Heavy Metals and Stormwater: An Investigation of Hobart, Tasmania, Australia

By

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A thesis submitted in partial fulfilment of the requirements for the Master of Science (Environmental Management)

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September, 2002

This thesis contains no material which has been accepted for the award of any other degree or graduate diploma in any tertiary institution and to the best of the author's knowledge and belief, the thesis contains no material previously published or written by other persons except when due reference is made in the text of the thesis.

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Abstract

Stormwater quality in the City of Hobart has been examined by past local studies. However, heavy metals were not critically examined in those studies. This research was undertaken to determine the levels of heavy metals discharged by three major rivulets namely, Sandy Bay Rivulet, Hobart Rivulet and New Town Rivulet into the Derwent Estuary.

Nine stormwater samples were collected through grab sampling during the first-flush period at three rivulet sites, including street runoff and stormwater in the suburbs. The sampling period took place from October 2001 till February 2002. Levels of pH and total suspended solids (TSS) concentrations were measured. Levels of heavy metals such as Al, Cd, Cr, Co, Cu, Fe, Mn, Ni, Pn and Zn were determined using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP) in the laboratory. Total metals concentrations, sediment and dissolved heavy metals were calculated and compared against international and national standards. In addition, studies from past stormwater studies, including local studies were used as a benchmark in this study.

Results show metals like Cu, Ni and Zn were found mainly in dissolved form while Pb, Al and Fe were mainly in particulate matter. High levels of dissolved Cu and Zn are found in Hobart and New Town Rivulets. Distribution and levels of heavy metals are found to be highly dependent on landuse across the three rivulets' catchments. High levels of Al and Fe were found to their abundance in the Earth's crust. High levels of Mn in Sandy Bay Rivulet were due to geologic makeup of Sandy Bay region. Other metals, excluding Cu, Pb and Zn are found to be within guidelines.

Non-point sources such as residential areas and point sources have been identified as potential sources of metals. Zn concentrations are significantly higher than Pb and Cu. Heavy metals in street runoff sample reveal higher levels of Cu, Ni and Zn than Atlanta streets. Comparison with local studies reveal an increase in TSS in Sandy Bay Rivulet, increass in Zn levels in Hobart Rivulet and an overall higher level of heavy metals in stormwater sediment as compared to sediments in the Derwent Estuary.

It is recommended reduction measures like efficient sediment traps should be installed at three rivulets, as well as source reduction programs to be adopted by the state government or local councils to curb the level of sedimentation, as well as the amount of heavy metals contaminated sediment from entering the Derwent Estuary.

Keywords

Urban Hydrology, Heavy Metals, Sediment, Urban Stormwater, First-flush, Street-runoff, Total Suspended Solids.

This research is dedicated to my parents for their undying support for me in the completion of this Masters degree.

Acknowledgements

It has been a wonderful experience working with Associate Professor John Todd. He has been more than a supervisor in this research. His guidance has contributed tremendously towards the completion this study. He has also provided a great learning experience during my education in Tasmania. It is a pity that he is retiring from teaching. I wish him the best in his future doings.

I would also like to convey my gratitude to Dennis Charlesworth who had assisted me in my laboratory work and always willing to impart laboratory techniques to me. Special thanks to Damien Norman from analytical services Tasmania who had been patience in explaining the complexity of chemical analysis process of the samples.

Lots of thanks to my family members, especially Mum and Dad who always wants the best for me and willing to part their hard-earned money to give the best education to me. I thanked them for that and I am glad to say, " I had done them proud" finally.

From the bottom of my heart, thanks to Jane Chan who is willing to accompany me out for sample collection during cold rainy days, preparing hot food when I comes back. You have been a pillar of support in this hectic year of study. It is a blessing for me to have you as a girlfriend.

Great thanks to Paviter Singh from Singapore who had sacrificed precious time in proof reading the chapters for me. You have been a great friend. Also thanks to his parents, Mr Sewaran Singh and Mrs Singh for the financial help in acquiring a laptop for myself. Their help will always remain in my mind and I applauded for their noble charitable acts.

Thanks for all the motivation from my small circle of friends in Hobart and faraway friends in Singapore. All of you have keep me going in these two years of study in Tasmania and all efforts have been paid off.

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CHAPTER 1 - Introduction

1.1 General Context

This study aims to investigate heavy metals contamination in urban stormwater in the City of Hobart, Tasmania (Australia). The research hypothesis will be explained in greater detail later in this chapter.

Water resources on Earth are equally precious when compared with other non-renewable resources. It is estimated that 75 percent of Earth's freshwater is 'locked' in glaciers or polar ice caps as ice (Dugan 1973), leaving the remaining 25 percent being distributed among the world's rising population needs. Water pollution is therefore an important issue, which needs to be examined, taking into strong consideration the scarcity of water resources. Water pollution could result in the loss of beneficial uses of water for drinking, fishing and shell fishing, swimming, boating, manufacturing process water and more (Heaney and Huber 1984).

There is an increasing environmental concern over urban stormwater pollution. This is because stormwater has the potential to contaminate downstream lakes, streams and reservoirs with urban pollutants (Parker *et al.* 2000). In fact, the impact of urban stormwater pollution was realized back in the 1950s by Akerlinch in Sweden, Shigorin in the Sovet Union and Palmer in USA. They found 5-day biochemical oxygen demand values in urban stormwater to be ten times the concentration of domestic wastewater receiving secondary treatment (Bradford 1977). At present, many management issues have targeted stormwater as a significant national problem. For instance, in France, the Ministry of Town Planning and Housing and the Secretariat of State for the Environment have conducted a five-year national research program on urban runoff pollution from 1978 to 1983 (Parker *et al.* 2000). In Arizona (USA), concern over urban stormwater is addressed in Section 402(p) of the 1987 Water Quality Act, which requires all municipalities with populations exceeding 100,000 to monitor the quality of stormwater being discharged into regulated streams (Parker *et al.* 2000). In the 1980s and 90s, rising pressure from urbanization has identified urban stormwater as a major environmental concern in Australia (Lawrence and Breen 1998). Every State in Australia now has or plans to put in place a state strategy against stormwater pollution. For instance, Tasmania is currently developing a State Stormwater Strategy (Green 2001), together with the Derwent Estuary Program, identifying urban stormwater as one of the factors contributing to pollution in the Derwent Estuary (Coughanowr and Green 2001).

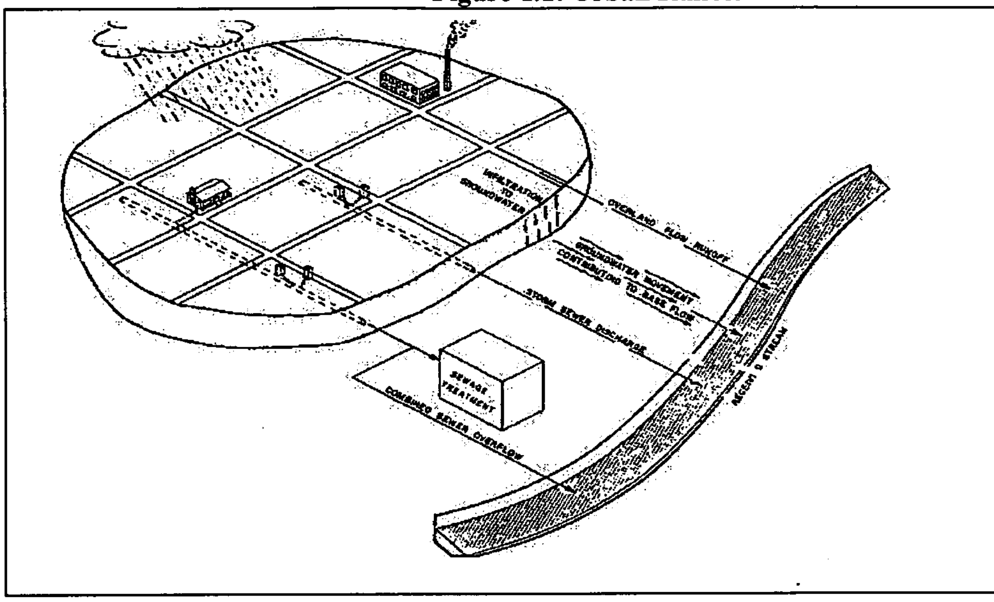
Urban stormwater and the urban hydrological cycle are intrically linked. The cycle may begin with rainfall being intercepted by various forms of vegetation. Rainfall may be stored temporarily in surface depressions and other retention areas or by evaporation where it goes back to the atmosphere. Rainfall that is not stored or evaporated, runs off as overland flow, either horizontally or vertically from the watershed (OECD 1986). Overland flow in an urban environment is categorized as urban stormwater. It includes urban runoff flowing into constructed drains and into receiving waters. Vertical flow can be described as runoff infiltrating permeable surfaces, recharging groundwater and contributing to base flow (Figure 1.1). In addition, it is possible to display the effects of urbanization using a runoff hydrograph between pre-urbanization times as opposed to post-urbanization (Figure 1.2). Increased urbanization increases the extent of impervious surfaces in the environment which contribute to a higher and faster horizontal runoff.

In the past, urban stormwater was usually dealt with as flood management. However, several urban stormwater studies have shown that urban runoff quality is deteriorating and needs urgent attention. Many countries are unable to meet national or international water quality guidelines in stormwater. Many lack effective stormwater programs to counteract stormwater pollution. These inadequacies are outlined in Chapter 2 (Section 2.3).

1.2 Urban Stormwater Pollutants and their Sources

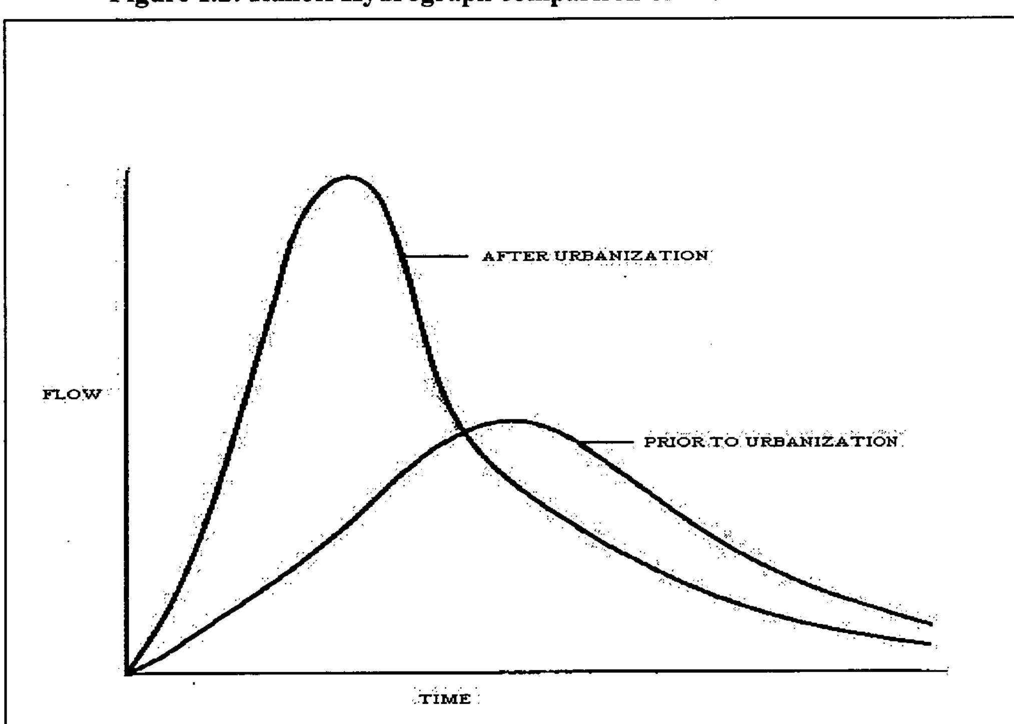
Rainwater becomes slightly acidic from the dissolution of atmospheric carbon dioxide (CO_2) (De Luca *et al.* 1991). The quality of rainwater deteriorates as they washed off pollutants with them into the stormwater. These pollutants, most of it comes from u sources that are difficult to identify (De Luca *et al.* 1991; OECD 1986). It was believed from several stormwater studies conducted; half of the contaminant load in urban runoff is contributed from non-point sources (Whipple *et al.* 1974; Wanielista *et al.* 1977, AWRC 1983). A study has been made by Colston (1974) to show the impact of non-point source on stormwater pollution. He removed 100% of organic matter and suspended solids from streets. However, this does not prevent stormwater from not having elevated levels of pollutants. Stephenson (1981) also described urban runoff as highly contaminated even if no sewage or waste water is discharged into the system. This is due to contribution by non-point sources namely; animal faeces, garden fertilizers, soil erosion, motor vehicles and atmospheric deposition.

Figure 1.1: Urban Runoff



Source: OECD (1986)

Figure 1.2: Runoff Hydrograph comparison of Pre vs Post Urbanization



Source: OECD (1986)

Similarly, Barton (1978) commented that the United States Environmental Protection Agency (U.S EPA) has listed urban runoff as rival to agriculture being the worst contributor of non-point pollution, as well as a far more serious polluter in many areas. In addition, Allison *et al.* (1998) have also shown that non-point source pollution is a major problem. Their study on nutrient contribution by leaf litter has shown that a 90% removal of leaf litter from stormwater does not produce a significant result in reduction of nutrient enrichment of urban stormwater.

Even though non-point sources are the main contributing factors in stormwater pollution. There is generally a pool of sources that contribute towards pollutants in stormwater (OECD 1986). They are the following:

- Everyday urban activities,
- Transportation activities,
- Atmospheric fallout,
- Corrosion,
- Industrial/ Commercial activities (Waste Landfill, Raw Material Stockpile and Contaminated Land), and
- Construction Activities/ Soil Erosion.

1.2.1 Everyday Activities

Daily urban activities have resulted in a build up of pollutants on ground surfaces. These contaminants include chemical fertilizers, insecticides or herbicides used in residential gardens and litter discarded on the ground. Highly impervious surfaces in urban areas increased the rate of overland flow which accelerated the amount of suspended solids washed into urban runoff. Organic deposition, especially animal faeces when washed into stormwater increases the level of organic contamination (De Luca *et al.* 1991; Green 1999; Green 2001). Green (1999) in his study of Springfield catchment in Tasmania (Hobart) measured facecal coliform counts well above the recommended guidelines for primary and secondary recreation contact of 150cfu/100mL and 1,000 cfu/100mL respectively. Also, it was estimated that urban runoff delivered approximately 90% of the total faecal coliform load to the Derwent Estuary in Tasmania (Green 2001).

1.2.2 Transportation Activities

Transportation activities are one of the major sources of urban stormwater contamination (Brinkmann *et al.* 1985; OECD 1986; Muschack 1990; TIEA 1995; Viklander 1998; Mársalek *et al.* 1999; Polkowska *et al.* 2001). Brinkmann *et al.* (1985) claimed that vehicular traffic is responsible for liquid, solid and gaseous pollutants in urban catchments. They occur in the form of combustion exhausts, leakages, and abrasion products from vehicles (tire wear, brake linings) or roads (pavement wear). In cold regions, build-up of pollutants is created by anti-skid compounds and de-icing chemicals (OECD 1986). These chemicals includes Cl^-, Na^+ and Ca^{2+} which are found in all samples collected during winter from road run off (Polkowska *et al.* 2001). Leakages of fuels, motor oils, and lubricants occur everywhere on roads and the greatest contribution comes from parking lots, petrol stations, car repair shops and near traffic lights. These pollutants are partly volatized (degraded with time), when exposed to strong heat (absorption of sunlight on dark-colored pavements) (Brinkmann *et al.* 1995). In addition, a study on highways by Marsalek *et al.* (1999) revealed that highway runoff included solids, hydrocarbons (including polycyclic aromatic hydrocarbons- PAHs), heavy metals, nutrients, deicing agents, phenols and herbicides applied on highway verges. Specific metal concentrations like zinc are found to be higher in street runoff as opposed to total urban runoff in Atlanta in USA (Rose *et al.* 2001). Benzene is also found in high concentrations due to its widespread use as an octane booster and lead substitute in gasoline (Polkowska *et al.* 2001). Viklander (1998) showed that tire wear from vehicles releases rubber particles with an average diameter of 20 μm in diameter and emissions from vehicles yield two lead associated particle sizes: One smaller than 1 μm and one 5-50 μm. Also, it is found that in stormwater 92% of the lead is associated with particles larger than 20 μm in diameter Viklander (1998).

1.2.3 Atmospheric Fallout

De Luca *et al.*'s (1991) study of rain quality in an urban catchment indicates pollution possibly contributed from atmospheric deposition. Anthropogenic activities create an imbalance in the atmosphere, increasing the amount of atmospheric pollutants. Sulphur oxides (SO_x) are emitted mainly by stationary sources. Nitrogen oxides (NO_x) are emitted by both stationary and mobile sources. Both are able to increase the acidity of rain (De Luca *et al.*

1991). In addition, fly ash and dust from industries, and vehicles' emissions can contribute high concentration of trace heavy metals, such as zinc (Zn), lead (Pb), cadmium (Cd) or beryllium (Be) in rainfall (De Luca *et al.* 1991; Green 1999).

1.2.4 Corrosion

As surfaces are corroded by daily atmospheric conditions, corroded particles accumulate on the ground surface and building materials. They are eventually washed off during rain events, together with the urban runoff (OECD 1986). Malmquist and Svensson (1977) have shown that corrosion of building materials has increased the amount of heavy metals like zinc and copper which are common constituents of building materials in Sweden. Roof runoff has also been investigated. It has been found that runoff flowing off roof tops contains heavy metals. For example, Yaziz *et al.* (1989) analyzed roof runoff during rainfall events in Malaysia and identified the first flush to contain high concentrations of zinc.

1.2.5 Industrial/ Commercial Activities (Waste Landfill, Raw Material Stockpile and Contaminated Land)

Industrial and commercial activities are definite sources of contamination. These sources are site-specific and contain many chemical toxins and heavy metal materials. They pollute receiving water bodies and groundwater through leachate discharges (OECD 1986). Green (1999) reported, in the study of Prince of Wales Bay (Tasmania), that a landfill site was partly responsible for contaminating the Derwent Estuary. There is evidence of soil contamination with heavy metals in this reclaimed landfill site and metals leaching into groundwater from the landfill. There is also risk of heavy metals being flushed by tidal patterns into the Estuary from the landfill site (Simmons 1996). Pasminco Metals is a major polluting zinc smelter before 1990s, sparking high levels of heavy metals like cadmium, copper, mercury, lead and zinc in Derwent Estuary. Since then, improvements were made towards responsible management practices. However, accident occurs on November 13th 2001 when over 4,000 m^3 of contaminated water over-flowed from the Pasminco site (2,780 m^3 from the contaminated pond. (Green and Coughanowr 2002).

1.2.6 Construction Activities/ Soil Erosion

Studies have shown that sediment contamination is a serious problem in urban stormwater (Helsel *et al.* 1979; Waller and Hart 1986; Bhaduri *et al.* 1995; Crawford *et al.* 1995; Parker *et al.* 2000). For example, Maricopa County in Arizona (Parker *et al.* 2000), northern Ohio (Bhaduri *et al.*1995) and Halifax in Canada (Waller and Hart 1986). It has been determined that there is a strong relation between the chemical characteristics of urban stormwater and suspended solids concentration in the stormwater (Hall and Anderson 1988; Parker *et al.* 2000). Construction activity could generate high sediment concentrations of between 2 and 10 times, and occasionally 100 times greater runoff compared to undisturbed land (Bhaduri *et al.* 1995). Waller and Hart (1986) have estimated an average concentration of 0.04kg/ha-yr phosphorus in sediment generated by construction activities. Similarly, soil erosion could also arise from extensive vegetation clearance, stream bank erosion and tracks in catchments.

1.3 Impacts of Polluted Urban Stormwater

The sight of dirty stormwater flowing into receiving waters is unappealing. It is normally accompanied by the 'first-flush' effect that encompasses large materials like plastic bottles, metal cans, cigarette butts and leaf litter. These large items may be removed by pollutant traps. However, small suspended sediment, dissolved heavy metals, organic matter, grease and oil continue to reach receiving waters and pose high risk to the environment. The impact generated by these contaminants are usually more acute and wide-ranging due to their nature and will be explained in the following sections.

1.3.1 Heavy Metals

The presence of heavy metals in stormwater is a threat to the marine environment and human health. Metal ions like aluminum, arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel and zinc listed as high risk pollutants (Ministry for the Environment 2002) are a higher threat in urban stormwater. They attached themselves to bottom sediments in freshwater, consumed by benthic biota and becomes increasingly concentrated up the food chain (Helsel *et al.* 1979). Several studies have documented the impacts of heavy metal pollution in bays and estuaries from stormwater. For example, the Derwent Estuary recorded high levels of heavy metal concentrations and listed shellfish, mussels and oysters to be unsafe for human consumption (Coughanowr and Green 2001). Medeiros and Coler (1982) also reported heavy metal concentrations from urban runoff in Green River of Massachusetts being responsible for the loss of some invertebrates from artificial substrates. Specific heavy metal pollution like mercury (Hg) has traditionally been of public health concern. There have been several cases in the past of mercury poisoning from discharges by industries. The Minamata and Niigata Bays (Japan) in 1950s recorded more than 100 Japanese deaths and a case of a mysterious neurological illness from mercury poisoning (Dugan 1973). A similar incident of mercury poisoning was also seen in the 1960s in Sweden. The source was traced back to the utilization of phenyl mercuric acetate (PMA) as a fungicide and the subsequent ingestion of the contaminated seeds by birds and fishes which caused a great decline in their numbers (Krenkel 1974).

1.3.1.1 Sources, Background levels, Toxicity Levels and Bigeochemcial Processes of Metals

Critical metal ions differ in their level of toxicity in several areas, in terms of human consumption, risk to aquatic life and livestock, agricultural purposes and recreational purpose. In general, these metals occur naturally. The most commonly natural sources of metals are surface waters, soils and vegetation, volcanic activity and forest fires. In the surface waters metals originate, to a large extent, from bedrock, surface runoff and from atmospheric deposition (Beijer and Jernelőv 1979). Table 1.1 shows the various background levels and sources of these metals. Table 1.2 shows the toxicity levels of individual metals and impacts to aquaculture species and humans.

