THE BIOAVAILABILITY OF TRACE METAL CONTAMINANTS IN THE BRUNETTE RIVER WATERSHED

by

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Abstract

Urban expansion with the development of our transportation network and its associated impervious surfaces, that readily transport surface runoff to our urban streams, has become the major non-point source of pollution in our urban watersheds. Trace metals and organic contaminants are of particular importance due to their potential toxic effects on aquatic organisms. The association of these contaminants with suspended solids and bed sediments, and the dynamic nature of the stream environment, has generated an interest in determining if these contaminants are available to aquatic organisms.

The objective of this study was to investigate the potential bioavailability of the trace metals, copper and zinc, in stormwater runoff and the streams of an urban watershed. Two techniques, namely metal speciation and dialysis with resin receiver were employed in the Brunette River watershed located mainly in the metropolitan area of Great Vancouver, British Columbia. Stormwater and baseflow samples were collected along a hydrologic gradient and the trace metals partitioned into chelex resin extractable, dissolved and particulate components. The suspended solids, filtered from samples, were subjected to geochemical sequential partitioning into the exchangeable, easily reducible and residual trace metal phases. Chelex resin placed in dialysis tubes was deployed in streams and sediment traps for periods of a week to complex "available metals" during dry summer baseflow and wet winter stormrunoff periods. Manganese and iron were also investigated since they could affect the geochemical partitioning of the more toxic trace metals. Recent studies have demonstrated that manganese is accumulating in the Brunette watershed probably as a result of the gasoline additive MMT.

The results of this study indicate that both Cu and Zn are at relatively high concentrations in this watershed, compared to the relevant water quality and toxicity criteria. The concentrations of these two metals decreased along the urban hydrological gradient, with highest level in the street surface runoff, decreasing in Still Creek and still further in the Brunette River as a result of sedimentation in Burnaby Lake. There was a high correlation of suspended sediment (SS) and the concentration of the four metals Cu, Zn, Mn and Fe in

surface runoff, which indicated that the trace metals were mostly associated with the particles flushed from impervious surfaces and transported in the urban streams.

Analysis of trace metal speciation demonstrates that only about 10 % of Cu was found in the immediate bioavailable form (resin extractable) at all sites. The particulate bioavailable fraction of Cu (exchangeable and reducible components) only accounted for 30% in street runoff and less than 10% in streams. Fifty percent of the Zn was observed in the immediate bioavailable form (resin extractable) in the watershed. The particulate bioavailable fraction of Zn accounted for 11-24% along the watershed. Both these trace metals showed potential toxic effects to organisms in the Brunette River watershed, especially in streetrunoff and upstream in Still Creek when compared to the relevant criteria. Copper contributed a higher toxic effect to the aquatic life than zinc in this watershed since it was proportionally higher compared to the criteria.

There was no clear relationship between Mn and the bioavailable fractions of Cu and Zn within the watershed observed in this study. However, there was an increase in particulate easily reducible Cu and Zn (manganese bound metal fraction) during stormflow conditions when compared to baseflow.

In stream resin uptake experiments clearly demonstrated that the trace metal uptake rates were high during storm flow, especially when there was a long dry period before the rainfall. However, there was still considerable uptake of trace metals under baseflow conditions. The good correlation between bioavailable metal species in stream and metal uptake by the receiver resin suggested that both approaches are useful in evaluating the bioavailability of trace metals in the urban aquatic environment and can be used as tools to assess the impact of trace metal on the aquatic organisms in the urban receiving water.

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Chapter 1

Introduction

The growth of population and intensive human activities are a typical feature of the urban watershed. Following the rapid industrial expansion since World War II, industries have been the major contaminant sources, referred to as point sources, and responsible for much of the pollution in the urban watershed. Over the last two decades, pollution abatement efforts have identified, regulated and mitigated many of these point sources to our waterways (McCallum 1995). However, the increase of non-point source pollution, in the form of urban runoff, has been recognized as a major continuing source of contaminants to urban streams (Gibb et al. 1991). As many investigators have pointed out, pollution from non-point sources in an urban area can account for over half of the contaminant load entering the water system (Whipple et al. 1974, Wanielista et al. 1977). Colston (1974) also found significant contribution of urban non-point sources to receiving creeks. He showed that even if 100% of the pollutants from raw municipal wastewater was removed, the total reduction of contaminants discharged to the receiving creek would only be 52% for chemical oxygen demand (COD), 59% for biochemical oxygen demand (BOD_5), 5% for suspended solids, and 9-43% for toxic trace metals such as Cr, Cu, Pb, and Zn (Colston 1974).

Numerous contaminants exist in urban runoff, they include hydrocarbons, nutrients, pesticides and toxic trace metals (Hunter et al. 1979, Hoffman et al. 1982, Bedient et al. 1980, Murphy and Carleo 1978, Wilber and Hunter 1979). Contaminants, such as trace metals, are deposited on urban impervious surfaces and are transported to the receiving water during stormwater runoff periods (MacDonald et al. 1997, IRE 1997). The data from the US Environmental Protection Agency's (EPA) nationwide urban stormwater runoff monitoring

program indicated that the most prominent toxic trace metals, namely copper, zinc and lead, exceeded the freshwater acute toxicity criteria 50, 12, and 27% of the time, respectively (Cole et al. 1984). Similar levels of toxicity criteria exceedance have been reported in various urban watershed studies (Morrison 1985, Jarvis 1992, MacDonald et al. 1997). In British Columbia the monitoring data from the Brunette River watershed indicated that among 13 stations within the watershed, copper concentration exceeded the 2 ug/L water quality objective (WQO) in 60 of 103 samples (58%) under baseflow conditions. The average zinc concentration exceeded 30 µg/L WQO in the Still Creek, a tributary to the Brunette, and an average copper concentration of 50 µg/L was observed during stormflow (MacDonald et al. 1997). The sediments in streams and lakes in the watershed also showed high level of trace metals. McCallum (1995) reported that the contamination of Burnaby Lake surface sediments with Pb, Cu, Zn, and Cd is indicated by their respective enrichment factors of 10, 6, 3.8, and 1.5, respectively, while stream contamination is indicated by the failure of all 33 stream stations to meet watershed sediment criteria for Pb, Cu, Zn.

The ultimate concern of trace metal contaminants in the receiving water is their toxic impact on the aquatic organisms and fish species (Morrison et al. 1987, Revitt et al. 1987, Kushner 1993, Bindra and Hall 1977). The toxic impact of the trace metals is caused by the accumulation of metals in the organisms. This process is referred to as bioaccumulation. Traditionally, total trace metal concentrations in water were used as environmental criteria for controlling metal pollution (Morrison 1985). However, researchers have demonstrated that the total trace metal concentration provides little information on metal toxicity, since only metal species termed "bioavailable metal form" play a key role for the toxicity estimation of metals to organisms in the water system (Bindra and Hall 1977, Morrison et al. 1987).

Trace metals in water generally exist in two phases. In the dissolved phase the metal is dissolved in the water column. In the particulate phase, the metals are either bound by the suspended particles, or deposited in the bed sediment. It has been recognized that the dissolved metal fractions are considered potentially more hazardous because they can be taken up directly by the aquatic organisms (Bindra 1983, Morrison 1985). Although the

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sediment-bound metals appear to be of little concern upon preliminary considerations, later investigations have shown that particulate metal might prove to be very important. This is due to the fact that sediments often contain 100 times higher concentrations of trace metals than that in the water column (Bindra 1983), and the release of trace metals from sediment into the water may happen under certain environmental conditions. Also ingestion of sediment particles by filter feeding organisms can provide another route for bioaccumulation.

Morrison (1985) suggested that storm runoff over the urban impervious surface brought large amount of trace metals into the receiving water, of which metals in the dissolved phase might cause an acute toxic impact on the organisms. On the other hand, the metals in particulate phase led to the accumulation of these metals in the stream sediment. Aquatic organisms can either directly ingest these sediments or assimilate the dissolved metals released from sediment to the water column.

The existing trace metal forms and their concentrations in the water and sediment can be affected by various physical-chemical factors. In an urban watershed, these factors include the metal sources discharged from different land use areas, such as the industrial, commercial and residential lands; the transport pathways by the urban hydrological characteristics, such as creeks, drainage channel, and the lakes; and the water chemistry, such as pH, hardness, dissolved oxygen; as well the effects of inorganic and organic substances and other metal species. All of these are considered as regulators of trace metal species and their toxic effect in the urban aquatic environment (Morrison 1985, MaCdonald et al. 1997, IRE 1997, Solo-Gabriele and Perkins 1997, Yuan et al. 1999)

Water chemistry plays a key role in metal bioavailability in the water system. It is generally accepted that trace metals will be more toxic at lower pH values, where most of the trace metals will exist in a free ionic form. Increases in pH may lead to the formation of insoluble hydroxides and oxides of the metal which prevents the metal of being assimilated by the aquatic organisms, thus reducing the toxicity of the trace metals (Gadd and Griffiths 1978). A laboratory bioassay study supported this conclusion by finding an increase of metal toxicity with a decrease of pH from 8.0 to 5.0 (Hall and Anderson 1987). The effects of water

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hardness on toxicity of trace metals to fish and invertebrates have also been noted. Moore and Ramamoorthy (1984) reported that the increasing hardness could reduce the toxicity of Cu^{2+}, Pb^{2+}, Ni^{2+}, and Zn^{2+}. Collins and Stotzky (1989) also suggested that metallic cations are more toxic to many microorganisms in soft than in hard water, because of the higher bicarbonate / carbonate contents of the latter. The redox condition of the sediment has been shown to be an important factor in controlling the chemical exchange reactions, which affect the transport of trace metals across the sediment water interface (Bindra 1983). Gibbs (1973) found that Fe and Mn existed in sediments as hydrous oxide coatings on particles. One typical example is that the release of manganese (Mn) and iron (Fe) from the sediment to the water column was accompanied by the depletion of dissolved oxygen in the water (Chen et al. 1976). Morgan and Stumm (1964) reported that under anoxic conditions, Fe and Mn in sediment become unstable and the mobilization of associated trace metals occurs. Singh and Subramanian (1984) concluded that manganese and iron play a significant role in influencing the distribution and transport of a variety of metal ions in the water system, since manganese oxides, along with iron oxides, are well known as the scavengers of the trace metals.

Trace metal pollution has been studied in the Brunette River watershed in the metropolitan region of Vancouver, British Columbia, since 1970's. Considerable data of water quality, urban hydrology, and trace metals both in water and in sediment have been collected over a twenty-year period (McCallum 1995). High concentrations of manganese have been observed in the stream sediment within the Brunette River watershed in recent years. The methylcyclopentadienyl manganese tricarbonyl (MMT), a manganese based gasoline additive used in the automobile since 1970's, may account for this finding (Mattu unpublished data). The high level of manganese in the Brunette water system may be the consequences of combustion products from MMT, possibly in the forms of Mn-phosphates, Mn-oxides, and Mn-sulphates (Ethyl 1997). These are deposited on the urban impervious surface, and discharged into the water by surface runoff. Since manganese is one of the regulators for the trace metal toxicity, the examination of metal manganese in the water system is also an important part of trace metal bioavailable studies.

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This thesis focuses mainly on the examination of bioavailable trace metal species in the waterway and their distribution under different flow and chemical conditions in the Brunette River watershed. Two approaches were employed in the study. The first is the speciation of trace metals in the water samples. The information on possible forms of bioavailable trace metals existing in urban storm runoff and in streams can be obtained with this physico-chemical analytical technique. The second is dialysis with receiver resin technique. Through this technique, the uptake of trace metals by aquatic organisms is simulated. The results of this approach are to provide more meaningful expression of the potential availability of trace metal contaminants in an urban watershed, especially during intermittent stormflow conditions.

