chromium relative to other embayments (Taylor, 2000). Estuarine sediments in Lane Cove River had comparatively low concentrations of chromium (Taylor, 2000) and do not reflect the high loadings of chromium estimated for this river. Sediment data were not available for arsenic.

Parramatta and Lane Cove Rivers had high annual loadings of cadmium and nickel. Dobroyd Canal had significantly higher per hectare loadings of cadmium than other sampled stormwater channels. Powells Creek, Hawthorne Canal and Parramatta River also had high per hectare loadings of cadmium. Distributions of cadmium in estuarine sediments in Port Jackson generally reflect locations of stormwater channels discharging high annual and per hectare loadings of cadmium. Elevated concentrations of cadmium were reported in estuarine sediments in Lane Cove River, Iron Cove adjacent to Dobroyd and Hawthorne Canals and Homebush Bay adjacent to Powells Creek (Taylor, 2000). Elevated concentrations of cadmium were also detected in localised areas of estuarine sediment in Duck and Parramatta Rivers (Taylor, 2000) where high annual stormwater loadings were reported. The localised area of cadmium contamination in Duck River (Taylor, 2000) does not correspond to elevated concentrations of cadmium in stormwater and may be indicative of a discrete point source. Sediment data were not available for nickel.

Annual stormwater loadings of copper and lead were significantly higher in Parramatta, Lane Cove and Duck Rivers than other sampled subcatchments. Duck River had the highest per hectare loading of copper, followed by Dobroyd Canal and Powells Creek. Dobroyd Canal had the highest per hectare loading of lead, followed by Powells Creek and Duck River. Data in Taylor (2000) indicates high concentrations of copper and lead occur in fluvial sediments in Massey Park and Cintra Park Canals and Dobroyd and Hawthorne Canals. High concentrations of copper and lead also occur in estuarine sediments in Hen and Chicken Bay and Iron Cove (Taylor, 2000). The high concentrations of copper and lead in fluvial sediments in Massey Park and Cintra Park Canals and estuarine sediments in Hen and Chicken Bay are not matched by high loadings of copper and lead in stormwater discharging from Massey Park and Cintra Park Canals. This may be due to the absence of stormwater data for Massey Park and Cintra Park Canals under medium/high-flow conditions and the use of average copper and lead concentrations to calculate loadings for these canals. A better correlation may be obtained if stormwater data specific to these canals are collected. In the upper reaches of Parramatta, Lane Cove and Duck Rivers, concentrations of copper in fluvial and estuarine sediments were comparatively low (Taylor, 2000) and do not match to the high loadings of copper reported for these rivers in the current investigation. In contrast, concentrations of lead in fluvial and estuarine sediments in the upper reaches of Parramatta, Lane Cove and Duck Rivers were comparatively high (Taylor, 2000) and reflect the high loadings of lead discharged from these stormwater channels. The better correlation observed for lead in the upper reaches of these rivers is probably due to the preferential partitioning of lead in stormwater to the particulate phase.

When stormwater discharges to the estuarine system, particulate-bound heavy metals will readily accumulate in bottom sediments through depositional processes (Salomons et al., 1987).

Parramatta River had the highest annual loading of zinc, followed by Lane Cove River. Dobroyd Canal and Powells Creek had high per hectare loadings of zinc. Massey Park and Cintra Park Canals had high average concentrations of zinc under low-flow conditions. Distributions of zinc in fluvial and estuarine sediments are consistent with locations of stormwater channels discharging high annual and per hectare loadings of zinc, with high concentrations of zinc occurring in estuarine sediments throughout the upper harbour and in the southern embayments of Hen and Chicken Bay and Iron Cove (Taylor, 2000).

Results of the current investigation support conclusions of previous investigations (Birch and Taylor, 1999; Taylor, 2000), i.e. that stormwater discharges of heavy metals correspond to spatial distributions and mixes of heavy metals in fluvial and estuarine sediments of Port Jackson estuary, indicating stormwater is likely to be a major source of heavy metals to Port Jackson estuary. Elevated heavy metal concentrations in stormwater is consistent with investigations in the Port Jackson estuary catchment, which detected high concentrations of copper, lead and zinc in soils and road dust (Scollens, 1998; Birch et al. 1999). Leachates from reclaimed land adjacent to stormwater channels are another potential source of heavy metals in stormwater (Suh et al. 2003a, b; 2004a, b; Scollens, 1998; Birch and Taylor, 1999).

4.3.2 Partitioning

Heavy metals may occur in stormwater in association with suspended particulates or in dissolved phase as free metal ions, inorganic complexes, organic complexes and compounds, or colloidal matter (Connell, 1993). Partitioning of heavy metals between dissolved and particulate phases is influenced by flow regime (Sansalone et al. 1996) and stormwater conditions including pH, redox conditions, temperature, concentrations of particulates (Warren and Zimmerman, 1994; Simpson et al., 1998).

Stormwater loadings of heavy metals have been correlated to loadings of total suspended solids (Williamson, 1985; Yuan et al. 2001). However, considerable variability in partitioning of heavy metals between dissolved and particulate phases has also been observed (Tanizaki et al., 1992; Barry et al., 1999; Hatje et al., 2001b; Warren and Zimmerman, 1994).

In the current investigation, lead was found to be predominantly associated with particulates under low- and medium/high-flow conditions, whereas nickel and cadmium were predominantly in the dissolved phase. The partitioning of other heavy metals between dissolved and particulate phases varied, although dissolved phase concentrations of arsenic and chromium were particularly high relative to particulate phase concentrations in Cintra Park Canal and Massey Park Canal under low-flow conditions, and Dobroyd Canal and Hawthorne Canal under medium/high-flow conditions. Copper and zinc partitioning was intermediate in all stormwater channels sampled under low-flow and medium/high-flow conditions.

Average proportions of heavy metals in particulate phase under low- and medium/high-flow conditions are provided in Table 25. Ranges of average proportions for the sampled subcatchments are also provided.

Flow	As	Cd	Cr	Cu	Ni	Pb	Zn
Low	**0.44** (0.08-0.75)	**0.22** (0.19-0.28	**0.28** (0.03-0.45)	**0.46** (0.30-0.68)	**0.18** (0.05-0.40)	**0.89** (0.78-0.98)	**0.54** (0.31-0.73)
Medium/High	**0.46** (0.17-0.77)	**0.32** (0.04-0.84)	**0.41** (0.17-0.75)	**0.66** (0.59-0.73)	**0.41** (0.28-0.50)	**0.96** (0.93-0.99)	**0.63** (0.42-0.80)

Table 25: Proportion of heavy metals in particulate phase

There is considerable variation in the proportion of heavy metals partitioning to the particulate phase. However, results suggest heavy metals in stormwater entering Port Jackson estuary preferentially partition to the particulate phase in the order:

$$Pb > Zn > Cu > As > Cr > Cd > Ni$$

Results also suggest heavy metals have a stronger association with particulates under medium/ high-flow conditions.

Findings of previous investigations on partitioning of heavy metals in stormwater vary and are not always consistent with results of the current investigation. Mosely and Peake (2002) found lead was predominantly associated with suspended particulates in stormwater under medium/ high-conditions, supporting the finding in the current study. However, Lawson et al. (2001) and Sansalone et al. (1996) found the partitioning of lead between dissolved and particulate phases was intermediate.

Sansalone et al. (1996) found cadmium, copper, nickel and zinc were predominantly in dissolved form under medium/high-flow conditions. This is consistent with observations for cadmium and nickel in the current study, but not for copper and zinc. Bodo (1989) found copper was predominantly in dissolved phase under low-flow conditions and particulate phase under medium/high-flow conditions, contradicting the findings of Sansalone et al. (1996) and the current investigation. The variations in results indicate there is considerable variability in the partitioning of heavy metals in stormwater.

4.3.3 Variability

Concentrations of heavy metals in stormwater are inherently variable (Warren and Zimmerman, 1994; Hall and Anderson, 1988). Under low-flow conditions, concentrations of heavy metals will vary depending on activities within the catchment, such as permitted and illegal discharges, excess irrigation and automobile washing, and the composition of groundwater discharging to canals (McPherson et al., 2005; ARMCANZ/ANZECC, 2000a). Under high/very high-flow conditions, concentrations of heavy metals will vary depending on the availability of metals in the urban contributing area, metal characteristics, antecedent dry period length, rainfall volume, duration and intensity, and catchment size and slope (Kayhanian et al., 2007; Yuan et al., 2001; Brezonik and Stadelmann, 2002).

Low-Flow vs Medium/High-Flow Conditions

In Port Jackson estuary catchment, concentrations of heavy metals in stormwater were generally higher under medium/high-flow conditions than under low-flow conditions. This is consistent with findings of other investigations and is explained by accumulation of pollutants on urban surfaces during dry weather and removal by rainfall runoff during wet weather (Charaklis and Wiesner, 1997). Heavy metals accumulate on urban surfaces as a result of traffic, atmospheric deposition, soil erosion and industrial activities (Water Board, 1993b; Birch et. al., 1999; McPherson et al., 2005).

Medium/High-Flow Events

Multiple medium/high-flow events were sampled in four stormwater channels in the Port Jackson estuary catchment. Time-weighted event mean concentrations of heavy metals for each event are presented in Figures 11A-F. The events sampled were not the same for each of the stormwater channels, e.g. Event 1 for Dobroyd Canal may not be the same event as Event 1 for Parramatta River. The event mean concentrations used to calculate loadings in the current investigation are also shown in Table 15.

Results indicate considerable variability in event mean concentrations of heavy metals for different storm events sampled. Variations between storm events are most likely indicative of differences in length of the antecedent dry period (during which heavy metals accumulate on urban surfaces) and variations in rainfall intensity (McPherson et al., 2005; Kayhanian et al., 2007). Higher rainfall intensity has been linked to higher removal of particulates from urban impervious surfaces and higher event mean concentrations of heavy metals in stormwater (Yuan et al., 2001).

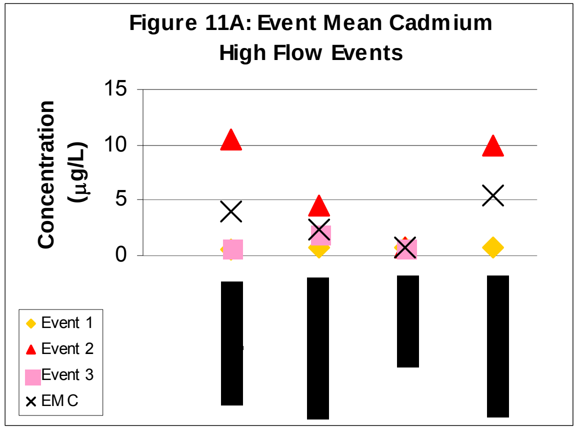


Figure 11A: Event Mean Cadmium
High Flow Events

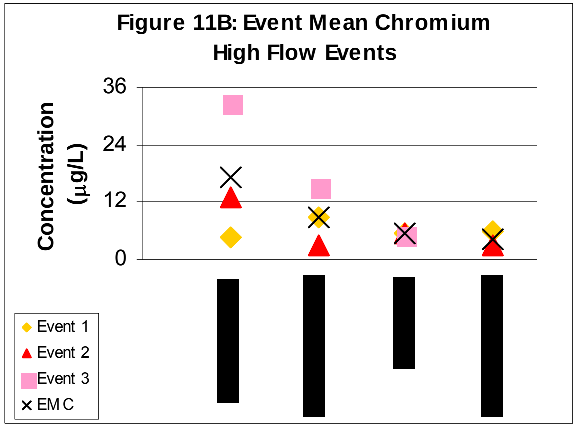


Figure 11B: Event Mean Chromium
High Flow Events

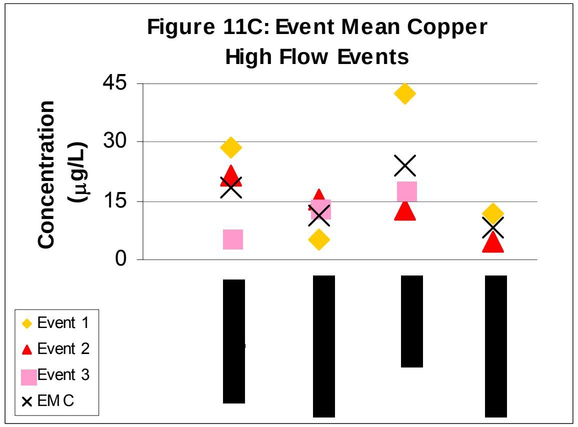


Figure 11C: Event Mean Copper
High Flow Events

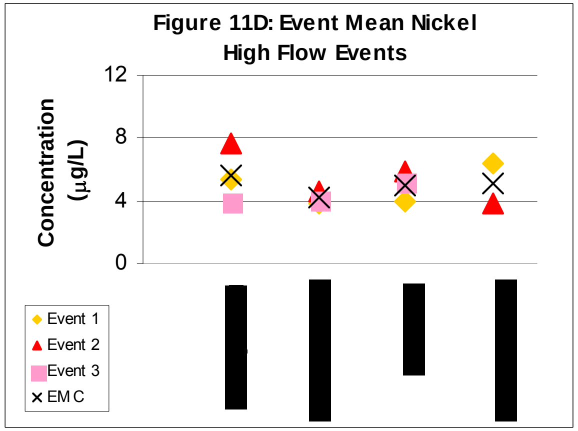


Figure 11D: Event Mean Nickel
High Flow Events

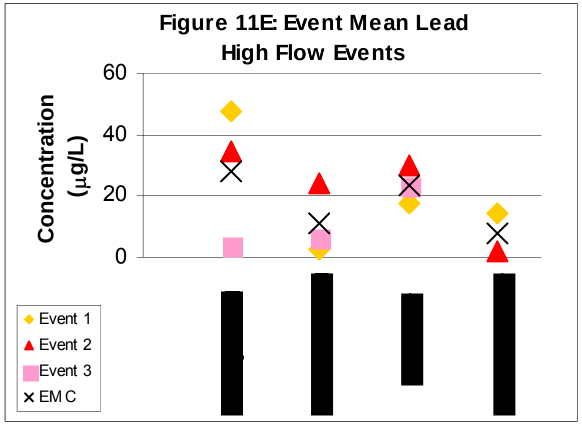


Figure 11E: Event Mean Lead
High Flow Events

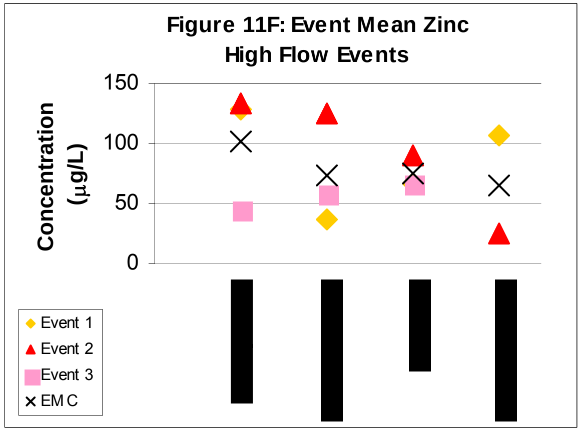


Figure 11F: Event Mean Zinc
High Flow Events

Nickel was an exception to the observed variability in heavy metal concentrations between storm events. Event mean concentrations of nickel were similar for all storm events and stormwater channels sampled. This may indicative of the preferential partitioning of nickel to dissolved phase in stormwater. Variations observed for other heavy metals between storm events may be associated with variations in suspended solids concentrations due to differences in the length of the antecedent dry period and rainfall intensity (McPherson et al., 2005; Kayhanian et al., 2007).

Concentrations of heavy metals varied during medium/high-flow events. Variations in concentrations of copper, nickel lead and zinc over a 12 hour period following commencement of medium/high-flow events in Dobroyd and Hawthorne Canals and Duck and Parramatta Rivers are presented in Figures 12A-D, 13A-D, 14A-D and 15A-D.