Metals in the aquatic environment may exist in the dissolved form, as free hydrated ions, complex and chelated ions with inorganic ligands including OH-, Cl- or organic ligands including amines, proteins, humic and fulvic acids, organic molecules or in particulate form. Nevertheless, these metals undergo various physical and chemical changes and are controlled by environmental variables such as pH, redox potential (dissolved oxygen, ionic strength) salinity, alkalinity and hardness, the presence of organic and particulate matter, and biological activity. For example, the loweing of pH will cause a release of metals from complexes and particulate matter (Beijer and Jernelőv 1979).

Many metals enter the environment as relatively non-toxic forms. Subsequently they may acquire an enhanced toxicity as organometallic compounds through environmental interaction involving both biological and non-biological processes. In this way, such pathways may combine and serve as a means for metal transport across sediment-water-organism interfaces. In these processes, the metals are undergoing biogeochemical process (Beijer and Jernelöv 1979).

Certain metals are known to undergo biogeochemical process through methylations. For instance, arsenic, lead and mercury. The synthesis of methylmercury requires the work of microbial activity under natural conditions. For example, the potential for microbial methylation of mercury by fungi and bacteria has been shown to exist under aerobic as well as anaerobic conditions. Arsenic under anaerobic conditions are readily methylated by the methanogenic bacterium *Methanobacterium*, strain MOH. The inorganic arsenic forms were reduced and gradually methylated to dimethylarsine. Similarly, evidence has been presented showing microorganisms in lake sediments can tranform certain inorganic and organic lead compounds into volatile tetramethyllead by bacterial isolates from Lake Ontario (Beijer and Jernelöv 1979).

Table 1.1: Background levels and Sources of Metals

Metal	Background levels	Natural occurrence
Aluminum	Ocean water – 1 mg/L Soil – 150 –600 g/kg	❖ Most common metal in the earth's crust (8.13 %). ❖ Found commonly in bauxite and cryolite.
Arsenic	Earth's crust - <2 mg/kg Uncontaminated soil - <40 mg/kg	❖ Occurs in environment in inorganic and organic compounds. ❖ Usually exist in nature in sulfide ores (Arsenopyrite).
Cadmium	Non-polluted waters- < 1 μg/L Uncontaminated soil - < 1 mg/kg	❖ Obtained as a by-product from refining zinc, and other metals, particularly copper and lead.
Cobalt	Soil – 8 mg/kg Water in Sweden lakes – 3.57 μg/L	❖ Seen as a rare element in the Earth's crust.
Chromium	Rivers and lakes – 1-10 μg/L Sea-water - <0.1 – 5 μg/L Soil - 250 mg/kg Earth's crust – 125 mg/kg	❖ Occurs in trivalent state as chromite ore.
Copper	Seawater – 1-5 μg/L Soils vary 1 – 100 mg/kg	❖ Principal ores are cuprite, malachite, azurite, chalcopyrite and bornite. ❖ Also occur in nature as pure state.
Iron	Rivers – 0.67 mg/L Seawater – 1-60 μg/L Earth's crust – 50 mg/g Soil – 7-550 mg/g	❖ Occurs in abundance like aluminum in the Earth's crust. ❖ Obtained from iron ores.
Manganese	Seawater – 2 μg/L Soil – 600 – 900 mg/kg	❖ Occurs in modules in the bottom of ocean and in most iron ores. ❖ Found in many minerals. For example pyrolusite, as the oxide, and rhodochronite, as the carbonate.
Nickel	Seawater – 0.1 – 0.5 μg/L	❖ Found in sulfide ores, mainly those mined underground, and in oxide ores, which are mined in open pits. ❖ Seldom identified in groundwater.
Lead	Surface waters - <100 μg/L	❖ Obtained from lead minerals, namely, galena, cerrusite and anglesite.
Zinc	Seawater, freshwater – 10 μg/L Earth's crust 40 mg/kg Soil – 10 300 mg/kg	❖ Found in sulfides.

Source: Friberg *et al.* (1979)

Table 1.2: Heavy Metals Guidelines and Toxicity Impacts on Humans and Aquatic Species (Continued at page 12)

Metals	Guidelines for aquatic species (mg/L)	Types of aquatic species	General impacts on aquatic species	Guidelines for humans	Impacts on humans
Aluminum	0.003	Rainbow trout	❖ Impacts are generally uniform throughout all species. ❖ 30%-50% heavy metals ingested by fishes tend to accumulate at the gills of the fish. ❖ Excessive metals at gills will reduce respiratory effectiveness of fishes, thus leading to fish kills. ❖ 10%-20% of metals will be accumulated in fish, tissues, however, accumulation will increase over long term period. ❖ Accumulation of metals in crustaceans, shellfish and mussels tissues are more likely to be higher than fish species given	❖ Drinking water: < 100 µg/L	❖ Fatal lung damage ❖ Pulmonary
	0.1	Freshwater species			
Arsenic	<0.05[1,2]	Freshwater species		❖ 70-80 mg (Arsenic trioxide) ❖ Drinking water: 0.007 mg/L **Threshold limit** ❖ Arsenic: 0.5 mg/m^3 ❖ Calcium arsenate: 1 mg/m^3 ❖ Lead arsenate: 0.15 mg/m^3	❖ Damage to respiratory system upon inhalation. (i.e. lung cancer) ❖ Irritation of exposed skin or mucous membranes from exposure to airborne dust ❖ Heart malfunction, liver damage and Anemia
	<0.03[1,2]	Saltwater species			
Cadmium	< 0.0002	Salmonids		❖ 50-500 mg/kg ❖ Drinking water: 0.002 mg/L **Threshold limit** ❖ Metal dust: 0.2 mg/m^3 ❖ Oxide fume: 0.1 mg/m^3	❖ Acute gastrointestinal effects ❖ Chronic renal and lung disease
	< 0.001	Rainbow trout			
	< 0.003	Silver perch			
	<1.0	No effect limit for salmonids			
	0.004	All freshwater species in soft waters			
	0.012	All freshwater species in hard waters			
	< 0.15	Freshwater crustaceans			
Chromium	< 0.05	Rainbow trout		❖ 0.5 – 5 g/kg, Cr(VI) ❖ Drinking water: 0.05 mg/L **Threshold limit** ❖ Chromium: 1.0 mg/m^3 ❖ Chromates and chromic acid: 0.1 mg/m^3 ❖ Chromic and Chromous salts: 0.5 mg/m^3	❖ Skin ulceration, irritative dermatitis, allergic skin reactions and allergic asthmatic reactions
	< 0.1	No effect on salmonids			
Cobalt		-		❖ 50-500 mg/kg ❖ Drinking water standards still under review **Threshold limit** ❖ Cobalt: 0.1 mg/m^3	❖ Myocardial effects – heart failure, polycythemia and thyroid lesions
Copper	< 0.006	Silver perch		❖ 8 g, $CuSO^4$ ❖ Drinking water: 2 mg/L	❖ Metal-fume fever upon inhalation
	< 0.03	Rainbow trout			
	< 0.1	No effect for salmonids			

Continued from page 11

Metals	Guidelines for aquatic species (mg/L)	Types of aquatic species	General impacts on aquatic species	Guidelines for humans	Impacts on humans
Copper			that they feed mainly from sediment bed	**Threshold limit** ❖ Copper fume 0.1 mg/m^3 ❖ Dust and mist: 1 mg/m^3	❖ Ingestion of large amounts of copper salts lead to gastrointestinal disturbances ❖ Systemic effects, esp. hemolysis, liver damage and renal damage
Iron	< 0.1	Rainbow trout		❖ 0.5-5 g/kg, $FeSO^4$ ❖ Drinking water – 1 mg/L **Threshold limit** ❖ Iron: 10 mg/m^3	❖ Metabolic acidosis. Shock and toxic hepatitis ❖ Long term effects – hemosiderosis cirrhosis of liver
	< 0.5	Silver perch			
	< 0.01	No known adverse effect			
	< 0.1	No effect for salmonids			
Lead	0.004 – 0.008	Salmonids		❖ Drinking water: 0.01 mg/L **Threshold limit** ❖ Metallic lead: 0.15 mg/m^3 ❖ Tetra ethyl lead: 0.075 mg/m^3	❖ Anemia ❖ Gastrointestinal colic
	< 0.003	Silver perch			
	< 0.01	Rainbow trout			
	< 0.1	No effect for salmonids			
Manganese	< 0.01	Silver perch		❖ 0.5 – 5 g/kg, Mn compounds ❖ Drinking water – 0.5 mg/L **Threshold limit** ❖ Manganese: 5 mg/m^3	❖ Pneumonia and bronchitis ❖ Parkinson's disease
	< 0.02	Rainbow trout			
	< 5.0	Fish hatchery			
Nickel	0.02	Trout		❖ Daily intake 0.3 to 0.5 mg ❖ Drinking Water – 0.02 mg/L **Threshold limit** ❖ Nickel: 1 mg/m^3	❖ Pneumoconiosis and asthmatic problems ❖ Pulmonary damage
Zinc	< 0.01	Rainbow trout		❖ 1.9 – 2.2 mg/kg, $ZnSO^4$ ❖ Drinking water – 15 mg/L **Threshold limit** ❖ Zinc chloride: 1 mg/m^3 ❖ Zinc oxide: 5 mg/m^3	❖ Gastrointestinal disorders including vomiting and diarrhea ❖ Metal fume fever ❖ Acute damage to mucous membranes of the nasopharynx and respiratory tract
	< 0.1	Silver perch			
	< 0.05	Salmonids			

Source: ANZECC (2000), Friberg *et al.* (1979), NHMRC and ARMCANZ (1996), WHO (1971) and Trevethick (1973)

1.3.2 Suspended Solids (Sediment)

Fine suspended solids are introduced to the aquatic ecosystems via many routes (e.g. effluent discharge, ocean and lake disposal, non-point sources and airborne deposition). Such input of contaminated sediment into marine environment is potentially far-reaching in its environmental issue of national and international importance (Power and Chapman 1992). Sedimentation alone alters channel morphology and smothers insect life. Water draining these catchments remains very turbid, upsetting the river ecosystem (Williamson 1993). Low clarity in murky waters causes riverbed plants to reduce food making in photosynthesis process. Direct effects on fish may not be significant, however the reduction in productivity of the river eventually will affect them. An increase in sedimentation in riverbeds also causes reduction in bentic invertebrates (Lynard *et al.*1980 and Cline *et al.* 1982).

Sedimentation poses economic problems. Excess deposits of sediment clog harbours and other water transport routes and reduce the storage capacity of reservoirs. This costs governments billions of dollars each year in dredging operations. For instance, it costs U.S. Army Corps of Engineers $180 million annually to dredge 83 million cubic yards of sediment linked to pollution sources. Costs are further incurred due to improper disposal of dredged sediments which are laden with nutrients, heavy metals and toxic chemicals (NRDC 2000).

Sediments act as a medium of transport for contaminants. For instance, heavy metal contamination in sediments that are transported into receiving waters. Its impacts have been discussed in Section 1.3.1 which include the high build up of toxic metals in the marine food chain that also endangers human health.

1.3.3 Organic Matter/Nutrients

The presence of organic pollutants in water has a detrimental effect on oxygen levels. This is because oxygen has a relatively low solubility in water. It is rapidly depleted during waste organic oxidation. Water becomes anaerobic which endangers fishes and other marine fauna (Dugan 1973). In addition, high organic pollutant loads in marine environment accelerate the eutrophication process. Eutrophication is a natural process which occurs as a result of the geological aging of a body of water such as a lake (Krenkel 1974). As a lake ages, plants along with sedimentation accumulate and thus extinction of the water body can occur. Such a process is observed with the large growth of blue-green algae that metabolize heterotrophically in the dark under anaerobic conditions. In addition, such algae are relatively resistant to rapid degradation and tend to settle to the bottom of a lake. After a prolonged period, these algae will accumulate in the lake as dead matter, transforming the water bodies into bogs or swamps (Dugan 1973). Blue-green algae blooms also cause an increase in Cl_2 concentration, including other problems relating to coagulation in water treatment plants, possible taste, odor and turbidity problems (Krenkel 1974). Incidents of eutrophication have been recorded at Lake Eloa (Florida) as a result of residential/ commercial runoff (Yousef *et al.* 1981).

Incident of depressed oxygen levels (Eutrophication process) is also observed in Derwent Estuary. Such phenomenon occurs seasonally during summer months and low flow times. It is believed this is due to a natural tendency towards oxygen depletion in the upper reaches of stratified estuaries, combined with the effects of the Norske Skog paper mill effluent (DEP 2001).

1.3.4 Oil and Grease

Oil and grease in runoff cause unsightly oil films on water bodies in receiving waters. Major disasters arising from oil spills from oil tankers cause major marine flora and fauna upsets. However, direct discharge of oil and grease into urban runoff could still pose a threat to the ecology of beaches. The effects on water fowl are quite apparent. For example, as the oil coats a bird's body, it breaks down the body's natural oils and waxes and disables it from flying and prevents it from maintaining normal body temperature (Krenkel 1974). Impacts of oil and grease on water bodies have an indirect impact on the food supply of fish. Fish can swim away to avoid a polluted area but plankton cannot. Crude oil is found to be toxic to zooplankton, including fish eggs at concentrations ranging from 10 ppb to 10 ppm. Effects on phytoplankton, photosynthesis and growth have been reported at concentrations typically on the order of 0.1-10 ppm. An oil spill in Buzzards Bay (Massachusetts) in 1969, also caused shellfish to be found unfit for human consumption. In addition, an oil spill is not confined to a limited area. Sediment stained with oil and grease normally is washed to other shores and bays, causing similar consequences (Laws 1993).

An excellent local example was focused on Prince of Wales Bay which receive runoff from an adjoining light industrial area, Derwent Park. The bay provides a graphic example of the problems hydrocarbon contamination can cause in waters close to large urban areas. The accumulation of contamination over many years is evidenced by the darkly stained oiled shores, oil slicks on the water, the smell of hydrocarbons near the bay, and warning signs of health hazards.Sampling of the sediments found that most of the accumulated hydrocarbons in Prince of Wales Bay sediments are compounds that are resistant to bacterial breakdown. These compounds are typical of road run-off and lubricating oils, and low-level industrial discharge (CSIRO Marine Research 1998).

1.4 Research Hypothesis and Aims

This proposed study using heavy metal a parameter is seen of great importance in Hobart (Tasmania) given that there are several stormwater outfalls into the Derwent Estuary. In total, the Derwent Estuary receives stormwater from 57 urban and suburban catchments by way of 13 major rivulets and over 270 outlet pipes (Coughanowr and Green 2001). The Derwent Estuary is the largest estuary in southeastern Tasmania, covering an area of 200 square kilometers and is an integral part of Tasmania's cultural, economic and natural heritage (DEP 2001). However, it is also internationally known for heavy metals pollution, in mercury, cadmium, copper, lead and especially, zinc recording the highest concentrations among all. The problem arises from long historic development in Norske Skog Paper Mill (at Boyer) and Pasminco Hobart Smelter (at Risdon) along the Derwent Estuary and until 1980s, treatment to industrial discharges has been limited. (Coughanowr and Green 2001). This henceforth limits the Derwent Estuary in its potential as a prime location for recreational fishing and swimming. In addition, its extensive and productive ecosystem which supports a wide range marine species was affected by its extensive pollution problems, leading to seafood deem unfit for consumption (DEP 2001).

Since 1996, reduction of pollution in the Derwent has improved significantly, particularly with respect to heavy metals discharged by industry (greater than 50% reduction) and pathogens discharged by municipal wastewater plants (greater than 90% reductions). These improvements are result from a large degree from site improvements at the Pasminco Hobart Smelter, as well as the upgrading and effluent reuse from several sewage treatment plants (Coughanowr and Green 2001).

These improvements are highly commendable but at present, situation still persist in the following matters:

1. Sewage treatment plants discharge the majority of nutrients,
2. Stormwater accounts for the majority of faecal bacteria,
3. Pasminco discharges the majority of heavy metals (primarily as diffuse emissions), and
4. Norske Skog discharges the majority of organic matter and resin acids.

In view of these persisting matters, it is worth examining the presence of heavy metals in stormwater discharging from City of Hobart catchment. Such work is in conjunction with past urban stormwater studies conducted in Hobart (Jenkins 1991; Blacklow 1995 and Green 1998). In addition, provide small but valuable data on levels of heavy metals entering Derwent Estuary from stormwater. Similarly, the question of whether heavy metal pollution in stormwater is a significant problem in Hobart City will be addressed. The objectives of the research are:

1. Investigate the level of heavy metals concentrations in urban stormwater in three major rivulets located in the City of Hobart.
2. Determine the level of criticalness in specific heavy metal concentrations from comparison with international standards, national standards, international literature and local literature.
3. From reviewed stormwater literature, identify possible sources of heavy metal pollution.
4. Recommend suitable management options in tackling heavy metal pollution in urban stormwater in studied sites in the City of Hobart.

CHAPTER 2 - Literature

2.1 Background Context

Urbanization creates great disturbance to land surfaces and also accelerates the generation of higher rates and volumes of runoff than would occur in other environments. This results in the increase of erosion and sedimentation rates by a factor of one hundred or more as cover is removed and streams convey greater sediment to receiving waters causing clogs and scouring (Pilgrim 1987). This calls for considerable flood management measures to tackle the sedimentation problem. The flood management issue has been a major concern in cities for some time. In view of this matter, several cities have modified and re-designed urban drainage networks to tackle this problem. As mentioned in Chapter 1, urban stormwater pollution has evolved as a major area of concern in all cities requiring urgent attention. Guidelines have been put into place by world health organizations for assessing the quality of stormwater. The variables that are most significant for planning and use of resources as well as for general pollution abatement are nutrient levels, presence of toxic materials, presence of unpleasant materials, organic oxygen requirements, suspended solids and bacterial counts (Cordery 1977; Randall *et al.* 1977). Other parameters, which include pH, overland flow, temperature and conductivity of stormwater, are also used in stormwater quality assessment (Deletic and Maksimovic 1998). Apart from these parameters, high heavy metal concentration is another strong indicative of stormwater quality.

2.2 Relation Between Sediment and Heavy Metal Contamination

The mobilization of heavy metals in stormwater occurs in both dissolved and particulate form (Brinkmann *et al.* 1985). Metals that are transported in particulate form are usually attached to sediments. Sediments are heterogeneous matrices of detrital, inorganic and organic particles eventually settling on the bottom of a body of water (Power and Chapman 1992), such as rock and shell fragments, minerals, plant detritus and animal waste, and anthropogenically derived substances. Sizes of sediments vary from silts (<63 μm) to sand or rock particles (>1 mm). Denser particles settle and accumulate faster at the bottom of a water column. On the other hand, fine particles like silt, stay in suspension for a longer period and are transported with greater ease to other receiving waters or into open seas (Maher *et al.*

1999). In this way, fine sediments that eventually settle and form the sediment bed, act as either a sink from catchments or a source that modifies the chemistry of overlying water. Such modification of geochemistry of sediment and water places the aquatic environment at risk (Horowitz and Elrick 1987). For instance, sediment laden with heavy metals has been shown to be a source which modifies the river quality of the Odra river basin (Berlin) when flood carries away contaminated sediments from mining and smelting industries sites in the basin (Müller and Wessels 1999).

Power and Chapman (1992) have shown that fine particles have a greater capacity to retain insoluble metals than coarser particles. This is due to both physical (e.g. grain size, surface area, surface charge) and chemical (e.g. composition, cation exchange capacity) properties of fine particles. The strongest correlation with trace elements occurs with particle sizes of <63 μm and <123 μm. The coarse fraction is composed primarily of stable, inorganic silicate materials that are noncohesive and generally not associated with chemical contamination. However, the fine fraction consists of particles with a relatively large surface area to volume ratio and, frequently, surface electric charges (Fe and Mn oxides and hydroxides) that cause these particles to be more chemically and biologically reactive than coarser sands and this increases the likelihood of sorption and de-sorption of contaminants (Power and Chapman 1992).

Together with several other investigators, Kersten *et al.* (1991), Viklander (1998) and Bennett *et al.* (1999) showed that concentrations of heavy metals increase when the grain size of sediments become smaller (Table 2.1 and 2.2). However, trace metals Cu and Cd exhibited a different pattern. This is because they are bound predominately to organic matter, therefore, correlations between surface area and sample chemistry were found to be less significant. Walker *et al.* (2001) study of pollutants in urban stormwater in South Australia also revealed that finer fractions (< 75 μm) were most contaminated, and they are more likely to be transported and deposited in bays or open seas. This is because they are least likely to be trapped in conventional sediment traps due to their low settling velocity.

Table 2.1: Concentrations of Metals in Street Sediments Swept by Machine

Composite Sample	Cu (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Housing area, 5,000 vehicles/day				
<1 mm	36	0.099	8.1	54
<2 mm	35	0.08	6.6	49
City Centre, 4,500 vehicles/day				
<1 mm	83	0.06	11	88
< 2 mm	73	0.049	8.4	72
City Centre, 20,000 vehicles/day				
<1 mm	61	0.23	55	123
< 2 mm	56	0.22	43	104
< 4 mm	47	0.19	34	83

Source: Viklander (1998)

Table 2.2: Heavy Metals in relation to Sediment trapped in Pollutant Trap (All units in mg/kg Dry Matter Basis)

Metals	Coarse Silt	Fine Silt	Suspended
As	4	7	49
Cd	5	17	185
Co	7	9	32
Cr	42	9	218
Cu	45	70	605
Mn	116	143	310
Ni	138	8	93
Pb	66	130	1270
Zn	439	1230	10300

Source: (Bennett *et al.* 1999)

Besides increasing metal concentrations with decreasing particle size, Wiber and Hunter (1979) believe that particle size plays a role in reflecting the source of contamination. It was found that larger size sediment fractions (> 420 μm) studied in Saddle River near Lodi (New Jersey) show a greater metal enrichment than the smaller sediment fractions as one proceeds downstream through the urban area. It was believed that these larger sediment fractions are least affected by scouring and transport, therefore they may best reflect the impact of urbanization on the distribution of heavy metals over an extended period of time at a given location.

2.3 Heavy Metals in the Urban Catchment

An urban catchment which comprised multi faceted human activities provides an ideal place for numerous human pollutants to be generated. Among these pollutants, heavy metals are the common ones. Heavy metals in the City of Hobart, as is the case in other industrialized countries' cities are derived from the activities reviewed in the following sections.