This study is expected to provide more information on trace metal partitioning in the typical urban water system, and gain insight into the spatial (along the metal transport route from street runoff to stream) and temporal (stormwater, snowmelt, as well as baseflow) distribution of the potential toxic effects of the trace metals to the aquatic organisms. The specific objectives of this study are:

(1) To characterize the bioavailability of trace metal contaminants (Cu, Zn, Mn, and Fe) in the Brunette River watershed by following the hydrological gradient through the watershed.

(2) To collect information on the potential metal uptake by the organisms during baseflow, stormwater runoff, and snowmelt conditions using dialysis with the receiver resin technique.

(3) To investigate the influence of manganese on the bioavailability of trace metal copper and zinc in the water stream.

The thesis is organized in the following sequence. In Chapter 1, the general introduction of trace metal bioavailability in the aquatic system and the objectives of this study are presented. Chapter 2 reviews the relevant literature on research on metal toxicity, the techniques used to measure bioavailable trace metals, and mechanisms of trace metal transportation in urban water system. The background information of metal contamination in

the Brunette River watershed and relevant water quality are also reviewed in this chapter. Chapter 3 describes the methodology of this study, which includes sampling programs, *in situ* dialysis with resin receiver experiment, and the speciation techniques. Chapter 4 presents the results of the trace metal speciation and the *in situ* resin receiver experiments. The bioavailability of trace metals Cu and Zn in Brunette River watershed, the effects of metal manganese in regulating the partition of trace metals Cu and Zn in the water system, the control factors affecting the trace metal uptake and partitioning, and the metal transport in the surface runoff are also discussed in this chapter. Chapter 5 draws the conclusions from this study and makes recommendations for further monitoring and research.

Chapter 2

Literature Review

Stormwater runoff in the urban watershed contributes significant amounts of trace metals to the receiving waters by washing off from impermeable surfaces. The monitoring data in various urban watersheds demonstrate that these intermittent trace metal discharges may exceed defined chronic and acute criteria for protection of aquatic life when compared to relevant water quality standards (Morrison 1985). Florence and Batley (1980) pointed out that in the case of metal toxicity, the determination of the total concentration of trace metal in a water sample provided very little information about the toxicity of the water. It is generally accepted that only the metals in specific forms can be assimilated by the organisms, which are termed bioavailable metal forms.

In natural surface water, trace metals present in a wide range of chemical forms, which are generally grouped into dissolved and particulate phases (Morrison 1989). The dissolved phase consists of hydrated ions, inorganic and organic complexes, together with species associated with heterogeneous colloidal dispersions and organometallic compounds. On the other hand, the particulate phase contains elements in various chemical associations, ranging from weak adsorption to binding in the detritus mineral matrix. The definition for these two phases is based on the conventional concept that the "dissolved" metals are all metal species that pass through 0.45-μm filter, and the remaining metals on the filter are called "particulate" metals.

When relating metal levels to toxic effects in the aquatic system, it is important to recognize the phase of the metals. It has been found that the dissolved metal can be taken up by the aquatic organisms more directly and easily, which may cause acute toxicity if there are

sufficient dissolved metal species in the water column (Morrison 1989). However, it has been noted that high levels of trace metals are in the particulate phase either suspended in the water column or deposited into the bottom as the bed sediment depending on the particle size. In the urban watershed, a considerable loading of dissolved metals in storm discharges has been observed (Morrison 1985). The particulate metal may also be mobilized into the dissolved phase under certain hydrological and chemical conditions, or ingested directly by the organisms. The accumulation of trace metals in the organisms through uptake of both dissolved and particulate metal species cause the toxic impact on the aquatic ecological system.

2.1 Trace metals in the urban water system

Trace metal contaminants have been regarded as the typical non-point source pollution to the receiving water from urban watershed (Macdonald et al. 1997, IRE 1997). The impacts of trace metal pollution on the urban water system is determined by the trace metal load from the urban watershed area and the metal concentration in the urban stream. Considerable research has been conducted on the heavy metal pollution in urban watersheds (Sartor and Boyd 1972, Hall et al. 1976, Harrison et al. 1981, Morrison 1985, Morrison and Revitt 1987, Jarvis 1992, Solo-Gabriele and Perkins 1997). These studies demonstrated that trace metal characteristics, the availability of the metals from the urban contributing area, and the urban hydrological conditions are the major factors which control the cycling and transportation of the heavy metals in the urban environment.

Urban impervious surfaces such as highway, street and parking lot are recognized as the major metal contributing area, where the heavy metal emissions from urban transportation are deposited on these surfaces and transported to the receiving waters through surface runoff

(Morrison and Revitt 1987). Sartor and Boyd (1972) found that highway surface sediments often contain elevated levels of trace metals. Similar observations were made by Harrison et al. (1981), namely that heavy metals on the road surface, derived mainly from vehicular emissions, are largely adsorbed onto or associated with highway particulate. A monitoring program conducted in 1997 (Hall unpublished data) in the Brunette River watershed, a highly urbanized area in B.C. Canada, demonstrated that the discharges of metal zinc and the total suspended sediment in storm runoff were highly correlated. These findings were also supported by other studies (Morrison 1985, Jarvis 1992, Solo-Gabriele and Perkins 1997). It is expected that the suspended sediments play the key role on the metal transport during storm events.

The rainfall volume, rainfall intensity, watershed size, and slope as well as the antecedent dry period have all been identified as controlling factors in regulating the loading of heavy metals from an urban area (Sonzogni et al. 1980, Jarvis 1992, McDonalds et al. 1997). Sartor and Boyd (1972) concluded that the quantity of materials existing on the urban street was dependent on the length of time elapsed since the last rain. Jarvis (1992) suggested that washoff of the highway pollutants is generally assumed to be a function of the amount of pollution on the highway surface at the time of the storm, and the rainfall intensity.

Considerable research and modeling have also been done to predict the trace metal loading in the urban watershed, and the transportation of trace metals in the urban watershed (Solo-Gabriele and Perkins 1997, Yuan et al. 1999).

2.2 Toxicity of trace metals to aquatic organisms

Bioavailable trace metals refer to the fraction of the trace metals in their surrounding environment that are able to be taken up by organisms. The surrounding environment may include water, sediment, suspended particles, and food items (Spacie and Hamelink 1984). Toxicity occurs when the organisms are unable to cope with the trace metals that are taken up and accumulated in their body. The toxicity of the trace metal to the aquatic organism is

determined by the bioavailability of the trace metal species in the water environment, and the uptake of the metal by the aquatic organisms. The definitions of toxicity and bioavailability of the trace metals and their relations are reviewed as follows.

2.2.1 Bioaccumulation

The toxic impact of trace metals on the aquatic organisms is due to the accumulation of trace metals in the organisms, which is referred to as bioaccumulation. Bioaccumulation occurs when the uptake of a chemical by an organism exceeds its elimination (Spacie and Hamelink 1984). Two mechanisms are involved in the bioaccumulation process, namely bioconcentration and biomagnification. The first mechanism refers to the process that, through direct adsorption and/or partitioning from the aquatic environment, the contaminants dissolved in water or bound to the sediment are taken up directly by the organisms and accumulated in their body (Tinsley 1979). The second mechanism is due to the pollutant distribution in different levels of the food chain, and is referred to as food chain biomagnification. Tinsley (1979) stated that accumulation in a food chain depends on the movement of mass through the food chain, and on the fact that less than 50% of this mass is converted into tissue of organisms in the next higher level. The uptake of contaminants in each level in the food chain leads to the accumulation of the contaminants in the higher level of predator, and finally the toxic effect to the organisms. A typical example of trace metal bioaccumulation was found for mercury (Hg), or more accurately methylmercury, which is accumulated through the aquatic food chain. Even in an extremely low level in natural water, bioaccumulation of mercury occurs. This is because mercury, when methylated, is very effectively absorbed by a variety of aquatic organisms. Wren et al. (1995) reported that aquatic organisms accumulated mercury from food, water and sediments. They found that even though most of the mercury in water is in the divalent inorganic form, the mercury in the methylated forms predominates in tissues of aquatic biota. Cox et al. (1975) measured concentrations of total mercury and methylmercury in aquatic biota collected from a stream receiving a continuous input of 0.8 μg of mercuric chloride per liter. They found that the bioconcentration factors of mercury ranged from 75 for *water boatmen* to 29,000 for *damselfly nymphs*.

2.2.2 Bioavailability of trace metals

Observations of trace metal toxicity impact demonstrated that the accumulation of metals in organisms was correlated to the metals in some specific forms rather than the total metal concentration. The term "bioavailability" of trace metals existing in the aquatic environment may represent those metal species that can be taken up and accumulated by the aquatic organism. Further partitioning of metals in dissolved and particulate phases shows the possible forms of trace metal in surface water, which are presented in Table 2-1 (Florence and Batley 1980, Morrison 1989).

Table 2- 1 Possible Forms of Trace Metal in Water

Phase	Chemical form	Example	Approximate diameter (nm) (Molecular weight)
Dissolved	Simple ionic species	$Zn(H_2O)_6^{2+}$	0.8 (0-150)
	Simple inorganic or organic complexes	$Zn(H_2O)_5 Cl^+$ Cu-glycinate	1-2 (0-150)
	Weak complexes Lipid-soluble complexes	Cu-Fulvic acid CH_3HgCl	2-4 (0-150)
	Adsorbed on inorganic and organic colloidals	$Cu-Fe(OH)_3$ – humic acid Pb^{2+}-humic acid	10-500 $(150-10^7)$
Particulate	Metals adsorbed onto or contained within clay and/or organic particles	Retained by 0.45 μm filter	>450 $(>10^7)$

Three groups of metal species in dissolved phase have been identified as having contributions to the bioavailability of the metals, and are listed in Table 2-1 (Florence and Batley 1980, Morrison 1989). They are metals in simple ionic form, metals in weak complexes, and metals in lipid-soluble complexes. The reason to classify these three metal forms as "bioavailable" is based on the transport mechanisms of trace metal through bio-

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membrane, e.g. transport by passive diffusion; transport by carrier-mediated pathways; and active transport process. Morrison (1987) suggested that the passive diffusion might dominate metal transport across the membrane of a living cell. In the passive diffusion process, the rate of diffusion is determined by the molecular size. As such, free metal ions can diffuse through a membrane fast, while the colloidal species cannot move easily across the membrane because of their larger size. For lipid-soluble complexes, a rapid penetration pathway was provided by the passive diffusion process so that the highly toxic effects of these species to the organisms were observed. The other two transport routes such as carrier-mediated pathways and the active transport process are also favored for the transport of free and weakly complexed metal forms. More transport mechanisms were described in detail by Luoma (1983), Viarengo (1985), Spacie and Hamelink (1984) and Morrison (1989).

As mentioned above, the soluble form of the trace metal accounts for only a small portion in the water system, most of the metals actually exist in the particulate phases that are bound to the sediment. Therefore the ingestion of particulate trace metal by the aquatic organisms is also a very important part for the studies of trace metal bioavailability.

2.2.3 Trace metal toxicity studies

Trace metal toxicity studies have found that various factors can affect trace metal accumulation and its toxicity to the aquatic organism. They include (1) existing trace metal forms in the water environment, (2) the type of the aquatic organisms exposed to the trace metals, and (3) the physical-chemical conditions of the water. Numerous studies have already been conducted to investigate the effects of these factors on trace metal toxicity.