In Dobroyd Canal, heavy metal concentrations were considerably higher in the first hour of Events 1 and 2 than in subsequent hours (Figures 12A-D). A similar trend was observed for copper, lead and zinc in the first two hours of medium/high-flow events in Hawthorne Canal (Figures 13A-D). This initial period of stormwater runoff, during which concentrations of pollutants were substantially higher than during later stages, is referred to as a ‘first flush’ (Lee et al., 2002). The concept of a first flush is based on the premise that much of the material that accumulates on surfaces of the urban environment during periods of dry weather is removed in the runoff from a new rainfall event (Kim et al., 2007; Characklis and Wiesner, 1997; Solo-Gabriele and Perkins, 1997).

A first flush is not always observed (Characklis and Wiesner, 1997). In the current investigation, concentrations of heavy metals in Duck and Parramatta Rivers were higher in the later stages of medium/high-flow events than in the first two hours (Figures 14A-D and 15A-D). The absence of a first flush in Duck and Parramatta Rivers may be related to the large size of the subcatchments. Characklis and Weisner (1997) showed that the absence of a first flush in the Brays Bayou catchment was due to the large size of the catchment. The investigation undertaken by Lee et al. (2002) in Korea had similar findings, with the first flush phenomenon exhibiting more prominently in smaller subcatchments. Soller et al. (2005) suggested this was due to pollutants being more rapidly delivered to the point of discharge within smaller catchments.

In addition to subcatchment size, variations in the occurrence of a first flush in stormwater channels entering Port Jackson estuary may be due to variations in storm event characteristics