2.3.1 Landfill Contamination

All countries generate large quantities of agricultural, industrial and municipal wastes. These wastes are either treated or incinerated before being released into the environment. However, in several countries land is viewed as not only an attractive avenue to dispose these wastes but a first choice. With the lack of proper environmental management and legislation concerning refuse disposal, illegal landfills are becoming a major problem. For example, uncontrolled sanitary landfills and waste dumps are established in Buenos Aires Province (Argentina) as a result of inadequate environmental legislation. These areas accept demolition materials as well as industrial, commercial, and domestic refuse with no control of unloading (Magdaleno and De Rosa 2000). This mode of treatment allows leachates (Table 2.3) with a wide range of physical, chemical and biological characteristics to contaminate aquifers and stormwater around the world (Cameron and McLaren 1997).

Table 2.3: Typical Composition of Leachates (g/m^3) from Landfill Sites

Species	UK	NZ	Species	UK	NZ
pH	8-8.5	6-8	Manganese	0.5	5-50
COD	850-1350	500-5000	Iron	10	50-400
BOD	80-250	100-4000	Nickel	0.04	0.1-1
Volatile acids	20	20-200	Copper	0.09	0.05-0.5
Ammonium N	200-600	100-1000	Zinc	0.16	1-100
Chloride	3400	200-2000	Cadmium	0.02	0.01-6
Sulphate	340	200	Lead	0.1	0.05-0.5
Sodium	2185	200-2000	Monocyclic phenols	0.01	n.d.
Potassium	888	100-1000	Total cyanide	0.01	n.d.
Magnesium	214	50-400	Organochlorine pesticides	0.01	n.d.
Calcium	88	100-1000	Organophosphorus pesticides	0.05	n.d.
Chromium	0.05	0.05-0.5	PCBs	0.05	n.d.

Source: Smith (1995)

Hazards of landfills have been widely studied. Hernández *et al.* (1998) reported landfill contamination hazards in central Spain. They traced contamination of dry weather flow of urban stormwater from groundwater to landfills in Spain's urban areas. Heavy metals such as boron and zinc are found at high levels. It is very likely that this is due to landfill leaching (Hernández *et al.* 1998).

The problem of landfills is further raised by Magdaleno and De Rosa (2000) who survey sanitary landfills and waste dump grounds in Buenos Aires Province (Argentina). There is no control over unloading of waste dumped from industries and domestic sources which leads to water pollution in rivers. Leachate samples were taken at three times (Table 2.4). It was believed that samples taken in 1997 were of lower concentrations due to dilution by rainfall, draining them into stormwater, followed by stormwater that created a flushing effect, possibly washing the toxicants into receiving waters.

Table 2.4: Leachates Samples in Buenos Aires Province (Argentina)

	Date		
	Concentrations (mg L^{-1})		
	June 1996	September 1996	August 1997
pH	7.2	7	7.3
COD	4640	3470	502
Total nitrogen	123	165	1.45
Ammonia- N	26.5	35	---
Total Phosphorus	15	16.55	0.02
Dissolved matter	5679	---	---
Suspended matter	1010	--	--
Sulphate	2.8	<0.02	<0.02
Copper	<0.05	0.14	0.38
Cadmium	0.038	0.015	0.06
Zinc	0.11	0.085	0.01
Chromium	0.004	0.021	<0.001
Manganese	0.53	0.047	0.06
Nickel	0.01	0.067	<0.001
Lead	0.15	0.17	1.45
Iron	0.96	1.1	0.604

Source: Magdaleno and De Rosa (2000)

2.3.2 Atmospheric Deposition

The presence of heavy metals in the urban catchment may also be attributed to atmospheric deposition. The atmosphere is seen as an excellent medium for transportation of fine pollutants from local and distant industries, as well from vehicular emissions.

Vehicular emissions have been characterized as a major source of heavy metals in urban catchments. As mentioned in Section 1.2.2, transportation's contribution of heavy metals comes mainly from motor oil leakages, brake linings and exhaust emissions. Heavy metals like Cr, Cu, Ni, Pb and Zn are found at high levels in several road studies literature (Hedley and Lockley 1975; Muschack 1990; Viklander 1998). Lead (Pb) especially is commonly emitted into the environment through the exhaust system as aerosols and tar products. Pb being not easily soluble in water is found mainly attached to soil and plants in the immediate vicinity of roads (Muschack 1990). This causes a problem in countries with lax vehicle laws that are unable to reduce Pb through cleaner emissions from motor vehicles.

The significance of atmospheric deposition of heavy metals by industries cannot be underestimated. Several studies have shown that heavy metal contamination comes from both local industries and distant industries (Ragaini *et al.* 1977; Polemio *et al.* 1982; Díaz-Barriga *et al.* 1997; Steinnes *et al.* 1997; Manz *et al.* 1999).

Industrial activities produce large amounts of pollutants that are airborne and deposited in urban catchments. It was believed that the main source of pollutants in several environments, including the urban environment, was the result of the deposition of these airborne pollutants from local or distant industries. These pollutants, comprising mostly of heavy metals (As, Cd, Ni, Pb and Zn), once deposited in urban soil or impervious surfaces, run the risk of being transported in stormwater during storm events.

The Díaz-Barriga *et al.* (1997) study on El Paso lead smelter in Texas (USA), showed that atmospheric deposition from cross border American industries has a huge impact on both soil contamination and children's health in Mexico. Contamination levels of soil across three sectors of varying distance from the smelter (sector I within 600 m, sector II between 600 m and 1200 m, and sector III between 1200 m and 1800 m) were studied. A control area was identified at 25 km from the smelter. Results are summarized in Table 2.5.

It was estimated that the smelter has emitted 1012 metric tons of lead, 11 tons of cadmium and 1 ton of arsenic into the atmosphere over a 3 year period from 1969 to 1971. From a monitoring program, it was also found that total lead uptake was four times lower for 1994 than for 1974. In 1974 when the lead smelter was still in operation, air was the principal pathway of exposure, and soil/dust became the second most important. The reverse happened in 1994, as soil/dust became the principal pathway and air the second. This is consistent with the Integrated Exposure Uptake Biokinetic (IEUBK) Model results. These results show that 82.7% of the total lead uptake in children can be attributed to the lead content in soil (Díaz-Barriga *et al.* 1997). A similar incident of high lead levels in blood was also reported in 90% of Kellogg preschool children in Idaho (Ragaini *et al.* 1977). In addition, patterns have shown that soil lead levels increase, as the distance to the smelter decreases. The same pattern did not hold true for household dust. This goes to prove that the primary source of lead is contaminated soil, through airborne pollutants from industry emission (Díaz-Barriga *et al.* 1997).

Table 2.5: Lead, Arsenic and Cadmium Levels in Surface Soil and Household Dust

	n	Mean (mg/kg)	SD (mg/kg)	Range (mg/kg)
Lead				
Soil-				
Sector I	6	302	111	150-425
Sector II	8	241	174	28-537
Sector III	8	81	58	31-197
Control	3	43	21	26-73
Dust-				
Sector I	3	285	8	280-295
Sector II	7	356	176	215-721
Sector III	9	202	121	21-363
Arsenic				
Soil-				
Sector I	8	25.2	17.1	5-51
Sector II	7	21.4	14.7	3-36
Sector III	4	19.5	6.2	13-27
Control	3	8.6	6.7	2-18
Dust-				
Sector I	4	38.7	17.5	30-65
Sector II	6	29.5	23.0	3-67
Sector III	4	18.7	6.5	13-27
Cadmium				
Soil-				
Sector I	8	6.9	5.5	0.5-16
Sector II	7	8.2	4.5	1-13
Sector III	4	5.5	3.7	2-9
Control	3	2.5	2.2	0.4-6
Dust-				
Sector I	4	10.0	4.4	6-15
Sector II	6	6.8	4.8	0.1-12
Sector III	4	6.2	1.0	5-7

Source: Díaz-Barriga *et al.* (1997)

Long range atmospheric transportation of pollutants is also recorded by Steinnes *et al.* (1997) in the natural soils of Norway. It was discovered that soils of southernmost Norway have a higher level of heavy metal contamination as compared to areas further north. Levels of concentration are higher for Pb, Zn, Cd and As. From the assessment of different regions of Norway, it was found that soils are exposed to atmospheric transport pollution by distant industries like Russian copper-nickel smelters which are situated close to the Norwegian border and other industries from other parts of Europe that are heavily industrialized and populated. Table 2.6 summarizes the findings of the study.

Table 2.6: Heavy Metals in Norway Soils and their Sources of Pollution

Element	Variability	Type of contamination	Source
Copper (Cu)	Small	Local	Russian copper-nickel smelter on Kola Peninsula Sulitjelma copper smelter in Nordland (closed in 1987) Kristiansand copper-nickel smelter in the south
Zinc (Zn)	Great	Long range Local	Sulitjelma smelter Zinc smelter at Odda
Arsenic (As)	Great	Long range	
Selenium (Se)	Great	Long range	From ocean to atmospheric (considered as a geographical factor)
Cadmium (Cd)	Great	Long range	-----
Antimony	Small	Local	Unknown
Lead (Pb)	Great	Long range	-----

Source: Steinnes *et al.* (1997)

Manz *et al.* (1999) report that fly ash emission from industrial areas, associated with mining and usage of lignite in Germany, causes hazardous acidic soils and accumulating levels of heavy metal concentrations in topsoil as time passes. Faraway sites from industries are also examined and it was discovered that metal contamination in topsoil is comparable to local sites nearer to the industrial area. Polemio *et al.* (1982) study on industrial and rural areas of Italy proved that higher contamination levels of Cd, Cu, Hg, Mn, Ni and Zn reside in industrial soils than rural soils. However, concentrations of As, Bi, Cu, Hg, Pb and Zn for both areas are higher than the mean world soil concentrations. This indicates a possibility of high atmospheric deposition of heavy metals from distant industries.

The problem of uncontrolled heavy metals emission from industries originates mainly in poor environmental controls in legislation and companies' lack of environment friendly practices. For example, there is no strong binding legislation to ensure compliance from plants in Kellogg (Idhao) and Bangkok (Thailand) in meeting emission standards from metal smelting (Ragaini *et al.* 1977; Wilcke *et al.* 1998). In addition, Hršak *et al.* (2000) demonstrated that lead smeltery companies in Kellogg (Idhao) with efficient bag filters installed lead to an improved reduction of lead, zinc and cadmium content in suspended particles (by 92, 94 and 89% respectively), and to a lesser extent in deposition (by 79, 75 and 68% respectively). Therefore, atmospheric deposition by industries is not an inevitable consequence only if industrial owners embrace ecological friendly practices and management.

2.3.3 Discharge from Industries

Besides atmospheric deposition which posed a risk to environment from industrial emissions, thoughtless disposal and storage of industrial wastes in the environment is also a major contributor of pollution into the environment. Studies have found evidence of bays and estuaries being contaminated with heavy metals transported via stormwater from nearby industries. Sediment tests from soil cores extracted from bays and estuaries indicated high heavy metal concentrations in sediments. These are the result of industries discharging wastes into open sewers. For instance, sediment tests from Garonne River (France), soil cores in the tributaries show high concentrations of metals, reflecting the impact of historic and present polluting upstream industrial activities that range from mining, calamine smelting, zinc works and more (Grousset *et al.* 1999). In Hobart, industries are supposed to disposed their waste proper into designated sewers. However, there are some cross-connections between stormwater and sewerage systems that also contribute to pollution levels (Coughanowr and Green 2001). Andronikov *et al.* (2000) also conducted a study of a historic industrial site near Falkirk (Central Scotland) which possessed chemical and iron works industrial plants between 1860 right up till the late 1960s. Results showed that the site is heavily contaminated with heavy metals that exceed threshold limits for domestic gardens, parks and open spaces. Water samples from a drain in the investigated site showed very high concentrations of Cr, As, Se and Br with values 22 820, 245, 350 and 6085 mg/L respectively.

Klein *et al.* (1974) studied electroplating plants sites in New York City and found out 250 plating firms had been discharging heavy metals directly into the sewers. The loadings of these metals into the stromwater are as follows: cadmium 30 kg; copper, 227 kg; nickel 477 kg and zinc 304 kg. Eighty five percent of these totals reached the treatment plants to be treated while the remaining 15 % was discharged into the harbor as untreated wastewater.

Lan *et al.* (2000) studied the country of Vietnam and showed that Ho Chi Minh City with the population of 5 million inhabitants, 700 big factories and 22,500 artisanal plants is mounting great pressure on the water sources (Saigon River) of the city. Pressure arises from limited controls of industrial and domestic waste discharges into these rivers. The irresponsible discharge of heavy metals into the environment is also reported by Chen *et al.* (1999). In the provinces of Jiangxi, Guizhou and Shengyang (China), many mining and smelting industries employ only simple indigenous techniques and crude equipment in extracting metals like mercury, zinc and cadmium. The recovery rate of these metals from metal ores was only 30-45% with the rest discharged into the environment, contributing to serious urban soil and stormwater contamination.

In Hobart, two main industries namely, Pasminco Hobart Smelter and Norske Skog Paper Mill have a long historic development in Tasmania. These developments along the Derwent Estuary have accounted for a high level of pollutants generated in the Derwent Estuary, especially heavy metals which has been an ongoing state concern. Since 1996, improvements has been made by these industries to reduce pollutant loads into the Derwent. Norske Skog has made an effort to treat wastewater at primary level (removal of solids and some resin acids and organic matter) prior to discharge but this effluent still contains large amounts of organic matter. Pasminco had reduced its pollutant loads by over 50% from several site improvements, including covering of stockpiles, rehabilitation of the Loogana area and construction of a second contaminated water pond. Nevertheless, despite these improvements, treated effluent from Norske Skog still contains large amounts of organic matter (approximately 95% of total anthropogenic Biochemical Oxygen Demand load) and some resin acids. Pasminco Smelter still accounts for much of the anthropogenic zinc load to the estuary (Coughanowr and Green 2001).

2.3.4 Building Materials/ Road Construction

Studies have shown that both landscape planning and building materials of urban environment play a crucial role in trapping and releasing heavy metal pollutants into the environment. Viklander (1998) discovered in his study of heavy metals in street sediments that sidewalks along roadsides promote the accumulation of sediments ladened with heavy metals generated by traffic flow. It was believed that sidewalks could have acted as barriers for larger particles that had not obtained enough energy from the vehicles to pass the curbstone. In this way, lighter particles are washed off first by water velocities. In addition, designs of roads have an impact on heavy metals concentrations in street sediments. For instance, in a street where the pattern of the road calls for the driver to apply the brakes very often, it is highly likely that Cu will show a greater concentration of sediments. Other heavy metals such as Cd, Pb and Zn are also most prominent in street sediments (Sartor *et al.* 1974; Morrison *et al.* 1984). Deletic and Maksimovic (1998) attempted the study of pollutant build-up and wash off on paved areas in urban cities and found that the accumulation of pollutants on impervious surfaces are very important.

Good (1993) and Herrmann *et al.* (1994) both investigated building materials and showed that buildings also promote the release of heavy metals. For example, it was found that high levels of Cu, Pb and Zn were detected in runoff from galvanized roof tops. Similarly, Karlén *et al.* (2001) commented that zinc as a metal with its good corrosion resistance has found widespread use in many buildings in the world. However, in assessing the potential risk of zinc corrosion, it is important to distinguish between corrosion and runoff. Runoff is the amount of metal being released from the corrosion-product layer during precipitation, and corrosion is the total amount of metal that has been oxidized. Potential risks include both metal runoff and metal incorporated in corrosion products. Past studies based on 1-5 years record show that initially runoff rate to be lower than corrosion rate. However, runoff rates remain constant whereas corrosion layer increases in thickness as corrosion rate decreases. After a number of years, the runoff rate and corrosion rate will be approximately equal. Thus, it is important to use runoff rates, rather than corrosion rate to assess the amount of metal dispersion from buildings. Table 2.7 shows chemical characterization of roof runoff.

Table 2.7: Chemical Characterization of Roof Runoff of the Sampling Period

Chemical species	October 1998	June 1999
Zinc (mg/L)	0.2 – 8.3	0.3 – 11.8
pH	5.1 – 6.3	5.9 – 6.9

Source: Karlén *et al.* (2001)

Another study of roof runoff involves the measurement of suspended solids and lead runoff from rooftops with different materials namely, tar felt, pantile, fibre cement, zinc sheet and flat gravel. It was found that suspended solids for each material recorded 260%, 210%, 280%, 400% and 26% respectively, compared to average concentrations of 17 mg/ L during the first 0.25 mm rainfall. Also, concentrations of particulate Pb differ greatly. This can be explained by different amounts of dry deposition before onset of rain and different washoff efficiency of suspended solids caused by roof roughness and resistance to flow (Quek and Förster 1993).

2.4 Urban Catchment As Heavy Metals Source in Stormwater

As described in Section 2.3, urban catchments have been collecting heavy metal pollutants from differing anthropogenic activities. These pollutants are not just trapped in the environment but also constantly mobilized through agents of wind and water. In this study, the importance of water as an agent is focused on. Heavy metal pollutants are constantly washed into stormwater during rain events. In such manner, the urban catchment becomes a source of heavy metals.

Brinkmann *et al.* (1985) and Walker *et al.* (2001) commented that roofs, walls, pavements and roads produce a "landscape of microdepressions", the surfaces of which are considerably rough. Low-intensity rainfall and frequent drying-rewetting procedures trap dissolved solids and suspended matter in these "microdepressions". Only heavy rains and strong winds are able to release the attached compounds from the urban watershed. Similarly, several factors like rain intensity and dry antecedent period will affect the level of sediment loadings in the stormwater. Therefore suspended sediment concentrations in stormwater fluctuate commonly in a rain hydrograph. This implies a sudden outbreak of high sedimentation could occur anytime in a storm event (Grimshaw and Lewin 1980).

There have also been vast amounts of work done in monitoring contaminated sediment runoff from urban cities into estuaries and bays (Christensen *et al.* 1978; Owe *et al.* 1982; Bhaduri *et al.* 1995; Crawford *et al.* 1995; Deletic and Maksimovic 1998; Lan *et al.* 2000; Parker *et al.* 2000). Deletic and Maksimovic (1998) highlighted that sediment transportation during storm runoff in urban areas is significant in terms of mass and has additional importance because other pollutants, such as heavy metals, are primarily associated with fine suspended particles.

Lan *et al.* (2000) study of Vietnam indicates stormwater pollution is clearly evident as toxicity levels in sediments from canals in the urban areas (where industrial and domestic activities are concentrated) are higher than the sediments in the river bed. As similar situation of urban runoff carrying trace metals is also reported by Owe *et al.* (1982) claming bottom sediments downstream of a highly urbanized area tends to have higher levels of metal concentrations than upstream sediments. This is due mainly to accumulation of pollutants from atmospheric fallout on urban surfaces that were washed off during rainfall. Another case study by Stark (1998) demonstrates the problems of urban runoff. It was found that urban runoff from urbanized catchments in Sydney (Australia), comprised of both dissolved metals in runoff and small grain size particle with trace metals attached to them, has been polluting bays and estuaries. Concentration of Cu is 3-14 times that of unpolluted bays, Pb is 3-12 times and Zn is 8-24 (Stark 1998).

Christensen *et al.* (1978) investigated the rate of sedimentation at Upper Newport Bay in California and found it to be 2.0 ± 1.0 cm/yr. High levels of Zn and Pb were recorded. The highest level of Pb (132 ppm) was found close to the mouth of the channel draining an urban area. It was found that lead contamination is associated closely with large grain size (> 0.45 μm), indicating these coarser materials are transported during intense storm events. Crawford *et al.* (1995) who also studied sediment pollution in New Jersey found that heavy metal contamination at Newark Bay was lower than its tributaries. Highest metal concentrations were found in the lower Passic River, Arthur Kill and Hackensack River. For example, Pb and Hg concentrations (3209 ppm and 31 ppm respectively) in Arthur Kill are higher than Newark Bay (24 ppm and 0.1 ppm). It is believed that sewage discharge produced by the expanding population accounts for the water quality of Newark Bay. In addition, with the combined sewer overflows which are prevalent in New Jersey, discharge from industries in high volumes over short period of time cause great deterioration of urban stormwater discharging into the estuary.

Bhaduri *et al.* (1995) explored the transportation process of sediment from construction sites and commented that sediment size of 43 microns in urban stormwater represents only 5.9% by weight of the total solids but contains 50% of the heavy metals and 33% to 50% of the algal nutrients. This suggests runoff leaving a basin with little sediment may still carry large chemical pollutant load.

It has been found that toxicity of stormwater does not rely solely on individual metals but was also dependent on the presence of other heavy metals. For instance, the presence of Pb increased the toxicity of Cu and Zn, there was also an increase in metal toxicity as pH decreased from 8 to 5, and toxicity increased when suspended solids concentrations increased from 50 to 200 mg/L.

Researchers have investigated the complexity of heavy metals in stormwater. Studies have shown that certain heavy metals transported in stormwater exhibited higher concentrations in particulate form than dissolved form, or vice-versa. Harrison and Wilson's (1985) study on trace metals from highways explains that major ions namely, potassium (K) and magnesium (Mg) occurred in dissolved form and trace metal, Mn is predominately dissolved too. At the same time trace metals, Pb and Fe were largely in particulate form (>0.45 μm). Metals which showed an intermediate behaviour were Cu and Cd. It was also found that the first-flush seems to contain more of the dissolved components. Morrison *et al.* (1984) conducted a study on dissolved and suspended heavy metals through an urban hydrograph, commented that metals namely, Zn, Cd and Cu are found to be present mainly in the dissolved phase. A higher concentration of Pb was associated with the suspended solid phase. However, it was also found that Pb in dissolved phase is more dominantly available during the later stage of a storm event. Also, high levels of metals, particularly Cu, are found in stormwater solids which may be due to the high percentage of particulate organic material in the runoff. Fine particles that predominate in stormwater solids are generally enriched with heavy metals. Therefore, leading to higher metal levels in stormwater solids than in corresponding raw street sediment.

Besides urban catchments, residential catchments with a small amount of light industries were also examined for heavy metals in stormwater. Mosley and Peake (2001) conducted such a residential catchment stormwater study in Dunedin (New Zealand). Results show highest concentration in Fe, followed by Zn, Cu and Pb (Table 2.8). During both base-flow and storm-flow conditions, Fe and Pb were predominantly associated with >0.4 μm particulate material. In contrast, Cu and Zn was found in < 0.4 μm fraction during base flow. However, during storm-flow, these metals increased in concentrations significantly.