2.2.3.1 Trace metal forms

Trace metals in different forms have different accumulation rates and thus have different toxicity to organisms. Bindra and Hall (1977) monitored Pb levels in *chironomids* sampled from two watersheds – one in urban and one in rural areas of Lower Mainland of British Columbia. They found that Pb concentration ratio of animals to sediments was 2.76:1 in the urban watershed, while it was relatively low in rural watershed with the range of 0.27:1 to

0.34:1. They concluded that the large difference in the accumulation of Pb in those two watersheds was probably the result of the different forms of Pb in the sediments.

a) Ionic metal

The ionic form of dissolved metal is often considered the most readily available and toxic form. In the early toxicity studies, Petersen (1982) found that free Cu ion was toxic in the range of 10^{-10} to 10^{-12} mole to the freshwater alga, *Scendesmus quadricauda*. Zevenhuisen et al. (1979) reported that the concentrations of 10^{-6} to 10^{-10} mole free Cu ion were found to inhibit bacterium, *Klebsiella aerogenes*. Freedman et al. (1980) demonstrated that the mortality of the *amphipod Hyallela azteca* strongly correlates to ionic Pb concentration.

b) Weakly bound metal forms

It has been found that the weakly complexed metal species can also be assimilated by aquatic organisms. Theis and Dodge (1979) observed the uptake of $CuOH^+$ and Cu^{2+} by the midge larva, *Chironomous tentans*. Guy and Kean (1980) showed that five organic ligands with relatively high Cu stability constants were toxic at a concentration of 10^{-8} M Cu. Luoma (1983) found that the toxicity was higher for citric acid (10^{-10} M Cu) and ethylenediamine (10^{-9} M Cu) which have low stability constants with Cu. He suggested that these small organic ligands may transport Cu into the cell via the biological membrane. By using EDTA as the complexing ligand to simulate the uptake by organisms, Allen et al. (1980) found that $ZnOH^+$ and Zn^{2+} were the toxic species to the alga *Microcystis aeruginosa*. Both the carbonate and free ionic forms of Pb have been reported as toxic to rainbow trout (Davies et al. 1976)

Humic substances act as the important complexation ligands for trace metal ions in natural water (Morrison 1989). It is believed that complexation of metals by humic substances reduces the metal bioavailbility, and thus the potential toxicity. Winner (1985) observed that a linear relationship between the LC_{50} value with increasing humic substance concentration, which reduced both the acute (3-day) and chronic (42-day) toxicity of Cu to the crustacean *D. pulex*.

C) Metal bound in Sediment

Metals bound in sediment are classified as the particulate form. It has been found to be an important source for the metal accumulation in aquatic organisms. Although there was no straightforward relationship between trace metal levels in organisms and total levels of metals in the sediment (Thomas 1997), the high metal levels both in the tissue of organisms and in the sediment in which they were exposed, suggested the uptake of trace metals by the organisms (Stecko and Bendell-Young 1999, Thomas 1997, Bindra 1983). The mechanisms of metal accumulation in organisms through sediment ingestion are complicated and this process is controlled by various factors. One example of sediment ingestion by worms was shown by Luoma and Bryan (1979). They found that Cu released from ingested sediments by stomach acids is readily absorbed by the tissue of the worms. Bindra (1983) reported that some organisms like *chironomids*, which constituted a major food source for freshwater and estuarine fish, could accumulate toxic trace metals from contaminated sediment substrates. In the process, toxic elements may be mobilized directly from sediments to food chain which is linked to the human aquatic food source.

It has been recognized that there is a clear relationship between the trace metal level in the organisms and the specific metal-binding forms, called 'biological relevant' components, in the sediment (Thomas and Bendell –Young 1998, Bindra and Hall 1977, Bindra 1983, Stecko and Bendell-Young 1999). Thomas and Bendell-Young (1998) found that the copper concentration in the tissue of bivalves correlated positively with ER-Cu (Mn-oxide bound) and RED-Cu (Fe-oxide bound) copper in the sediment. The amount of copper recovered in the RED phase (RED-Cu) accounted for 38% of the variability in tissue levels. The major interests of the bioavailability studies on the particulate metals have now focused on what kind of metal-binding forms in the sediment, and how easy they can be released to the water column under various physical, chemical and biological conditions, or to the sediment geochemistry.

2.2.3.2 Aquatic organisms

Bioavailable trace metal species in the water may not be taken up by all of the organisms living in the water environment. Rand and Petrocelli (1984) reported that substantial

assimilation differences might exist among individual organisms. For example, not all organisms respond in a quantitatively identical manner to the same concentration of a toxicant. The effects of such an exposure might vary from very intense in some organisms to minimal or none in other organisms. That is, some organisms may die and others survive with apparently minimal adverse effects. The observation by Bindra (1983) in his microcosm studies indicated that contaminated sediments were most toxic to the *opossum shrimp*, but were much less toxic to the *oligochaetes worm*, since the *oligochaetes worm* appeared to have the higher capacity to mobilize and excrete trace metals from its tissue. Due to this characteristic, some organisms, such as worms, molluscs and aquatic insects, are usually used as indicators to determine the trace metal availability in the aquatic system.

Bryan (1971) proposed that the *polychaete* worm, *Nereis diversicolor*, seemed to reflect the extent of Cu contamination of its environment and can be used as one of the suitable indicator organism species for metal contamination of sediments. In his study, *polychaetes*, sampled from two estuarine sediments had Cu concentration of 407 and 49 µg/L, had Cu contents of 22 and 9 µg/L, respectively.

The results of studies on Zn accumulation in *oligochaetes* are often contradictory. Ray et al. (1979) reported that Zn in *Nereis virens* remained constant when exposed to water containing 1.0 mg/L of Zn. Guthrie et al. (1979) attributed the high concentration of Zn in polychaetes from a marine microcosm to its ability to accumulate Zn from both sediment and water.

Molluscs are filter feeders or deposit feeders. They depend upon the ingestion of sediment or suspended particulate matter for their food supply. It has been reported that mussels from the waters close to major population and industrial centers often contain high concentrations of Cu (Fowler et al. 1974, Anderson 1977, Popham et al. 1980). Fowler and Oregioni (1976) attributed the accumulation of Cu by mussels to their feeding habit and their slow uptake and excretion mechanisms. Oysters are known to accumulate high concentrations of Cu and appear to reflect the levels in the environment. In 22 weeks of exposure of oysters to contaminated seawater and sediment, the concentration of Cu in the oysters ranged from < 40 µg/L to 600 µg/L (Watling and Watling 1976).

Freshwater clams and mussels are known to have a high affinity for the metal Zn (Forester 1980). Anderson (1977b) reported Zn concentration in six species of freshwater clam and sediments collected from the Fox River near Chicago. Zinc levels in clams were greater than that in the sediments. Anderson (1977b) found that the distribution of Zn in various organs of two species of clams (*Anodonta marginata* and *Lasmigona complanata*) indicated maximum concentrations in gills and viscera, which suggested that Zn uptake was mainly through food intake.

Chironomids, a kind of aquatic insect, was also found to accumulate the trace metal Cu. Bindra and Hall (1977) found considerable accumulation of Cu by these organisms, created bioaccumulation ratios ranging from 1.1 to 4.5 under field conditions. The accumulation of zinc in aquatic insects was also reported by Namminga and Wilhm (1977). In their study, the zinc levels were found in *chironomides* and sediments collected from Skeleton Creek, Oklahoma. The mean concentration of Zn in the organisms was 57 µg/L, 3.6 times higher than that in the sediments. Bindra and Hall (1979) studied the distribution of trace metals in various geochemical phases of sediments and in the burrowing oligochaete worms, collected from various watersheds of the Lower Mainland of British Columbia. Sediments were characterized for a number of chemical and physical parameters such as percent organic and inorganic carbon, pH, redox potential, and particulate size distribution. No single parameter appeared to control Zn in the worms.

2.2.3.3 Environmental control factors

Numerous factors such as temperature, pH, salinity, hardness, dissolved oxygen etc. in the aquatic environment influence the toxicity of pollutants to organisms. Two selected examples of these effects are illustrated below.

a) Water pH

Water pH is an important factor in regulating bioavailable metal forms and their toxicity. Allard et.al. (1987) reported that in normal freshwater pH condition, Cu mostly existed in the

particulate phase, and jumped from 60% to 90% when the pH increased from 5.5 to 7. The particulate Zn, on the other hand, increased from 10% to 70% with pH change in the same range. Morrison (1989) proposed that hydrogen ion competes with free metal ion for cellular binding sites at low pH, thereby reducing metal toxicity; whereas above pH 6.5, the free metal concentration decreases due to the presence of Cu hydroxide complexes which may not be toxic. Fleming and Trevor (1989) found that water pH greatly affects copper speciation. Petersen et al. (1984) reported that Cu toxicity to the green alga *S. quadricauda* increases from pH 5.0 to pH 6.5 and is constant above pH 6.5. Harrison et al. (1986) found that a decrease of pH from 7 to 5 led to a 50 % to 60 % reduction of Zn flux into the alga *Chlamdomonas variabilis*.

b) Water hardness

Water hardness, usually expressed as mg/L $CaCO_3$, substantially affects metal toxicity. The almost universal observation on the relation of water hardness to metal toxic effects is that metals are less toxic in hard water, provided the pH is kept constant. The effect of hardness varies with the metal, being most dramatic with cadmium, because of its precipitation in hard water (Rattner and Heath 1995). Copper and zinc are intermediate in their interaction with hardness (Brown 1968, Miller and Mackay 1980, Bratley and Sprague 1985a). In the case of zinc, the effect of hardness seems to rest with changes in the fish gills rather that with metal speciation. Increasing hardness reduces the uptake rate of zinc by gill tissue, the prime target organ for zinc becoming lethal (Bratley and Sprague 1985b). Playle et al. (1992) found that calcium (but not $CaCO_3$) reduced gill accumulation of copper at pH 4.8, but not at pH 6.3. Apparently, both calcium and hydrogen ions compete with copper for binding sites on gills.

2.2.3.4 Manganese and iron oxide control the trace metal bioavailability

Manganese-oxide, as well as iron-oxide have been recognized as important controlling factors in trace metal bioavailability and toxicity. Singh and Subramanian (1984) pointed out that the incorporation of trace metals into hydrous manganese or iron oxide was due to adsorption (specific or electrostatic), ion-exchange or co-precipitation. The low solubility of hydrous Mn and Fe oxides together with their large surface area approximately 300 m^2 /g,

i.e., small grain size (of the order of 100 A^0) and favorable surface change in the pH range generally found in natural aquatic systems make these hydrous oxides efficient scavengers of trace metals.

Thomas and Bendell-Young (1998) investigated the trace metal partitioned in the surficial sediment and linking these metal forms to the deposit feeder *Macoma balthica* at 26 locations in the intertidal region of the Fraser River estuary in B.C. Canada. Three biologically relevant sediment components, named easily reducible Mn (ER-Mn), reducible Fe (RED-Fe) and organic matter, were characterized with chemical extraction procedure. The trace metal Cd, Cu, Pb, Ni and Zn were separated and measured in these three fractions in the sediment. The analysis clearly indicated that metal levels in the tissue and shell of *M. balthica* were best related to the concentration of metal associated with the ER-Mn components of the sediment.

Studies suggested that trace metals associated with the iron and manganese oxides in the sediment are most available to deposit feeding organisms (Thomas 1997). Bendell-Young and Harvey (1994) found that zinc and copper concentrations in *chironomids* correlated with zinc and copper concentration associated with the manganese oxide portion as modified by amounts of organic matter. Luoma et al. (1995) reported that the concentration of silver associated with the iron and manganese oxides was a reasonable good predictor of silver bioavailability to *Macoma balthica*.

2.3 Techniques used to determine bioavailable metal species

With the realization that bioavailable metal species depend on their chemical form, various physio-chemical separation methods and associated analytical techniques have been developed (Florence and Batley 1980, Morrison 1985, Bendell-Young et al. 1992). Numerous studies on trace metal toxicity and bioavailability have been based on these techniques (Bindra and Hall 1977, Florence and Batley 1980, Harrison et al. 1981, Morrison 1985, 1987, 1989, Bendell-Young et al. 1992, Thomas and Bendell-Young 1998, Stecko and

Bendell-Young 1998). These techniques are still widely used in the study of metal bioavailability.

2.3.1 Separation of metal species in dissolved phase

Florence and Batley (1980) summarized commonly used separation techniques in speciation of metals in the dissolved phase, such as liquid-liquid extraction, dialysis, ultrafiltration, centrifugation, and ion-exchange. Of all these physio-chemical separation techniques, ion-exchange using Chelex resin to separate bioavailable metals from other forms was recommended because of its selectivity.