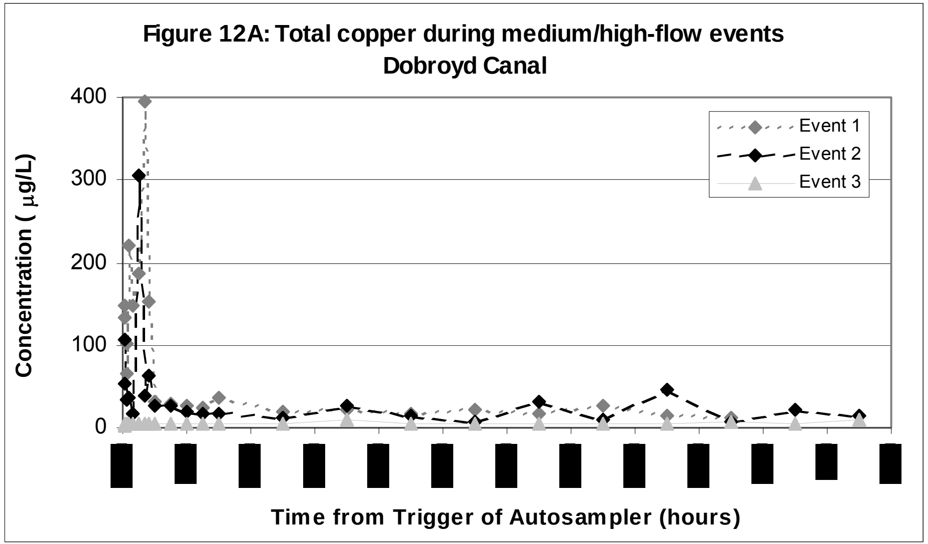


Figure 12A: Total copper during medium/high-flow events
Dobroyd Canal

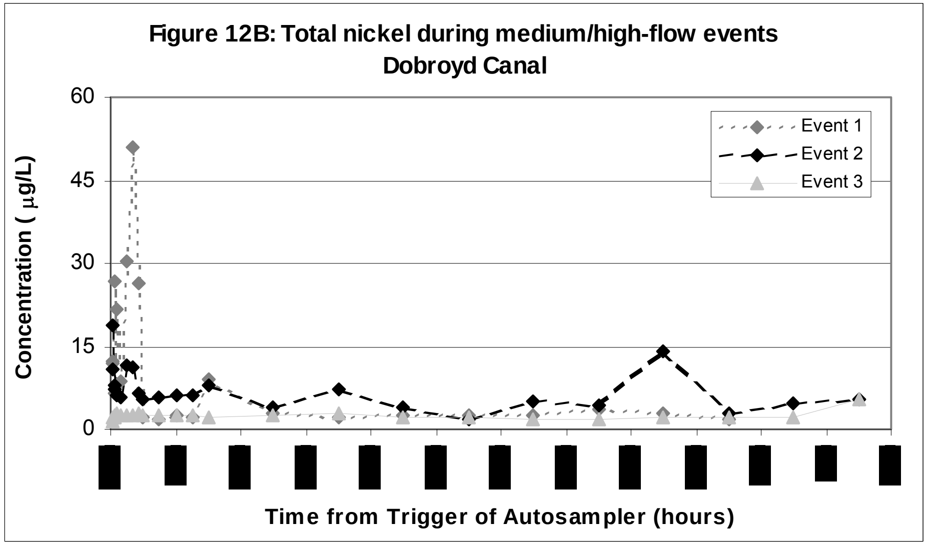


Figure 12B: Total nickel during medium/high-flow events
Dobroyd Canal

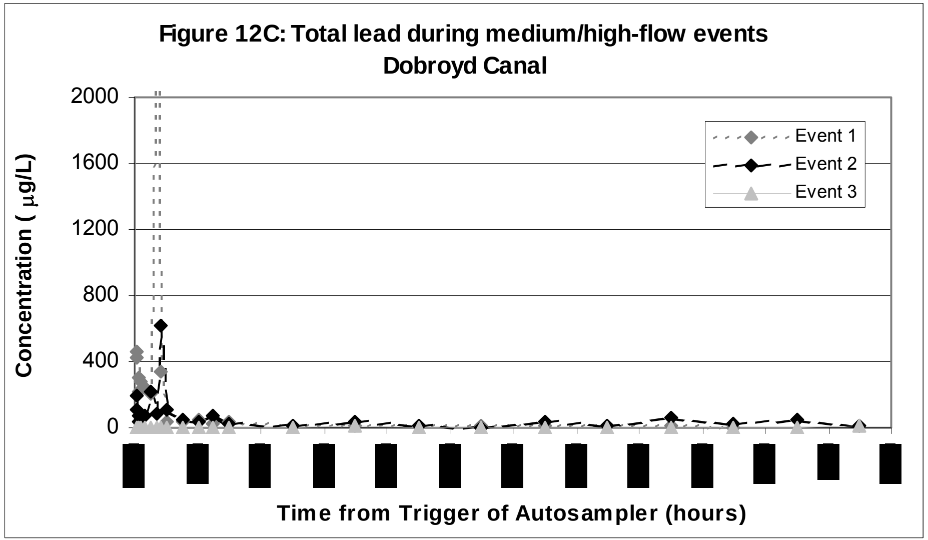


Figure 12C: Total lead during medium/high-flow events
Dobroyd Canal

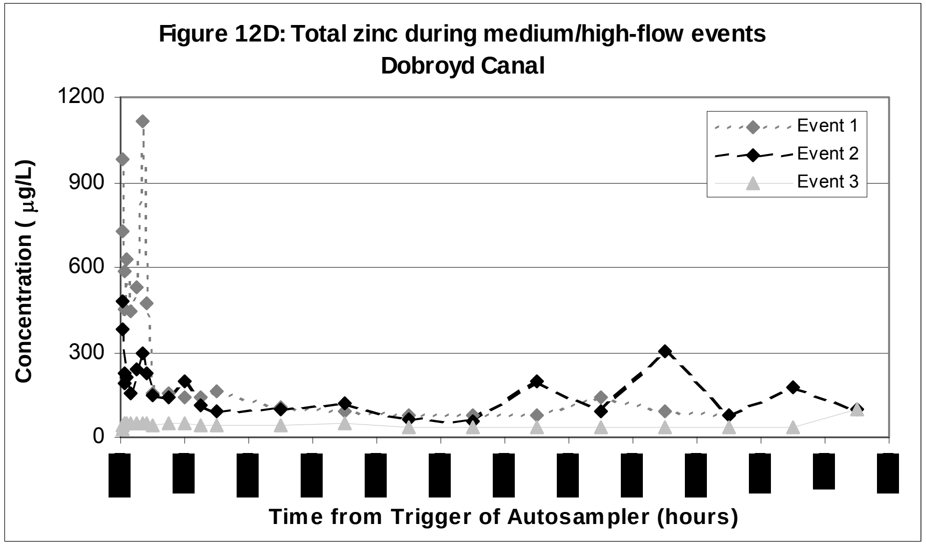


Figure 12D: Total zinc during medium/high-flow events
Dobroyd Canal

Figure 13A: Total copper during medium/high-flow events Hawthorne Canal

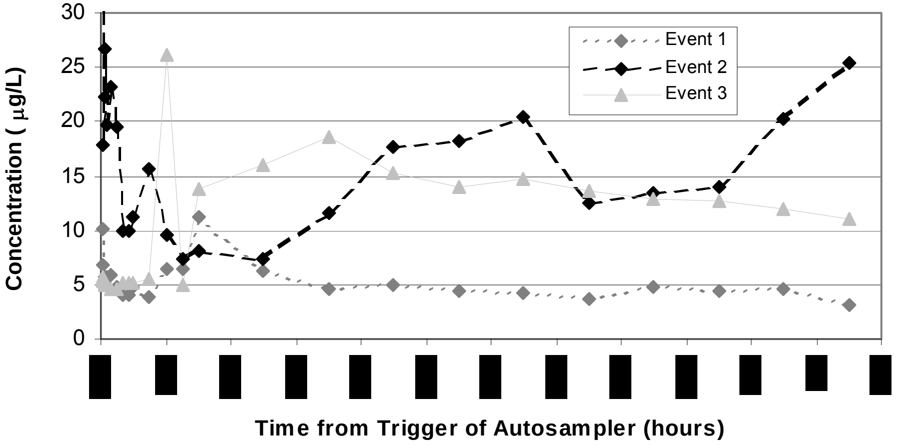


Figure 13B: Total nickel during medium/high-flow events Hawthorne Canal

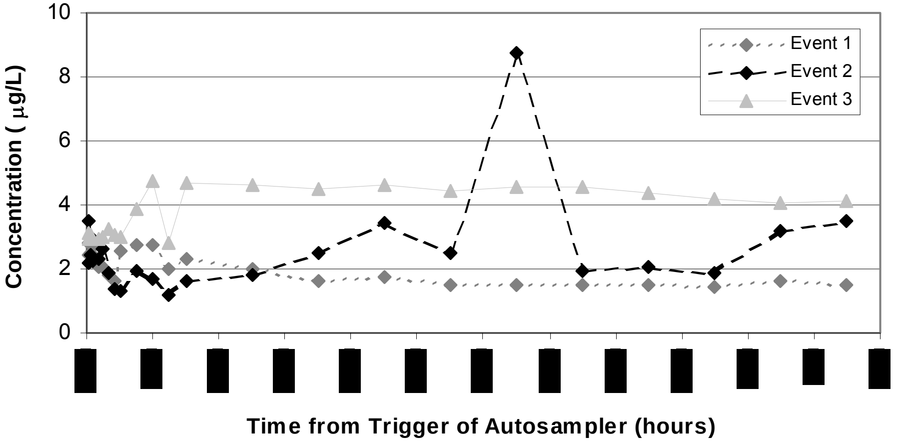


Figure 13C: Total lead during medium/high-flow events Hawthorne Canal

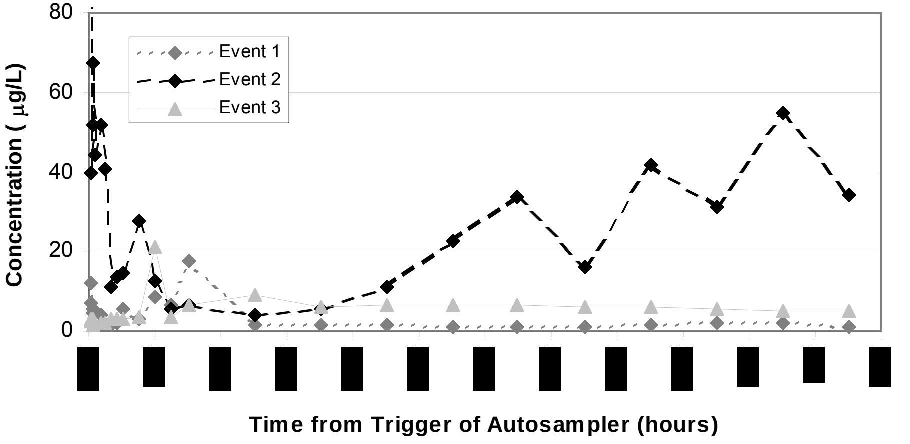


Figure 13D: Total zinc during medium/high-flow events Hawthorne Canal

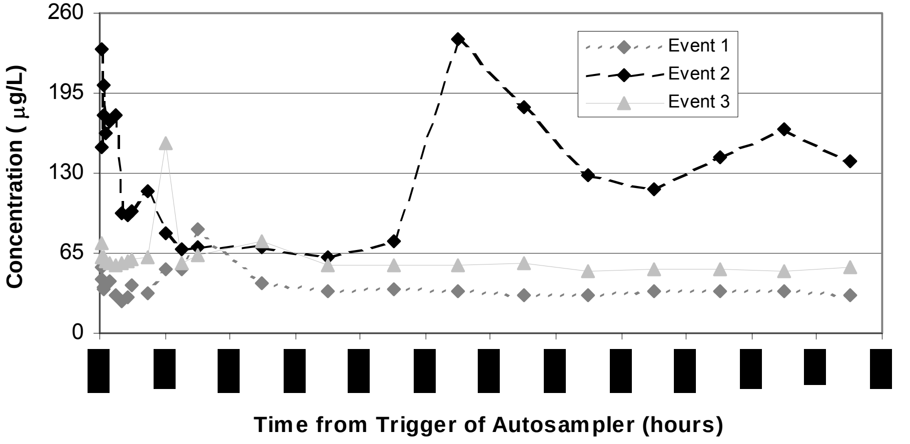


Figure 14A: Total copper during medium/high-flow events
Duck River

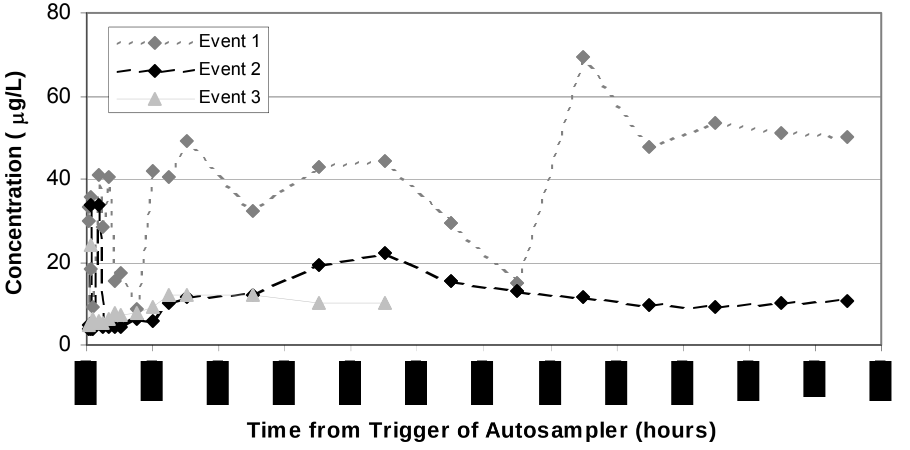


Figure 14B: Total nickel during medium/high-flow events
Duck River

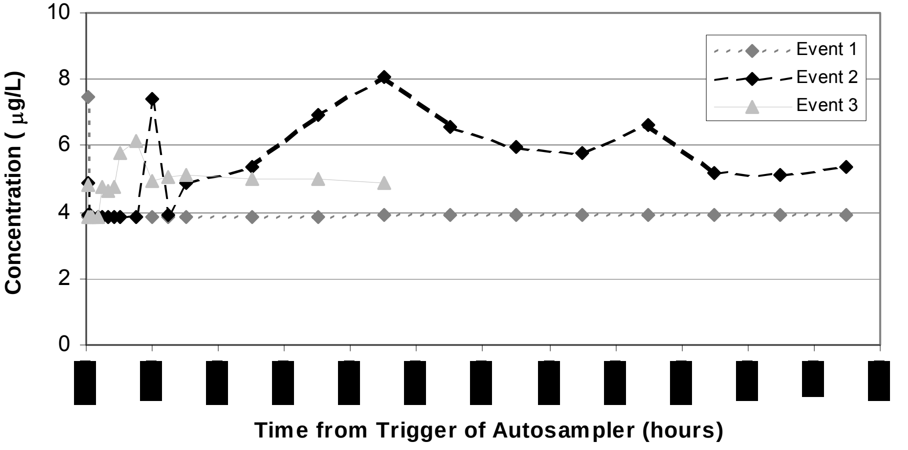


Figure 14C: Total lead during medium/high-flow events
Duck River

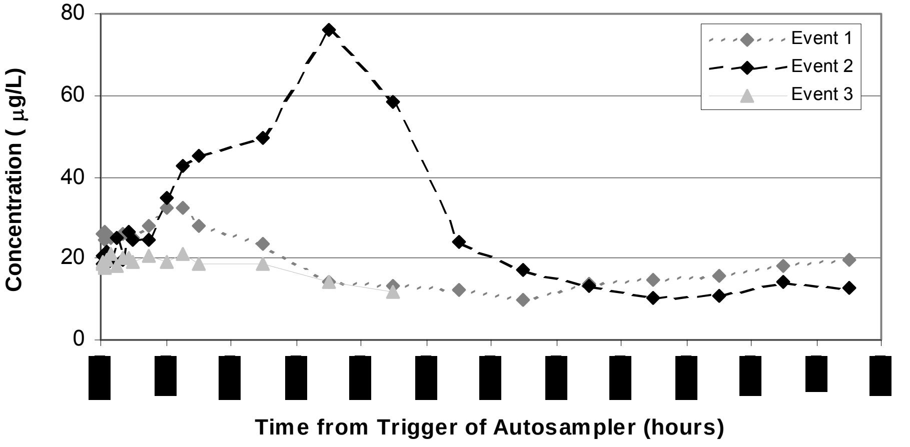
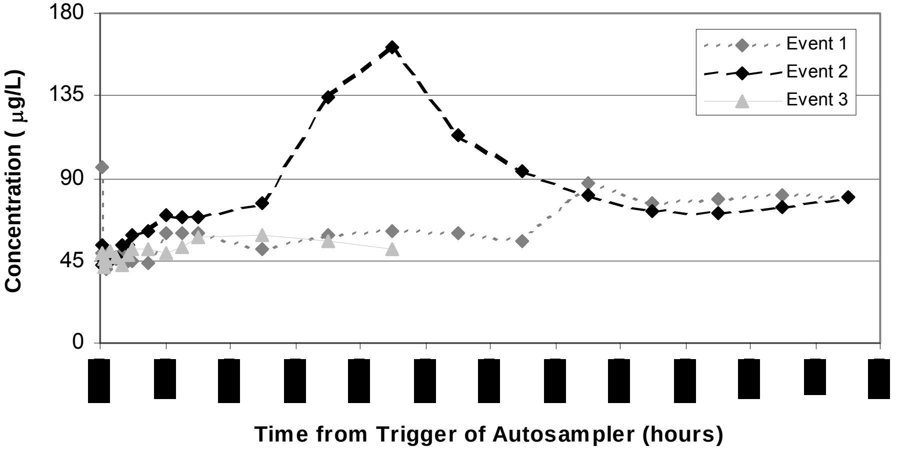


Figure 14D: Total zinc during medium/high-flow events
Duck River



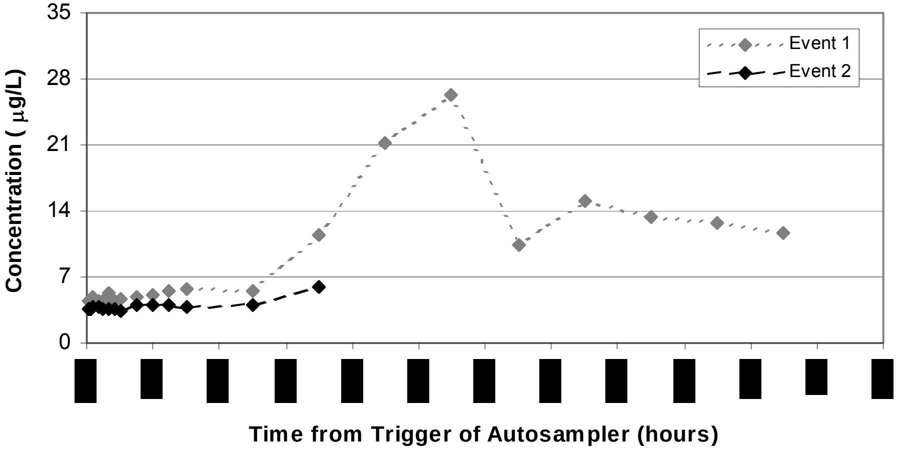


Figure 15A: Total copper during medium/high-flow events
Parramatta River

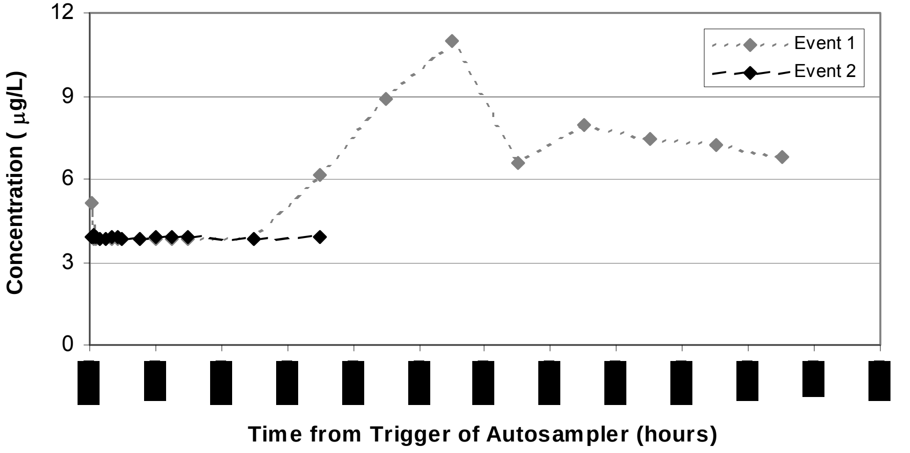


Figure 15B: Total nickel during medium/high-flow events
Parramatta River

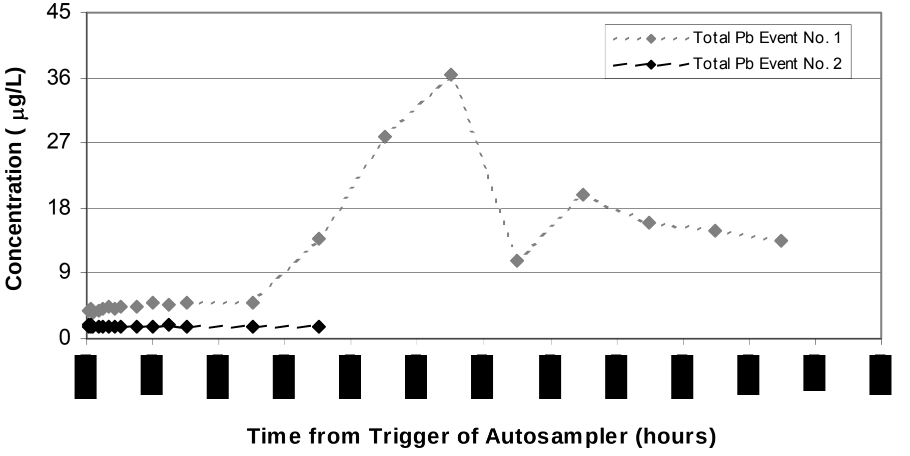


Figure 15C: Total lead during medium/high-flow events
Parramatta River

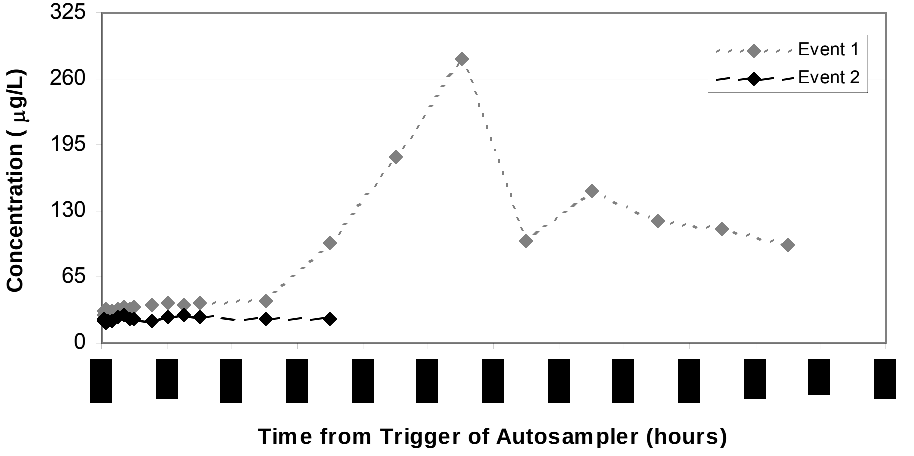


Figure 15D: Total zinc during medium/high-flow events
Parramatta River

(antecedent dry period, rainfall intensity), subcatchment characteristics (impervious area) and heavy metal partitioning (dissolved or particulate phase) (Kayhanian et al., 2007; Lee et al., 2002; Soller et al., 2005). The effect of storm event characteristics on the occurrence of a first flush has not been assessed in the current study, as data were not available. However, the effects of impervious area and pollutant characteristics have been considered.

The occurrence of a first flush has been linked to high proportions of impervious coverage within catchments (Lee et al. 2002) as pollutants are more easily washed off impervious surfaces (Soller et al., 2005). In the Port Jackson estuary catchment, the proportion impervious area is unlikely to be a significant factor contributing to observed differences in occurrence of a first flush. This is because proportions of impervious area were similar for all subcatchments sampled, ranging from 49 % for the Parramatta River catchment to 55 % for Hawthorne Canal catchment.

The occurrence of a first flush has also been linked to partitioning of heavy metals between dissolved and particulate phases. Concentrations of dissolved and particulate phase heavy metals over a 12 hour period following commencement of medium/high-flow events in Dobroyd and Hawthorne Canals are presented in Figures 16A-D and 17A-D. Results indicate that in Dobroyd and Hawthorne Canals, the first flush observed for arsenic, cadmium and chromium was predominantly for dissolved phase concentrations, with dissolved phase concentrations significantly higher than particulate phase concentrations. These results support the findings of Soller et al. (2005) and Sansalone and Buchberger (1997). Soller et al. (2005) suggest dissolved phase metals exhibit the strongest evidence of a first flush because dissolved metals are more easily eroded from impervious surfaces and entrained in surface water runoff than particulate phase metals.

However, the first flush observed in Dobroyd Canal for copper, nickel, lead and zinc was predominantly for particulate phase concentrations. These results are consistent with the observation that copper, lead and zinc have a close association with particulates in stormwater, although nickel was found to preferentially partition to dissolved phase. The removal of particulates from urban surfaces increases with rainfall intensity (Soller et al., 2005). Stormwater concentrations of heavy metals associated with particulates may therefore increase with higher rainfall intensity during the early stages of a storm (Kayhanian et al., 2007; Lee and Bang, 2000).