Table 2.8: Total Metals in Urban Stormwater from Kaikorai Valley, Dunedin (New Zealand)

Metals	Base Flow		Storm Flow	
	Median	Range	Median	Range
Fe (Total) (μg/L)	674	643 - 932	1833	575 - 1706
(<0.4 μm)(μg/L)	243	188 - 261	171	98 - 645
Pb (Total) (μg/L)	4.9	3.7 – 13.9	34.0	5.7 – 94.5
(<0.4 μm)(μg/L)	0.8	0.3 – 2.4	2.9	0.3 – 16.5
Cu (Total) (μg/L)	3.2	2.8 – 4.3	21.9	4.5 – 56.4
(<0.4 μm)(μg/L)	3.1	2.4 – 4.0	9.7	4.1 – 15.7
Zn (Total) (μg/L)	46	32 - 81	233	101.0 – 883.3
(<0.4 μm)(μg/L)	43	22 - 66	107	74.2 – 243.5

Source: Mosley and Peake (2001)

2.4.1 The First-flush of Stormwater

The first-flush effect of stormwater is based on the premise that much of the material that accumulates on the surfaces of the urban environment during dry weather period is swept up in the first wave of runoff from a new rainfall. This suggests that a disproportionately large fraction of contaminants might be removed through treatment of the stormwater eluting during the earliest stages of a storm (Helsel *et al.* 1979; Characklis *et al.* 1997). Gupta *et al.* (1999) study of Talkatora Lake, Jaipur found the first-flush of stormwater from the adjoining residential and commercial area was a major cause of pollution in the lake. On the other hand, Deletic and Maksimovic (1998) in their study of two small urban catchments at Belgrade in Yugoslavia and another in Lund in Sweden do not detect a first-flush effect in their stormwater. It seems that the first-flush effect is more likely to occur during large storm events with higher intensity.

Helsel *et al.* (1979) explain that defining first-flush is problematic when we define first-flush in terms of concentration because concentration is flow dependent. For example, a storm discharge could possibly have the highest Total Suspended Solids (TSS) concentration in the beginning of the storm and also obtained similar TSS concentrations in another time period during the same storm. Perhaps, the first-flush should be defined as the out flush of pollutants and TSS during the initial stage of the storm. If this first-flush is found to be significantly lower than rise in TSS concentration in the later stage of the storm, it may be considered as a "weak" first-flush (Sansalone *et al.* 1997). First-flush effect varies according to different land uses. However, it has been hypothesized that first-flush effect will increase as urbanization increases. For instance, commercial sites were found to have shown a first-flush effect 90% of the time, considering all extractable metals. High rise and other residential sub-basins indicated an extractable metal first-flush in an average of 80% of all storms. The agricultural sites averaged 64%, and the forested site 0% for all storms. The frequency of soluble metals in the first-flush were lower than extractable metals. Commercial high-rise, townhouse/apartment, and high-density residential sub basins averaged a 78% incidence of soluble metal first-flush. The agricultural and residential stations averaged a 52% flush frequency, while the forested site again showed no first-flush (Helsel *et al.* 1979).

Wiber and Hunter's (1975) study on two sub catchment basins in Lodi (New Jersey) found that first-flush effect is evident shortly after the initation of runoff, usually within the first 30 minutes. Land use patterns between the two sub basins varies as follows: sub-basin 1 (size: 18 acres, residential 30%, commercial: 58% and industrial: 12%) and sub-basin 2 (size: 25 acres, residential 53%, commercial: 42% and industrial: 5%). Both sub-basins produced a peak concentration of heavy metals, lead, zinc and copper in the first-flush. On the other hand, such hypothesis is not always true. There are only some studies that show evidence of the first-flush phenomena (Weibel *et al.* 1964; Whipple and Hunter 1977 and Hunter *et al.* 1981) and it seems to date that phenomena of first-flush effect have been largely limited to watersheds smaller than 10 km^2 (Characklis *et al.* 1997).

2.5 Local Context

The vast literature of stormwater studies has indeed proved stormwater quality is an important aspect that should be undertaken and managed in every state and nation. In Hobart, the Derwent Estuary Program is designed to reduce pollution in the Estuary. One of main objectives is to reduction pollution in stormwater flowing into the Derwent (Coughanowr and Green 2001).

To counteract the issue of stormwater pollution in Derwent is a costly project to undertaken. It is not possible to treat all stormwater discharges given the large number of catchments and stormwater outfalls that drain to Derwent. Regional strategy has been implemented to minimize the amount of discharges by new developments, to localized practices in land use management. Reduction of pollutants is carried out through new technologies including gross pollutant traps, stormwater reuse, education programs, constructed wetlands and catchment management (Coughanowr and Green 2001). On the other hand, new proposed strategies and actions have been outlined. They are the following:

1. Improve existing monitoring to better assess stormwater pollutant loads and ecosystem effects,
2. Develop and implement stormwater planning controls for new developments,
3. Prioritise stormwater catchments as a basis for management,
4. Develop stormwater catchment management plans,
5. Target land uses and land use practices that generate significant stormwater flows and pollutant loads and develop/implement source control strategies,
6. Reduce sewage/stormwater cross connections to minimize faecal contamination of stormwater, encourage stormwater reuse initiatives, particularly at source, and
7. Educate and inform businesses, contractors and the community about how their actions can reduce stormwater impacts and about the potential risks of stormwater pollution.

2.5.1 Local Studies Undertaken

Similarly, there have been studies of urban stormwater pollution in Hobart. Jenkins (1991) conducted a study of urban stormwater from general land use comprised of mostly residential use, with light industries occupying 5% of the total study site. It was found that total suspended solids at baseline prior to floodflow was 10 mg/L. It rises to a maximum of 114 mg/L and coincides with the peak flow of the hydrograph. Incidentally, the increase in metal pollutants in urban stormwater also increases. Concentrations of zinc and lead were 0.25 mg/L and 11 μg/L respectively during baseline levels. Concentrations increased similar to TSS, reaching their maximum of 2.74 mg/L and 50 μg/L during the peak flow of the hydrograph. We could infer a positive relationship between TSS and heavy metal concentrations in urban stormwater quality of Hobart. In his study, Jenkins used pH, temperature, conductivity, TSS, zinc, lead, nitrate and phosphate as parameters. An increase in pollutants towards the city centre was noted, however no pollution sources were described.

Tuit (2001) also investigated TSS concentrations in Sandy Bay Rivulet and recorded the highest TSS concentration of 621 mg/L. However, nothing is mentioned with regard to heavy metals concentrations in relation to sediment.

Blacklow (1995) has conducted a microbiological study of a Hobart major urban stream, the Hobart Rivulet. The main conclusions of the study were that human sewage contaminated soils were thought to be the primary contributor to faecal contamination of the rivulet during dry weather but during wet weather the main source was animal faecal material from surface runoff.

Green (1998) conducted a study on faecal and hydrocarbon pollution in urban stormwater discharge to the Derwent Estuary. Results showed that animal faecal input into the Derwent Estuary reaches 10 tonnes in Hobart every day. For hydrocarbons, it was estimated to be an annual input of 245 and 293 tonnes. However, the hydrocarbon assessment did not take into account specific potential inputs from tanker operations, runoff from factory sites or from boating and shipping activities.

In the Prince of Wales Bay project in Tasmania, Green (1999) also reported high pollution levels of Prince of Wales Bay in the Estuary. It is believed that runoff from urban areas and historic landfills and industries (Pasmico zinc works) located close to the bay are responsible for heavy metal pollution. It has also been found that sediment from stormwater drains at Prince of Wales Bay site is also contaminated with heavy metals. Studies by Hanslow (1994), Pirzl (1996) and Derwent Estuary Program study (2000/2001) have shown a decrease in heavy metals concentration in sediment from the Derwent Estuary since 1975. However, present concentrations are still at high levels, especially Zn. The decrease in heavy metal concentrations is mainly due to reductions in heavy metals discharge by Pasminco Zinc Works. On the other hand, show sediments in the Derwent Estuary are still heavily enriched with heavy metals even though they are of lower concentrations than previous years (Table 2.9). Study by Pirzl (1996) studied a total of 38 sites and found highest contamination is found in Sites 14, 15 and 18. This is because of their proximity to Pasminco Metals and Sites 20 and 22 are sites of lower contamination. The lowest levels of heavy metals are found in Sites 39 and 40 which are far from Pasminco Metals. Certain sites are near to discharge points of three rivulets sampled in this study. They are Sites 14 and 15 which are near discharge point of New Town Rivulet. Site 18 is near discharge point of Hobart Rivulet and site 22 is near Sandy Bay Rivulet. Similarly, State of Derwent Report (2001) has also indicated heavy metals are still a problem in the Estuary (Table 2.10). Even though heavy metal concentrations were studied in the receiving environment of the Derwent Estuary, there is no mention of the role of stormwater towards these levels of heavy metals.

Table 2.9: Distribution of Heavy Metals in Derwent Estuary

Site	Zn (mg/kg)	Cd (mg/kg)	Mn (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	Al (mg/kg)	As (mg/kg)
14	19201	134.2	780.5	529.9	53811	2078	29622	20.90
15	6163	43.26	527.8	232.7	48610	1108	29122	12.13
18	1932	8.676	149.1	167.9	30799	684.8	21662	0.304
20	1858	7.339	264.9	90.18	25610	525.7	15761	0.370
22	761.7	2.826	104.6	38.74	23783	228.2	17300	0.205
39	26.80	0.000	69.93	1.471	6837	11.01	2758	0.117
40	33.98	0.117	65.86	1.172	4926	9.375	1727	0.076

Source: Pirzl (1996)

Table 2.10: Area of Derwent Estuary Sediments as compared to Probable Ecological Effects Guidelines

Metal	Negligible Effects	Low to Medium	Medium to High
Mercury	1%	34%	65%
Lead	23%	38%	39%
Zinc	32%	20%	48%
Cadmium	36%	52%	12%
Copper	74%	23%	4%
Arsenic	79%	14%	7%

Source: DEP (2001)

CHAPTER 3 – Methodology

3.1 Climate

The study is conducted in the City of Hobart which is the capital city of Tasmania. Tasmania is an island lying adjacent to the Tasman Sea; south of the southeast corner of the Australian mainland (Figure 3.1). It is the smallest of Australia's six states. The City of Hobart (Latitude 42° 55' 0S, Longitude 147° 19' 60E) (Figure 3.2) situated in south eastern Tasmania is dominated by the geographical presence of Mount Wellington. Tasmania has a mountainous topography so it comes as no surprise that Mount Wellington exerts a significant influence on the climate of Hobart. Hobart experiences orographic rainfall generated by Mount Wellington which generates an average annual rainfall of 624 mm. This makes it the second driest capital city in Australia besides Adelaide which records 555 mm (CBMA 2001). With regards to the orographic precipitation, rainfall decreases as distance from Mount Wellington increases. Therefore, higher rainfall is experienced in the Western shore of the city (i.e. suburbs such as Sandy Bay and West Hobart) than compared to the Eastern shore of Hobart (i.e. suburbs such as Lindisfarne and Rosny) (Tuit 2001). Yearly rainfall is distinctive with lower rainfall experienced from January to May and higher rainfall from June to December (CBMA 2001).

Figure 3.1: Location of Tasmania in Australia

Figure 3.2: Location of Hobart in Tasmania

3.2 Catchment Characteristics

The City of Hobart is characterized by 27 sub catchment basins and 49 stormwater outfalls into the Derwent Estuary (Figure 3.3). Every catchment basin is drained by a creek, gully and then a rivulet which together form the hydrological network of the City of Hobart. Three major rivulets namely, Sandy Bay Rivulet, Hobart Rivulet and New Town Rivulet flow through the City of Hobart, discharging their flows into the Derwent Estuary. Each rivulet draws its source from Mount Wellington as well as other creeks and gullies, which flow through varying land use in its catchment. Land use of these catchments could generally be classified into the following:

1. Commercial,
2. Light density residential,
3. High density residential,
4. Rural,
5. Recreation,
6. Service and light industry, and
7. Special use.

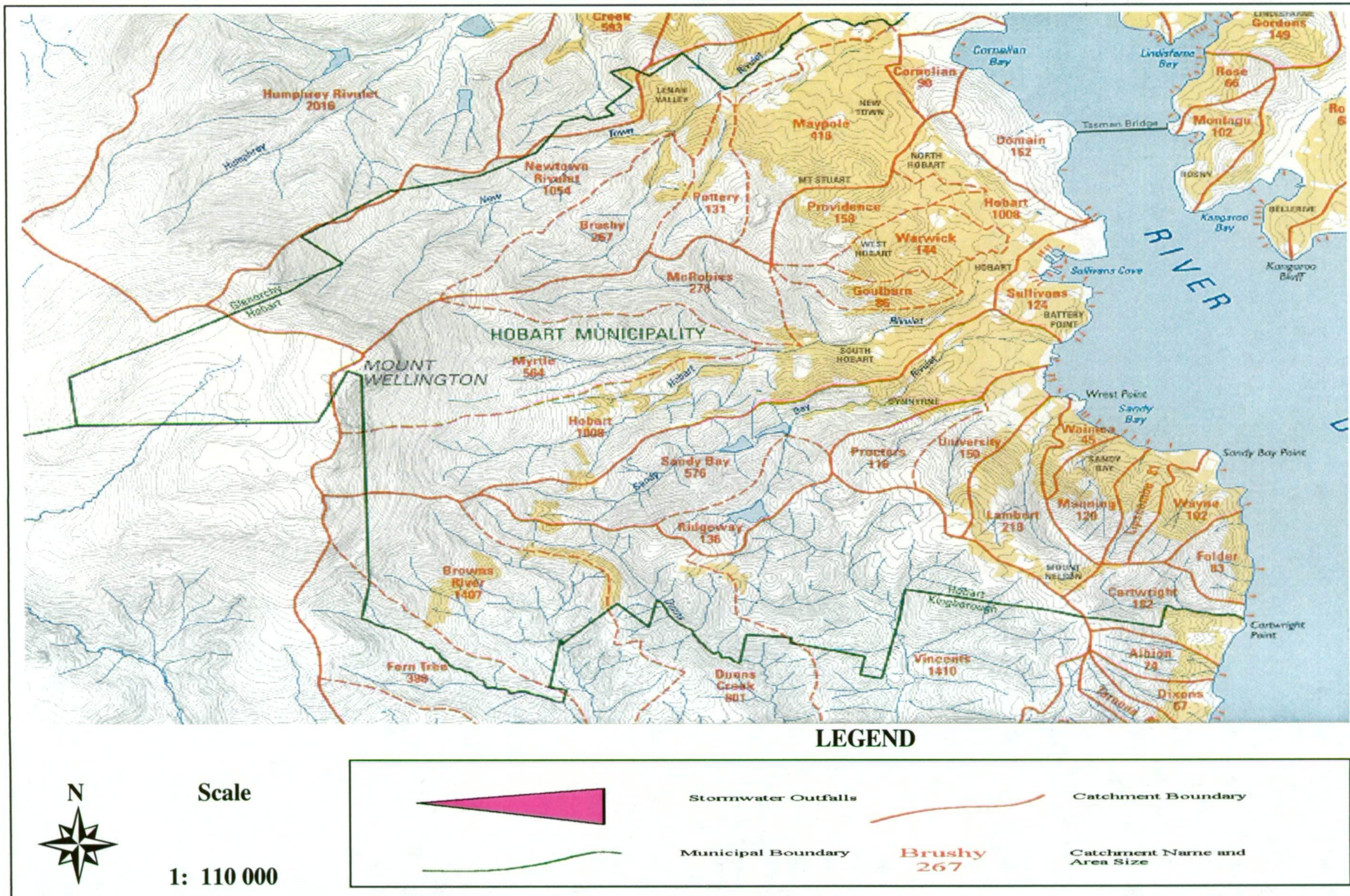
In the City of Hobart, light industries occupy only a small percent of area in the catchment basins. There are 3 major industrial developments in Hobart which are located along the Derwent Estuary. They are, Pascminco Metals – EZ Zinc Refinery at Risdon, Cadbury Chocolate Factory at Dogshear Point and Norske Skog Newsprint Mill at Boyer. It is believed that majority of zinc concentrations in Derwent Estuary still originates from Pasminco Metals (Coughanowr and Green 2001).

Table 3.1 presents a summary of land use patterns in the three catchments as shown in Figure 3.4. The percentages of each landuse in the catchments are calculated as a rough estimate from Figure 3.4. Each catchment is briefly described in the following sections.

Table 3.1 Summary of Landuse in each Catchment

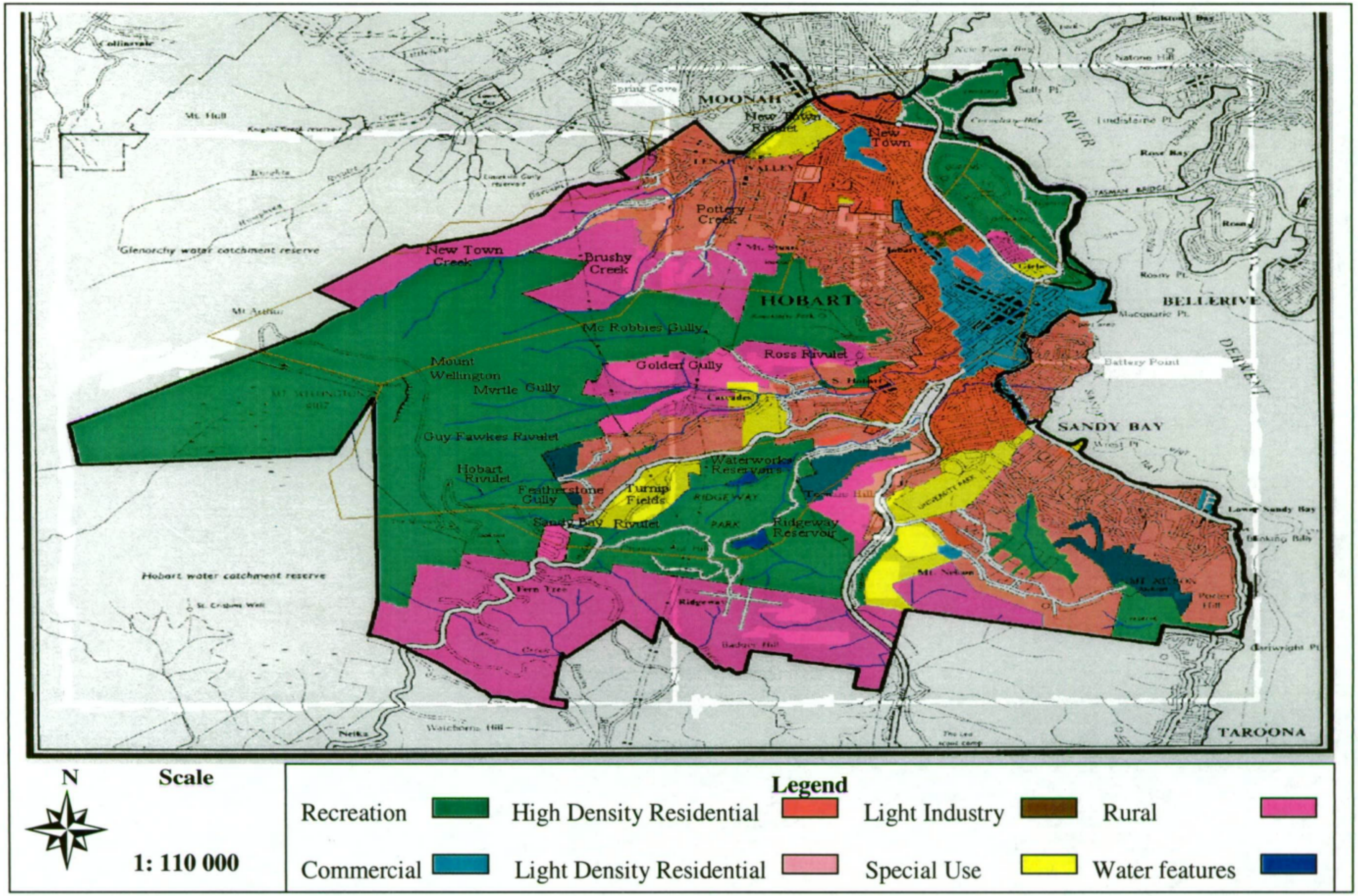
Land use	Sandy Bay (712 ha)	Hobart (1572 ha)	New Town (1868 ha)
Recreation	55 %	50 %	35 %
Rural	3 %	10 %	30 %
Lower Density Residential	20 %	15%	15 %
Higher Density Residential	10 %	8 %	10 %
Special Land use	10 %	5 %	5 %
Commercial	2 %	10 %	5 %
Light Industry	----	2 %	----

Figure 3.3: Catchments of City of Hobart



Source: Service Tasmania (2001)

Figure 3.4: Land Use Pattern of City of Hobart



Source: Hobart City Council 2001

3.2.1 Sandy Bay Rivulet Catchment

The Sandy Bay Rivulet is a waterway flowing from the slopes of Mount Wellington bypassing Ridgeway Reservoir and Waterworks Reserve. The source comes from the Springs of Mt Wellington. It flows a distance of approximately 7.5 km in length and drains two catchments namely, Sandy Bay and Ridgeway. The areas of the two catchments are 576 ha and 136 ha respectively (Figure 3.3). The waterway passes through the suburbs of Sandy Bay and ends its course at Marieville Esplanade. Industries are absent from the catchment with exception of four old and disused quarries located at Ridgeway Reservoir, Waterworks Reservoir, Old Waterworks Road and Stoney Steps Road. These quarries provided the bulk of granite for the construction of Ridgeway and waterworks reservoirs in the past.

Land use of Sandy Bay Rivulet catchment can be divided into 5 distinct categories. From the headwaters, it is dominated by E.Pulchella grassy woodland forest to Waterworks Reserve. The forest catchment is reserved for nature conservation and water catchment. It is also allocated as public recreation with small walking tracks located within and around the reserve. Rural landuse is also found in the reserve between Halls Saddle and Mountainside Saddle (Figure 3.4). From the forest catchment, the rivulet passes through Turnip Fields (special use) which comprises several small farms. As the rivulet flows through Sandy Bay to Battery Point, landuse changes from light density residential to high density residential. In addition, draining a small commercial landuse in Battery Point and Sandy Bay Road. Plate 3.1 shows the site of sample collection in Sandy Bay Rivulet.