Chelex chelating resin is classed as a weakly acidic cation exchange resin by virtue of its carboxylic acid groups. The resin is made by copolymers of styrene divinylbenzene. The paired iminodiacetate ions contained in the resin act as chelating groups in binding polyvalent metal ions (BIO-RAD), which gives it a higher binding strength to the metal. The mechanism of resin selectivity for trace metals is due to its structure with homogeneous pores down to 1.5-3.0 nm (Morrison 1985). The stability of the iminodiacetate groups in the resin (log k $\approx$ 13 for Cu) is such that weakly complexed metals may be dissociated and preferentially associate with the Chelex-100 (Morrison 1985). When polluted water contacts the resin, the metal ion may adsorb either to the resin surface or to the resin pore surface by diffusion. The transport of metal ions into the resin pore is driven by a strong diffusion gradient and then undergoes rapid chelation. The metal in colloidal forms is prevented from adsorption by the resin because of their large molecular size. The efficient separation of metal species in seawater by Chelex resin was found with pore size structure of resin about 1.5 –3.0 nm to bind metal in the ionic form (small size) and prevent binding of colloidal metal in the large molecular size (Florence and Batley 1976).

Morrison (1985) employed Chelex –100 resin in the metal partitioning of stormwater. In his study, three dissolved metal fractions were separated, which were termed electro-chemically available metal fraction, representing the metal in ionic form; chelex removable fraction, representing ionic and weakly bound inorganic and organic low molecular weight form; and

colloids (strongly bound fraction). The determination of chelex removable fraction is by passing stormwater through a resin column, trace metals in the water are exchanged with the cation such as Ca^{2+} or Na^+ on the resin and become complexed with the resin. The trace metal in the resin can then be eluted with acidic solution. The metals in acidic elutant are referred to as the resin removable or resin extractable fraction, which implies that they are the potentially bioavailable metal species in the stormwater. By using this separation scheme, the metal in the resin removable fraction was found to represent a significant proportion of total metal for both Zn (48%) and Cd (57%) in the urban stormwater, which showed the potential toxic impact on receiving water (Morrison 1985, Morrison and Revitt 1987).

The high selectivity of Chelex resin to the freshwater trace metals, such as Cd, Cu and Zn, was described in the manufacturer's instruction manual (BIO-RAD). The recovery test of metal copper and zinc from Chelex resin in stormwater suggested that the resin can be used as an efficient tool for the determination of bioavailable metal species in the urban freshwater environment (Morrison 1985, Morrison and Revitt 1987).

2.3.2 Speciation of metal species in the particulate phase

Speciation techniques account for the most sediment bioavailable trace metal studies since anthropogenic metals introduced into the aquatic environment occur either in particulate form or are rapidly sorbed to particles (Regnier and Wollast 1993). Stecko and Bendell-Young (1999) pointed out that once the trace metals enter water, they are adsorbed relatively fast and contribute to the pool of metals associated with either suspended particulate matter (SPM) within the water column or are ultimately incorporated into deposited sediments (DS). The ingestion of SPM or DS by organisms as their food source will lead to the trace metal accumulation in the organism and possible transfer via the food chain to a higher trophic level. On the other hand, the geochemically unstable metal fraction in SPM or DS may release trace metals to the dissolved bioavailable forms under certain conditions (Morrison and Revitt 1987).

The sequential selective extraction procedure (SEQ) with atomic absorption spectrophotometry (AAS) analysis for the geochemical speciation of metal species in the particulate phase has been developed and widely applied (Tessier et al. 1979, Harrison 1981, Bendell-Young 1992). In general, six geochemical forms have been classified by extraction with selected reagents for the metal associates, which are termed exchangeable form, carbonate form, easily reducible form (bound to Mn-oxide), reducible form (bound to Fe-oxide), organic form and residual form. The modifications of this analytical method have been conducted by various researchers based on their particular interest on the sediment metal geochemistry and bioavailability (Harrison et al. 1981, Morrison 1985, Bendell- Young et al. 1992, Thomas and Bendell-Young 1998, Stecko and Bendell-Young 1999). Bendell-Young et al. (1992) proposed the simultaneous sediment extraction procedure (SIM). Comparing it to SEQ, they suggested that for sediment with low carbonate content, the SIM is a more efficient partitioning method because the loss of metal due to the "in between reagent rinses" in each fraction by SEQ can be overcome, and also SIM needs less time for the sample processing. However, a larger sediment sample is needed when using the SIM method.

The sediment speciation technique has been widely used to define geochemical components related to various soils, deposited sediment and suspended sediment in the water system. Harrison (1981) investigated the chemical association of lead, copper, zinc and cadmium in the street dusts and roadside soils by using sequential extraction procedure. He found that, by partitioning metals into five fractions, lead, cadmium and zinc were predominantly associated with carbonates and Fe-Mn oxides, whereas copper was largely in organic association.

Stecko and Bendell-Young (1999) studied the geochemistry of suspended particulate matter (SPM) contrasting to the deposited sediment (DS) in the Fraser River estuary, BC, Canada. A distinct difference was found in the geochemistry between these two particulate phases. Concentrations of organic matter and reducible Fe (R-Fe) in SPM were significant higher in the winter months than in the rest of the year, while the organic matter has no seasonal change in the DS. Concentrations of Cu, Zn and Pb in SPM were up to 17 times greater than

that in DS, with a higher proportion of these metals associated with the easily reducible component (oxides of Mn and amorphous forms of Fe oxides) during winter as compared to summer months. The findings of this study suggested that the seasonal change in the partitioning of metals, in addition to greater proportion of the metal occurring in an easily reducible form in SPM relative to DS, has potentially important implications for sediment ingesting organisms capable of filter-feeding on both SPM and DS (Stecko and Bendell-Young 1999).

Morrison (1987) partitioned the suspended sediment from urban stormwater into three fractions, namely exchangeable, hydrous oxide, and organic fractions, by using a selective sequential extraction technique. He suggested that the exchangeable fraction may represent the bioavailable metal source because metals in this fraction may exchange or complex with anions, so that they might be released into the soluble phase under normal pH conditions. The hydrous oxide (Mn-oxide or Fe-oxide) and organic fractions contain more strongly bound metals and are unlikely to have any immediate biological impact, but are potentially released into the water column when there is a significant drop in pH or redox potential in the water or sediment environment.

2.3.3 Dialysis with resin receiver – simulation of metal uptake by the organisms

Bioassays are considered an accurate method for studying trace metal bioavailability, though they are time consuming, and sometimes are species-specific that lead to the misunderstanding of potential trace metal impacts in the water environment (Florence and Batley 1980). A dialysis with resin receiver approach has been developed to simulate the uptake of metal species by the aquatic organisms (Morrison 1987). It is generally accepted that metal species either in ionic form or bound to small inorganic or organic molecules, such as weak complexes or lipid soluble forms, with molecular weighs less than 1000, can be assimilated by a living cell. The dialysis membrane bag (MWCO (molecule weight cut off value) = 1000) can be used since it provides a fairly efficient separation between colloidal and ionic species (Morrison 1985). The Chelex resin is encapsulated in the bag to make it the

receiver. The consideration for the receiver structure is that the dialysis membrane has been designed to simulate the membrane of the living cell, and the Chelex resin within the bag as the constituent of the cell. When exposed *in situ* for a certain time, the trace metal species will penetrate the dialysis membrane and become chelated by the resin inside the bag. The concentration gradient of the membrane bag causes metal species to traverse the membrane from the polluted water since the resin chelates the metal continuously inside the bag creating a diffusion gradient. The trace metal assimilated by the receiver represent the metal species that is bioavailable in the aquatic environment, and can be quantitatively expressed as the metal uptake rate by the organisms (pg metal $mm^{-2}.hr^{-1}$) based on the bag area and the exposure time. Morrison (1987) suggested that the dialysis with receiver resin technique should be particularly suitable for stormwater studies over a long time sampling period where intermittent discharges of metal are experienced. These may normally be missed by a grab sample during stormflow. In addition to the resin uptake of trace metals, the membrane uptake rate can also be examined and expressed in pg metal $mm^{-2}.hr^{-1}$. The uptake of metal by membrane surface may represent those metal species that are available to the surface of the organism but may not readily penetrate a membrane (Morrison 1987).

By applying dialysis with resin receiver technique in the urban stormwater, Morrison (1987) reported that an increase of bioavailable metal uptake rate was observed during experiment periods containing rainfall events, while the low and fairly constant uptake rates were found during baseflow. The sensitivity of metal uptake by the receiver with the metal level in the water was also tested in the field under stormflow conditions. The results are given in Table 2-2.

Table 2- 2 Uptake of metals by Chelex-100 in a 3500 MWCO dialysis bag
(Morrison 1985)

Time period	Runoff volume (m^3)	Metal uptake rate, pg / mm^2. hr			
		Zn	Cd	Pb	Cu
Nov.22-26, 1984	650.4	73.1	0.12	0.51	19.3
Nov.26-29, 1984	169.2	26.5	0.05	0.25	2.03

The data in Table 2-2 indicate an increase in metal uptake during the period of higher storm runoff. It may therefore be concluded that the dialysis with resin receiver is sensitive to the increased intermittent stormwater discharge (Morrison 1985).

2.4 Trace metal studies in Brunette River watershed

The Brunette River watershed is located in the geographic center of the Great Vancouver Regional District (GVRD). It is a small tributary system to the lower Fraser River with an area of 98 km^2 (Fig. 2-1). The watershed is highly urbanized, and is within the municipalities of Burnaby, Vancouver and New Westminster. Four predominant land uses within the watershed include residential (42%), industrial (5.5%), commercial (15%), and open space and forested (31%) (MacDonald et al. 1997). Highway 401 and Lougheed Highway following the lower elevation contours around both sides of Burnaby Lake, as well as the streets and alleys, occupy approximately 15% of the total land within the watershed, and make up significant impervious surfaces for stormwater runoff (Hall and Anderson 1988). Two shallow lakes, namely Burnaby Lake (120 ha) and Deer Lake (80 ha) are the prominent features of this drainage basin (Bindra and Hall 1977). The main tributary up-stream of Burnaby Lake is called Still Creek. This creek collects the major stormwater from watershed upstream and discharges it into the west-end of the Burnaby Lake, while the Brunette River at the downstream of the Burnaby Lake enters the Fraser River with all the flow from the watershed. The streams and lakes within the watershed have been classified as the storm sewer by the Great Vancouver Regional District (GVRD).