Figure 16A: Dissolved and particulate arsenic Med/high-flow in Dobroyd Canal

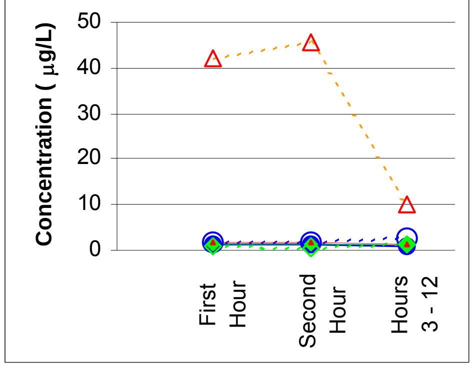


Figure 16B: Dissolved and particulate cadmium Med/high-flow in Dobroyd Canal

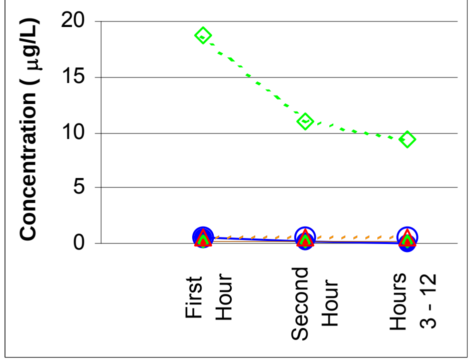


Figure 16C: Dissolved and particulate chromium Med/high-flow in Dobroyd Canal

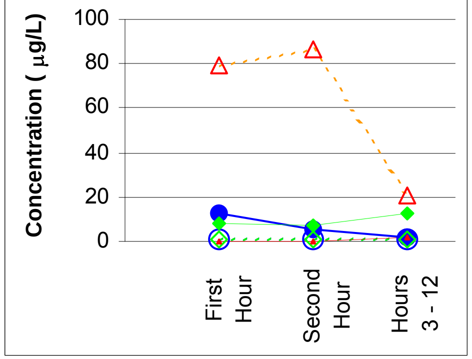


Figure 16D: Dissolved and particulate copper Med/high-flow in Dobroyd Canal

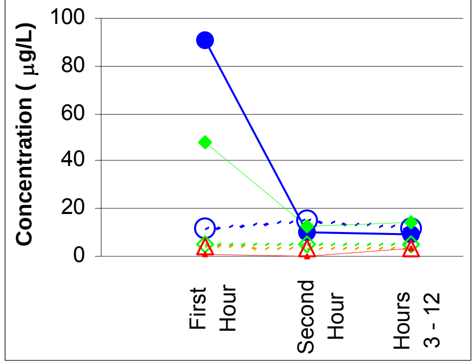


Figure 16E: Dissolved and particulate nickel Med/high-flow in Dobroyd Canal

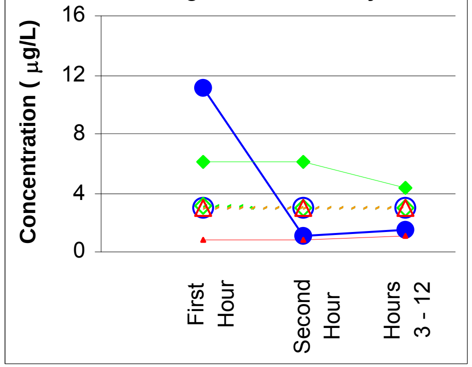


Figure 16F: Dissolved and particulate lead Med/high-flow in Dobroyd Canal

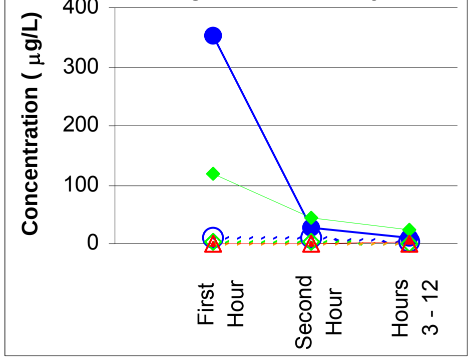


Figure 16G: Dissolved and particulate zinc Med/high-flow in Dobroyd Canal

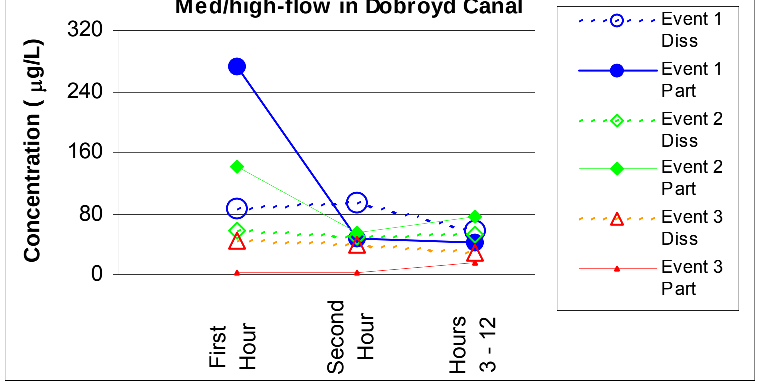


Figure 17A: Dissolved and particulate arsenic Med/high-flow in Hawthorne Canal

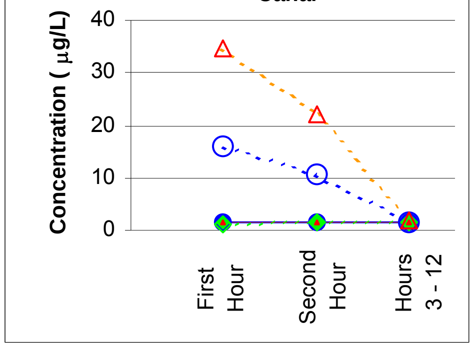


Figure 17B: Dissolved and particulate cadmium Med/high-flow in Hawthorne Canal

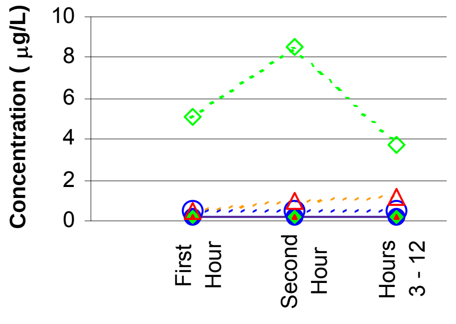


Figure 17C: Dissolved and particulate chromium Med/high-flow in Hawthorne Canal

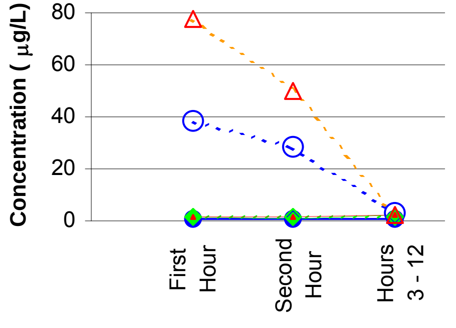


Figure 17D: Dissolved and particulate copper Med/high-flow in Hawthorne Canal

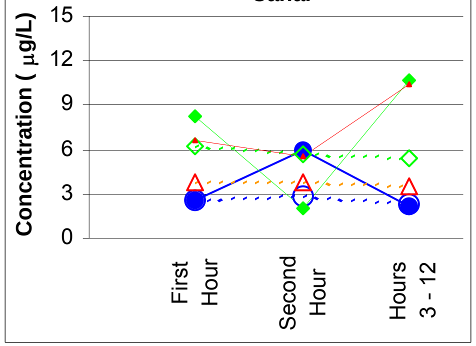


Figure 17E: Dissolved and particulate nickel Med/high-flow in Hawthorne Canal

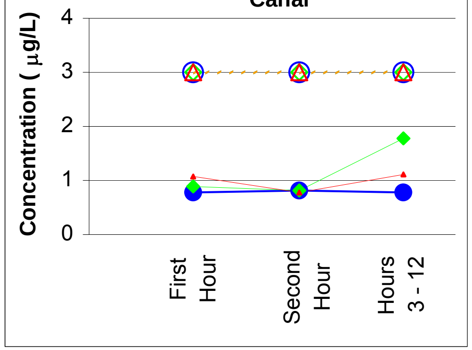


Figure 17F: Dissolved and particulate lead Med/high-flow in Hawthorne Canal

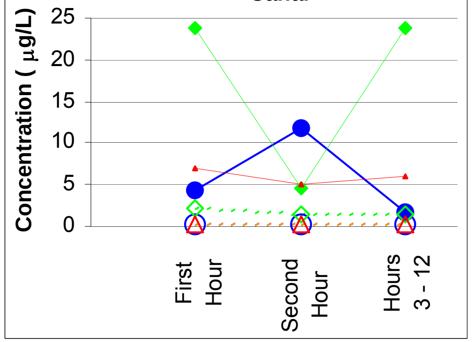
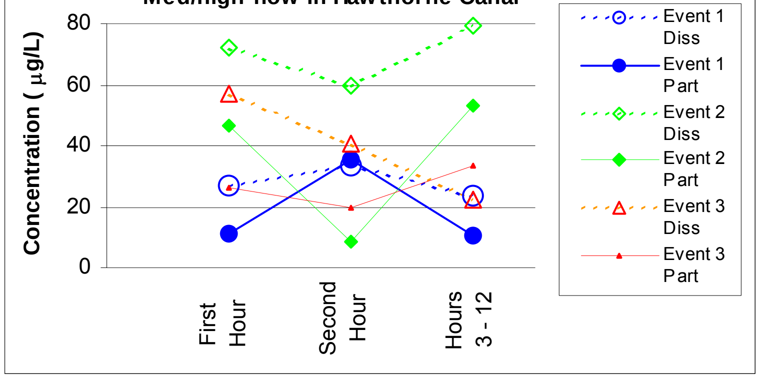


Figure 17G: Dissolved and particulate zinc Med/high-flow in Hawthorne Canal



4.3.4 Risk to Riverine Ecosystems

Elevated concentrations of heavy metals may present a threat to healthy functioning of aquatic ecosystems (Pesch, 1990; Riesh and Gerlinger, 1984; Bryan and Langston, 1992). Heavy metals may be toxicants, i.e. chemical contaminants that have the potential to exert direct toxic effects on organisms by interfering with physiological activity (ANZECC/ARMCANZ, 2000b). Heavy metals also have the potential to bioaccumulate and biomagnify up the aquatic food chain (ANZECC/ARMCANZ, 2000b).

The toxicity of a heavy metal to an aquatic organism is dependent on the concentration and bioavailability of the metal. Bioavailability is a function of speciation and partitioning of a heavy metal. The speciation and partitioning of heavy metals in the aquatic environment is influenced by physical and chemical conditions of the system, including suspended sediment, dissolved organic matter, salinity, pH, redox potential, temperature, hardness and dissolved oxygen (Turner et al., 1992; Stumm and Morgan, 1996). Some species of metals are more toxic than others, e.g. chromium (IV) is more toxic than chromium (III). Dissolved phase metals are more bioavailable than particulate phase metals (ANZECC/ARMCANZ, 2000b).

The quality of stormwater in streams entering Port Jackson estuary has been assessed using the Australian and New Zealand Environment Conservation Council (ANZECC) and Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ) (2000b) *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*. ANZECC/ARMCANZ (2000b) water quality guidelines provide trigger values for heavy metals, which represent dissolved phase concentrations that should not be exceeded. The values are estimates of concentrations that should have no adverse effects on the aquatic ecosystem for chronic (sustained) exposures, and if exceeded, trigger further investigation to evaluate risk to the ecosystem. Such an investigation may include assessment of bioavailability, biological uptake, or toxicity of the heavy metal in context of physical and chemical conditions of the waterway.

Trigger values used to assess the quality of stormwater in this study are those for fresh waters with a 95% level of protection (where the protection level signifies the percentage of species predicted to be protected). These values have been selected because the stormwater is fresh, and because a 95% level of protection is recommended for slightly disturbed systems.

Cumulative frequency graphs are presented in Figures 18A-L showing the proportion of stormwater samples that exceed ANZECC/ARMCANZ (2000b) trigger values. Concentrations of dissolved phase heavy metals under low-flow and medium/high-flow conditions are presented for each of the stormwater channels sampled.

Arsenic

Arsenic occurs in natural waters in many forms, depending on the redox conditions and pH. Arsenic (III) and arsenic (V) are the most common forms, with arsenic (III) being more toxic. Arsenic tends to bind to carbon to form organo-arsenic compounds and it may bioaccumulate in organisms (ANZECC/ARMCANZ, 2000b).

ANZECC/ARMCANZ (2000b) provides high reliability trigger values for arsenic (III) and arsenic (V) in fresh waters of 13 μg/L and 24 μg/L, respectively. Stormwater samples collected in the present investigation were not analysed for speciated arsenic and the proportion of arsenic (III) and arsenic (V) is unknown. Total dissolved arsenic concentrations have been compared to trigger values to provide an indication of potential risk to the aquatic ecosystem.

Under low-flow conditions, 53% of stormwater samples collected from Massey Park Canal exceeded the ANZECC/ARMCANZ (2000b) high reliability trigger value for arsenic (III), with 36 % of samples also exceeding the high reliability trigger value for arsenic (V). At all other locations sampled, none of the samples collected exceeded the low reliability trigger values for arsenic (III) and arsenic (V) under low-flow conditions. Under medium/high-flow conditions, less than 12% of samples collected from Dobroyd and Hawthorne Canals exceeded the trigger value for arsenic (III) and less than 10% of samples exceeded the value for arsenic (V). Samples collected from Duck River and Parramatta River under medium/high-flow conditions did not exceed the trigger values for arsenic.

Results indicate a potential risk to the aquatic ecosystem in Massey Park Canal due to dissolved arsenic concentrations in stormwater under low-flow conditions. It is not possible to determine whether there is a potential risk from stormwater in Massey Park Canal under medium/high-flow conditions, as stormwater samples were not collected under these conditions. A better indication of potential arsenic toxicity would be obtained through further sampling of stormwater from Massey Park Canal under low- and medium/high-flow conditions, and analysis of the samples collected for speciated arsenic.

Cadmium

Cadmium occurs predominantly in divalent form in natural waters, as a range of inorganic and organic compounds. Cadmium is adsorbed strongly by suspended material and may be accumulated by a number of aquatic organisms (ANZECC/ARMCANZ, 2000b).

ANZECC/ARMCANZ (2000b) provides a high reliability trigger value for cadmium of 0.2 µg/L. As the trigger value for cadmium is less than the laboratory limit of reporting used in the current investigation (1.0 µg/L), and concentrations of cadmium were lower than the laboratory limit of reporting in all samples collected under low-flow conditions and 27 % of samples collected under medium/high-flow conditions, it is not possible to determine whether potential impacts to aquatic ecosystems in the sampled stormwater channels exist. Further analyses of dissolved cadmium in stormwater using a lower detection limit are required to assess risks due to cadmium.

Chromium

Chromium occurs in natural waters in trivalent (III) and hexavalent (VI) forms. Chromium (VI) is more toxic to aquatic organisms than chromium (III). Chromium (VI) is quite soluble, existing in solution as a complex ion, whereas chromium (III) is readily removed from the water column by dissolved organic matter, suspended material or precipitation.

ANZECC/ARMCANZ (2000b) provides a low reliability trigger value for chromium (III) of 3.3 µg/L and a high reliability trigger value for chromium (VI) of 1.0 µg/L. The stormwater samples collected in this investigation were not analysed for speciated chromium and so the proportion of chromium (III) and chromium (VI) in the samples is not known. Total dissolved chromium concentrations have been compared to the trigger values to provide some indication of potential risk to the receiving waters.

Under low-flow conditions, all stormwater samples collected from Cintra Park and Massey Park Canals exceeded the trigger value for chromium (III). All stormwater samples collected from Massey Park Canal, and over 90% of samples collected from Cintra Park Canal, also exceeded the trigger value for chromium (VI) under low-flow conditions.

Between 15 and 72% of samples collected from Dobroyd and Hawthorne Canals and Powells and Haslams Creeks exceeded the trigger value for chromium (III) and less than 6% exceeded the value for chromium (VI) under low-flow conditions. None of the stormwater samples collected from Duck, Parramatta and Lane Cove Rivers exceeded the trigger values for chromium (III) or chromium (VI) under low-flow conditions.

Under medium/high-flow conditions, less than 50% of all samples collected exceeded the trigger value for chromium (III) and less than 20% of samples exceeded the value for chromium (VI) for all subcatchments sampled.

The results indicate that dissolved concentrations of chromium in stormwater under low-flow conditions may pose a risk to the aquatic ecosystems in Cintra Park and Massey Park Canals. As there were no stormwater samples collected under medium/high-flow conditions, it is not possible to determine whether there is a potential for impacts from stormwater in Cintra Park and Massey Park Canals under medium/high-flow conditions. Further analyses of stormwater from these canals would be required to determine the proportion of chromium (III) and chromium (VI) and potential risk to aquatic ecosystems.

Copper

Copper is an essential trace element required by many aquatic organisms, however the concentrations required for optimum growth are not much less than those that are toxic. The most toxic forms of copper in natural waters are free hydrated copper ions and copper hydroxy species. Copper is adsorbed strongly by suspended material and is readily accumulated by plants and animals (ANZEC/ARMCANZ, 2000).

The ANZECC/ARMCANZ (2000b) trigger value for dissolved copper in fresh waters is 1.4 µg/L. Under low-flow conditions, all samples collected from Dobroyd and Hawthorne Canals, Powells Creek and Cintra Park Canal exceeded the trigger value for copper. More than 93% of samples collected from Haslams Creek, 72% of samples collected from Massey Park Canal and Parramatta River and 54% of samples collected from Lane Cove River exceed the trigger value for copper. Under medium/high-flow conditions, all samples collected exceeded the trigger value for copper.

The aquatic ecosystems in streams entering Port Jackson are potentially at risk due to dissolved concentrations of copper in stormwater under low- and medium/high-flow conditions. However, further sampling of stormwater under medium/high-flow conditions is required to assess the potential impacts of dissolved copper in Cintra Park and Massey Park Canals, Powells and Haslams Creeks, and Lane Cove River.

Nickel

In aquatic environments, nickel occurs in divalent form, the most toxic form of nickel, and is generally associated with particulate matter (ANZECC/ARMCANZ, 2000b). The ANZECC/ARMCANZ trigger value for nickel is 11 µg/L.

None of the stormwater samples collected under low or medium/high-flow conditions exceeded the trigger value for nickel. This indicates that there is unlikely to be any potential impacts to the aquatic ecosystems in streams entering Port Jackson due to concentrations of dissolved nickel in stormwater.

Lead

In natural waters, lead occurs in the +2 and +4 valency states. Lead is strongly complexed by dissolved organic matter and adsorbed by suspended clay, humic substances and other suspended material. The toxicity of lead to aquatic organisms is reduced by the low solubility of its many forms in water (ANZECC/ARMCANZ, 2000b). The ANZECC/ARMCANZ trigger value for lead is 3.4 µg/L.

Less than 20 % of stormwater samples collected had concentrations of dissolved lead that exceeded the trigger value for lead under both low- and medium/high-flow conditions. This suggests that there is a low potential for impacts to aquatic ecosystems in streams entering Port Jackson due to concentrations of dissolved lead in stormwater.

Zinc

The predominant species of zinc in natural waters is Zn^{2+}. This is also the most toxic form of zinc to aquatic organisms. However, zinc forms complexes with dissolved organic matter and is adsorbed by suspended material, which typically reduces the uptake and toxicity of zinc to aquatic organisms (ANZECC/ARMCANZ, 2000b).

The ANZECC/ARMCANZ (2000b) trigger value for zinc in marine waters is 8 µg/L. The proportion of stormwater samples exceeding this trigger value under low-flow conditions ranged from 95% for Dobroyd and Hawthorne Canals, Cintra Park and Massey Park Canals and Duck River to 33% for Lane Cove River. Under medium/high-flow conditions, all samples collected from Dobroyd and Hawthorne Canals exceeded trigger value for zinc, and more than 80% of samples collected from Duck and Parramatta Rivers exceeded this value.

Results indicate that stormwater concentrations of dissolved zinc have the potential to cause impacts on the aquatic ecosystems of streams entering Port Jackson, particularly in Dobroyd and Hawthorne Canals, Cintra Park and Massey Park Canals, and Duck River. More sampling of dissolved zinc in stormwater under medium/high-flow conditions is required to better characterise potential risks to the aquatic ecosystems in Cintra Park and Massey Park Canals, Powells and Haslams Creeks, and Lane Cove River.