Plate 3.1: Site of Sample Collection at Sandy Bay Rivulet

3.2.2 Hobart Rivulet Catchment

Hobart Rivulet is a waterway that flows a distance of approximately 8.5 km in length and drains two catchments namely Myrtle and Hobart. The area of these two catchments are 564 ha and 1008 ha respectively (Figure 3.3). Similar to Sandy Bay Rivulet, its source comes from Mount Wellington but is joined by several other smaller flowing waterways namely, Guy Fawkes Rivulet, Featherstone Gully, McRobies Gully and Ross Rivulet (Figure 3.4). With a bigger catchment area, the landuse of the catchment is also more varied and includes a significant area of light industry and commercial use.

Hobart Rivulet starts its course from mountain reserve (Betts Vale Track), which is reserved for recreational use before being joined by Featherstone Gully whose source comes from a light residential area and the northern side of Turnip Fields. McRobies Gully drains a catchment which Hobart City Council describes as recreational zone. However, the Gully drains a large controlled disposal area. Materials disposed of at McRobies Gully include, domestic refuse, secondary treated sewage sludge, lime slurry, medical waste (including infectious waste) and hazardous materials (Jenkins 1991). The Hobart Rivulet later drains through light density residential housing followed by Cascade Brewery (Special land use), which uses the waterway for cooling purposes (Figure 3.4). Hobart Rivulet later is joined by Guy Fawkes Rivulet draining water from Old Farm Track of the Mountain Park and flows along Old Farm Road providing drainage for the rural land use. Headwaters of Guy Fawkes Rivulet comes from Myrtle Gully which runs along Myrtle Gully track located on the slope of Mt Wellington, and Golden Gully which drains water from Wellington Park cutting across middle Island Fire Trail. The Hobart Rivulet then continues its course through light density residential in South Hobart before entering high density residential at Central Business District (CBD) along Macquaire Street and Davey Street. The CBD area is characterized by large commercial and retail service shops and various light industries. For example, automobiles repair centres and small hardware workshops. It also provides drainage for both high and low density residential areas of West and North Hobart. Plate 3.2 shows the site of sample collection in Hobart Rivulet

Plate 3.2: Site of Sample Collection at Hobart Rivulet

3.2.3 New Town Catchment

The New Town Rivulet is a waterway which flows a distance of approximately 9.5 km in length and drains New Town Rivulet, Brushy, Pottery and Maypole catchments. The sizes of these catchments are 1054 ha, 267 ha, 131 ha and 416 ha respectively (Figure 3.3). Like Sandy Bay and Hobart Rivulet, its headwaters begin at Mount Wellington and it flows through the suburbs of Lenah Valley and New Town. Like Hobart Rivulet, it is joined with other smaller watercourses. New Town Rivulet begins as a small creek from Mount Wellington. It is connected with three creeks namely Brushy Creek and Pottery Creek which form into New Town Rivulet at Lenah Valley Road, and is connected with Maypole creek before it reaches its mouth. These creeks drain their respective catchments as shown in Figure 3.3.

Land use of New Town Rivulet catchment could be described as follows; New Town Creek starts its course as mountain park and rural land. Drainage of the catchment's recreation and rural land use comes mainly from Brushy Creek and Pottery Creek. New Town Rivulet continues its course draining lower density residential areas at Lenah Valley Road and light industries For instance, a dairy factory is also located at Lenah Valley. The New Town catchment also includes special land use area which is characterized by brickworks (drained by Maypole Creek) and Department of Primary Industries Laboratories. Landuse changes into higher density residential and small commercial area. The mouth of the rivulet ends at New Town Bay concurrently draining recreational land (Rugby Park) at Cornelian Bay. Plate 3.3 shows the site of sample collection at New Town Rivulet.

Plate 3.3: Site of Sample Collection at New Town Rivulet

3.3 Sampling Techniques

In this study, rainfall events with 3 antecedent dry days or more are selected for sampling. It is assumed that the first flush of the rain event takes place during the first 30 minutes of the rain event and samples are collected within this time period. The method of grab sampling is done by dipping a water bucket manually at a depth of 10 cm from the water surface in order to collect fine suspended sediments in stormwater. The dipping action is repeated till 5 - 15 litres of stormwater is collected and stored in plastic containers. After collection, the stormwater samples are stored in the dark at a temperature of 9 ^{0}C. All stormwater containers, before use, were sterilized by rinsing with 10% nitric acid (HNO_3) (i.e. 1 L of distilled water mixed with 100 mL of concentrated HNO_3), followed by rinsing with distilled water.

In total 11 stormwater samples were collected at differing rainfall intensities. They include: 4 samples from Hobart Rivulet (Samples 1,2, 4 and 9), 3 samples from New Town Rivulet (Samples 6, 7 and 13), 2 samples from Sandy Bay (Samples 8 and 12), 1 from street runoff from Davey Street in the suburbs (Sample 10) and 1 sample from Hobart Rivulet before entering the urban catchment and is used as the background sample in this study (Sample 11). However, only 9 samples are considered as suitable and accurate. They include samples 2, 6, 7, 8, 9, 10, 11, 12 and 13. Samples 1 and 4 are considered unsuitable for comparisons in this study. This is because Sample 1 is collected at different site even though it is collected from Hobart Rivulet. Sample 4 is collected an hour after Sample 2 is collected. Therefore, Sample 4 is not considered as first flush sample in this study. Details of data collection process is shown in Table 4.1.

Suspended sediment is extracted from the collected stormwater samples through a filtration process. Membrane filter papers of 0.45 μm pore size are used for filtering. These filter papers are dried under 105 ^{0}C for 24 hours and weighed before use. The filtration is carried out by 250 mL capacity inlet into a 2-litre vacuum flask which is emptied when it fills up. The vacuum flask is kept under vacuum constantly by connecting it to a water hose which in turn is connected to a running water tap. The 250 mL inlet is constantly being fed by an inverted 2 litre glass bottle filled with stormwater sample (Plate 3.4). The stormwater plastic containers are shaken to get a well mixed suspended sediment in the stormwater before filling the 2 litre glass bottle.

Clean filters are replaced after every 24 hours to accelerate the filtration process. After every filtration, filters with sediment residues were dried at a temperature of 105^{0}C for 24 hours, followed by dessication and reweighed to determine the weight of residue sediment. The volume of filtered stormwater is measured. Together with the weight of sediment, suspended solids concentration could be calculated. pH of both unfiltered stormwater and filtered stormwater are measured using a pH meter (model pH 320). The pH meter was calibrated using the buffer solutions with pH values of 4 and 7.

Plate 3.4: Filtration Process

3.4 Chemical Analysis

Filtered sediment (0.03 - 0.1 g) and filtrate are sent to Analytical Services Tasmania for heavy metals analysis. Sediment is analyzed using United States Environmental Protection Agency (USEPA) standards using standard method 200.7. This method is known as Aqua Regia Digestion process which is explained in detail in sections 3.4.1 and 3.4.2.

3.4.1 Sediment Analysis

Sediments are mixed with 5 mL of acid solvent which is comprised of concentrated nitric acid (16 molarity) and concentrated hydrochloric acid (12 molarity) at ratio of 1: 3 respectively. The mixture is digested at a temperature of 100 degrees Celsius for 4 hours (Plate 3.5). After 4 hours, de-ionised water is added to the mixture to make up 50 mL (Plate 3.6). This 50 mL of solution will be sent through the Inductively coupled Plasma-atomic Emission Spectrometry (ICP) to be analyzed for heavy metal concentrations (Plate 3.7).

Plate 3.5: Digestion of Samples in Nitric Acid in Process

Plate 3.6: Samples in Test-tube after Digestion ready for ICP Analysis

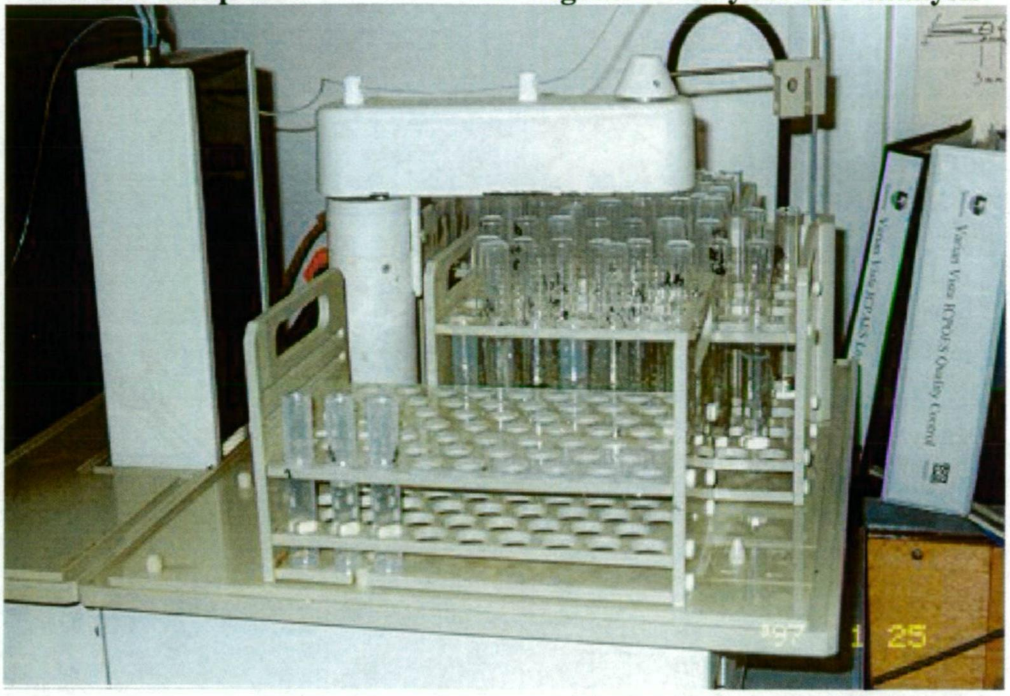
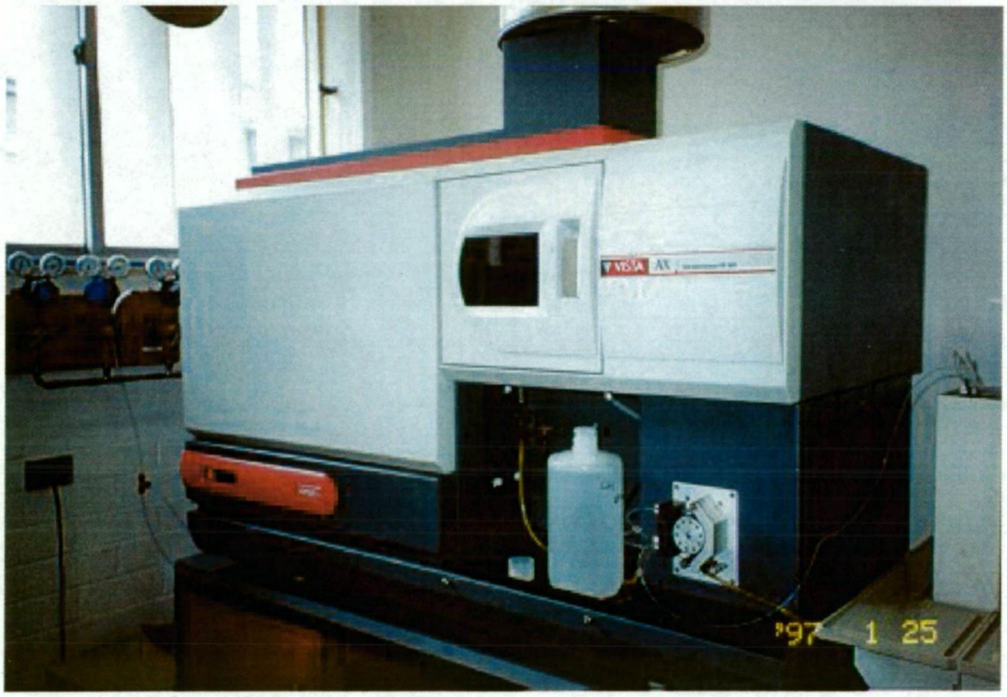


Plate 3.7: Inductively coupled Plasma-atomic Emission Spectrometry



3.4.2 Filtrate Analysis

In the digestion of an aqueous solution, 5 mL of 10% acidified nitric acid is added to 50 mL of sample. The mixture is heated at a temperature of 95 degrees Celsius until the mixture is reduced to 30 mL. De-ionised water is added to the 30 mL digested mixture to make up 50 mL. This is followed by analysis of heavy metals by the ICP.

CHAPTER 4 - Results

4.1 Data Collection

The data collection process is shown in Table 4.1. To ensure that significant amount of pollutants were washed off from the catchment for collection as first-flush stormwater samples, light drizzle rainfalls were neglected. Therefore, only stormwater during medium and high intensity rainfall events were sampled.

Table 4.1: Data Collection Process

Sample	Date	Time (hrs)	Rainfall (mm)	Rain intensity	Antecedent Dry Period (Days)	Sediment Weight (g)	Stormwater filtered (L)	Location
2	05/11/01	1850	11.8	Medium	4	0.0988	5.28	Hobart Rivulet
4	05/11/01	2235	11.8	High	4	0.0456	7.72	Hobart Rivulet
6	11/01/02	2100	15.8	High	3	0.273	11.19	Maypole Creek
7	08/02/02	1330	0.2	High	4	0.2507	15	New Town Rivulet
8	19/02/02	1340	No readings as recorded	High	3	0.7569	6.33	Sandy Bay Rivulet
9	28/02/02	1845	0.4	Medium	7	0.9126	9.15	Hobart Rivulet
10	28/02/02	1825	0.4	Medium	7	2.1661	5.12	Street Runoff
11	28/02/02	1825	0.4	Medium	7	0.0982	14.94	Hobart Rivulet in Suburbs Environment
12	11/03/02	2020	4.8	High	4	10.7055	4.49	Sandy Bay Rivulet
13	11/03/02	2040	4.8	High	4	0.8549	6.86	New Town Rivulet

Results of sediment and filtrates obtained from samples are shown as follows: Table 4.2 shows dissolved heavy metals concentrations (< 0.45 μm fraction), Table 4.3 and 4.4 show results of heavy metals concentrations in particulate form (> 0.45 μm fraction). Table 4.5 shows results of total metals concentrations in samples. Table 4.6 shows mean and standard deviation of heavy metal concentrations in filtrates, sediments and total metals of samples.

Table 4.2: Dissolved Heavy Metal Concentrations (µg/L) (< 0.45µm fraction)

Samples/ Metals	2F	4F	9F	6F	7F	13F	8F	12F	10F	11F
Al	26	27	43	<20	139	45	92	36	34	41
As	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Cd	<1	<1	<1	<1	<1	2	<1	1	<1	<1
Co	<1	<1	<1	<1	<1	1	<1	1	1	<1
Cr	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cu	18	12	13	13	5	10	11	8	12	1
Fe	47	55	36	28	78	75	62	69	225	184
Mn	6	<5	14	8	<5	108	85	463	41	<5
Ni	3	4	2	<1	2	2	3	3	4	<1
Pb	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Zn	321	326	370	294	84	250	47	89	391	39

Table 4.3: Heavy Metal Concentrations in Sediment (mg/kg)

Metals/ Samples	2S	4S	9S	6S	7S	13S	8S	12S	10S	11S
Al	22166	30701.8	36598.7	32710.6	23374.6	24798.2	26952	28303.2	27745.7	24949.1
As	<10.1	<21.9	6.6	11	12	5.9	6.6	3.8	3.2	<10.2
Cd	<10.1	<21.9	5.5	7.3	12	9.4	4	2.5	6.5	<10.2
Co	10.1	21.9	18.6	22	23.9	23.4	19.8	7.4	10.6	20.4
Cr	40.5	87.7	52.6	62.3	39.9	44.5	31.7	10.7	25.9	50.9
Cu	334	482.5	335.3	359	175.5	512.3	204.8	109.3	113.1	122.2
Fe	32894.7	50657.9	47775.6	NA	63422.4	42461.1	36596.6	36429.9	32131.5	37576.4
Mn	334	1030.7	336.4	725.3	188.7	428.1	1317.2	797.7	170.4	967.4
Ni	20.2	43.9	29.6	36.6	31.9	25.7	25.1	7.8	18	40.7
Pb	587	921.1	484.3	597.1	239.3	423.4	410.9	119.6	217.4	203.7
Zn	4210.5	4473.7	4459.8	5750.9	2321.5	2316.1	1625	1429.2	2114.4	1252.6

Table 4.4: Heavy Metal Concentrations in Sediment (µg/L)

Metals/ Samples	2S	4S	9S	6S	7S	13S	8S	12S	10S	11S
Al	414.8	181.4	3650.3	798	390.7	3173.7	3222.7	67483.3	11738.3	164
As	<0.2	<0.1	0.7	0.3	0.2	0.8	0.8	9.1	1.4	<0.07
Cd	<0.2	<0.1	0.6	0.2	0.2	1.2	0.5	6	2.7	<0.07
Co	0.2	0.1	1.9	0.5	0.4	3	2.4	17.6	4.5	0.1
Cr	0.8	0.5	5.3	1.5	0.7	5.7	3.8	25.6	10.9	0.3
Cu	6.3	2.9	33.4	8.8	2.9	65.6	24.5	260.6	47.9	0.8
Fe	615.5	299.2	4765		1060	5434.1	4376	86859.7	13593.8	247
Mn	6.3	6.1	33.6	17.7	31.5	54.8	157.5	1902	72.1	6.4
Ni	0.4	0.3	3	0.9	0.5	3.3	3	18.5	7.6	0.3
Pb	11	5.4	48.3	14.6	4	54.2	49.1	285.1	92	1.3
Zn	78.8	26.4	444.8	140.3	38.8	296.4	194.3	3407.6	894.5	8.2

Table 4.5: Total Metal Concentrations (µg/L) in Individual Sites

Parameter		Background	Percent	Hobart Rivulet Mean	Hobart Rivulet Range	Percent	New Town Rivulet Mean	New Town Rivulet Range	Percent	Sandy Bay Rivulet Mean	Sandy Bay Rivulet Range
TSS	mg/L	6.6		59.2	18.7-99.7		70.4	16.7-124		1252	119.6-2384.3
pH		7.2		7.1	6.6-7.6		7.1	6.9-7.3		7.4	7.3-7.5
Al (Total)	µg/L	4063.8		2067	440.7-3693.3		1522	529.7-3218.7		35417	3314.7-67519.3
(<0.45 µm)	µg/L	41	***1.7***	35	27-43	***4.5***	68	<20-139	***0.2***	64	36-92
As (Total)	µg/L	<6		5.5	5.2-5.7		5.3	5.3-5.7		10	5.8-14.1
(<0.45 µm)	µg/L	<5	***89***	<5	<5	***36.7***	<5	<5	***49***	<5	<5
Cd (Total)	µg/L	<1.9		1.4	1.2-1.6		1.8	1.2-3.2		4.3	1.5-7
(<0.45 µm)	µg/L	<1	***64.3***	<1	<1	***72***	1.3	<1-2	***23.5***	1	<1-1
Co (Total)	µg/L	<2.5		2.1	1.2-2.9		2.2	1.4-4		11	3.4-18.6
(<0.45 µm)	µg/L	<1	***42.9***	<1	<1	***40.9***	0.9	<1-1	***9.1***	1	<1-1
Cr (Total)	µg/L	4.8		4.1	1.8-6.3		3.5	1.7-6.7		15.7	4.8-26.6
(<0.45 µm)	µg/L	<1	***22***	<1	<1	***25.7***	<1	<1	***5.7***	<1	<1
Cu (Total)	µg/L	17.4		70.7	24.3-46.4		35.1	7.9-75.6		152.2	35.8-268.6
(<0.45 µm)	µg/L	1	***21.2***	15	12-18	***26.6***	9.3	5-13	***6.2***	9.5	8-11
Fe (Total)	µg/L	4842.6		2731.8	662.5-4801		3323.5	1138-5509.1		45683.4	4438-86928.7
(<0.45 µm)	µg/L	164	***1.7***	45.5	36-55	***1.8***	60.3	28-78	***0.1***	65.5	62-69
Mn (Total)	µg/L	29.7		30	12.3-47.6		75	25.7-162.8		1303.8	242.5-2365
(<0.45 µm)	µg/L	<5	***33.3***	10	6-14	***53.7***	40.3	<5-108	***21***	274	85-463
Ni (Total)	µg/L	3.6		4.2	3.4–5		3.2	1.9-5.3		13.8	6-21.5
(<0.45 µm)	µg/L	<1	***71.4***	3	2-4	***50***	1.6	<1-2	***21.8***	3	3
Pb (Total)	µg/L	31.5		34.7	16-53.3		29.2	9-59.2		172.1	54.1-290.1
(<0.45 µm)	µg/L	<5	***4.3***	<5	<5	***16.7***	<5	<5	***2.8***	<5	<5
Zn (Total)	µg/L	345.6		577.3	339.8-814.8		367.8	122.8-546.41		1869	241.3-3496.6
(<0.45 µm)	µg/L	39	***60.3***	348	326-370	***57***	209.3	84-294	***3.6***	68	47-89

Total metals from the three rivulets are plotted against background levels in Figures 4.1, 4.2, 4.3 and 4.4. In addition, concentrations of 5 significantly high metals Cu, Pb and Zn, and Ni and Mn are shown in Figures 4.5 and 4.6 respectively. Results of dissolved heavy metals (< 0.45 μm fraction) are shown in Figures 4.7, 4.8, 4.9 and 4.10.

Table 4.6: Mean Concentrations and Standard Deviations of Filtrates and Sediment among three rivulets

	Total Metals (μg/L)		Filtrates (μg/L)		Sediment (mg/kg)	
Heavy Metals	Mean	Std Deviation	Mean	Std Deviation	Mean	Std Deviation
Al	11362.1	± 24803.6	57.3	± 42.9	27843.3	± 5209.4
As	6.6	± 3.3	4.9	0	8	± 3
Cd	2.9	± 2.3	1.1	± 0.4	7.2	± 3.4
Co	4.6	± 6.25	0.9	± 0.06	17.9	± 6.6
Cr	7.1	± 8.8	0.9	0	40.3	± 16.3
Cu	68.6	± 90.8	11.1	± 4.1	290	± 136.1
Fe	17246.2	± 34196	56.4	± 19.7	43263.4	± 11189.7
Mn	413.2	± 864.9	98.4	± 166.2	589.6	± 388.9
Ni	6.5	± 6.8	2.3	± 0.8	25.3	± 9.3
Pb	71.5	± 98.5	4.9	0	408.8	± 175.8
Zn	865.1	± 1181.2	207.9	± 131.4	3159	± 1646.9

4.2 Partitioning of Metals

Results from Table 4.5, show that Cu, Zn and Ni are more dominantly found in dissolved form (< 0.45 μm fraction) in Hobart and New Town Rivulets while heavy metals in Sandy Bay Rivulet are predominately attached to particulate matter (> 0.45 μm fraction). Overall, Al, Fe, Pb and Mn all predominate in particulate matter in the three rivulets. However, in sample 13, Mn is shown to also occur strongly in dissolved form. High levels of Cu, Pb and Zn are found in particulate matter from street-runoff (Sample 10).