Stream flow characteristics are highly dependent on the region's topography and climatic conditions. Within the watershed, while the steep gradients of the land in the upper reaches of both Still Creek and the Brunette River cause high stream flow, the lower reaches of Still Creek (from Gilmore Avenue to Burnaby Lake) experience near-quiescent conditions during dry periods leading to a variation in stream velocities (McCallum 1995). The maximum discharges occur during the high precipitation winter months, and the minimum discharges are in the summer.
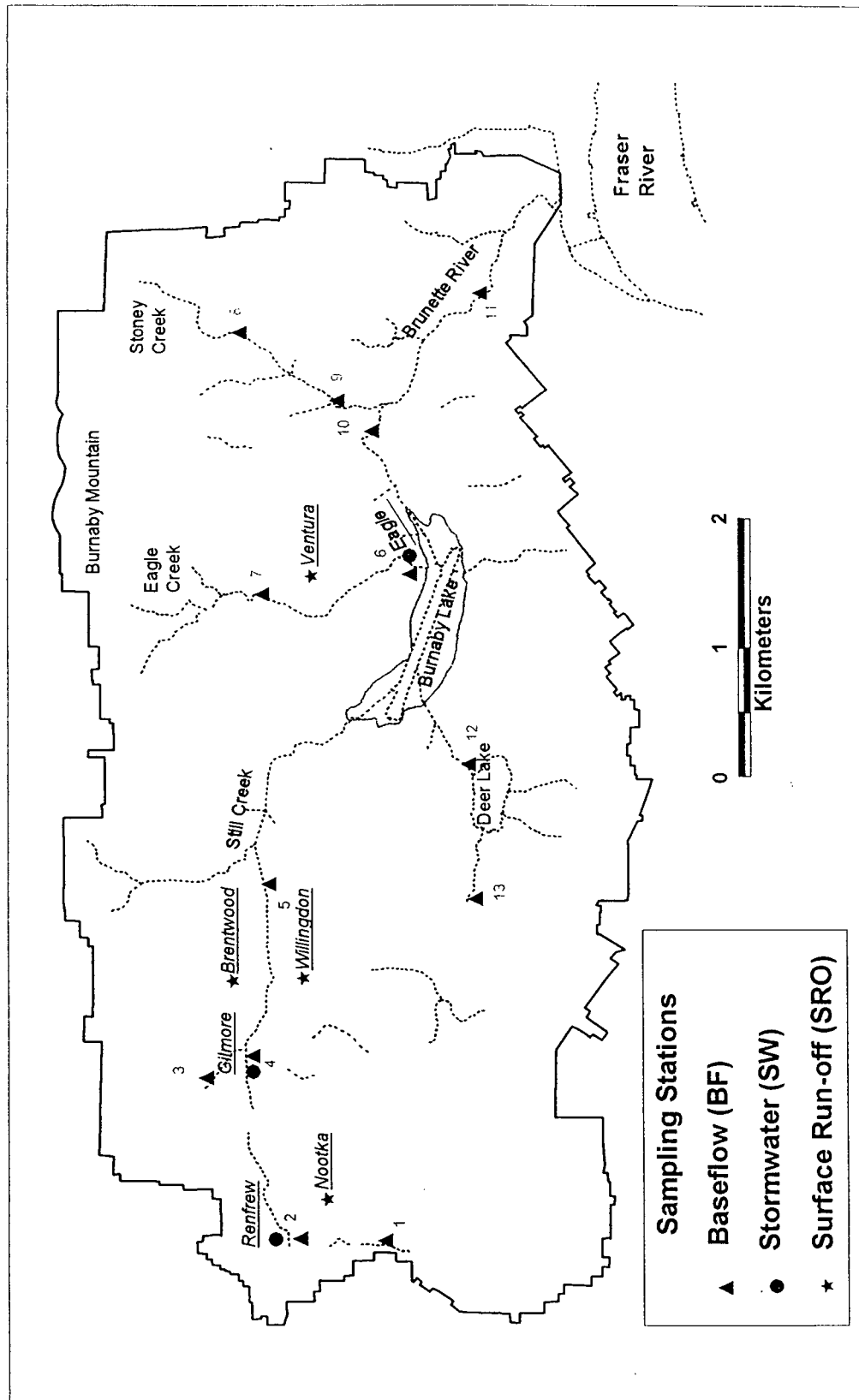
Figure 2- 1 Brunette River Watershed

Stormwater contaminants in Still Creek have been an issue since the beginning of urbanization in the region. The first zoning of industrial land in the watershed (Still Creek area) in 1947 marked the beginning of a prolonged commercial and industrial expansion (Dawson et al. 1985). The dramatic increase of the population in the Lower Mainland caused the rapid increase of automobile traffic. The associated problems of roadway congestion and air and water pollution are a major concern in the Brunette watershed as a result of large traffic volumes throughout (McCallum 1995).

There were significant changes in wildlife populations following the clearing and settlement of the region. Water pollution and habitat destruction caused the complete elimination of the salmon population in Still Creek and in Brunette River during 1960-1970's. After the efforts of Sapperton Fish and Game Club to clear river debris, eliminate point sources of contamination, and re-stock fish from hatcheries, a few salmon have returned to the Brunette River recently (Rudolph 1995).

The examination of water quality and trace metal contamination in the Brunette River watershed started in 1970's (Hall et al. 1976). Based on the contaminant transport characteristics in the urban area (see Fig. 2-2), contaminants have been examined in various components such as baseflow, stormflow, street sediment, stream sediment, lake sediment, as well as fish tissues and benthic invertebrate. The trace metals Pb, Cu, Zn, Cd, Ni and Hg have been studied since they are the predominant contaminants in the urban watershed.

In order to examine water quality and the influence of non-point source pollution from urban stormwater runoff on the aquatic ecosystem, a comprehensive monitoring program was conducted by Fraser River Action Plan and Fraser Pollution Abatement Office of Environmental Canada from 1994 to 1995 (MacDonald et al. 1997). The report of this study indicated that under baseflow condition, dissolved oxygen in the lower reaches of Still Creek and in the upper reaches of Brunette River threatens the safe passage of fish during the summer. The levels of oxygen in the surface waters of lower Still Creek drop to <5 mg/L (50% saturation), while the bottom waters are often depleted. Fish kills have been observed in this reach of the river. The low dissolved oxygen (2.6 mg/L, 30% saturation) in the

Brunette River was also observed in summer, which was due to the highly colored water (avg. 70 mg/L) from Burnaby Lake that prevented light from penetrating into the water column and limited photosynthesis. The monitoring data showed that copper at all three stormwater sampling stations exceeded the water quality criterion of 2 μg/L for the protection of aquatic life.

During rainfall, the high concentrations of trace metals were found in the stormwater. The average total zinc concentration was found to exceed the safe criterion (30 μg/L) in both Still Creek and Eagle Creek during storm runoff period. The average copper concentration in Still Creek exceeded 50 μg/L, which is far higher than the water quality criterion for copper. Even though lead additives have been removed from gasoline, the average concentration of 10 μg/L lead in Still Creek was still detected, which exceeded the water quality criterion of 4 μg/L for the protection of aquatic life (Macdonald et al. 1997).
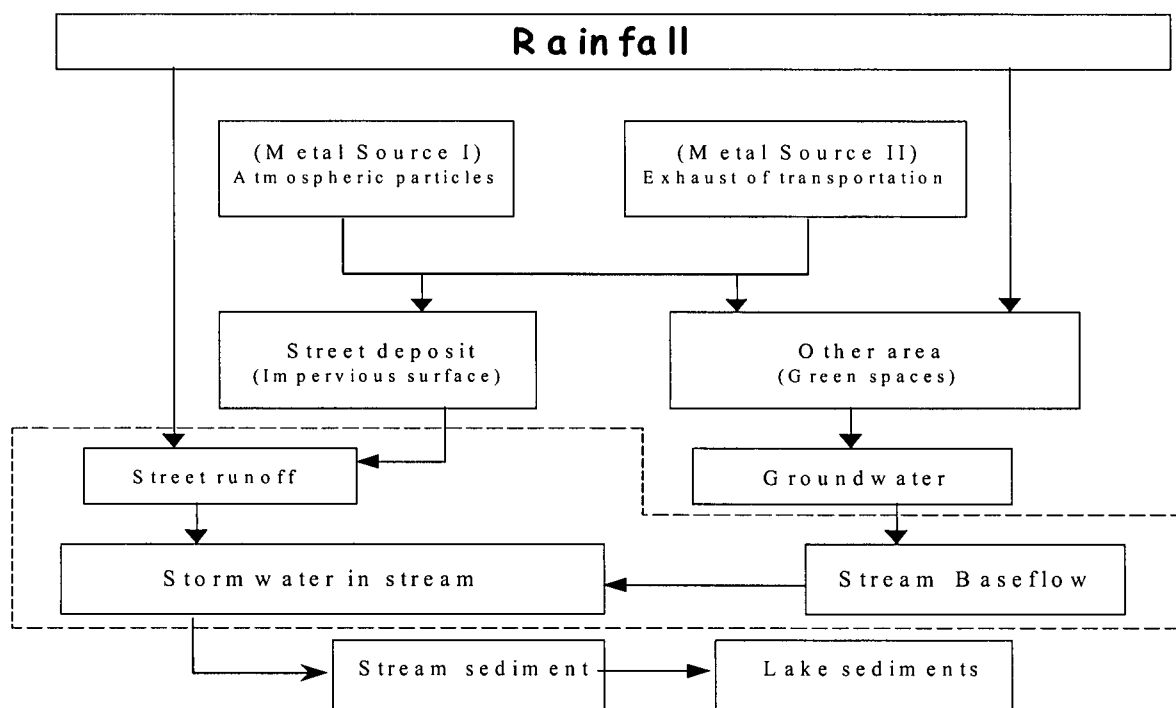
Figure 2- 1 Trace metal source, sink and transport in the urban area.

In earlier studies (Hall et al. 1976), a series of stream sediments and street surface materials were collected for one year period from July 1973 to June 1974, and 11 trace metals were analyzed. In this research, the relatively high levels of trace metals, especially copper, lead and zinc were found in the Still Creek stream sediments that were related to industrial activity and heavy traffic flow in this area. The low flow areas of both Still Creek and Brunette River were areas of trace metal sedimentation in the stream bed. The study indicated that the street surface materials appear to be one of the major sources of trace metal contamination.

Bioassay tests (Hall and Anderson 1987) using the *cladoevran*, *Daphnia* and stormwater indicated that the suspended sediments were toxic to aquatic organisms, as most contaminants in the stormwater were associated with these particles. Macdonald et al. (1997) reported that the suspended sediment at the Gilmore stream station (Still Creek) had an EC_{50} of 1-2%, which was characterized as a slightly toxic response. The suspended sediments sampled in runoff from a highly traveled roadway (Willingdon Ave.) were considered moderately toxic (EC_{50} 0.1-0.9%).

Manganese in the watershed water system is another contaminant of concern. The replacement of MMT (Mn based fuel additive) with lead since 1970's in Canada leads to the increase of manganese in the Brunetter River watershed. Data from McCallum (1995) and Schreier (1991) have reported an increase in Mn concentration in the stream sediments. A 2600% increase in the acid extractable Mn between 1973 and 1993 was reported by McCallum (1995). The observations from a recent manganese study within the watershed suggested that the lightly bound Mn in the acid extractable fraction may have an effect on trace metal dynamics in the system since Mn-oxides are scavengers of other trace metals (Mattu and Hall 1999).

2.5 Relevant environmental criteria for assessing trace metals

The establishment of criteria for the assessment of metal bioavailability must consider the effect of toxic metals on the organisms, and the interaction of the metal with surrounding organic and inorganic substances (Morrison 1985). The problems encountered in the assessment of metal toxicity may be caused by (1) chemicals in the water environment affecting the trace metal toxicity, and (2) trace metals exhibiting an extremely variable toxicity between species (Borgmann 1983). One example is that the humic acid causes a significant reduction of Cu toxicity to *Daphnia magna*. It is generally accepted that metal toxicity decreases with increasing water hardness. The relevant water quality criteria based on the water hardness were used for the freshwater toxicity assessment and are listed in Table 2-3 (Swain 1989), Table 2-4, and Table 2-5 (Morrison 1985).

Table 2-3 provides the specific trace metal objectives for the Brunette River system, which was established by Swain (1989) and reiterated by the Fraser River Estuary Management Program (FREMP) in 1991. The values listed in the table are for protection of freshwater aquatic life and wildlife, and for the secondary contact recreation (MacDonald *et al.* 1997).

Table 2- 3 Water Quality Objectives in the Brunette Water System (total metal)

Hardness (mg/L as $CaCO_3$)	Cu (μg/L)		Zn (μg/L)	Pb (μg/L)		Cr (μg/L)
	Long term Ave.	Long term Maximum	Maximum Value	30 day Ave.	Maximum Value	Maximum Value
	2		30	4	18	20
≥ 20		4				
≥ 30		5				

The US EPA trace metal criteria under different water hardness is presented in Table 2-4. Since these criteria take into account the effect of intermittent total metal discharges, it is considered to be more realistic for the assessment of stormwater impact.