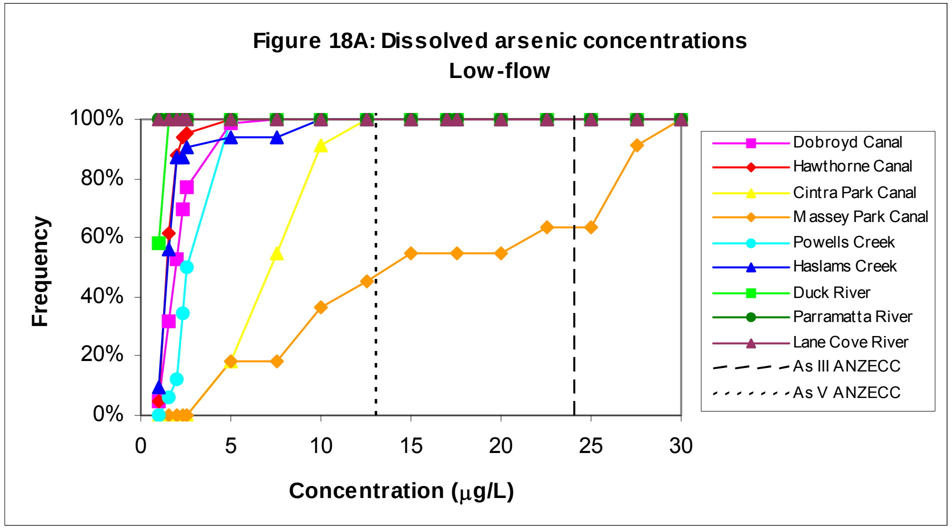


Figure 18A: Dissolved arsenic concentrations
Low-flow

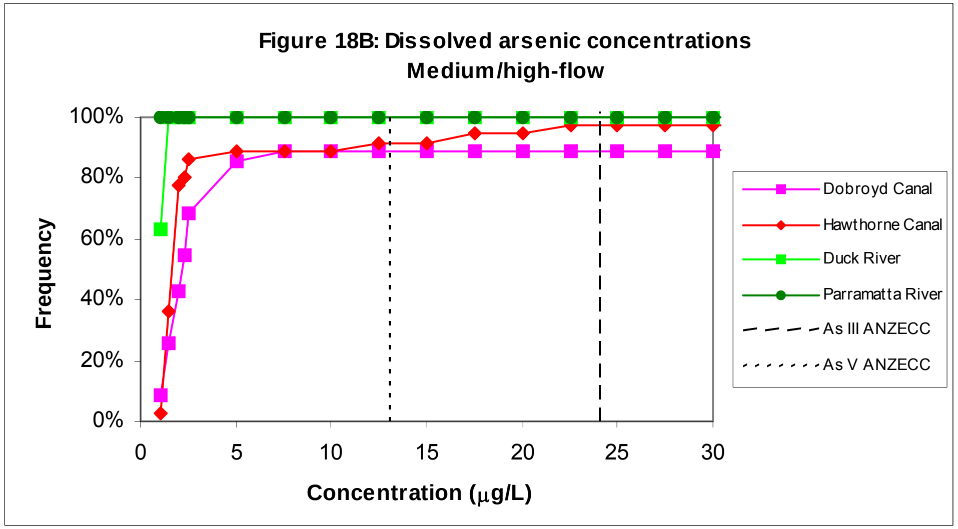


Figure 18B: Dissolved arsenic concentrations
Medium/high-flow

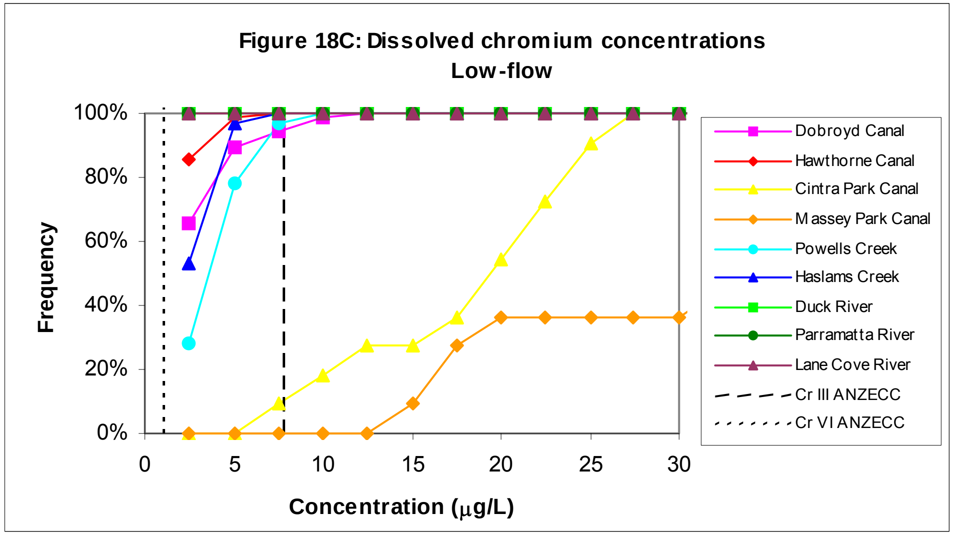


Figure 18C: Dissolved chromium concentrations
Low-flow

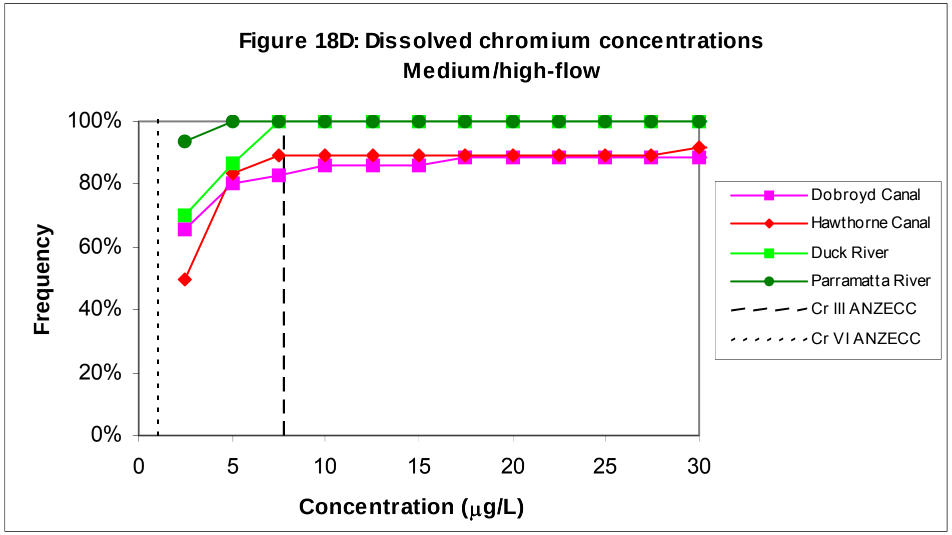


Figure 18D: Dissolved chromium concentrations
Medium/high-flow

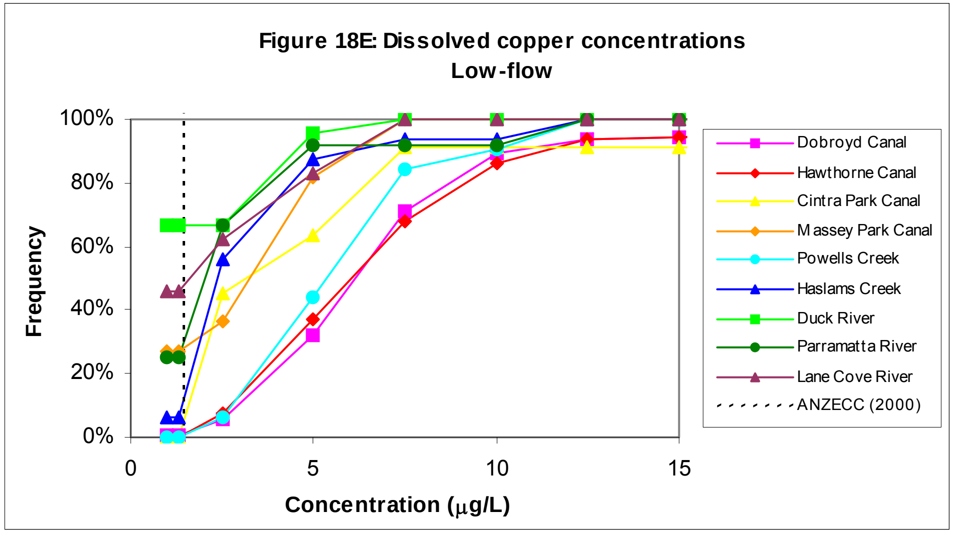


Figure 18E: Dissolved copper concentrations
Low-flow

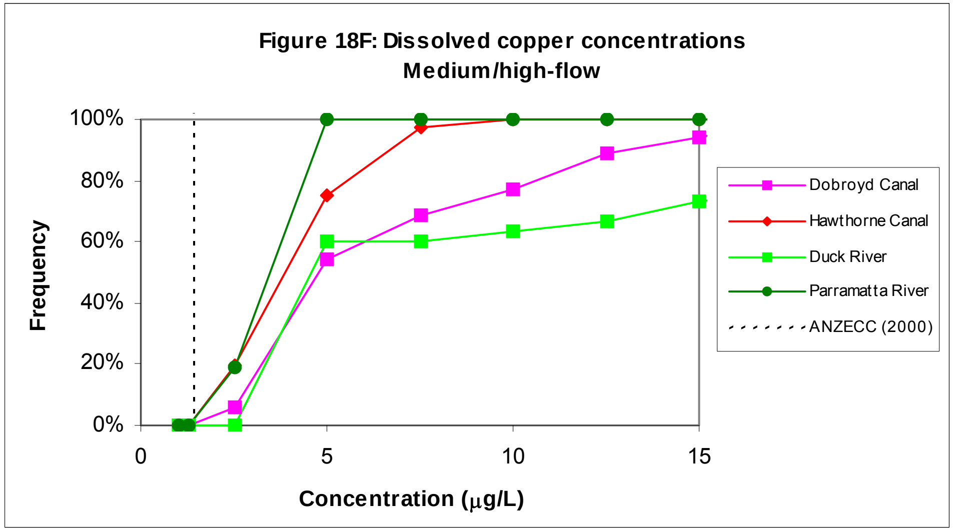


Figure 18F: Dissolved copper concentrations
Medium/high-flow

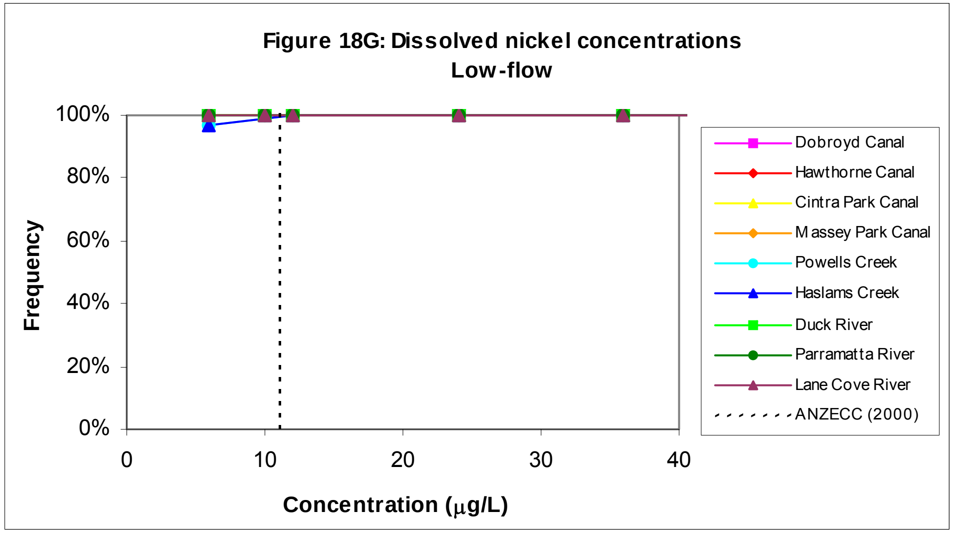


Figure 18G: Dissolved nickel concentrations
Low-flow

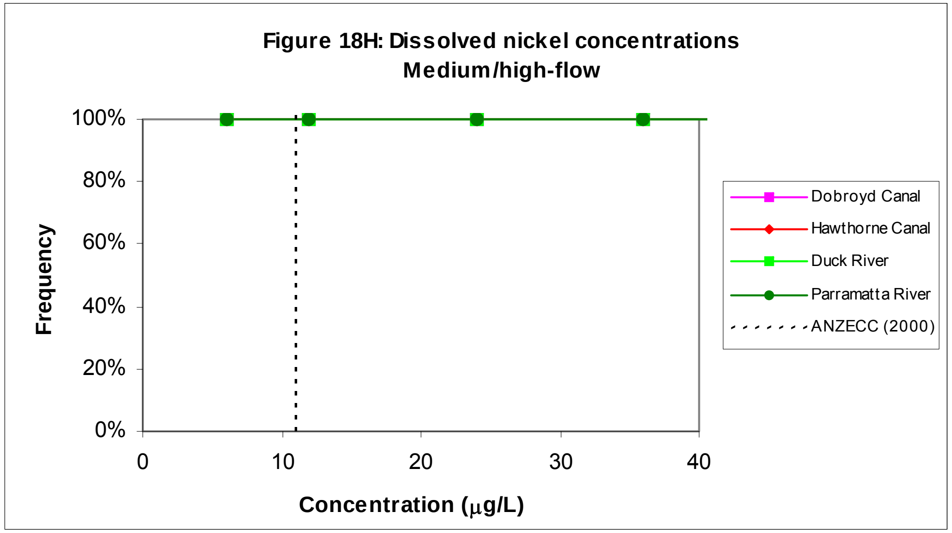


Figure 18H: Dissolved nickel concentrations
Medium/high-flow

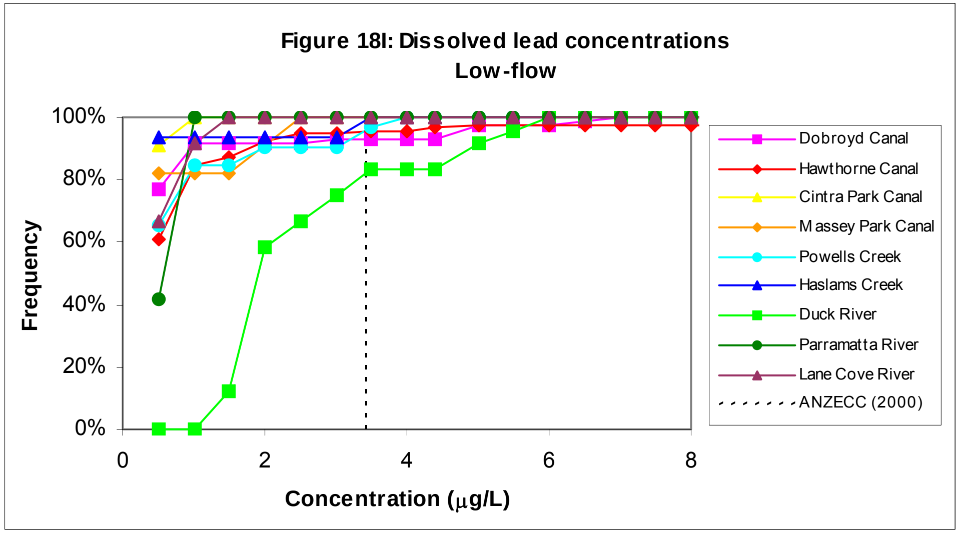


Figure 18I: Dissolved lead concentrations
Low-flow

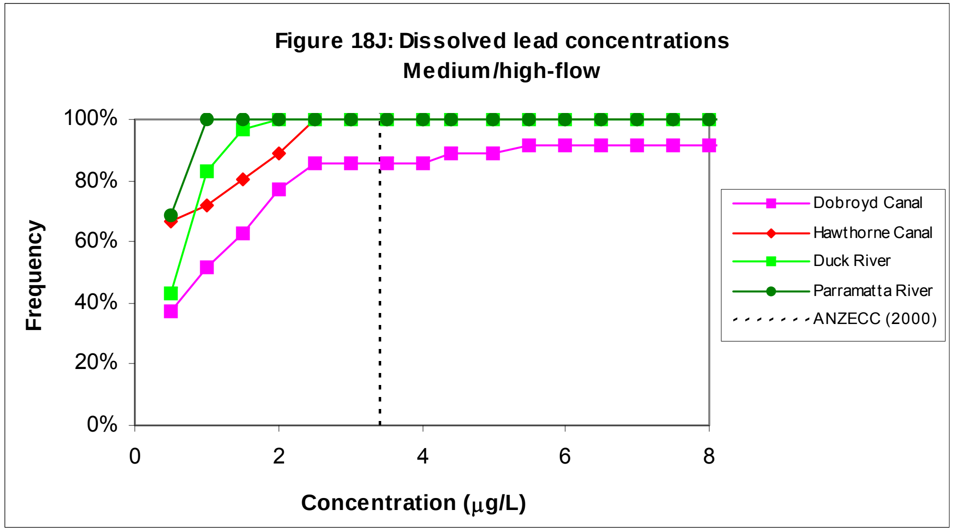


Figure 18J: Dissolved lead concentrations
Medium/high-flow

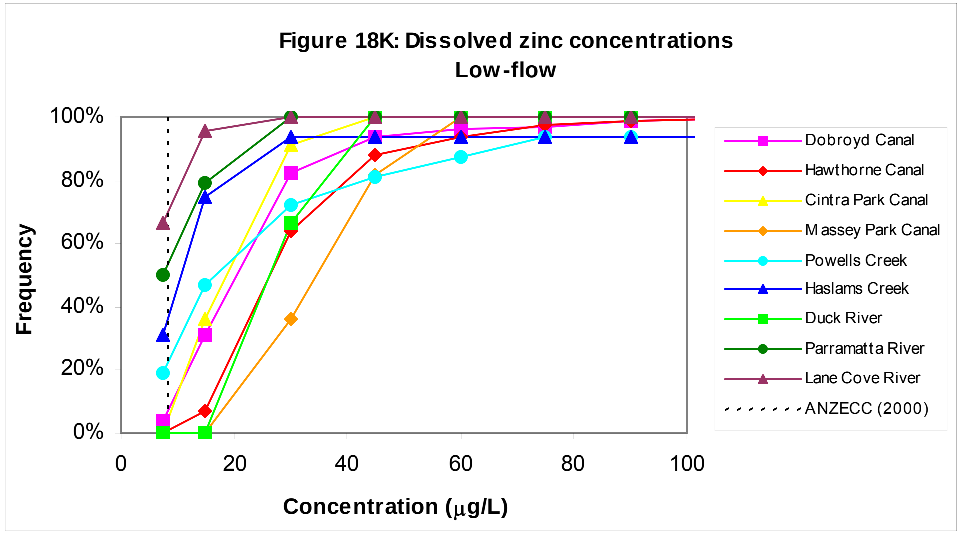


Figure 18K: Dissolved zinc concentrations
Low-flow

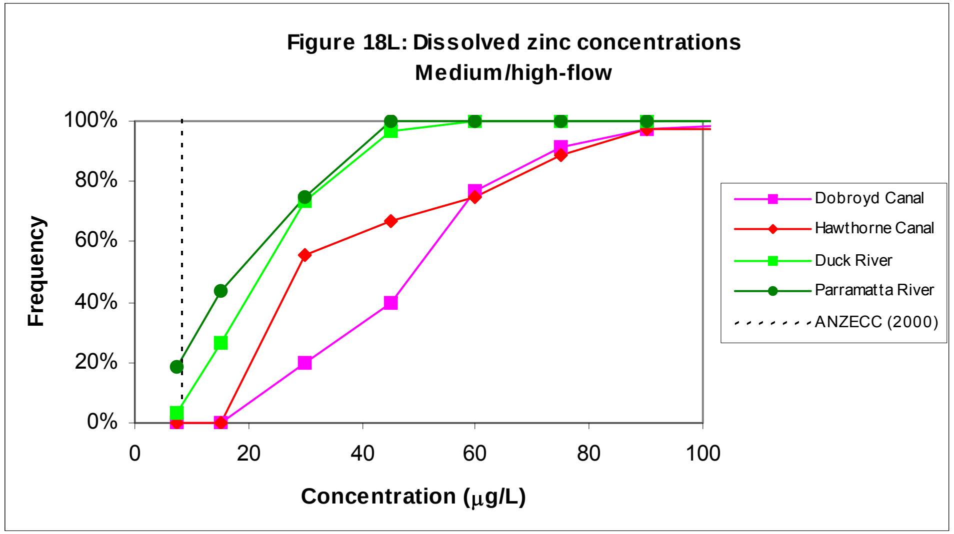


Figure 18L: Dissolved zinc concentrations
Medium/high-flow

Comparison of stormwater heavy metal concentrations from the current study to trigger values in ANZECC/ARMCANZ (2000b) indicates there are potential risks to the health of aquatic ecosystems in streams entering Port Jackson due to dissolved phase concentrations of copper and zinc in stormwater. Potential risks were identified under low- and medium/high-flow conditions for all stormwater channels sampled, where data were available.

Potential risks to the health of aquatic ecosystems were also identified for Cintra Park and Massey Park Canals due to dissolved phase concentrations of chromium, and Massey Park Canal due to dissolved phase concentrations of arsenic, under low flow conditions. However, as total dissolved chromium and arsenic concentrations have been compared to trigger values for speciated chromium and arsenic, further sampling of stormwater and analyses for speciated chromium and arsenic are required to assess potential risks to the aquatic ecosystems in these canals.

Data were not available for Cintra Park and Massey Park Canals, Powells and Haslams Creeks, and Lane Cove River under medium/high-flow conditions. Further sampling of these streams under medium/high-flow conditions is required to better characterise potential risks to aquatic ecosystems due to stormwater heavy metals.

4.3.5 Fate of heavy metals in stormwater

Stormwater enters Port Jackson estuary via stormwater canals and rivers discharging at the ends of embayments, or as runoff from adjacent land. The fate of heavy metals transported by stormwater to the Port Jackson is controlled by salinity changes, physical mixing and dilution, flushing of the estuary, and chemical processes such as sorption, complexation, cation exchange and redox reactions (Turner et al., 1992). Depending on the fate of stormwater heavy metals discharged to Port Jackson estuary, there may be impacts on the estuarine ecosystem. In general, heavy metals in estuarine systems occur in greater concentrations in the sediments than the water column (Morse et al., 1993).

Estuarine Mixing

Heavy metals transported by stormwater enter Port Jackson estuary in association with particulates, or as dissolved species (Förstner et al., 1994).

The fate of particulate bound heavy metals will depend on the nature and size distribution of the particulates. Larger solids transported by stormwater are likely to be deposited at the mouths of stormwater channels or the receiving estuary, whereas smaller colloidal particles may remain in suspension and be transported much greater distances (Characklis and Wiesner, 1997). Investigations in Port Jackson estuary indicate particulate bound heavy metals are deposited where stormwater channels discharge to the estuary. High concentrations of heavy metals occur in estuarine sediment adjacent to the mouths of stormwater channels and there are strong declining heavy metal trends away from stormwater channels. The sedimentation of particulates from stormwater discharging to the estuary has led to the accumulation of heavy metals in bottom sediments of the estuary (Taylor, 2000; Birch and Taylor, 1999). Dissolved heavy metals in stormwater entering the estuary may also be trapped in interstitial water (porewater) during sedimentation (Salomons et al., 1987).

Heavy metals deposited where stormwater channels discharge to Port Jackson estuary are likely to be associated with larger particulates. However, an investigation of road surfaces as a primary source of particulate heavy metals to stormwater in the Port Jackson estuary catchment indicated heavy metals are predominantly associated with the fine fraction (<62.5 µm) (Birch and Scollen, 2003). These results support the findings of investigations in other catchments, which indicate a significant proportion of particulate-bound heavy metals in stormwater are associated with fine particulates (0.45 – 75 µm) (Herngren et al., 2005; Characklis and Wiesner, 1997). This is due to an exponential increase in surface area and increased surface charge, with decreasing particle size (Ball et al. 1996).

During estuarine mixing, the fate of stormwater heavy metals bound to fine particulates is controlled by hydrological processes (Characklis and Wiesner, 1997) and chemical changes associated with increasing salinity (Barry et al., 2000). An investigation of heavy metal partitioning in stormwater discharged from Dobroyd and Hawthorne Canals to Port Jackson estuary found copper and zinc were repartitioned from the particulate phase to the dissolved phase during estuarine mixing (Barry et al., 1999; Barry et al., 2000). Hatje et al. (2003) confirmed these findings, identifying maxima in dissolved cadmium, copper and zinc concentrations in the upper estuary. Maximum concentrations of dissolved phase heavy metals at the discharge point of stormwater channels is probably due to flocculation and coagulation of colloids releasing metals and lowering the rate of scavenging, and competition for active particle surfaces by a range of cations other than heavy metals (Hatje et al., 2003; Barry et al., 2000).