4.3 Total Metals

Sandy Bay Rivulet recorded the highest level of total metals discharged into the Estuary, followed by Hobart and New Town Rivulets. In Sandy Bay Rivulet, Cu recorded 8.7 times higher than background levels. Likewise, Mn is 43.9 times higher, Ni is 3.8 times higher, Pb is 5.5 times higher and Zn is 5.4 times higher. Hobart Rivulet records Cu being 2 times higher than background levels. Likewise, Mn, Ni and Pb show identical levels and Zn is 1.7 times higher. New Town Rivulet records Cu being 2 times higher than background levels.

Likewise, Mn is 2.5 times higher. Ni, Pb and Zn show identical levels when compared to background levels (Table 4.5).

However, these levels are only mean concentrations of samples taken from different rain events. The following shows the highest level of total metal concentrations for individual rivulets at different rain events. For Sandy Bay Rivulet, highest Cu concentrations exceed background levels by 15.4 times, Mn by 79.6 times, Ni by 6 times, Pb by 9.2 times and Zn by 10.1 times. Highest Cu concentrations recorded in Hobart Rivulet exceed background levels by 2.7 times. Likewise, Mn by 1.6 times higher, Ni by 1.4 times higher, Pb by 1.7 times higher and Zn by 2.4 times higher. In New Town Rivulet, highest Cu concentrations exceed background levels by 4.3 times higher, Mn by 5.5 times higher, Ni by 1.5 times higher, Pb by 1.9 times higher and Zn by 1.6 times higher (Table 4.5).

4.4 Sediment

Three metals, namely Cu, Pb and Zn, show elevated concentrations in sediments in the three Rivulets. Ranking highest when compared with background levels (Sample 11) is Hobart Rivulet, followed by New Town Rivulet and Sandy Bay Rivulet (Figure 4.5). Referring to Table 4.3, Hobart Rivulet, levels of Cu are 2.5 – 4 times higher, Pb 2.5 – 4.5 times higher and Zn 2 – 3.6 times higher. For New Town Rivulet, levels of Cu are 3 – 4 times higher, Pb 2 – 3 times higher and Zn 1.8 – 4 times higher. For Sandy Bay Rivulet, levels of Cu are 1.7 times higher, Pb 2 times higher and Zn 1.3 times. Ni concentration is recorded highest in New Town Rivulet, followed by Hobart Rivulet. Sandy Bay recorded a significantly higher level of Mn compared to the other two rivulets as well as background levels (Figure 4.6).

4.5 Dissolved (< 0.45 μm fraction)

Four metals, namely Cu, Mn, Ni and Zn, show high concentrations in dissolved form (< 0.45 μm fraction). Hobart Rivulet recorded the highest concentrations, followed by New Town Rivulet (Figures 4.7, 4.8, 4.9 and 4.10). The samples collected from varying rivulets are clearly distinguished by colours in these figures. Hobart Rivulet is represented by red, New

Town Rivulet in purple, Sandy Bay Rivulet in yellow, background sample in blue and street runoff in black. In Hobart Rivulet, levels of Cu are 15 times higher, Mn 2 times higher, Ni 3 times higher and Zn 9 times higher. In New Town Rivulet, Cu is 9 times higher, Mn 11 times higher and Zn 5 times higher. In Sandy Bay Rivulet, Cu is 9.5 times higher, Mn 56 times higher, Ni 3 times higher and Zn 2 times higher. Pb recorded < 5 µg/L in all samples (Table 4.2).

4.6 Street Runoff

Street sample (Sample 10) indicates high levels of Cu, Ni and Zn (Table 4.2). Levels of dissolved Cu and Zn are comparable to levels of contaminants from studied sites (Hobart and New Town Rivulet). However, levels of heavy metals in sediment collected from street runoff are found at lower concentrations than sediment collected from three rivulets.

4.7 pH and Total Suspended Solids (TSS) Concentrations

The pH of three rivulets range from 6.6 – 7.5. This is almost identical with background level of 7.2. Sandy Bay recorded the highest total suspended solids concentrations (TSS). It recorded 190 times higher than background level of 6.6 mg/ L. New Town and Hobart record 11 and 9 times higher than background levels respectively (Table 4.5).

Figure 4.1

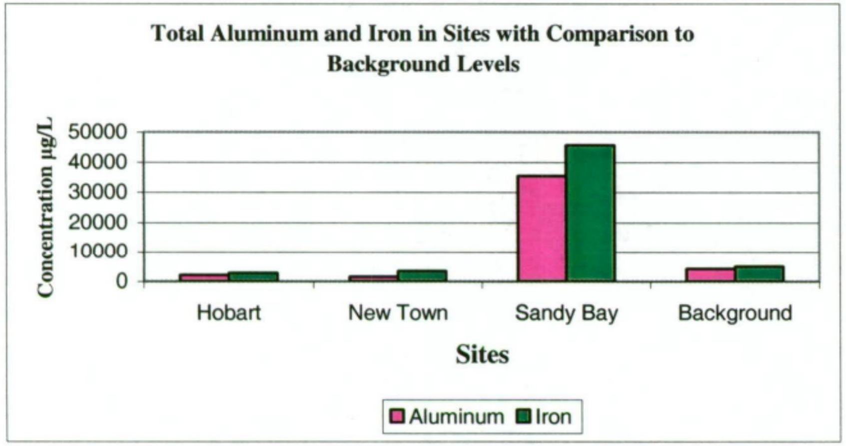


Figure 4.2

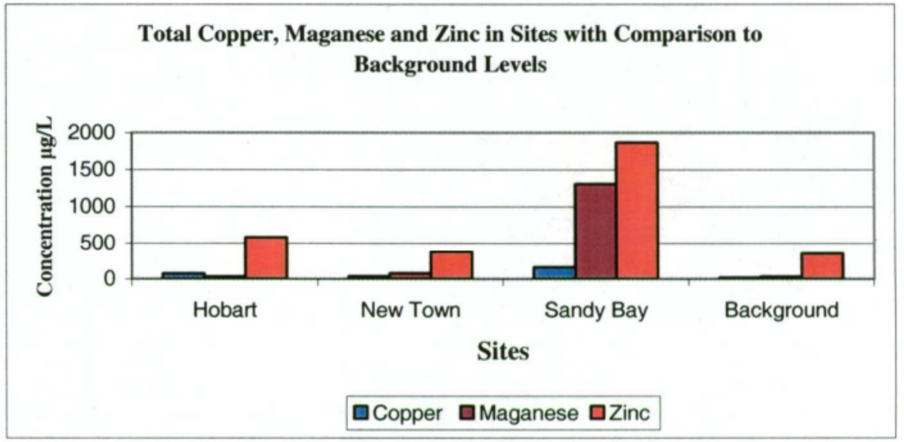


Figure 4.3

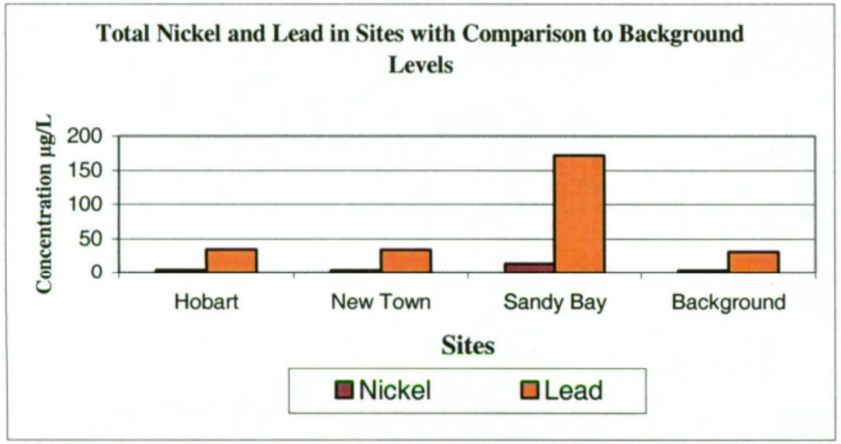


Figure 4.4

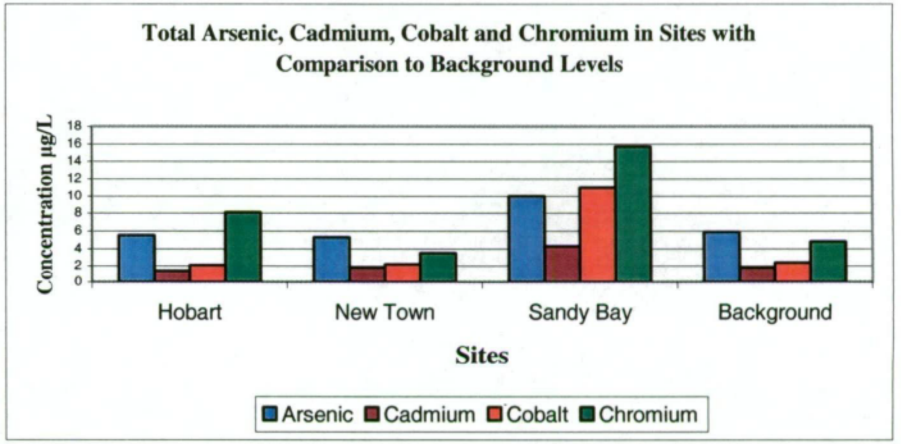
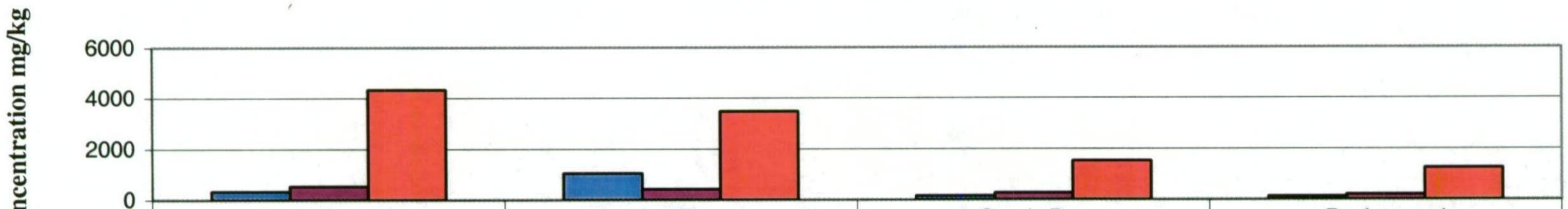


Figure 4.5

Concentrations of Copper, Lead and Zinc in Sediment



	Hobart	New Town	Sandy Bay	Background
Copper	334.7	1046.8	157.1	122.2
Lead	535.7	419.9	265.3	203.7
Zinc	4335.2	3462.8	1527.1	1252.6

Sites

Figure 4.6

Concentrations of Nickel and Manganese in Sediment

	Hobart	New Town	Sandy Bay	Background
Nickel	24.9	31.4	16.5	40.7
Manganese	335.2	447.4	1057.5	967.4

Sites

Figure 4.7

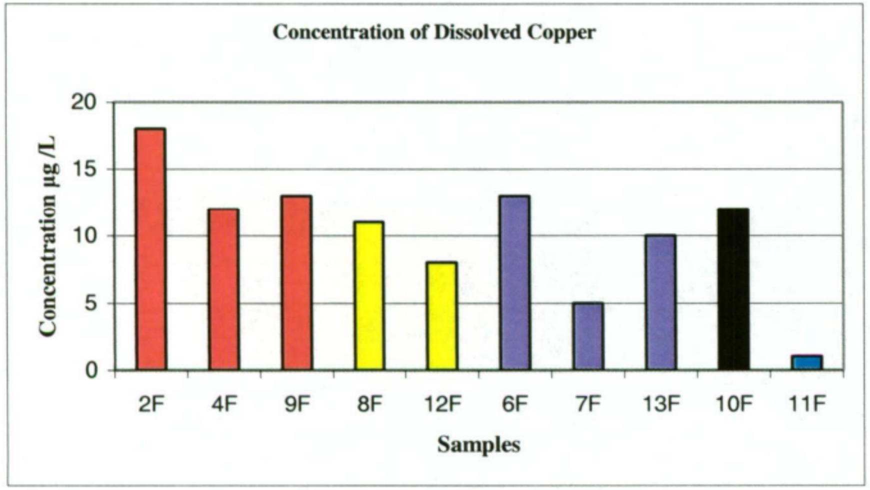


Figure 4.8

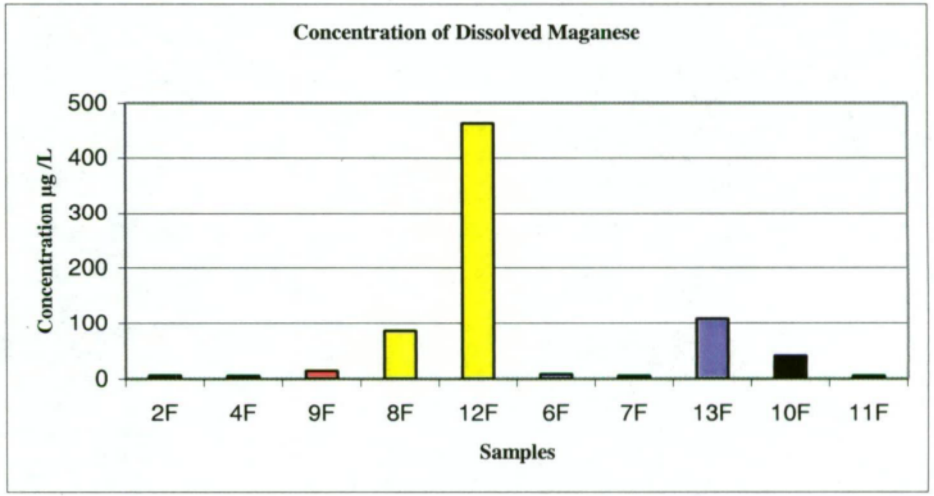


Figure 4.9

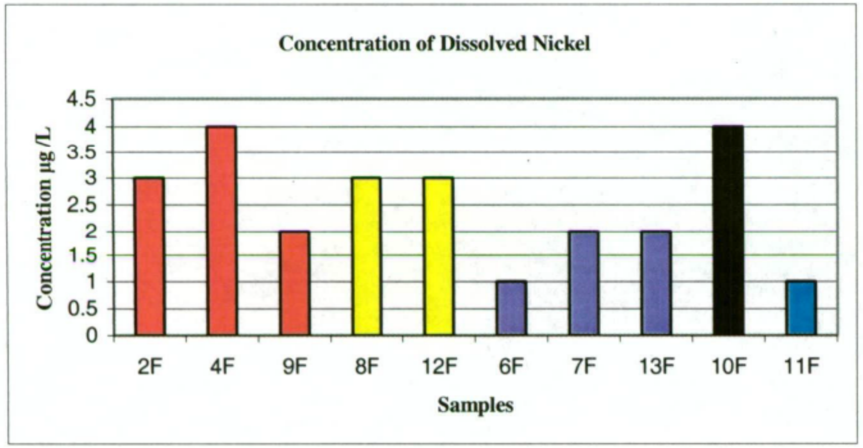
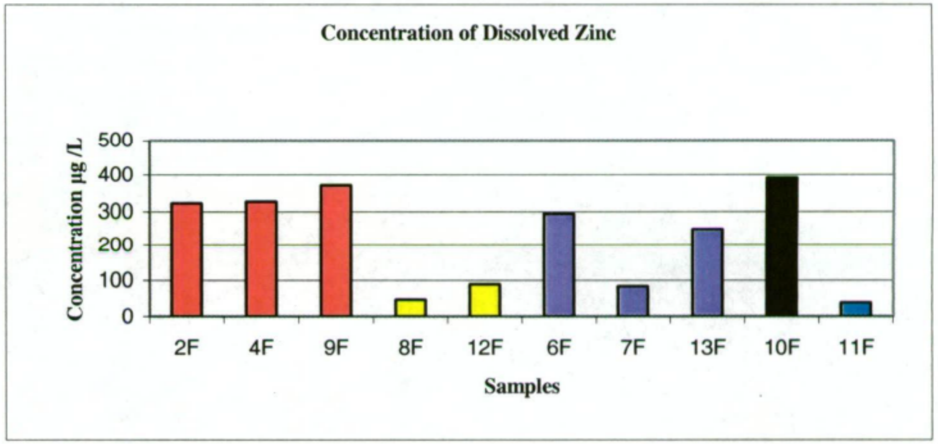


Figure 4.10



4.8 National and International Standards

In an attempt to reduce pollution, international and national guidelines have been established. These guidelines in Tables 4.7, 4.8, 4.9, 4.10 and 4.11 aid in providing information with regard to sediment and stormwater heavy metals contamination. Similarly, they also provide toxicant guidelines for recreational purposes (Table 4.10). Table 4.7 was complied by Moen *et al.* (1984) using their knowledge of sediment contamination. This allowed responsive actions to be taken according to different levels of soil contamination. Table 4.8 indicated international sediment quality guidelines followed by the Netherlands. Tables 4.9, 4.10 and 4.11 showed The Australian and New Zealand Environment and Conservation Council (ANZECC) 2000 water quality guidelines which is adopted by the Ministry for the Environment in Australia. ANZECC 2000 water quality guidelines is an updated and revised version of the ANZECC 1992 water quality guidelines. Table 4.12 was derived from Australian Water Resources Council's workshop on water pollution guidelines for urban stormwater.

Table 4.7 : Standards for Soil Contaminant Action

Heavy Metals	A	B	C
Copper (mg/kg)	50	100	500
Lead (mg/kg)	50	150	600
Zinc (mg/kg)	200	500	3000

A = Reference below which soils are probably uncontaminated
B = Value above which there is need for further investigation
C = Value above which a clean-up is necessary
Source: Moen *et al.* (1984)

Table 4.8 : Selected Sediment Quality Criteria in Netherlands

Metals	Target Value (mg/kg)	Limit Value (mg/kg)	Intervention Value (mg/kg)
Cadmium	0.8	2	12
Copper	36	36	190
Lead	85	530	530
Zinc	140	480	720

Source: Risk Assessment and Environmental Quality Control (1994)

Table 4.9 : Sediment Quality Criteria in Australia

Metals	ISQG-Low (Trigger value) (mg/kg)	ISQG-high (mg/kg)
As	20	70
Cd	1.5	10
Cr	80	370
Cu	65	270
Ni	21	52
Pb	50	220
Zn	200	410

Source: Ministry for the Environment (2002)

Table 4.10: Summary of Water Quality Guidelines for Recreational Purposes

Metal	Concentration (μg/L)
Al	200
As	50
Cd	5
Cr	50
Cu	1000
Fe	300
Mn	100
Ni	100
Pb	50
Zn	5000

Source: Ministry for the Environment (2002)

Table 4.11: Summary of Heavy Metals Concentrations Guidelines Entering Freshwater and Saltwater

Metal	Concentration (μg/L)
Al	Freshwater - < 30 Saltwater - < 10
As	
Cd	Freshwater - < 0.2 – 1.8 Saltwater - < 5
Cr	Freshwater and Saltwater - < 20
Cu	Freshwater and Saltwater - < 5
Fe	Freshwater and Saltwater - < 10
Mn	Freshwater and Saltwater - < 100
Ni	Freshwater and Saltwater - < 100
Pb	Freshwater - < 1 Saltwater - < 20
Zn	Freshwater - < 10 Saltwater - < 100

Source: ANZECC (2000)

Table 4.12: Total Heavy Metals in Stormwater in Australia

Metals	Urban Runoff Concentrations (μg /L)	Dry Weather (Urban) (μg /L)
Cadmium	6	<0.4
Chromium	170	<10
Copper	40	<10
Lead	200	25
Zinc	200	<125

Source: Australian Environment Council (1988)

Levels of heavy metals in this study are compared against national and international standards for total, dissolved and sediment metals. The Australian Environment Council (1988) (Table 4.11) is used as the standard for total metals and results are shown in Figures 4.11 and 4.12. Standards from Risk Assessment and Environmental Quality Control (1994) (Table 4.8) are used for comparing heavy metals in sediments and results are shown in Figures 4.14 and 4.15. Similarly, ANZECC 2000 guidelines are also put to test and results are shown in Figure 4.16. Dissolved metals (Table 4.2) are compared against Tables 1.2 and 4.10. Results are shown in Figure 4.13.

4.8.1 Total Metals

A comparison of findings from Table 4.5 against standards from Table 2.13 shows metals like Cd, Cr and Pb are within safe limits. There is no specific standard for metal Mn. Thus, we could only compared it to background samples. However, metals like Cu and Zn exceeded guidelines. Sandy Bay Rivulet shows the highest concentrations in both metals, followed by Hobart and New Town Rivulets (Figures 4.11 and 4.12).