Table 2- 4 EPA Water Target Concentrations (total metal) (EPA 1983)

Heavy metal	Total hardness (mg/L)	Freshwater toxic criteria (µg/L)		Intermittent discharge criteria (µg/L)	
		24 hour	Maximum	Threshold	Significant mortality
Copper	50	5.6	12	20	50-90
	100	5.6	22	35	90-150
	300	5.6	62	115	265-500
Zinc	50	47	180	380	870-3200
	100	47	321	680	1500-4500
	300	47	800	1700	3850-11000
Cadmium	50	0.01	1.5	3	7-160
	100	0.02	3.0	6.6	15-350
	300	0.08	9.6	20	45-1070
Lead	50	0.75	74	150	350-3200
	100	3.8	172	360	820-7500
	300	50.0	660	1400	3100-29000

The proposed value of environmental quality objective by European Economic Council (EEC) is given in Table 2-5. Under different total water hardness, the dissolved rather than total metal concentration was set up to protect freshwater organisms against toxic trace metals. However, the intermittent metal discharge was not considered in the criteria. The relevant freshwater toxicity criteria for trace metals have been set for some particular trace metals.

Table 2- 5 EEC proposed EQO* Values for Protecting Freshwater Life against Heavy Metals (Mance and O'Donnell 1983)

Total Hardness (mg/L)	Dissolved Pb (μg/L)	Dissolved Zn (μg/L)	Dissolved Cu (μg/L)
0-50	50	70	1
50-100	125	170	6
100-150	125	250	10
150-200	250	250	10
200-250	250	250	10
250+	250	500	28

EQO – Environmental quality objective

The previous studies in the Brunette River watershed demonstrated trace metal contamination in the water system (MacDonald et al. 1997). It was found that under the same water hardness (0-100 mg/L as $CaCO_3$), both the total and dissolved concentration of Cu and Zn exceeded the BC criteria listed in Table 2-3 by several times among street runoff and in stream. The dissolved Cu also exceeded the corresponding EEC limitation listed in Table 2-5. The total Cu at the two stream sites also exceeded EPA's criteria for 24-hour average for freshwater toxicity. The total Cu in the runoff even significantly exceeds the threshold of the intermittent discharge criteria.

The concentration of total metal Zn, on the other hand, exceeded EPA's criteria for both the 24-hour and maximum values for freshwater toxicity in street runoff. The concentration in Still Creek exceeded the 24-hour limitation for freshwater toxicity, but lower than the maximum limitation of the same criteria. Total Zn in downstream in Brunette was safely lower than all the criteria listed in Table 2-5.

Chapter 3

Methodology

Two methods, namely metal speciation and dialysis with resin receiver, were used in this metal bioavailability study. While the metal speciation technique was used to characterize bioavailable trace metal species in the urban water; the resin receiver technique was used to simulate the uptake of these metals by the aquatic organisms. The potential toxic impacts of trace metals in the urban aquatic system were assessed with these two approaches.

Three sampling sites were selected within the watershed for this study. In order to characterize the bioavailable metal species in the Brunette River system, the sampling was conducted under baseflow, stormflow, and snowmelt conditions in the past one and half years. Each water sample was analyzed through the speciation technique with atomic absorption spectrophotometry(AAS) to identify the bioavailable species under different flow conditions. The in-situ experiments of dialysis with resin receiver were also conducted in all three sites under the same set of flow conditions.

3.1 Sampling sites

The locations of the three sampling sites are shown in Figure 3 –1. The site selection is based on the transport route of trace metals from urban non-point sources to the receiving water following the urban hydrologic gradient. Site #1 is a sediment trap of a road in a commercial land use area. This site was chosen to evaluate the trace metal contaminants from urban impervious surface through surface runoff. Site #2 is located in Still Creek – upstream of the lakes in the watershed. It was used to investigate the trace metal species from a highly

impervious sub-watershed. Located in Brunette River, Site #3 was selected to study the metal species in the downstream section of the Burnaby Lake before entering the Fraser River.
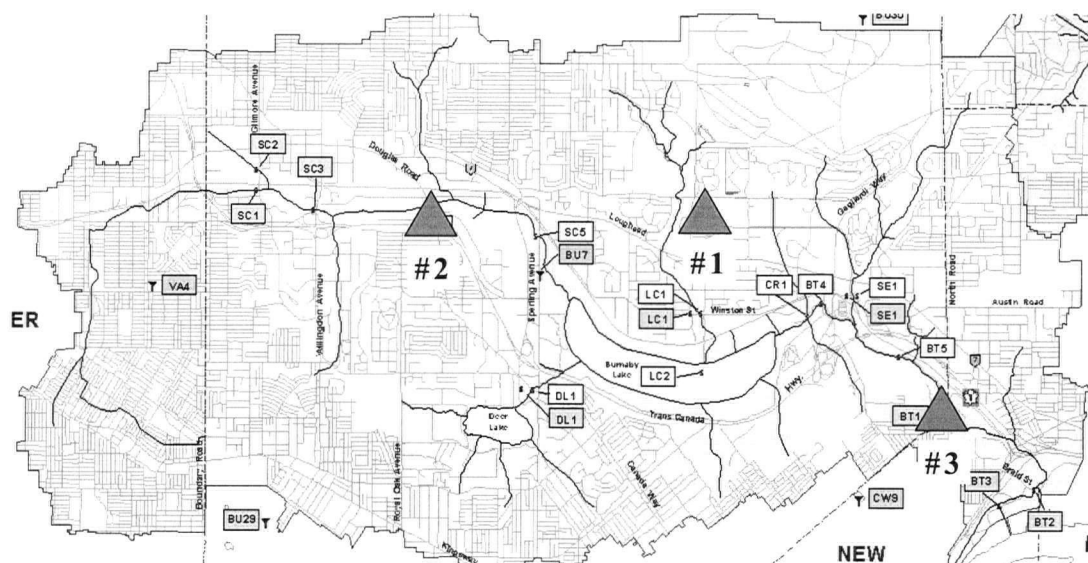
Figure 3- 1 Locations of the sampling sites in Brunette River watershed

Table 3- 1 Description of sampling sites

Station Number	Station Name	Location	Description
#1	Ventura	Ventura Drive and Lake City way SE. corner of intersection (On south slope of Burnaby Mountain)	• Light industrial area. • Representing the street runoff.
#2	Douglas Ave.	Still Creek at Douglas Ave.	• Industrial area. • Representing the watershed upstream of the lake.
#3	North Road	Brunette River at North Rd.	• Sampled within Hume Park. • Representing downstream of Burnaby Lake

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The detailed description for each site is given in Table 3-1. All the water sampling and receiver experiments of this study were conducted at these three sites. Another important consideration in selecting these three sampling sites is that considerable monitoring data are already available for comparison and analysis (MacDonald et al. 1997).

3.2 Trace metal speciation

The whole process of trace metal speciation consisted of three parts: water sampling, sample speciation and sample analysis.

3.2.1 Water sampling

Water was sampled at all the three sampling sites described in 3.1. Two sampling programs were conducted – grab sampling and intensive sampling. While the grab samples were collected in baseflow and stormwater conditions, the intensive water sampling was conducted over a typical storm event. The water samples were collected in a rotating sequence from site to site for one typical storm event. At each site, the water was sampled at intervals of approximately 40 min. The sampling procedure is shown in Figure 3-2.
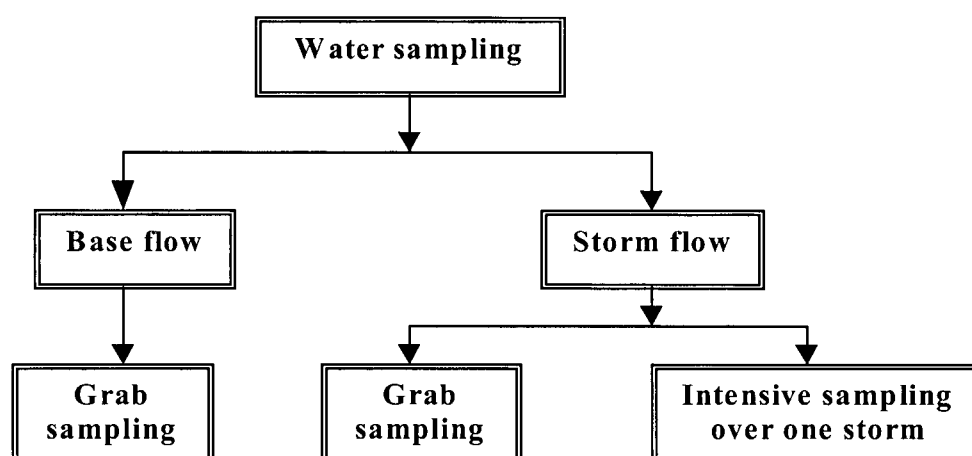
Figure 3- 2 Field sampling scheme

Both the water sampling and *in situ* receiver experiments were conducted from July 1998 to January 2000. They were designed to follow the precipitation patterns of the watershed, as shown in Fig. 3-3. Of the six grab-samplings, two were sampled under baseflow conditions, and four were collected in the early rainfall under stormflow conditions. Field receiver experiments were also conducted six times during the period. They were almost all started at the same time as the grab sampling, except for one in February 1999. The only intensive water sampling was carried out in November 1999, during a typical rain event of the wet season. The detailed sampling records are shown in Table 3-2.
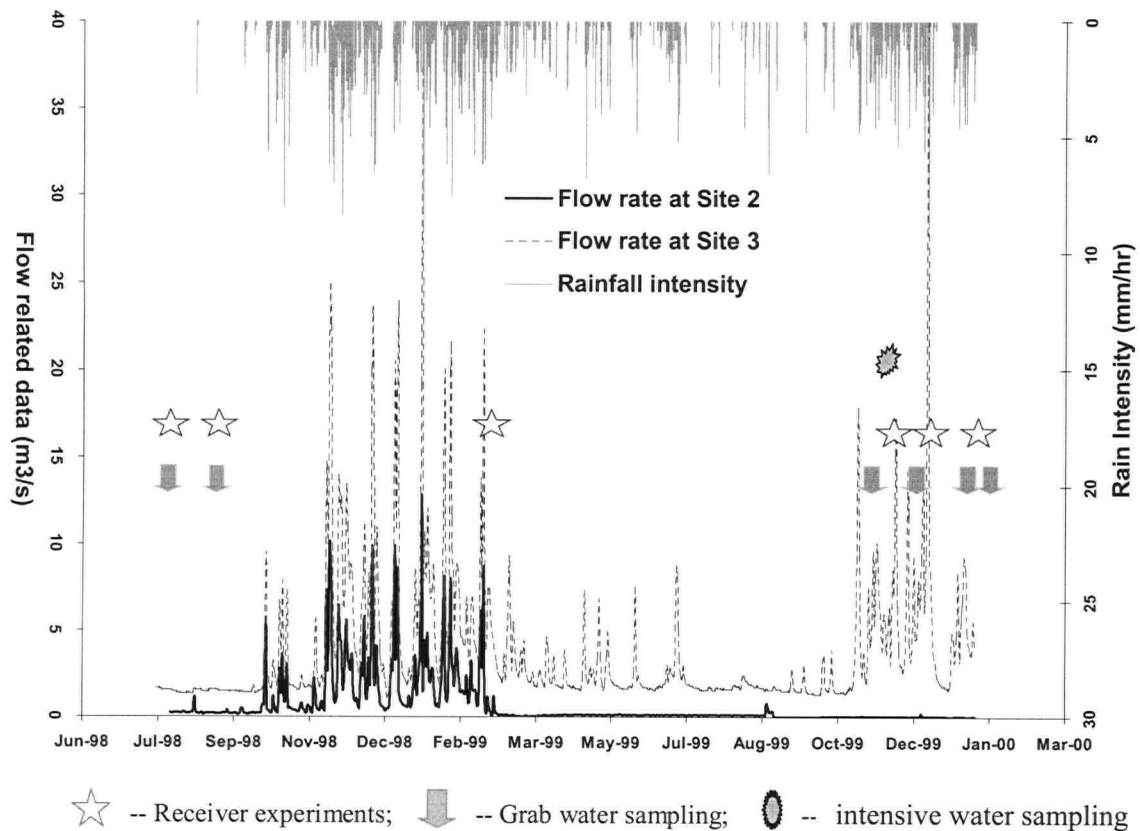
Figure 3- 3 Field samplings and *in situ* experiments

Table 3- 2 Water sampling during study period

Sampling date	Sampling station	Sample characteristics	Sampling point	Sample quantity (L)
July 23, 1998	#1	Baseflow Trap water	In the trap	1.0
	#2	Baseflow	In stream	4.0
	#3	Baseflow	In stream	4.0
Aug. 17, 1998	#1	Baseflow Trap water	In the trap	12.0
	#2	Baseflow	In stream	12.0
	#3	Baseflow	In stream	12.0
Oct. 23, 1999	#1	Street runoff	Free falling from road surface	10.0
	#2	Stormwater	In stream	10.0
	#3	Stormwater	In stream	10.0
Nov. 19, 1999 (intensive sampling)	#1	Street runoff	Free falling from road surface	4×4 +2×2*
	#2	Stormwater	In stream	4×4 +2×2
	#3	Stormwater	In stream	4×4 +2×2
Jan. 3, 2000	#1	Street runoff	Free falling from road surface	3.0
	#2	Stormwater	In stream	3.0
	#3	Stormwater	In stream	3.0
Jan. 3, 2000	#1	Street runoff	In the trap	2.0
	#2	Stormwater	In stream	2.0
	#3	Stormwater	In stream	2.0

*Six samplings in total. 4 L each in the first four and 2 L each in the rest two samplings.