Further seawards of where stormwater was discharged to the estuary, Barry et al. (2000) reported a strong decrease in dissolved phase concentrations of copper, lead and zinc. Dissolved phase heavy metals may be removed from solution by binding with anions to form insoluble oxyhydoxides and carbonates, or by adsorbing to, or coprecipitating with, suspended particulate matter (Singh and Subramanian, 1984) such as particulate organic carbon and iron (II) and manganese (IV) oxides and hydroxides (Tessier, 1992). Barry et al. (2000) attributed the decrease in dissolved metal concentrations in the lower estuary to high sediment mobility and water turbidity in Iron Cove, resulting in adsorption of heavy metals onto active particle surfaces, combined with mixing and dilution with estuarine waters. The hypothesis of readsorption by suspended particulate matter is supported by the findings of Hatje et al. (2003), which correlated a decrease in dissolved copper and zinc concentrations in the lower estuary to an increase in suspended particulate metal concentrations (Hatje et al., 2001b).

Influence of Flow Regime

Flow regime is expected to have a significant impact on the fate of heavy metals transported by stormwater to Port Jackson estuary.

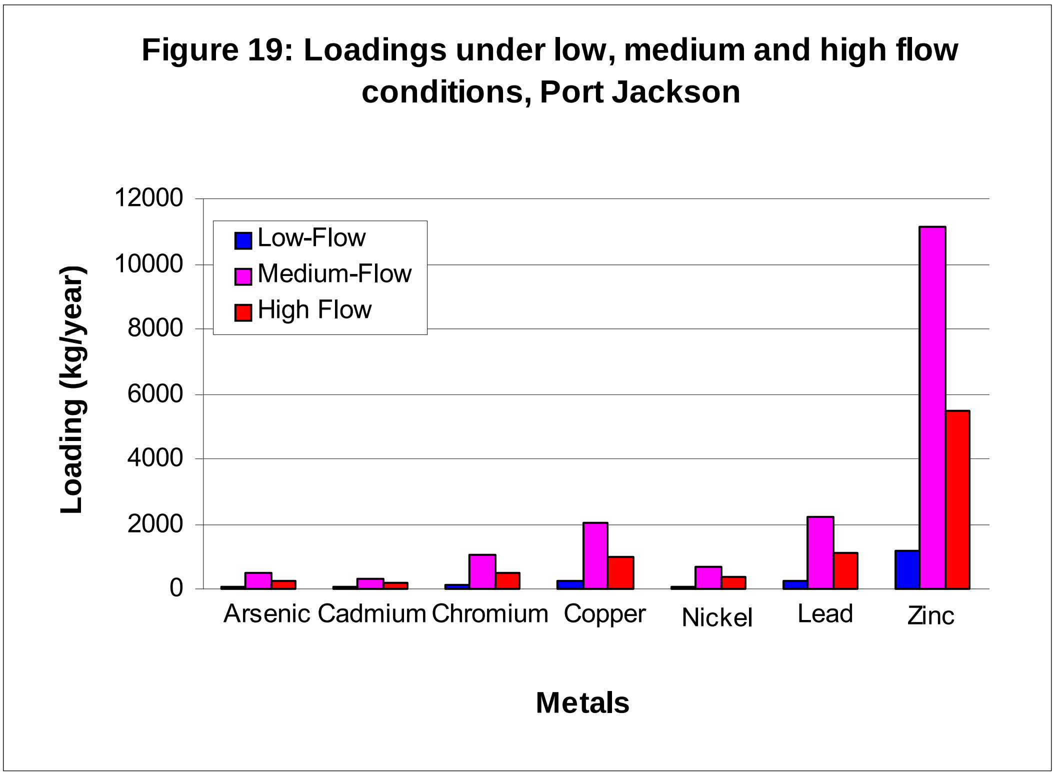
The typical pattern of stormwater discharge to Port Jackson estuary is one of low-flow conditions, with occasional, brief medium/high-flow events (Hatje et al., 2003). Under low-flow conditions, Port Jackson estuary is almost entirely saline and is well-mixed (Hatje et al., 2001b) due to low freshwater discharge and minimal tidal turbulence. However, under medium/high-flow conditions, the estuary becomes stratified, with a buoyant freshwater plume overlying a more dense saline water of the estuary (Pitbaldo, 1978). Sedimentation studies in Iron Cove found the normally well-mixed estuarine water column was stratified for up to two weeks after major rainfall events (Taylor, 2000).

Heavy metals transported by stormwater to Port Jackson estuary under high flow conditions are understood to be rapidly exported from the estuary in a discrete layer of turbid freshwater and not deposited in the estuary (Wolanski, 1977; Barry et al. 1999). Preliminary research suggests that under medium-flow conditions, particulate heavy metals bypass the embayments of Port Jackson and are deposited in the main channel.

Sedimentation rates in Iron Cove decreased by an average of 28% during high-flow events, suggesting the contribution of high-flow conditions to the accumulation of heavy metals in Port Jackson estuary may be less than the contribution of low-flow conditions (Taylor, 2000). Preliminary research suggests the contribution of medium-flow conditions to the accumulation of heavy metals in Port Jackson estuary is also likely to be lower than the contribution of low-flow conditions as particulate heavy metals deposited under medium-flow conditions are likely to be remobilised and removed from the main channel through resuspension processes.

Birch and Taylor (1999) suggested stratification of the estuary occurs when precipitation exceeds 40-60 mm in a day. Preliminary research suggests flows may bypass embayments when precipitation exceeds 5 mm in a day. Although likely to vary between subcatchments, influenced by factors including subcatchment area, impervious area, channel dimensions and rainfall event magnitude (Nezlin et al., 2005), these simple defining thresholds provides an initial guideline for analysis of (Cruickshank, 2006). Further research is required to establish more accurate thresholds for each subcatchment discharging to Port Jackson estuary.

To assess the influence of flow regime on the fate of stormwater heavy metals in Port Jackson estuary, heavy metal loadings were modelled for days where there had been less than 5 mm of rainfall in 24 hours (low-flow conditions), days where there had been between 5 mm and 50 mm of rainfall in 24 hours (medium-flow conditions), and days where there had been greater than 5 mm of rainfall in 24 hours (high-flow conditions). Results indicate 7 % of stormwater heavy metals loadings to Port Jackson estuary were discharged under low-flow conditions, 61 % under medium-flow conditions and 31 % under high-flow conditions (Figure 19).



Heavy metals in stormwater discharged to the estuary under medium- and high-flow conditions are inferred to be rapidly exported seaward from the estuary, posing no risk to the estuarine ecosystem, due to stratification of estuary and the removal of heavy metals deposited in the main channel through resuspension processes.

On this basis, the loadings of heavy metals to Port Jackson estuary are assumed to include heavy metals discharged under low-flow conditions only. Revised average annual loadings of heavy metals to Port Jackson estuary are presented in Table 26.

Port Jackson	**As**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
Average Annual Loading (tonnes)	0.05	0.04	0.11	0.22	0.08	0.24	1.2

Table 26: Predicted annual loadings of heavy metals to Port Jackson estuary during low-flow conditions only

4.3.6 Risk to Estuarine Ecosystem

In addition to posing a potential risk to riverine aquatic ecosystems, heavy metals in stormwater may pose a risk to the receiving estuarine environment. The fate of heavy metals transported by stormwater to Port Jackson estuary includes deposition in the sediments (Taylor, 2000; Birch and Taylor, 1999) and repartitioning to dissolved phase (Barry et al., 1999; Barry et al., 2000). Marine organisms may take up heavy metals associated with sediment through ingestion of particles as food, or through non-selective feeding habitats (Wang et al., 1999). Marine organisms are exposed to dissolved phase metals through overlying water or sediment porewater. Following uptake, heavy metals may exert direct toxic effects on organisms by interfering with physiological activity (ANZECC/ARMCANZ, 2000b).