Figure 4.11

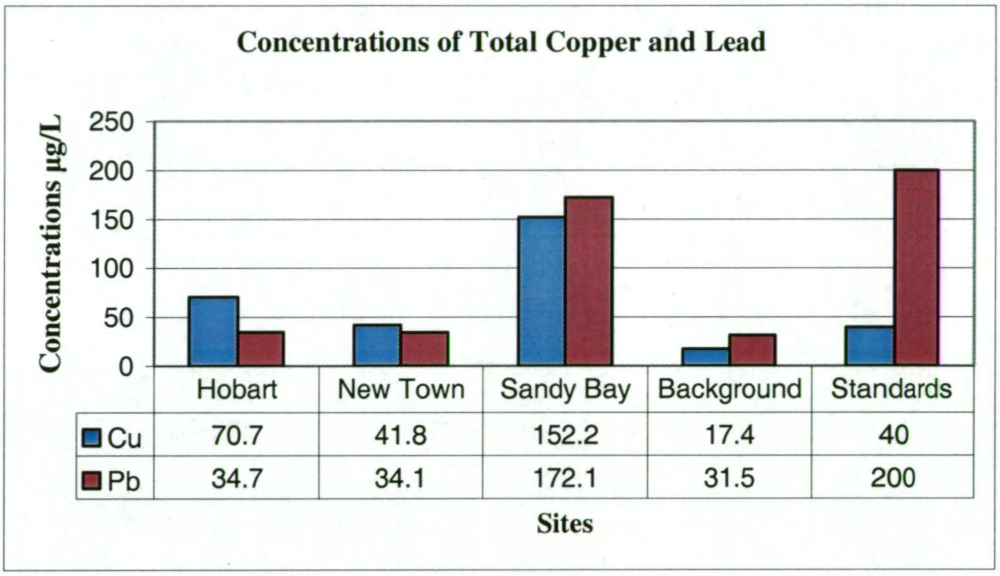
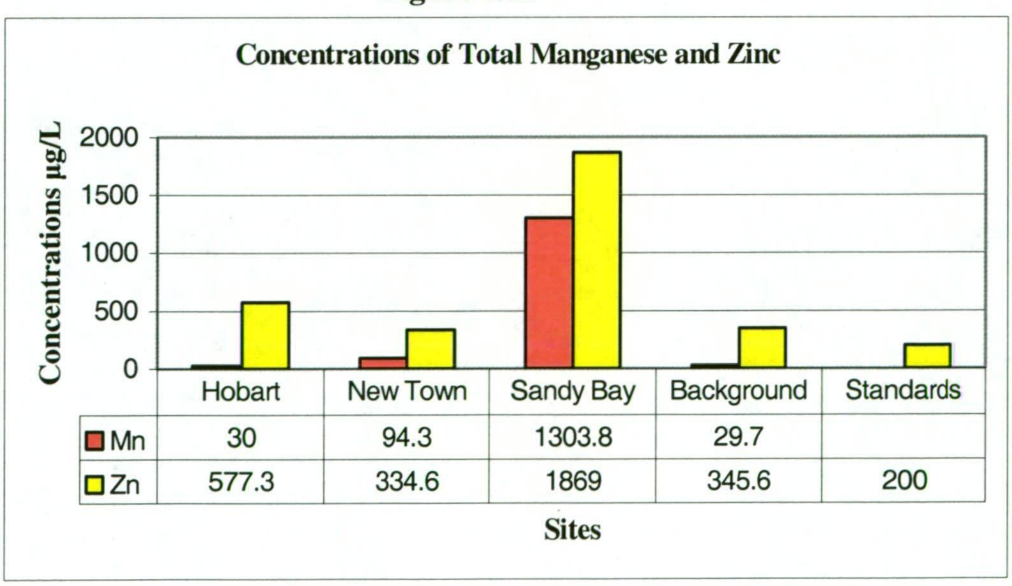


Figure 4.12



4.8.2 Dissolved Metals

A comparison of findings in Table 4.2 against standards in Table 1.2 indicate concentration of Zn is at risk to aquatic species. On the other hand, comparison with Table 4.10, indicate all metals analysis indicate no risk towards recreational purposes in dissolved metals. Dissolved Zn at all sites indicate high risk to aquatic species (Table 1.2), with Hobart Rivulet having the highest concentrations, followed by New Town Rivulet (Figure 4.13). However, certain metals (Table 4.5) indicate high levels of concentrations when compared against ANZECC 2000 water quality guidelines in Table 4.11. Metals like Al, Cu, Fe, Pb and Zn all exceeded guidelines for freshwater. Mn concentrations from Sandy Bay Rivulet is only one that exceeded freshwater guidelines (Table 4.13). For saltwater guidelines, metals like Al, Cu, Fe, Pb and Zn. Zn in Sandy Bay Rivulet is the only one that does not exceed saltwater guidelines but its Mn concentrations exceeded saltwater guidelines (Table 4.13).

Figure 4.13

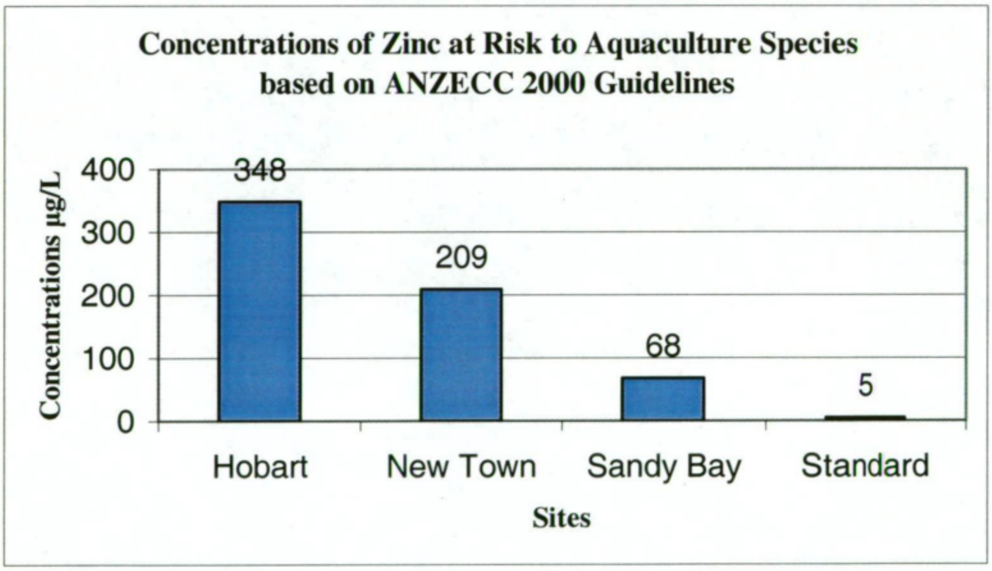


Table 4.13: Comparison of Mean Dissolved Concentrations of Heavy Metals in Individual Rivulets Against ANZECC 2000 Water Quality Guidelines

Metal	Concentration (μg/L)	Hobart Rivulet (μg/L)	New Town Rivulet (μg/L)	Sandy Bay Rivulet (μg/L)
Al	Freshwater - < 30 Saltwater - < 10	35	68	64
As	Freshwater - < 10 Saltwater – 1 – 5	< 5	< 5	< 5
Cd	Freshwater - < 0.2 – 1.8 Saltwater - < 5	< 1	1.3	1
Co	Freshwater and Saltwater - 0.1 – 0.5	< 1	< 1	1
Cr	Freshwater and Saltwater - < 20	< 1	< 1	< 1
Cu	Freshwater and Saltwater - < 5	15	9.3	9.5
Fe	Freshwater and Saltwater - < 10	45.5	60.3	65.5
Mn	Freshwater and Saltwater - < 100	10	40.3	274
Ni	Freshwater and Saltwater - < 100	3	1.6	3
Pb	Freshwater - < 1 Saltwater - < 20	< 5	< 5	< 5
Zn	Freshwater - < 10 Saltwater - < 100	348	209.3	68

4.8.3 Metals in Sediment

A comparison of findings in Table 4.3 against standards in Table 4.7 and 4.8, results show only Cu, Pb and Zn exceeding guidelines. However, Cu in Sandy Bay Rivulet (157.1 mg/kg) remains within guidelines when compared with international standards in Netherlands (Figures 4.14 and 4.15). When compared with Table 4.7, in the case of Cu, New Town Rivulet has exceeded level C. Both Hobart and Sandy Bay Rivulet exceeded level B. In the case of Pb, all three rivulets reached level B. In the case of Zn, Sandy Bay exceeded level B with 1527.1mg/ kg. Both Hobart and New Town Rivulets exceeded level C. Mn concentrations remain the highest in Sandy Bay Rivulet as compared to Hobart and New Town Rivulets (Figure 4.15). Similar results are seen when compared with ANZECC 2000 water quality guidelines in Table 4.9. Cu, Pb and Zn show concentrations higher than ISQG-high value. However, metals like Cd and Ni which show concentrations between ISQG – low and ISQG – high, indicating these metals also requires investigation at all three sites (Figure 4.16).

Figure: 4.14

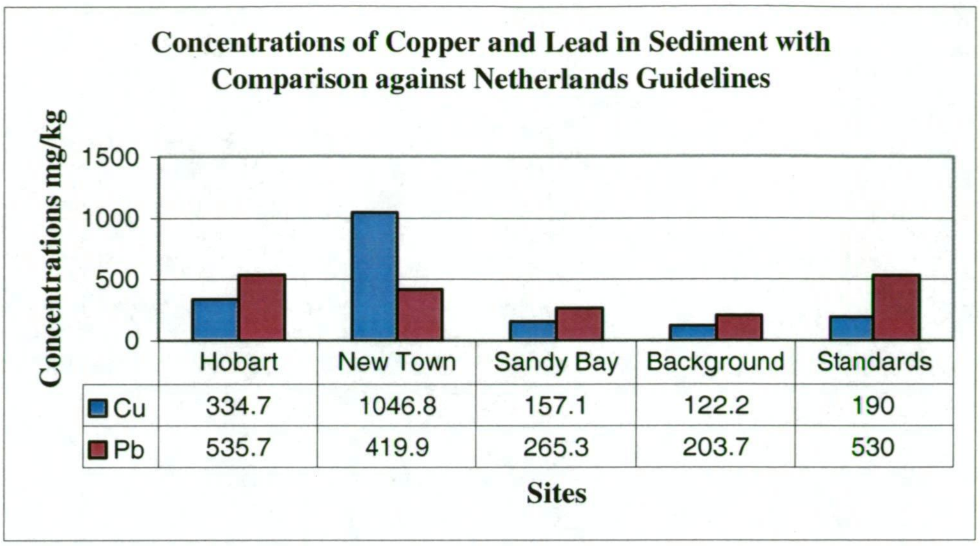


Figure 4.15

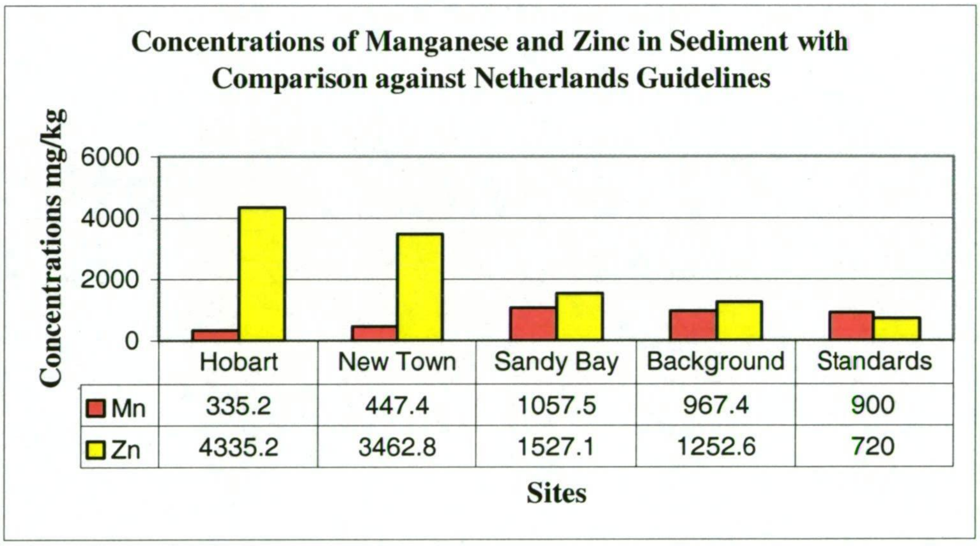
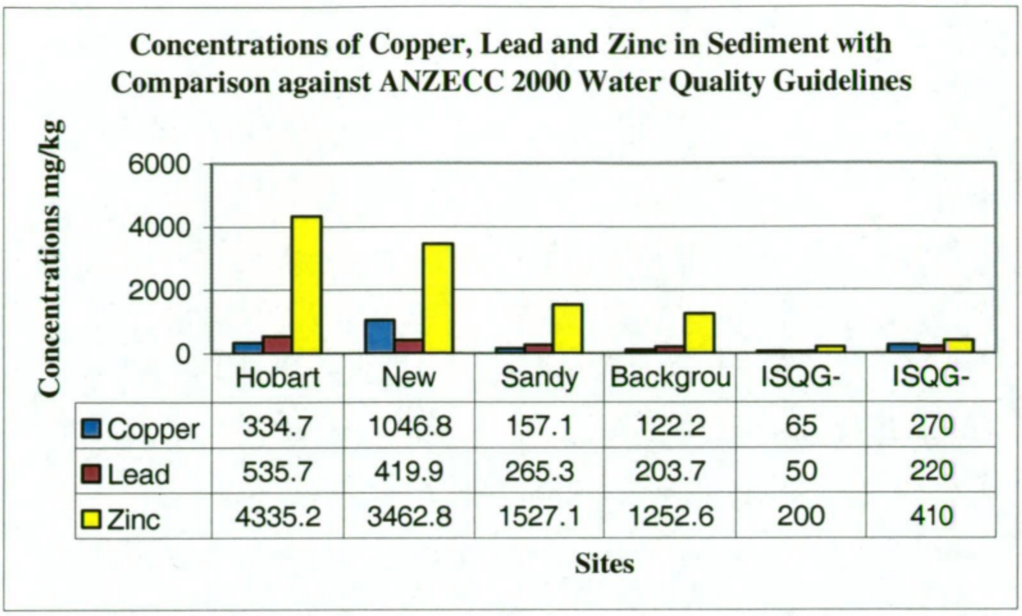


Figure: 4.16



4.9 Comparison with other Stormwater Studies

Findings in the study will also be compared with past stormwater studies. This would help in assessment of whether heavy metals in City of Hobart are higher or lower than other countries' cities. Commonly metals like Cd, Cu, Ni, Pb and Zn are used as parameters. Also, these stormwater studies are selected based on the similarity that they are either developed or developing economies.

Table 4.14: Dissolved Heavy Metals in Stormwater in other Industrial Cities

Countries	Cd (µg/L)	Cu (µg/L)	Pb (µg/L)	Ni (µg/L)	Zn (µg/L)	Comments
Sarnia (America) †	6.8	57.1	233	8.5	307	
Sault Ste Maria (America) †	6.0	69.6	97	31.3	274	
Windsor (America) †	5.4	57.1	154	27.8	234	
Brunette watershed (British Columbia) *	NA	450	4140	NA	3200	The highest level of metals

Source: † Marsalek (1991); * Hall and Anderson (1988)

Table 4.15: Street Runoff from three Locations in Metropolitan Atlanta

Locations	Median Cu (µg/ L)	Median Ni (µg/ L)	Median Pb (µg/ L)	Median Zn (µg/ L)
Shopping center parking lot	6.0	4.2	15.4	163
Suburban street runoff	1.5	1.8	3.8	118
Urban street runoff	16.9	4.0	11.4	905

Source: Rose *et al.* (2001)

Table 4.16: Heavy Metals in Sediment (mg/kg) in Stormwater in Industrialized Cities

Cities	Al	Fe	Mn	Cd	Cr	Cu	Ni	Pb	Zn
Bangkok (Thailand) †	1400 - 43400	3900 - 26700	50 - 810	0.05 – 2.53	4.3 – 57.4	5.1 – 283.0	4.1 – 52.1	12.1 – 269.3	3 - 814
London (Englsand) †	-	-	-	<1 - 40				28 - 13700	34 - 13100
Hamburg (Germany) †	6000	3600	750	2.00	95.4	146.6	62.5	218.2	516
Manila (Philippines)†	6900	7800	1990	0.57	114.1	98.7	20.9	213.6	440
Hong Kong †	-	-	-	0.94	-	16.1	-	89.9	58.8
Ho Chi Minh City (Vietnam) *	-	-	-	-	100.5 – 497.0	16.6 – 175.8	-	15.2 – 166.0	11.7 – 1420.5
Port Jackson (Sydney, Australia) ‡	-	-	-	-	-	150-350	400-800	-	400-1100

Source: † Wilcke *et al.* (1998); * Phuong (1998) in Lan *et al.* (2000); ‡ Stark (1998)

4.9.1 Total Heavy Metals

Findings from Table 4.5 when compared with Table 2.8, indicate Fe recording a lower concentration. However, metals Pb, Cu and Zn all exceeded results obtained by Mosley and Peake (2001) in Dunedin (New Zealand). Sandy Bay Rivulet shows the only exception with lower Zn concentration. Similar behaviour in metals Cu and Zn to be associated with dissolved form is observed in this study.

4.9.2 Dissolved Heavy Metals

Comparing findings from Table 4.2 against findings from Table 4.14, Hobart and New Town Rivulet have shown Zn concentrations to be higher than the listed industrialized cities. All other metals, Cd, Cu, Pb and Ni remained lower concentrations than the cities. However, Sandy Bay Rivulet recorded lower concentrations in all heavy metals than the other industrialized countries.

4.9.3 Heavy Metals in Sediment

Comparing findings from Table 4.3 and 4.6 against findings from Table 4.16, levels of heavy metals in sediment is found to be higher than certain industrial cities. It is found that City of Hobart generally records a higher level of Cu, Pb and Zn as compared to other industrialized countries, Ho Chi Minh City (Vietnam), Hamburg (Germany), Bangkok (Thailand), Manila (Philippines) and Hong Kong (China). City of Hobart apparently possessed similar levels of heavy metals concentrations to Port Jackson (Sydney, Australia).

Different from the rest, London (England) recorded higher levels of Cd, Pb and Zn than City of Hobart.

4.9.4 Street Runoff

Comparing the findings of this study for street runoff (Sample 10) findings (Table 4.2 and 4.3) against Table 4.13. In terms of dissolved heavy metals, Ni shows similar levels in three locations to Table 4.15. Pb shows lower contamination compared to Atlanta. However, levels of Cu and Zn are shown to be higher for the City of Hobart suburban streets compared to shopping center parking lot and suburban street runoff in Atlanta. However, both metals indicate a lower contamination when compared to urban street runoff.

4.9 Comparison with Local Studies

The results of this study show lower levels of Zn and Pb compared to findings by Jenkins's study on smaller catchments. However, a higher level of TSS concentration is found in Sandy Bay Rivulet compared to results recorded by Tuit (2001). Comparison with Pirzl (1996) heavy metals distribution in Derwent Estuary (Table 2.9) with Table 4.3, indicate concentrations of metals discharged by individual rivulets are higher than sediment found at respective rivulets' mouth. New Town Rivulet shows higher concentrations in Cu. Hobart Rivulet shows higher concentrations in Cu, Pb and Zn. Sandy Bay Rivulet shows higher concentrations in Cu, Pb and Zn. However, all metals concentrations remain lower than sediment concentrations found near Pascminco Metals – EZ Zinc Refinery.

CHAPTER 5 - Discussion

5.1 Results Analysis

This chapter deals with the problem of heavy metals in Hobart stormwater and attempts to identify the sources behind these contaminants. Levels of heavy metals will be discussed in the following sections,.

- Partitioning of total metals,
- Common metals,
- Total metals,
- Heavy metals in sediments,
- Dissolved heavy metals, and
- Street runoff.

In addition, the Hobart results will be compared with findings of other industrialized cities' and national and international stormwater guidelines.

5.2 Total Metals Partitioning

The importance of total metals partitioning is emphasized in the literature (Morrison *et al.* 1984; Sansalone *et al.* 1997; Mosley and Peake 2001). It has important implications for the potential toxicity of urban stormwater to organisms in receiving waters. Evidence suggests that it is the free metal ion concentrations that determine a metal's bioavailability rather than the total concentration (Campbell 1996). Because of this, certain metals may not be as toxic as high total concentrations may suggest. This indicates Cu, Ni and Zn which are predominately in the < 0.45 μm fraction should be a risk in both Hobart and New Town Rivulet. On the other hand, total metals which are highly associated with particulate matter in Sandy Bay Rivulet, may not be as critical compared to the other two rivulets. However, deposition of these sediments in the receiving environment (Derwent Estuary) will pose risk to marine health over a longer period. This is when heavy metals in the sediment become a source of contamination. The high occurrence of Cu and Zn in the < 0.45 μm fraction in this study is also observed by Morrison *et al.* (1984) and Mosley and Peake (2001).

Previous studies have also documented similar high occurrences in particulate matter for Fe (Yousef *et al.* 1984; Harrison & Wilson 1985 and Mosley and Peake 2001) and Pb (Morrison *et al.* 1984; Harrison and Wilson 1985; Mosley and Peake 2001). The adsorption of Pb to the surface of Fe oxyhydroxide particles (Erel *et al.* 1991) is a possible reason for the similar behaviours of Pb and Fe observed in the present study.

5.3 Common Metals

Fe, Al and Mn which have higher concentrations than other metals in this study, owe this phenomenon to their abundance in the Earth's crust. They are largely classified as secondary contaminates which do not pose high risk to human health (CPW 2001). It is found that the Earth's crust contains 8.13 % of Al (Norseth 1979) and 5 % of Fe (Elinder and Piscator 1979). They are commonly present in a number of different types of soil minerals. For instance Al is not found in an uncombined state in nature, but mostly in the form of various silicates. For example important aluminum-containing silicates are bauxite and cryolite (Norseth 1979).

Mn has also been reported by other stormwater studies as a natural occurring mineral (PSU 2001) which does not really pose a health risk. However, it does pose aesthetic problems to stormwater quality (CPW 2001).

5.4 Total Metals

Sandy Bay rivulet recorded the highest TSS concentrations and total mean heavy metals concentrations among the three rivulets. Results show all heavy metals discharged by Sandy Rivulet are associated with particulate matter (Table 4.5). This is despite Cu and Zn which have been observed in two other rivulets and other stormwater studies to be associated in dissolved form. For Hobart and New Town Rivulets, heavy metals like Cu, Pb and Zn are seen in higher concentrations in sediment (Figure 4.5 and Table 4.3) and higher concentrations of heavy metals Cu, Ni and Zn in dissolved form (Figures 4.7. 4.9 and 4.10) than Sandy Bay. However, these levels are insufficient to bring total metals concentrations of Hobart and New Town Rivulet higher than Sandy Bay Rivulet.

5.5 Heavy Metals in Sediment

It was believed that diverse land use in Hobart Rivulet catchment has a significant influence on heavy metal concentrations in the sediment. Sandy Bay which drains mainly recreational area (Ridgeway Park), light density residential, little high density residential and small area of commercial activity at Sandy Bay and Battery Point (Table 3.1 and Figure 3.3) understandingly shows the lowest sediment heavy metal concentrations among the three rivulets (Figure 4.5). However, Zn concentration is found exceeding standard limits and Cu almost reaching the risk level too.