3.2.2 Trace metal speciation

The major trace metals studied in this project were copper and zinc, because the high concentrations of these metals were observed within the watershed during previous studies (MacDonald et al. 1997). Manganese and iron were also analyzed to examine their effects of regulating the more toxic trace metals such as Cu and Zn in the aquatic environment.

The speciation procedure followed by this study is based on the scheme developed by Morrison (1985). Metals in the soluble phase were partitioned into resin extractable (or resin removable) fraction and residual dissolved fraction to distinguish bioavailable and non-bioavailable metal species. For particulate metals, three fractions, namely exchangeable, Mn-oxide bound and residual trace metals, were determined to evaluate the potentially bioavailable metals. The reason for studying the Mn-oxides bound fraction in the particulate phase was to evaluate the effect of manganese in regulating trace metals in this urban aquatic system. Figure 3-4 shows the flow chart of the speciation scheme. The detailed procedure for each analysis step is described below.
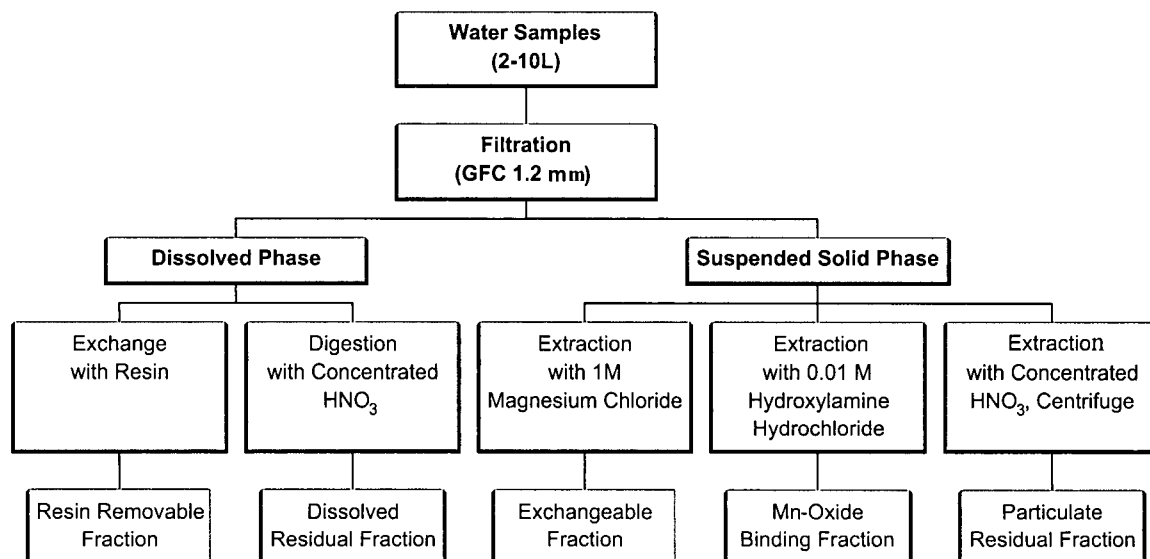
Figure 3- 4 The speciation scheme for the water sampling

3.2.2.1 Separation of the water samples into dissolved and particulate phases

Two to ten-liter water samples (baseflow or stormwater) were filtered through 1.2 μm glass fiber filters (GFC). The reason for using GFC filter rather than 0.47 μm polymer filter was to provide a large amount of filtrate for further bioavailable metal speciation in the dissolved phase.

3.2.2.2 Separation of trace metals in the dissolved phase

a) Chelex Resin removable fraction (RE)

1 – 3 L filtrates of stormwater (or 10 L of baseflow water) were exchanged with Chelex-100 resin (6 g) in a glass column of 25 cm in length and 1.5 cm in diameter. The flow rate was 5 – 10 mL/min. The resin after exchange with sample water was transferred into a 50 mL polyethylene tube. Twenty mL of 2M HNO_3 was added to the resin and shaken for 3 hours on a lateral action shaker (Eberbach Cop.) to elute the trace metals. The sample was centrifuged at 3000 rpm (BECKMAN Centrifuge J2-21M/E) for 20-30 min and the elutants were filtered through Whatman #4 filter paper into a 50 mL volumetric flask. The resin was extracted with 15 mL de-ionized water, shaken for half an hour and centrifuged for 20 min. The water extract was added to the acid in the volumetric flask and the sample made to volume. The Chelex resin extractable fraction was analyzed by atomic absorption spectrometer (SpectrAA-220FS) for Cu, Zn, Fe, and Mn to give bioavailable metal forms.

b) Residual dissolved fraction

Residual dissolved fraction indicates the metal species bound to the colloidal forms in the dissolved phase. It can be determined by the difference between total dissolved metal (TD) and resin removable metal (RE). Total dissolved metal was measured by the following steps. The filtrate (250-500 mL) was digested with 5 mL concentrated HNO_3, and evaporated to dryness on a hot plate. The residue in the digestion flask was dissolved in 10 mL of 1M HNO_3, rinsed with 10 mL of deionized water into a 25 mL volumetric flask, and then filtered

through a Whatman #4 filter paper. This sample was analyzed by AAS for Cu, Zn, Mn and Fe.

3.2.2.3 Speciation of suspended sediment

a) Exchangeable fraction

Trace metals in the exchangeable fraction were analyzed with the following procedure. First the filter containing the particulate residue was cut into small pieces and then placed into a polyethylene tube. Twenty mL of 1M $MgCl_2$ at pH=7 was added to the tube, the tube was then shaken at room temperature for 1 hour. The sample was then centrifuged at 10000 rpm for 30 min, and the extract was filtered through Whatman #4 filter paper into a 50 mL volumetric flask. The filter in the polyethylene tube was extracted with 20 mL of deionized water on the shaker for another 20 min and added into the volumetric flask. This extract was finally analyzed by AAS for Cu, Zn, Mn and Fe. The results represent the exchangeable fraction. The remaining filter residue was then used in the following analysis.

b) Hydrous manganese oxide fraction

The remaining filter in the polyethylene tube was used for further extraction. It was extracted with 20 mL of 0.01 M acidic hydroxylamine hydrochloride, $NH_2OH.HCl$ (dissolved in 0.01M HNO_3, pH=2) by shaking at room temperature for 0.5 hour. The sample was centrifuged at 10000 rpm for 30 min, and the supernatant was transferred to a 50 mL volumetric flask through Whatman #4 filter paper. The filter in the polyethylene tube was extracted with 20 ml of deionized water on the shaker for another 20 min and added into the volumetric flask. The sample was analyzed by AAS for Cu, Zn, Mn and Fe. The remaining filter residue is used in the following procedure.

c) Particulate residual fraction

The remaining filter was transferred to a porcelain crucible and digested with a 20 mL mixture of concentrated HNO_3 and HCl (4:1) on a hot plate till the solution evaporated. The

residue was dissolved in 15-20 mL of 0.05 M HNO_3, and diluted to 25 mL. The sample was analyzed by AAS as the particulate residual fraction for the metals Cu, Zn, Fe and Mn.

3.2.2.4 Total metal concentration

The total metal concentration ™ was determined in the water samples, and TM concentration is used to calculate the total particulate metal concentration (TP) in stormwater expressed as TP=TM-TD. A non-filtered water sample (250 mL) in an Erlenmeyer flask was digested with 5 ml concentrated HNO_3 and evaporated to dryness on a hot plate. The flask was rinsed with 10 mL 1M HNO_3 and 10 mL of deionized water and transferred to a 25 mL volumetric flask through a paper filter (Whatman #4, washed by de-ionized water). Cu, Zn, Fe, and Mn were analyzed with AAS.

3.2.3 Other water quality data

3.2.3.1 Suspended sediment (SS)

The suspended sediment was analyzed by following a standard analysis procedure (APHA 1981). The samples were filtered through GF/F glass fiber filter (0.7 µm). Total suspended sediments were measured for stormwater over a rain event..

3.2.3.2 pH

The pH of the water samples of the intensive sampling was measured in the laboratory with pH meter (ORION 420A), which was standardized with pH 4 and pH 7 buffers.

3.2.3.3 Precipitation data and flow data

Precipitation data and flow data from January 1998 to January 2000 were obtained from GVRD. The flow data of two stations, Station SC4 in Still Creek and Station BT5 in Brunette River, were collected. While Station SC4 was at exactly the same location as sampling site #2, Station BT5 was just upstream of sampling site #3. They were then used for the

stormflow and baseflow analysis. The rain gauge number BU7 was located in the center of the watershed, and provided the precipitation data.

3.3 Dialysis with resin receiver at field sites

The dialysis with resin receiver technique was used to measure the uptake rate of the trace metals copper, zinc, manganese, and iron in the urban water system. This technique is based on the fact that the chelating resins are able to reasonably simulate the cell uptake. It was conducted in two steps: the *in situ* receiver experiment and the laboratory analysis. The in-situ experiment was to expose the receiver to the water for a period of time, to simulate the metal uptake by aquatic organisms.

3.3.1 Field receiver experiment procedure

The *in situ* receiver experiments were conducted in the same three sites used for the water sampling. A total of six *in situ* receiver experiments were conducted under baseflow, stormflow and snowmelt conditions. The cellulose dialysis tubing bags within which one gram of Chelex resin (Chelex −100 in Na form) was encapsulated were emerged in the sediment trap and streams. After the exposure of a period of time (one storm, one week and two weeks), the receivers were returned to the laboratory for analysis. The description of all the in-situ receiver experiment is given in Table 3-3.

3.3.2 Receiver materials

The resin receiver was made from a Spectra/Pro wet dialysis membrane tubing, which has a diameter of 24 mm and the molecular weight cut-off value of 1000. The membrane tubing was treated with 0.01 EDTA overnight and washed with deionized water before use. The suitable tubing length of 60-80 mm (Morrison 1985) was accurately measured. The Chelex-100 chelating resin in Na form (1.0 g) was slurried into the bag with deionized water (approximately 20 ml). The tubing bag was tightly sealed at both ends and suspended within

a plastic tube. The plastic tubes were tied to concrete blocks and placed in the stream or sediment trap.