Sediment Quality

Elevated concentrations of heavy metals occur in sediments adjacent to stormwater channels in Port Jackson estuary (Taylor, 2000; Birch and Taylor, 1999). Comparison of heavy metal concentrations to the ANZECC/ARMCANZ (2000b) interim sediment quality guidelines (ISQGs) indicates extensive areas of sediment are potentially toxic to aquatic organisms (Taylor, 2000; Birch and Taylor, 2002a, b). The ISQGs provide low and high guideline values, which if exceeded, trigger assessment of bioavailability to investigate whether sediments pose a risk to benthic communities.

Concentrations of lead and zinc in surficial sediments exceed the ISQG-low and high values in Iron Cove, Hen and Chicken Bay and Homebush Bay, as well as in the upper harbour near Duck and Parramatta Rivers, the north shore near Lane Cove River, and most of the central channel (Taylor, 2000). Concentrations of copper in surficial sediment exceed the ISQG-high value in Hen and Chicken Bay, and the low value throughout most of the upper harbour. Bioavailability studies undertaken in Iron Cove by Taylor (2000) indicate approximately 70 % of the total mass of lead, 50 % of total zinc and <30 % of total copper in surficial sediment, are available to biota. Continued delivery of copper, lead and zinc to sediments in Port Jackson estuary via stormwater therefore poses a potential risk to the health of the aquatic ecosystem in Port Jackson.

Estuarine Water Quality

Comparison of dissolved concentrations of heavy metals in Port Jackson estuary to the ANZECC/ARMCANZ (2000b) water quality guidelines indicates concentrations of dissolved copper in the estuary exceed the trigger value (Hatje et al., 2003).

However, potential ecological risks due to dissolved copper are deemed to be low, as the speciation of dissolved copper in estuarine waters is dominated by the formation of relatively stable complexes with dissolved organic matter, which are not bioavailable (Hatje et al., 2003).

4.4 Remediation

Recent recognition of the significant problems associated with stormwater pollution in urban environments has led to implementation of the Urban Stormwater Program by the NSW government in 2001. This program requires local councils throughout the state to prepare and implement stormwater management plans to support improved urban stormwater quality management practices (Stormwater Trust, 2001; NSW Environment Protection Authority, 1997).

Stormwater remediation devices have been installed at several locations in the Port Jackson estuary catchment as a result of the Urban Stormwater Program. Devices currently in operation include gross pollutant traps, weirs, sand infiltration basins and constructed wetlands (Cruickshank, 2006; Birch et al., 2004; Birch et al., 2005). The effectiveness of these devices varies depending how well targeted the design of the devices are to hydrological conditions and the nature of contaminants in the stormwater.

In the current investigation, characterisation of heavy metals in stormwater has been undertaken to target remediation efforts in the Port Jackson estuary catchment and ensure optimum efficiency of new or retrofitted remediation devices in removing heavy metals. The findings of the current investigation should be considered in conjunction with the findings of other investigations of stormwater contamination in the Port Jackson estuary catchment. It is important that stormwater remediation devices are selected to addresses the range of contaminants that may be present in stormwater, including gross pollutants, nutrients, faecal coliforms, heavy metals, pesticides and polycyclic aromatic hydrocarbons.

4.4.1 Remediation Targets

Using the conceptual model of heavy metals in stormwater in the Port Jackson estuary catchment, specific targets for remediation have been identified.

Assessment of the ecological risk of stormwater to riverine and estuarine ecosystems has indicated copper, lead and zinc are the heavy metals of most concern in stormwater entering Port Jackson estuary and should be targeted for remediation.

Stormwater sampling and modelling undertaken in the current investigation, and assessment of the distribution of sediments contaminated by stormwater identified in previous investigations (Birch and Taylor, 1999; Taylor, 2000), has indicated most of the stormwater channels entering the Central and Upper Harbour, and the upper reaches of Middle Harbour, are of concern. This includes the stormwater channels entering the southern side of Port Jackson estuary upstream of subcatchment 67, and the northern side of Port Jackson estuary upstream of subcatchment 11. The stormwater channels of greatest concern are those entering embayments on the southern side of the estuary west of Darling Harbour, Duck, Parramatta and Lane Cove Rivers, and those entering Neutral, Long and Sugarloaf Bays in Central and Middle Harbours. These stormwater channels should be prioritised for remediation.

Investigation of the partitioning of heavy metals in stormwater entering Port Jackson estuary has indicated lead is predominantly associated with particulates, whereas copper and zinc are equally partitioned between dissolved and particulate phases. Remediation strategies that remove particulates from stormwater would effectively reduce heavy metal loads to Port Jackson estuary, particularly lead loads. However, as a significant proportion of particulate bound heavy metals in stormwater entering Port Jackson estuary are likely to be associated with fine particulates (Birch and Scollen, 2003), the particle size fractionation of particulate bound heavy metals should be considered when designing remediation devices. To effectively remove copper and zinc loads from stormwater entering Port Jackson estuary, remediation strategies should target both dissolved and particulate phases.

It has been suggested that heavy metals in stormwater discharged to the estuary under high-flow conditions (>50 mm of rainfall in 24 hours) are rapidly exported seaward in a discrete freshwater layer and not deposited in sediments of the estuary (Wolanski, 1977; Barry et al. 1999; Taylor, 2000). Preliminary research also suggests that under medium-flow conditions (between 5 and 50 mm of rainfall in 24 hours), particulate heavy metals bypass the embayments of Port Jackson estuary, are deposited in the main channel and subsequently resuspended and removed from the estuary. Stratification of the estuary is estimated to occur when precipitation exceeds 40-60 mm in a day (Birch and Taylor 1999), and bypass of embayments when rainfall exceeds 5 mm in a day, so it has been inferred that potential risks to the estuarine ecosystem due to heavy metals occurs under low-flow conditions (<5 mm of rainfall in 24 hours). On this basis, remediation devices should be designed to target low-flow events, allowing medium- and high-flows to bypass the estuary system.

4.4.2 Remediation Options

A range of potential remediation strategies exist for removal of contaminants from stormwater, including physical, biological and chemical treatment methods (Hvitved-Jacobsen, 1994). Usually a combination of these methods will be most effective in treating stormwater, as runoff from urban environments is a complex mixture of contaminants. Research has indicated that remediation strategies for the removal of heavy metals from stormwater should filter particulate bound metals and adsorb dissolved phase metals (Sansalone, 1999; Sansalone and Buchberger, 1995).

Remediation devices that promote sedimentation and settling of particulates are commonly used to remove particulate bound heavy metals from stormwater. Gross pollutant traps have been shown to be effective in removing coarse sediment and minor associated heavy metals from stormwater. The effectiveness of detention ponds and constructed wetlands in removing finer particulates and associated heavy metals from stormwater has also been demonstrated (Hvitved-Jacobsen et al., 1994; Ball et al., 2000; Revitt et al., 2004; Scholes et al., 1998; Birch et al., 2004), however the efficiency of these devices in removing heavy metals will vary depending on residence times in the pond/wetland, the size of the pond/wetland relative to catchment area, and the occurrence of hydrological conditions leading to remobilisation of particulates (Strecker et al., 1992; Birch et al., 2004).

The requirement for large areas of land to construct effective detention ponds and artificial wetlands (0.5-2.0% of the catchment) (Tilley and Brown 1998) decreases the utility of these approaches in fully developed areas such as the Port Jackson estuary catchment (Ball et al., 2000). Removal of particulates through filtration of stormwater may therefore be a more feasible option in the Port Jackson estuary catchment, particularly if filtration can occur on-line within stormwater channels. Filtration of stormwater using sand has been shown to remove over 75 % of suspended solids following pre-treatment for removal of coarse sediment and litter (EPA, 1997).

Filtration of stormwater through sand mixed with a sorbent medium can remove both particulate and dissolved phase heavy metals from stormwater. A sand infiltration basin on Whites Creek in the Port Jackson estuary catchment, comprising a mixture of sand and zeolite, was shown to be effective in removing copper, lead and zinc from stormwater (Birch et al., 2005). Filtration of stormwater through sand mixed with mulch was also effective in removing heavy metals. (Ray et al., 2006; Jang et al., 2005

Sand-sorbent filters are potentially a low-cost option for the removal of heavy metals from stormwater. Many of the sorbents trialled are waste products such as saw dust, fly ash or scrap metal, or commonly available, inexpensive materials such as bark, alumina or zeolite (Ray et al., 2006; Rangsivek and Jekel, 2005; Genc-Fuhrman et al., 2007; Jang et al., 2005). There is potential for sand-sorbent filters to be used on-line in stormwater channels, reducing the area of land required for stormwater remediation. Further research needs to be undertaken to assess the effectiveness of different sorbents in removing heavy metals from stormwater in the Port Jackson estuary catchment and to design a remediation device that targets low-flow events.

4.5 Limitations

The results of the present study are being used in the development of a numerical model to predict the transport and fate of contaminants in the Port Jackson estuary. The current research may also be used in the future for stormwater management or the design stormwater remediation works. It is important that the limitations of the current research are recognised so that they can be appropriately considered in any further work that uses data from the current study.

Comparison to other studies in the Port Jackson estuary catchment suggests average concentrations and loadings reported in the current investigation may be underestimations of actual values. Results of the current investigation should therefore be interpreted in consideration of the potential sensitivity of results, which has been estimated using average concentrations and loadings reported in other investigations.

Stormwater samples were collected from only nine of the 70 subcatchments modelled, and only four of these were sampled under medium/high-flow conditions. As a result, the average concentrations used to calculate loadings were averages of results from other subcatchments (except where sampled) and therefore not truly representative of stormwater discharge from each individual subcatchment.

The modelling package used (MUSIC) does not model heavy metals. For the purposes of this investigation, heavy metals were modelled using the simulation for total suspended solids. The main limitation of this approach is that loadings were not reported for pervious areas. MUSIC assumes that total suspended solids are filtered and captured by vegetated areas. Whilst this principle may be applicable to particulate bound heavy metals, it is not applicable to dissolved concentrations of heavy metals that may be present in stormwater runoff from pervious areas.

Stormwater improvement devices were not modelled in this investigation. A number of stormwater improvement devices are present in the Port Jackson estuary catchment including sand infiltration basins on Whites and Johnstons Creeks, and constructed wetlands on Whites, Powells and Toongabbie Creeks. As MUSIC does not model heavy metals, it could not be used to model the removal of heavy metals in the current investigation.

4.6 Recommended Future Research

Comparison to other studies in the Port Jackson estuary catchment suggests average concentrations and loadings of stormwater heavy metals reported in the current investigation are underestimations of actual values. It is hypothesised that this may be because the sampling design used did not allow assessment of variation at the annual scale. To obtain more accurate data on the quality of stormwater entering Port Jackson estuary, future research could use a sampling design that accounts for variation at the annual scale.

Stormwater sampling to verify the modelling in the current research could be undertaken in stormwater channels where sampling was not undertaken as part of the current investigation. The data collected could be used in conjunction with the data collected in the current investigation to adapt MUSIC for heavy metals assessment.

Other potential future research could investigate stratification of Port Jackson estuary. Conclusions of the current research were based on the assumption that heavy metals in stormwater discharged to the estuary under medium- (between 5 and 50 mm of rainfall in 24 hours) and high-flow conditions (>50 mm of rainfall in 24 hours) are not deposited in sediments of the estuary due to flows bypassing embayments or the estuary and resuspension processes. Although sedimentation studies in Ion Cove (Taylor, 2000) have provided some evidence of estuarine stratification, further research to better understand these processes and confirm the fate of heavy metals transported under medium- and high-flow conditions is required to confirm the conclusions of the current study. Subcatchment specific rainfall thresholds for stratification of the estuary and flows bypassing embayments could also be established to provide more accurate information for the targeting of stormwater remediation.

Further research could also be undertaken to design a stormwater remediation device that targets low-flow (less than 5 mm in 24 hours) events and effectively removes dissolved and particulate concentrations of heavy metals from stormwater entering Port Jackson estuary. This may include assessment of the effectiveness of different filters and sorbents in removing dissolved and particulate phase heavy metals.

5. Conclusion

Modelling of stormwater using the Model for Urban Stormwater Improvement Conceptualisation indicated the average annual discharge of stormwater from the Port Jackson catchment was 215,307 ML. Average annual loadings of arsenic, cadmium, chromium, copper, nickel, lead and zinc in stormwater discharging to Port Jackson estuary were 0.8, 0.5, 1.7, 3.2, 1.1, 3.6 and 17.7 tonnes per year, respectively, although comparison to other studies in the catchment suggests these values may be underestimations of actual loadings by 1.3 to 10 times. The proportion of heavy metals discharged under low-flow conditions (<5mm of rainfall in 24 hours), medium-flow conditions (between 5 and 50mm in 24 hours), and high flow conditions (>50 mm of rainfall in 24 hours) was 6.5%, 62.5% and 31%, respectively.

A conceptual model of heavy metals in stormwater entering Port Jackson estuary was developed to assist in identifying heavy metals, locations and flow regimes to be targeted for future remediation works. Stormwater loadings of copper, lead and zinc pose a risk to the health of riverine and estuarine ecosystems in the catchment and should be targeted for remediation. Stormwater channels that should be prioritised for remediation include the channels entering southern embayments west of Darling Harbour; Duck, Parramatta and Lane Cove Rivers; and the channels and rivers entering Neutral, Long and Sugarloaf Bays.

Stormwater loadings of lead are predominantly associated with suspended particulates; loadings of copper and zinc are equally partitioned between dissolved and particulate phases. Stormwater remediation strategies should target both dissolved and particulate phases to ensure effective removal of copper, lead and zinc.

Assuming heavy metals in stormwater discharged to the estuary under medium- and high-flow conditions are not deposited in sediments of the estuary due to flows bypassing embayments or the estuary and resuspension processes (Wolanski, 1977; Barry et al. 1999; Taylor, 2000), remediation should target low-flow events, allowing medium- and high-flows to bypass the system.

The findings of the current research could be used to identify appropriate remediation strategies for dissolved and particulate phase heavy metals in stormwater discharging to Port Jackson estuary. However, in designing stormwater remediation devices, consideration should be given to the range of contaminants that may be present in stormwater entering Port Jackson estuary.

6. References

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1. Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ) and Australian and New Zealand Environment and Conservation Council (ANZECC) (2000a) *National Water Quality Management Strategy, Australian Guidelines for Urban Stormwater Management*.

2. Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ) and Australian and New Zealand Environment and Conservation Council (ANZECC) (2000b) *National Water Quality Management Strategy, Australian and New Zealand Guidelines for Fresh and Marine Water Quality*.

3. Atlanta Regional Commission (2001) *Georgia Stormwater Management Manual, Volume 1, Stormwater Policy Guidebook*. First Edition.

4. Ball, J. E., Jenks, R. and Aubourg, D. (1996) Dry weather build-up of constituents of road surfaces. In: *Proceedings of the 7th international conference of urban storm drainage*. Hanover, Germany. 785-790.

5. Ball, J. E., Wojcik, A. and Tilley, J. (2000) *Stormwater quality from road surfaces – Monitoring of the hume highway at South Strathfield.* Report No. 204. NSW Roads and Traffic Authority.

6. Barry, S. C., Taylor, S. E. and Birch, G. F. (1999) *Heavy metals in urban stormwater canals entering Port Jackson, Australia, and their impact on the estuarine environment*. Proceedings of the eighth international conference on urban storm drainage, Sydney, Australia.

7. Barry, S.C., Taylor, S.E. and Birch G. F. (2000) Heavy metal supply to the Port Jackson estuary, Australia by stormwater. *Austr. J. Wat. Res*. **4**: 147-154.

8. Barry, S. C. and Birch, G. F. (2003) *Stormwater heavy metal loadings to Iron Cove, an embayment of Sydney Harbour* (unpublished and incomplete) School of Geosciences, University of Sydney.

9. Birch, G.F. (1996) Sediment bound metallic contaminants in Sydney's adjacent offshore, Australia. *Estuar. Coast. Shelf Sci*. **42**, 31-44

10. Birch, G.F., Evenden, D. and Teutsch, M.E. (1996) Dominance of point source in heavy metal distributions in sediments of a major Sydney estuary, Australia. *Sci. Total Environ.* **28**, 169-174.

11. Birch, G.F. and Taylor, S.E. (1999) Source of heavy metals in sediments of the Port Jackson estuary, Australia. *Sci. Tot. Environ*. **227**, 123-138.