New Town Rivulet which drains the biggest catchment 1868 ha reflects almost identical concentrations of metals in sediment as Hobart Rivulet. This could be explained largely by almost similar patterns of land use within the two catchments (Table 3.1). However, higher levels of Cu are shown to be 3.2 times higher than Hobart Rivulet and 8.5 times higher than background levels (Figure 4.5).

Samples from Hobart Rivulet and New Town Rivulets demonstrate the existence of an inverse relationship between sediment load and heavy metals concentrations. Hobart Rivulet, despite recording the lowest TSS concentration among three rivulets, records the highest level of Pb and Zn heavy metal contamination. Even though Cu concentration is lower than New Town Rivulet, it is considered at risk levels when compared to standards in Table 2.10 and 2.11. This indicates that a higher concentration of pollutants, despite small sediment load, could easily be washed off from impervious areas in commercial and highly urbanized catchments drained by Hobart and New Town Rivulets.

5.6 Dissolved Metals

Pb records < 5 µg/L dissolved concentrations in all samples (Table 4.2). This indicates a strong relation between the metal and particulate matter. Lead's low solubility in water was commonly observed by other stormwater studies (Morrison *et al.* 1984; Muschack 1990 and Mosley and Peake 2001). Morrison *et al.* (1984) found generally all metals, including Pb in the dissolved phase becomes quite significant towards the end of rain event. However, this could not be proved in this study as only first-flush samples were collected. High levels of dissolved Cu and Zn from Hobart and New Town Rivulets indicates clearly their bioavailability and further confirms strong sources of Cu and Zn in both Hobart and New Town Rivulets catchments.

5.7 Street Runoff

Results of suburban street runoff indicate street runoff in the City of Hobart is a strong contributing source of heavy metals in the three rivulets. This is especially so for Sandy Bay Rivulet catchment which is comprised of mainly recreation and residential, and very little commercial activity. Its high level of dissolved Cu and Zn, as compared to low levels of Cu and Zn contamination in sediment, emphasize further the strong bioavailability behaviour of the two metals.

5.8 Comparison with Past Stormwater Studies

Comparing this study's results against other stormwater studies shows dissolved Cu and Zn, and sediment concentrations of Cu, Pb and Zn, remain critical. Most significant is Zn concentration in Hobart is higher than London.

5.9 Comparison with Local studies

Lower levels of contamination when compared with Jenkins (1991) could be explained in two ways. Firstly, levels of Zn and Pb have dropped. Secondly, results of Jenkins (1991) are based on the entire cycle of the urban hydrograph. This is in contrast to the present study which collects only first-flush samples of stormwater. It should be understood that there are possibilities of more than one peak flow during a rain hydrograph. This study which collects only first-flush samples during initial stage of rain events discounts other peak concentrations occurring during similar storm event.

TSS concentration in Sandy Bay Rivulet recorded in this study is 2 times higher than recorded by Tuit (2001). This further emphasizes the increasing acute erosion problem Sandy Bay Rivulet is facing. Certain consequences have surfaced from this erosion process. At present, Sandy Bay Rivulet is suffering from sedimentation problems at its rivulet mouth (Plate 3.1).

Comparison with heavy metals in Derwent Estuary sediments studied by Pirzl (1996) indicates high levels of contamination of stormwater in all metals. However, metals like Cu, Pb and Zn are more significantly higher. It is feared that heavy metals pollution in the Derwent Estuary may continue to escalate from the deposition of heavy metals contaminated sediment from stormwater. Over the years, it was found that levels of heavy metals are declining (Pirzl 1996). This drop in levels is due to an extensive improvement program implemented by Pascmico Metals (Hanslow 1994). In order to work in parallel with industrial improvements towards heavy metals reduction, the state government should concurrently enforce stringent environmental programs in curbing heavy metals in stormwater.

5.10 Potential Sources of Heavy Metals in Hobart

Results have shown that each rivulet is facing an acute problem of stormwater pollution. Even though, this study does not aim at collecting evidence of pollution from sources. Based on stormwater literature studied, potential sources of heavy metals in Hobart could still be drawn to account for the deteriorated stormwater.

High TSS concentration levels in Sandy Bay Rivulet may be due to high erosion process and as the shortest channel among three rivulets, possessed a higher ability to discharge sediment quicker than other two rivulets along the rivulet channel. Tuit (2001) studied sediment transportation in Sandy Bay Rivulet and also identified it as a pressing problem to be solved. The lack of erosion abatement measures may explain this problem. In additional, high sediment load might come from residential gardens. Similarly, the unusually wet months of October (2001), November (2001), January (2002) and February (2002) would have also contributed to a high erosion rate, greater than findings by Tuit (2001). A lower TSS concentration in Hobart and New Town Rivulets could be explained by the soil abatement measures undertaken in New Town Rivulet in using wire mesh to protect soil structure along some of its banks. In addition, the design of the rivulet also affect sediment transportation in stormwater. For instance, unlike Sandy Bay and New Town Rivulets, the winding channel of Hobart Rivulet promotes the deposition of sediment within the rivulet rather than a larger sediment load being discharged at the rivulet mouth.

High levels of Cu in Sandy Bay Rivulet possibly come from roof runoff from residential housing using galvanized roof tops that produce high levels of Cu, Pb and Zn (Good 1993; Herrmann *et al.* 1994). Nevertheless, contamination from roof runoff seems moderate as pH recorded for every stormwater sample ranges from 6.6 – 7.6 (Table 4.5). Sources of Cu and Zn in Sandy Bay Rivulet may have come from commercial retail shops and petrol stations along the Sandy Bay Road and Battery Point. Their small density as compared to Hobart Rivulet and New Town Rivulet catchments may contribute moderately high Cu and Zn. However, road runoff from highway road, Southern Outlet and Sandy Bay Road could be principal contributors of Cu and Zn in Sandy Bay Rivulet stormwater. Both roads command high daily traffic between suburbs and city. Southern Outlet Road especially has a long descent slope at a steep angle requires mandatory speed of 80 km/h from motor vehicles. It is believed along this section of the highway, drivers use heavily on their brakes to slow down. In this process, more wear on brake linings and tires would result in the release of heavy metals Cu and Zn being released on the road and washed into the rivulet. Similar findings of high Cu concentrations in street sediment resulting from heavy braking of vehicles were also found by Sartor *et al.* (1974). To further prove street runoff is also a strong origin of heavy metals and could directly influence the quality of stormwater, high levels of Cu, Ni and Zn in street runoff sample (Sample 10S) are recorded. This could be explained by the fact that Cascade Road leading to Macquarie Road commands a high level of daily traffic, as it is one of the main connecting roads from the suburbs to the city.

Sources of Cu also originate from domestic sources. Klein *et al.* (1974) also reported high levels of Cu and as well as Zn in domestic wastewater. Hobart's water supply is generally seen as "soft" water with higher alkalinity (pH 7) as compared to Australia's mainland's water. The higher alkalinity tends to dissolve Cu from the plumbing pipes from the water system in residential area. This problem becomes more occurring in older residential housing with older plumbing system.

High Mn concentrations as a secondary contaminant pose only aesthetic problems not a serious health risk. Its high concentrations are subjected to variations depending on geologic background and mining activities (Piscator 1979). Similarly, Wiber and Hunter (1979) also believed the enrichment of Fe and Mn in sediment could be explained by geologic factors. It was believed that the weathering of bedrock materials in Sandy Bay region produces Mn in storm water runoff or leached from mineral soils, given the geology of Sandy Bay region is comprised of basic igneous rock type (Tuit 2001). Such explanation is provided by PSU (2001). Sediments are another potential source of manganese. The manganese can adsorb to soil or sediment particles, and is then transported in the stream. Variations in the levels of heavy metals such as manganese in a stream are often related to variations in sediment concentrations. As sediment concentrations increases, then the concentrations of the heavy metals also increases. Decaying organic matter can also provide small amounts of soluble manganese. In addition, Manganese is found commonly in igneous rocks (PSU 2001).

Having high levels of Cu, Pb and Zn in both Hobart and New Town Rivulets reveals similar sources of contamination. For example, vehicle emissions, automobile workshops, commercial area and atmospheric deposition. The difference in concentration levels of metals only reflects a higher concentration of these sources in one catchment as compared to the other. For instance, a higher concentration of marine engine and automobile workshops in New Town Rivulet catchment probably account for the higher levels in Cu and Zn than Hobart Rivulet. Higher levels of Pb in both rivulets may come from numerous spray-paint shops located in the commercial landuse in the two catchments and high traffic patterns.

Hobart Rivulet, possessing the highest density of residential, commercial and light industries might account for the highest level of Zn among all three rivulets. The waste disposal area located at McRobies Gully is another specific source of contamination. Efforts by the Hobart City council to re-route the waterway from pollution by this landfill have not been really successful. Zn concentration flowing from McRobies Gully catchment is found to reach 300 μg/L in the study conducted by Jenkins (1991). Therefore, it is highly likely that heavy metals leaching from the site might have found their way into the stormwater. Similarly, Magdaleno and De Rosa (2000) observed heavy metals concentrations in landfills leachates after rain events (Table 2.5). Hernández *et al.* (1998) also reported, in their study of landfills, that Zn concentration could reach levels of 586.4 mg/kg. Thus, McRobies Gully disposal site poses a risk of heavy metals pollution in stormwater.

Atmospheric deposition is a likely contributor of heavy metal contamination for all three rivulets. It was suspected that Zn contamination may arise from atmospheric deposition from Pascminco Metals – EZ Zinc Refinery at Risdon in Derwent Estuary. However, no samples of Hobart City topsoil and air have been tested for Zn contamination as part of this study. Higher levels of Pb could be explained through older car fleet in Tasmania. Cars are not subjected to strict transportation laws that push for compulsory vehicle inspection annually in order to ensure vehicle emissions are not polluting. This is unlike countries such as Singapore. Old cars running on leaded petrol are allowed on to roads. In addition, usage of leaded petrol is still present during the period of sampling. The banned on leaded petrol only took place in January 2002, therefore Pb from leaded petrol in Tasmania is still a likely contributor of Pb in stormwater during the course of sampling. Older fleets of cars may also be contributing factors towards high levels of Cu, given that Cu is predominately used in brakes and tires of vehicles.

A possible explanation for the presence of high Cu concentrations in stormwater could be linked to high organic levels in Hobart stormwater Green (1998) had shown both faecal and hydrocarbon pollution are prevalent in Hobart stormwater. Investigators, Kersten *et al.* (1991), Viklander (1998) and Bennett *et al.* (1999) had shown Cu to bound predominately to organic matter. Therefore, it is also likely through organic matter; Cu has been transported into stormwater. However, organic matter is not sampled for heavy metals concentrations in this study.

CHAPTER 6 - Conclusion

6.1 Summary

This chapter addresses the objective outlined in the introduction and briefly summarizes overall results. This chapter also recommends on-going monitoring and better abatement measures of heavy metals in Hobart's stormwater.

We shall review again the objectives set in the study. They are the following:

1. Investigate the level of heavy metals concentrations in urban stormwater in three major rivulets located in the City of Hobart.
2. Determine the level of criticalness in specific heavy metal concentrations from comparison with international standards, national standards, international literature and local literature.
3. From reviewed stormwater literature, identify possible sources of heavy metal pollution.
4. Recommend suitable management options in tackling heavy metal pollution in urban stormwater in studied sites in the City of Hobart.

From these objectives, the study aims to contribute towards the work of monitoring the quality of stormwater runoff using heavy metal as the indicator parameter.

A total 11 samples were collected through grab sampling. 2 of these samples were however discarded. This was because Sample 4 did not represent a first-flush event and the other was collected at different site in the rivulet. Among the 9 samples were street runoff, a sample from a creek draining from the brickworks factory and a sample collected as background concentration from Hobart Rivulet before it enters the suburbs area. The unusually wet months (October 2001 – February 2002) and untimely night rains disallowed more samples from being collected. The study aimed at collecting first flush samples which made it important to have at least 3 dry antecedent days to allow sufficient accumulation of pollutants in the catchment. In some cases, this made it unsuitable collect samples from consecutive rain events.

Besides time as a factor, laboratory tests are also costly. Limited funds put a barrier on the sample numbers to be tested. The nine samples which were collected had been filtered through membrane filter papers of 0.45 μm pore size. After filtration, they were sent for laboratory test for heavy metals concentrations in both solid and dissolved form.

Results have been compared to national and international stormwater guidelines, other industrialized cities and local studies. From these comparisons, it was indicated that stormwater in Hobart is facing an acute problem in heavy metals pollution. This conclusion is based on findings that indicate sediment and runoff from Hobart stormwater has higher heavy metals concentrations than sediment in the specific sites of the Derwent Estuary (apart from sites near Pascminco Metals – EZ Zinc Refinery). Comparison with other industrialized cities also reflects Hobart's predicament with Cu, Pb and Zn all in high concentrations by world and national standards. Zn poses the most serious problem among the three metals.

High levels of Fe, Al and Mn are treated as secondary contaminants, given their abundance in the Earth's crust. High levels of Mn observed in Sandy Bay Rivulet are believed to come from weathering of parent bedrock material in the Sandy Bay region. Results also indicate different modes of heavy metals transportation by the three rivulets into the Derwent Estuary. Sandy Bay Rivulet has recorded the highest TSS and total metals concentrations among three rivulets (Table 4.5). This also indicates transportation of heavy metals are highly associated with particulate matter prevalent in the rivulet. Hobart and New Town Rivulets have shown high levels of heavy metals concentrations in both dissolved form and sediment which indicate both modes of heavy metals transportation are prevalent.

Sources of heavy metals were inferred from published papers as no direct samples were collected from individual sources. The lack of air and urban topsoil sampling in this research meant that no concrete evidence of atmospheric deposition of Zn by Pasminco Metals was available. No direct runoff samples were collected from the milk factory in Lenah Valley, Cascade Brewery, McRobies disposal site, automobile workshops, paint shops, housing gardens, roof runoff and shipyards to indicate their role in heavy metals pollution in Hobart. Sources sampling would require further funding which was not possible in this study. However, as identified by other stormwater and heavy metals studies, these sources are potential sources of heavy metals contamination in industrialized cities. Potential sources of contamination for respective rivulet catchments are summarized in Table 6.1.

Table 6.1: Inferred Sources of Contamination in Respective Catchments

Source	Sandy Bay Rivulet	Hobart Rivulet	New Town Rivulet	Metals
Housing	☼☼☼	☼☼	☼☼	Cu, Zn
Street runoff	☼☼☼☼	☼☼☼☼	☼☼☼☼	Cu, Pb, Zn
Automobile workshops	☼	☼☼☼	☼☼☼☼	Cu, Pb, Zn
Commercial	☼☼	☼☼☼☼	☼☼☼	Cu, Pb, Zn
Light Industries	NA	☼☼	☼☼☼	Cu, Pb, Zn
Erosion	☼☼☼☼☼	☼☼	☼☼☼	Mn, Al, Fe
Specific Sources		Landfill ☼☼☼		

P.S: Number of ☼ denotes the level of contribution a source to heavy metals in the catchment.

☼☼☼☼☼ = Serious ☼☼☼☼ = Very Strong ☼☼☼ = Strong

☼☼ = average ☼ = minimal

NA= Not Applicable

6.2 Management Options

There are several management options that can be deployed to reduce urban stormwater pollution. These have been discussed in detail in several urban stormwater management manuals (Degroot 1982; Goldman *et al.* 1986; Lawrence and Breen 1998 and NCSU 2001). These options are briefly discussed in the following sections. Generally, these management practices could be classified under two distinctive groups: preventive measures and control measures. It is advisable that management employ them appropriately to achieve best results in reducing stormwater pollution.

6.2.1 Preventive Measures

Preventive measures are management techniques that aim to reduce the exposure of materials to stormwater, thereby limiting the amount of pollutants washed off by stormwater. Preventive measures are cost effective ways to manage urban stormwater runoff and pollution (NCSU 2001). They could be implemented through source reduction and land use management practices.

6.2.1.1 Source Reduction Practices

Source reduction practices aim to prevent potential pollutants from entering stormwater at their source. This can be done through better curb designs which minimize runoff velocity thereby reducing sediment erosion (NCSU 2001). Frequent street cleaning can also be carried out. Revitt and Ellis (1980) claimed that there is a reduction in street loadings after cleaning runs by a mechanical rotary brush sweeper followed by high pressure jet flushing. It is found that street surface loadings for suspended solids and lead is reduced by 30% and 27 % respectively. A further reduction of 45% and 55% of suspended solids and lead is seen after flushing work has been done. To reduce the amount of metal pollutants in runoff, Elliott (1998) suggests that source abatement can be carried out. For instance, copper reduction could be achieved by reducing copper in brake shoes. Similarly, reducing the use of galvanized steel roofs and zinc-rich paints, and modifying the composition of rubberizing compounds in tires could reduce zinc concentrations in stormwater. The responsibility for carrying out other preventive measures lies heavily on industrial management in ensuring materials, stockpile and chemicals are kept well away from rain and exposure.

6.2.1.2 Land Use Management Practices

Land use management usually implies controlling or restricting the uses of land in the watershed to reduce pollution. Such methods are cost effective and require minimal maintenance. Sites could be designed to ensure minimum pollution impacts. They could be buffer zones, setbacks or easements.

Buffer zones are strips of vegetation, either natural or planted, around water bodies. They serve as infiltration zones which allow vertical infiltration and reduce horizontal overflow. Therefore, reducing sediment washed into receiving waters and allows recharging of groundwater (Goldman *et al.* 1986). Setbacks are established restrictions on development activities especially those which are located within specific distances of water bodies. They are usually aimed at minimizing sedimentation and associated nutrient enrichment downstream. Easements are strategies to prevent land from development. These lands are normally located near water bodies in fragile condition. Easements may be negotiated or purchased from landowners and passed on to future owners as part of the deed to the property. Easements could act as 'green belts' around water bodies and offer recreational opportunities for people (NCSU 2001).

6.2.2 Control Measures

Control measures are actions that reduce the level of pollutants in stormwater that have been exposed to pollutant sources. Control measures are mostly expensive and require ongoing maintenance. Sediment traps work on the principle that allows stormwater to enter allowing pollutant sediments to settle at the bottom before being released into stormwater channels. Such sediment retention structures could be dry detention basins, sediment traps or sediment barriers (Goldman *et al.* 1986). Other control devices employ the infiltration principle, allowing polluted stormwater to infiltrate through the soil profile, thereby removing pollutants through adsorption to soil particles. Examples of such control devices are infiltration devices, oil-water separators, sand filters, and porous pavements (NCSU 2001). Another form of control measure is the use of wetlands. Wetlands have proven successful in reducing nutrient and toxicity levels of stormwater through the use of natural physical, biological and chemical aquatic processes (NCSU 2001). Table 6.2 shows a summary on the efficiency of each management practice in pollutant removal in stormwater.

Table 6.2: Efficiency of Best Management Practices in removing Pollutants from Urban Stormwater.

Best management practices	Pollutant Removal						
	Trash	Solids (Sediments)	P	N	BOD	Metals	Bacteria
Percolation Trenches/Pits	■	■	■	□	■	●	■
Grassed Swales	NA	□	□	□	□	☼	□
Grassed Buffer Zones	NA	☼	☼	☼	☼	☼	☼
Pervious Pavements	■	☼	○	■	○	■	□
Infiltration Basins	■	■	■	□	■	○	■
Vegetated Waterways	NA	□	□	☼	□	☼	□
Inlet Controls/ Traps	●	□	☼	☼	□	☼	☼
Detentions Basins	NA	●	■	□	■	○	●
Retention Ponds/Wetlands	NA	○	■-○	□-■	□-■	○	■-●
Sand Filters	○	●	□-■	□-■	□-■	●	□-■
Aeration	NA	NA	NA	NA	●	NA	NA
Street Sweeping	○	□-■	☼	☼	☼	☼	☼
Key: Removal Efficiency ● 80-100% ○ 60-80% ■ 40-60% □ 20-40% ☼ 0-20% NA = Not Applicable							

Source: Lawrence *et al.* (1996); NCSU (2001).

6.3 Recommendations in Reduction Measures in this Study

From the earlier section on management practices, there are appropriate management techniques which we could choose for each individual rivulet. It is more advisable that in Sandy Bay Rivulet to practice erosion control methods or installation of sediment traps to curb the high level of sediment load during storm events. This is because heavy metals are more likely to be discharged into the Derwent Estuary using sediment as a substrate. Similar measures could also be adopted in Hobart and New Town Rivulets as sediment shows high levels of heavy metals in them too. Reduction of faecal deposition from birds and pets in Hobart could also help in reducing the availability of substrate in the transportation of Cu and Cd into stormwater. Such responsible pet owners are needed to clean up the faecal deposition by their pets on streets and parks.

High levels of dissolved Cu and Zn in both rivulets make it difficult to remove them from stormwater. Therefore, source reduction practices are more feasible solutions. Heavy metals could be reduced through more frequent road sweeping, reduction of Cu contents in brakes, reduction in use of galvanized steel materials, ensuring waste disposal site and other specific sources are kept well away and not polluting waterways, enforcement of stricter vehicles laws to stop pollution prone vehicles on the road and stricter enforcement of environmental compliance from industries.

Similarly, it would also be advisable to divert the first flush of stormwater for treatment of pollutants, most importantly removal of contaminated sediment before releasing it into receiving environment (Derwent Estuary).

6.4 Further recommendations

This research has proved its usefulness in stormwater quality monitoring in the City of Hobart. Knowing more about heavy metals discharged into the Derwent Estuary moves us a step closer towards solving the Estuary problems. While the study has been successful in fulfilling its aims and objectives in raising the awareness that stormwater is one of the routes whereby heavy metals enter into receiving waters in Hobart. However, more benefits from research in stormwater field could be reaped if better methodology techniques are employed and are available to the researcher.

- ❖ Research on heavy metals throughout an urban hydrograph will aid in better understanding of the mobilization, sources and concentrations of heavy metals discharging from a catchment. To be able to perform this task, better equipment is needed. For instance, the presence of an electronic data logger would be extremely beneficial in collecting stormwater samples. In this way, rain events during nights would not be missed. It also allows easier handling of sample collection with limited manpower as well as recording of other useful information like flow rate and the quantity of heavy metals loadings through stormwater.

- ❖ Sources, which include atmospheric deposition, roads, industries, workshops, roof runoff, housing and landfills, should be examined with the support of more funding for costly laboratory tests. This would provide identification of source contamination and helps in reduction of heavy metals pollution. Limited funding has also prevented more samples to be collected from individual rivulets, as well as background samples as wished.

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