12. Birch, G. F., Scollen, A., Snowden, R. and Suh, J. (1999) *Sources of heavy metals in stormwater draining into Port Jackson, Sydney, Australia*. Proceedings of the eighth international conference on urban storm drainage, Sydney, Australia.

13. Birch, G. F. and Taylor, S. E. (2000a) Marine pollution in Australia, with special emphasis on central New South Wales estuaries and adjacent continental margin. *Int. J. Environ. Pollut*. **13**, 1-3.

14. Birch, G.F. and Taylor, S.E. (2000b) The distribution and possible sources of organochlorine residues in sediments of a large urban estuary, Port Jackson, Sydney. *Austr. J. Earth Sci*. **47**, 749-756.

15. Birch, G. F., Matthai, C., Fazeli, M. S. and Suh, J. Y. (2004) Efficiency of a constructed wetland in removing contaminants from stormwater. *Wetlands*. **24**: 459-466.

16. Birch, G. F., Fazeli, M. S. and Matthai, C. (2005) Efficiency of an infiltration basin in removing contaminants from urban stormwater. *Environ. Monit. Assess*. **101**: 23-38.

17. Bodo, B. A. (1989) Heavy metals in water and suspended particulates from an urban basin impacting Lake Ontario. *Sci. Tot. Environ*. **87/88**: 329-344.

18. Brezonik, P. L. and Stadelmann, T. H. (2002) Analysis and predictive models of stormwater runoff volumes, loads and pollutant concentrations from watersheds in the Twin Cities metropolitan area, Minnesota, USA. *Water Res*. **36**, 1743-1757.

19. Brown, J. N. and Peake, B. M. (2006) Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff. *Sci. Total Environ*. **359**, 145-155.

20. Bureau of Meteorology and Cooperative Research Centre for Catchment Hydrology (2001) *Climatic atlas of Australia: Evapotranspiration*. Bureau of Meteorology.

21. Bureau of Meteorology (2004) *Climatic averages for Sydney (Observatory Hill).* Data accessed n\online via http://www.bom.gov.au/climate/averages/tables/cw_066062.shtml

22. Chambers, J. E. D. (2000) *Homebush Bay and its tributaries Haslams and Powells Creeks: A study of stormwater pollution and preliminary remediation techniques.* B.Sc. Honours Thesis (unpubl) School of Geosciences, University of Sydney.

23. Characklis, G. W. and Wiesner, M. R. (1997) Particles, metals and water quality in runoff from large urban watershed. *J. Environ. Engin.* **123**: 753-759.

24. Charbeneau, R. J. and Barrett, M. E. (1998) Evaluation of methods for estimating pollutant loads. *Water Environ. Res.* **70**, 1296-1302.

25. Chiew, F. H. S. and McMahon, T. A. (1999) Modelling runoff and diffuse pollution loads in urban areas. *Water Sci. Technol*. **39**, 241-248.

26. Connell, D. W. (1993) *Water Pollution. Causes and effects in Australia and New Zealand.* 3rd Ed. University of Queensland Press.

27. Cruickshank, B. (2006) *Modelling nutrient load to the Port Jackson estuary, Australia*. B. Sc. Honours Thesis (unpubl) School of Geosciences, University of Sydney.

28. Davis, A.P., Shokouhian, M., Ni, S. (2001) Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. *Chemosphere.* **44**, 997-1009.

29. Department of Local Government (2006) *Stormwater management service charge guidelines*. NSW Department of Local Government, Sydney.

30. EPA (1997) *Managing Urban Stormwater—Treatment Techniques*. Report No. 97/97. New South Wales Environment Protection Authority. pp 104.

31. Förstner, U., Calamano, W., Hong, J. and Kersten, M. (1994) Effects of redox variations on metal speciation – Implications on sediment quality criteria assessment. In: *Reviews on Analytical Chemistry*. Euroanalysis VII, Spec. Publ. R. Soc. Chem.

32. Genc-Fuhrman, H., Mikkelsen, P. S. and Ledin, A. (2007) Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from stormwater: Experimental comparison of 11 different sorbents. *Water Res*. **41**: 591-602.

33. Hall, K.J. and Anderson, B. C. (1988) The toxicity and chemical composition of urban stormwater runoff. *Can. J. Civ. Eng*. **15**: 98-106.

34. Hamilton, R. S., Revitt, D. M., Warren, R. S. and Duggan, M. J. (1987) Metal mass balance studies within a small highway dominated catchment. *Sci. Total Environ*. **59**, 365-368.

35. Hatje, V., Rae, K. and Birch G.F. (2001a) Trace metal and total suspended solids concentrations in freshwater: The importance of small-scale temporal variation. *J. Environ. Monit.* **3**, 251-258.

36. Hatje, V., Birch, G.F. and Hill, D.M. (2001b) Spatial and temporal variability of particulate trace metals in Port Jackson estuary, Australia. *Estuar. Coast. Shelf Sci*. **53,** 63-77.

37. Hatje, V., Apte, S. C., Hales, L. T. and Birch, G. F. (2003) Dissolved trace metal distributions in Port Jackson estuary (Sydney Harbour), Australia. *Mar. Pollut. Bull*. **46**: 719-730.

38. Herngren, L., Goonetilleke, A. and Ayoko, G. A. (2005) Understanding heavy metal and suspended solids relationships in urban stormwater using simulated rainfall. *J. Environ. Manag*. **76**: 149-158.

39. Huber, W. C. and Dickenson, R. E. (1988) *Storm water management model, Version 4, Part A, User's Manual*, *EPA-600/3-88-001a*. United States Environmental Protection Agency, Athens, Ga.

40. Hvitved-Jacobsen, T., Johansen, N. B. and Yousef, Y. A. (1994) Treatment systems for urban and highway runoff in Denmark. *Sci. Tot. Environ*. **146/147**: 499-506.

41. Irvine, I. and Birch, G.F. (1998) Distribution of heavy metals in surficial sediments of Port Jackson, Sydney, Australia. *Austr. J. Earth Sci.* **45**, 169-174.

42. Jang, M. A., Seo, Y. and Bishop, P. L. (2005) The removal of heavy metals in urban runoff by sorption on mulch. *Environ. Pollut.* **133**: 117-127.

43. Kayhanian, M., Suverkropp, C., Ruby, A. and Tsay, K. (2007) Characterisation and prediction of highway runoff constituent event mean concentration. J. *Environ. Manag.* **85**, 279-295.

44. Kim, L. H., Ko, S. O., Jeong, S. and Yoon, J. (2007) Characteristics of washed-off pollutants and dynamic EMCs in parking lots and bridges during a storm. *Sci. Tot. Environ.* **376**: 178-184.

45. Lawson, N. M., Mason, R. P. and Laporte, J.M. (2001) The fate and transport of mecury, methylmercury, and other trace metals in Chesapeake Bay tributaries. *Wat. Res.* **35**, 501-515.

46. Lee, J. H. and Bang, K. W. (2000) Characterization of urban stormwater runoff. *Water Res.* **34**: 1773-1780.

47. Lee, J. H., Bang, K. W., Ketchum, L. H., Choe, J. S. and Yu, M. J. (2002) First flush analysis of urban storm runoff. *Sci. Tot. Environ.* **293**: 163-175.

48. McCready, S., Slee, D., Birch, G.F. and Taylor, S.E. (2000) The distribution of polycyclic aromatic hydrocarbons in surficial sediments of Sydney Harbour, Australia. *Mar. Pollut. Bull.* **40,** 999-1006.

49. McPherson, T. N., Burian, S. J., Stenstrom, M. K., Turin, H. J., Brown, M. J. and Suffet, I. H. (2005) Trace metal pollutant load in urban runoff from a southern Californian watershed. *J. Environ. Engin.* **131**, 1073-1080.

50. Morse, J. W., Presley, B. J., Taylor, R. J., Benoit, G. and Santschi, P. (1993) Trace metal chemistry of Galveston Bay: Water, sediments and biota. *Mar. Environ. Res.* **36**: 1-37.

51. Mosley, L. M. and Peake, B. M. (2001) Partitioning of metals (Fe, Pb, Cu, Zn) in urban runoff from the Kaikorai valley, Dunedin, New Zealand. *New Zealand J. Mar. Fresh. Res.* **3**: 615-624.

52. MUSIC Development Team (2005) *MUSIC User Manual*. Cooperative Research Centre for Catchment Hydrology.

53. Nezlin, N. P., DiGiancomo, P. M, Stein, E. D. and Ackerman, D (2005) Stormwater runoff plumes observed by SeaWiFS radiometer in the Southern California Bight. *Rem. Sens. Environ*. **98**: 494-510.

54. NSW Environment Protection Authority (1997) Managing Urban Stormwater: Council Handbook.

55. Peterson, S. M. and Batley, G. E. (1992) *Road runoff and its impact on the aquatic environment*. Investigation Report CET/LH/IR0761. Centre for Advanced Analytical Chemistry, CSIRO, Lucas Heights, Australia.

56. Pitbaldo, R. M. (1978) Estuarine modelling: The development and validation of a two layer, real-time model for the Parramatta river estuary. Ph.D. thesis, University of Sydney.

57. Rangsivek, R and Jekel, M. R. (2005) Removal of dissolved metals by zero-valent iron (ZVI): Kinetics, equilibria, processes and implications for stormwater runoff treatment. *Water Res*. **39**: 4153-4163.

58. Ray, A. B., Selvakumar, A. and Tarufi, A. N. (2006) Removal of selected pollutant from aqueous media by hardwood mulch. *J. Haz. Mat*. **13**6: 213-218.

59. Revitt, D. M., Hamilton, R. S. and Warren, R. S. (1990) The transport of heavy metals within a small urban catchment. *Sci. Total Environ*. **93**, 359-373.

60. Revitt, D. M., Shutes, R. B. E., Jones, R. H., Forshaw, M. and Winter, B. (2004) The performances of vegetative treatment systems for highway runoff during dry and wet conditions. *Sci. Tot. Environ*. **334/335**: 261-270.

61. Salomons, W. E., de Rooij, N. M., Kerdijk, H. and Bril, J. (1987) Sediments as a source for contaminants. *Hydrobiol.* **149**: 13-30.

62. Sansalone, J. J. and Buchberger, S. G. (1995) An infiltration device as a best management practice for pollutants in urban highway runoff. *Water Sci. Technol.* **32:** 119–125.

63. Sansalone, J. J., Buchberger, S. G. and Al-Abed, S. R. (1996) Fractionation of heavy metals in pavement runoff. *Sci. Tot. Environ.* **189/190**: 371-378.

64. Sansalone, J. J. and Buchberger, S. G. (1997) Partitioning and first flush of metals in urban roadway storm water. J. *Environ. Engin.* **123**: 134-143.

65. Sansalone, J. J. (1999) In-situ performance of a passive treatment system for metal source control. *Water Sci. Technol.* **39:** 193–200.

66. Scholes, L., Shutes, R. B. E., Revitt, D. M., Forshaw, M. and Purchase, D. (1998) The treatment of metals in urban runoff by constructed wetlands. *Sci. Tot. Environ.* **214**: 211-219.

67. Scollens, A. (1998) *Heavy metal contributions to Port Jackson estuary from catchment road surfaces*. B.Sc. Hons. Thesis (unpubl) School of Geosciences, University of Sydney.

68. Sing, S. K. and Subramanian, V. (1984) Hydrous Fe and Mn oxides – scavengers of heavy metals in the aquatic environment. *CRC Crit. Rev. Environ. Control*. **14**: 33-90.

69. Soller, J., Stephenson, J., Olivieri, K., Downing, J and Olivieri, A. W. (2005) Evaluation of seasonal scale first flush pollutant loading and implications for urban runoff management. *J. Environ. Manag.* **76**: 309-318.

70. Solo-Gabriele, H. M. and Perkins, F. E. (1997) Watershed-specific model for streamflow, sediment and metal transport. *J. Environ. Engin.* **123**, 61-70.

71. Stein, E. D. and Ackerman, D. (2007) Dry weather water quality loadings in arid, urban watersheds of the Los Angeles Basin, California, USA. *J. Am. Wat. Res. Assoc.* **43**, 398-413.

72. Strecker, E. W., Priscoll, E. D., Shelley, P. E. and Gaboury, D. R. (1992) Use of wetlands for stormwater pollution control. U.S. Environmental Protection Agency.

73. Stormwater Trust (2001) *Urban Stormwater Program, Overview and Future Directions*.

74. Stumm, W. and Morgan, J.J. (1996) *Aquatic Chemistry: Chemical equilibria and rates in natural waters*. John Wiley & Sons, New York.

75. Suh, J., Brown, P. and Birch, G. F. (2003) Geochemical factors affecting leachate composition derived from soils in reclaimed land using laboratory freshwater and saline water column experiments. *Mar Fresh Res*. **54**: 885-893.

76. Suh, J., Brown, P. and Birch, G. F. (2003) Hydrogeochemical characteristics and importance of natural and anthropogenic influences on soil and groundwater in a reclaimed land adjacent to Port Jackson, Sydney, Australia. *Mar Fresh Res*. **54**: 767-779.

77. Suh, J., Birch, G. F., and Matthai, C. and Hughes, K. (2004) Spatial distribution and sources of heavy metals in reclaimed lands of Homebush Bay; the venue of the 2000 Olympic Games, Sydney, New South Wales. *Aust J. of Earth Sci*. **51**: 53-66.

78. Suh, J., Birch, G. F. and Hughes, K. (2004) Hydrochemistry in reclaimed lands of the 2000 Olympic Games site, Sydney, Australia. *J. Coast Res*. **20**: 709-721.

79. Tanizaki, Y. Shimokawa, T. and Yamazaki, M. (1992) Physico-chemical speciation of trace elements in urban streams by size fractionation. *Wat Res*. **26**: 55-63.

80. Taylor, S.E. (2000) *The source and remobilisation of contaminated sediment in Port Jackson, Australia*. Ph.D. Thesis (unpubl) School of Geosciences, University of Sydney.

81. Tessier, A. (1992) Sorption of trace elements on natural particles in oxic environments. In: *Environmental Particles*. Buffle, J. and van Leeuwen, H. P. eds, Vol 1, Chap 11, 425-453. Lewis Publishers, Michigan.

82. Tilley, D.R. and Brown, M.T. (1998) Wetland networks for stormwater management in subtropical urban watersheds. *Ecol. Engineer*. **10**: 131-158.

83. Turner, A., Millwatrd, G. E., Bale, A. J. and Morris, A. W. (1993) Application of the K_D concept to the study of trace metal removal and desorption during estuarine mixing. *Estuar. Coast. Shelf Sci*. **36**: 1-13.

84. Wang, W., Stupakoff, I. And Fisher, N. S. (1999) Bioavaiolability of dissolved and sediment-bound metals to a marine deposit-feeding polychaete. *Mar. Ecol. Prog. Ser*. **178**: 281-293.

85. Warren, L. A., and Zimmerman, A. P. (1994) The influence of temperature and MaCl on cadmium, copper and zinc partitioning among suspended particulate and dissolved phases in an urban river. *Wat. Res*. **9**: 1921-1931.

86. Water Board (1993a) Pollutant loadings into the waterways of Sydney and the Illawarra regions. Water Board Report.

87. Water Board (1993b) *Water Quality and Pollutant Loads in the Hawthorne Canal Stormwater Channel No 62*. Report No 93/67. Australian Water Technologies EnSight.

88. Williamson, R. B. (1985) Urban stormwater quality I. Hillcrest, Hamilton, New Zealand. *New Zealand J. Mar. Fresh. Res*. **19**: 413-427.

89. Williamson, R. B. and Morrisey, D. J. (2000) Stormwater contamination of urban estuaries, 1. Predicting the build-up of heavy metals in sediments. Estuaries, 23. 56-66.

90. Wolanski, E. (1977) The fate of storm water and stormwater pollution in the Parramatta Estuary, Sydney. *Aust. J. Mar. Fresh. Res*. **28**: 67-75.

91. Yuan, Y., Hall, K. and Oldham, C. (2001) A preliminary model for predicting heavy metal contaminant loading from an urban catchment. *Sci. Total Environ*. **266**, 299-307.