Table 3- 3 Field receiver experiments during the study period

Experiment date	Sampling station	Flow characteristics	Experiment place	Exposure time (days)	No. of dialysis receivers
July 23 – 30, 1998	#1	Baseflow	In the trap	7	4
	#2	Baseflow	In stream	7	4
	#3	Baseflow	In stream	7	4
Aug. 17 - Sept. 1, 1998	#1	Baseflow	In the trap	15	4
	#2	Baseflow	In stream	15	4
	#3	Baseflow	In stream	15	4
Feb. 11 – 18 1999	#1	Street runoff	In the trap	7	4
	#2	Stormwater	In stream	7	8
	#3	Stormwater	In stream	7	6
Oct. 27 - Nov. 3 1999	#1	Street runoff	In the trap	7	6
	#2	Stormwater	In stream	7	0
	#3	Stormwater	In stream	7	6
Nov. 19, 1999 (intensive sampling	#1	Street runoff	In the trap	7	4
	#2	Stormwater	In stream	7	4
	#3	Stormwater	In stream	7	4
Nov. 19 – 25, 1999	#1	Street runoff	In the trap	7	4
	#2	Stormwater	In stream	7	4
	#3	Stormwater	In stream	7	4
Jan. 3 – 10, 2000	#1	Street runoff	In the trap	7	4
	#2	Stormwater	In stream	7	4
	#3	Stormwater	In stream	7	4

3.3.3 Laboratory analysis

The trace metals were analyzed for both the receiver resin and membrane tubing. The sample preparations were conducted in a Soil Science laboratory and analyzed in a Environmental Engineering laboratory by atomic absorption spectrophotometry (AAS). The procedure of laboratory analysis is described below.

3.3.3.1 Analysis of resin

The resin was carefully released from the tubing bag into a beaker, and the bag was washed with 10 mL deionized water to transfer all residue resin into the beaker. The resin was transferred with water into a 25 mL plastic centrifuge tube, and the supernatant was removed with pipettes. Ten ml of 1M HNO_3 was added into the tube and the metals was eluted from resin by shaking 3- 4 hours. The sample was centrifuged at 3000 rpm for 20-30 min and the elutants were filtered through Whatman #4 filter paper into a 25 mL volumetric flask. Ten mL of deionized water was added to the tube, and shaken for another half an hour. The elutant was centrifuged and filtered into the acid extract. The sample was diluted to 25 mL, and analyzed by AAS for Cu, Zn, Mn, and Fe.

3.3.3.2 Analysis of trace metal in membrane

After the resin was released from the membrane bag, the bag was put into a 25 ml plastic centrifuge tube. The membrane bag was extracted with 10 mL of 2M HNO_3 by shaking for 3-4 hours. The elutant was filtered with the Whatman #4 filter paper into a 25 mL volumetric flask. Five mL of deionized water was added into the tube to rinse the bag by shaking for another half an hour. The elutants was filtered into the volumetric flask. The filtrate was diluted to 25 mL, and the sample was then analyzed by AAS for Cu, Zn, Mn, and Fe.

3.3.3.3 Exchange capacity and interference test for Chelex resin

The resin exchange capacity was tested to ensure enough Chelex resin was available in the dialysis bag for the targeted trace metal complexation. With the consideration that the

common divalent metals such as calcium and magnesium are dominant elements in the urban water, the interference of these metal species were tested in the laboratory to ensure that these metals had little interference on the trace metal copper and zinc complexation with Chelex resin. The results of these two experiments are given in the Appendix E.

3.4 QA/QC and statistics

All glassware was acid-washed before use. The blanks used in the speciation and elution processes went through the complete analytical procedure. Reproducibility of the analysis was measured on duplicate samples for the trace metals in the water sample. The receiver membrane was treated with 0.02M EDTA and washed with deionized water to eliminate metal contaminants adsorbed in the membrane surface before use. The replicates of receiver were used in each *in situ* experiment and the analysis.

The data obtained through the trace metal speciation of the water samples and the *in situ* receiver experiments, along with the precipitation and flow data, were analyzed statistically to obtain the following information on bioavailable trace metals in the watershed:

1. Correlation between metals Mn and Fe with trace metals Cu and Zn. It is to see how Mn and Fe regulate the toxicity of Cu and Zn.

2. Correlation between trace metals with suspended sediment transport over surface runoff.

3. Correlation of the two bioavailable trace metal study approaches, i.e. the relationship between the bioavailable trace metal speciation and the trace metal uptake.

Chapter 4

Results and Discussion

The results obtained from the two technical approaches - namely metal speciation and dialysis with resin receiver - are presented in this chapter. The speciation of trace metal in the water samples provides the information on the concentration of bioavailable trace metal species, in both dissolved form and the particulate form associated with suspended sediment. These forms were studied under baseflow, stormwater, and snowmelt conditions. The uptake rate of bioavailable metals measured in the field experiments using dialysis with resin receiver helps to evaluate the potential accumulation of trace metal species by the aquatic organisms throughout the drainage system of this highly urbanized watershed.

The behavior of trace metals and their potential bioavailability in the watershed are discussed in this chapter. This discussion includes their spatial distribution and seasonal variation, and their potential toxicity either through immediate cell uptake (dissolved metal) or through particulate metal ingestion. The focus of the discussion is on: 1) the bioavailable forms of trace metal in relation to their total concentration; 2) the discharge pattern of the trace metals through storm runoff; and 3) the potential toxic effects of the trace metals on the receiving water organisms. The possible control factors in regulating the bioavailable metal species and the uptake of these species by the receiver resin have also been analyzed. The correlation between dissolved bioavailable metal species and their uptake by receiver resin are also discussed.

Table 4-1 summarized the details of climatic and hydrological conditions during the water sampling and resin receiver experiments. The baseflow sampling were carried out in two ocassions under non rainfall period. There was a short rainfall during the August field experiment. Stormwater sampling was try to catch each storm at the starting of the rainfall, but due to the transportation delay, the sampling can only be conducted in the early storm. All storms were in the medium to large, except the storm in Feberary, 1999, which is relatively light comparing to the others.

Table 4- 1 Climatic and hydrological conditions during the sampling and receiver
          experiment (Need to put some data—check for data)

Sampling &Resin experime-ntal time (7 days exposure)	Dry period before rain (day)	Total rainfall over exp. period (mm)	Total flow/ exp. period @ Site #2 (m³)	Total flow/ exp. period @ Site #3 (m³)
Baseflow				
July, 98	7	0	102826	1091059
Aug., 98	30	16.8	379296	2232576
Stormflow				
Feb., 99	0	56.2	1731024	3462048
Oct., 99	12	85.2	2086128	4172256
Nov., 99	5	90.4	2181600	4363200
Jan., 00	0	83.2	2373840	4747680

4.1 Bioavailable metal study by trace metal partitioning

4.1.1 Total water fractionation

The series physical-chemical partitioning procedures were employed for all the water samples collected during baseflow and stormflow, which included grab water samples and the intensive stormwater samples. The results of the street runoff (Site #1) demonstrate the bioavailable trace metals discharged directly from the urban impervious surface; while the results obtained at Site #2 and Site #3 indicate the spatial variation of the bioavailable trace metals when they are transported through Brunette River water system. The metal

partitioning of the intensive stormwater samples provides insight into the variation of bioavailable trace metal species in both surface runoff and in stream water over a rain event.

4.1.1.1 Grab water samples

Grab samples were collected from stormwater and baseflow. The total (TM), total dissolved (TD), and resin extractable (RE) fractions for the trace metals copper, zinc, manganese and iron were measured in the water samples. The RE fraction measured the dissolved phase of each metal and was regarded as the most possible bioavailable trace-metal species that can be directly taken up through the cell of the organisms. The suspended sediments collected in each grab samples were analyzed with the speciation technique to understand the different geochemical binding forms of the particulate metals. The complete data set of these metal-partitioning results is given in Appendix A.

a. Metal partitioning in stormwater

Stormwater sampling was conducted four times through the whole study period (Tab. 4-1). The detailed sampling procedure was described in chapter 3 (Table 3-2). The partitioning of the four trace metals – Cu, Zn, Mn, and Fe – in stormwater was conducted on the grab samples collected on Jan. 3 and Jan. 10, 2000, respectively. The grab samples collected in October 1999 were used for the preliminary investigation of the study methods, therefore their results are not included in this chapter. The results of the intensive stormwater sampling program (November 1999), on the other hand, will be presented separately in section 4.1.1.2. The results of the mean concentrations of Cu, Zn, Mn, and Fe in their TM, TD and RE forms are presented from Fig. 4-1 to Fig. 4-4, with their 90% confident interval (n = 4).

Copper

As shown in Figure 4-1, it can be seen a significantly higher total copper concentration (TM-Cu) was observed at Site #1 than at the other two sampling sites. Of the two stream sites, a relatively higher level of total copper was found in Still Creek, upstream of Burnaby Lake (Site # 2), than that observed at the down stream site in the Brunette River (Site #3).
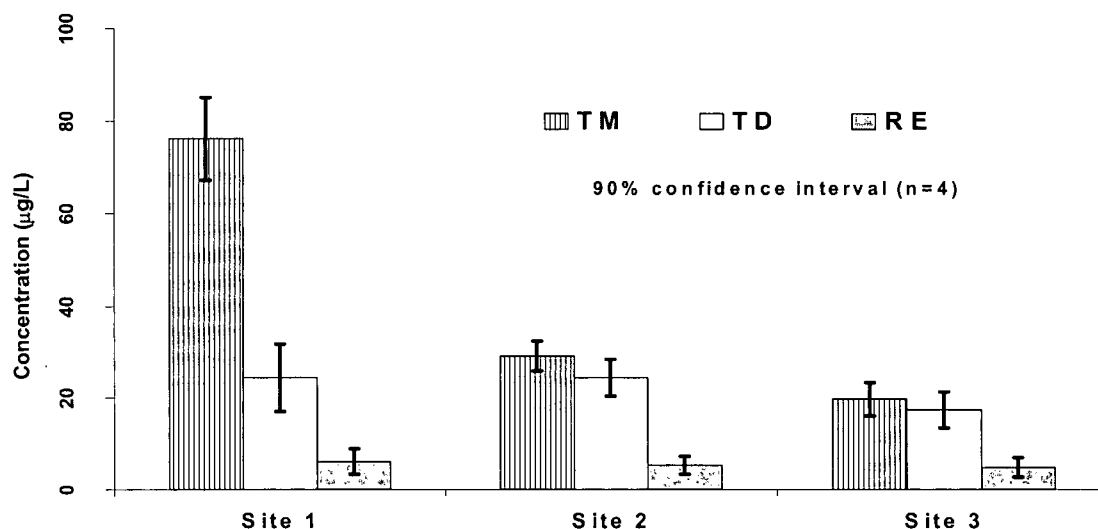
Figure 4- 1 Partitioning of Cu in stormwater sampled at three sites

There was no obvious difference of dissolved copper (TD-Cu) among the three sites. A quite similar mean TD-Cu concentration (24.5 μg/L) was detected at Site #1 and Site #2, but a slightly lower level of 17.4 μg/L was found at Site #3. The resin removable copper (RE-Cu) fraction, on the other hand, was at a very low level (below 10 μg/l) at all three sites.

Zinc

As shown in Figure 4-2, Zn behaved similarly to Cu. High TM concentration of zinc was found in the street runoff (Site #1) with the mean concentration of 369 μg/L. In the stream, the total zinc (TM-Zn) concentration was measured in the range of 80-188 μg/L in Still Creek (Site #2), and decreased approximately 40% to 37-59 μg/L downstream in Brunette River (Site #3). It can be seen in Fig. 4-2 that the total dissolved zinc (TD-Zn) was highly co-related to TM-Zn at all three sampling sites, which accounted for approximately 50-70% of the TM-Zn concentration. Zinc in the resin removable fraction (RE-Zn) was also closely co-related to the dissolved zinc, accounting for about 60-70% of total dissolved zinc (TD-Zn) at all three sites. The higher RE-Zn fraction in dissolved phase indicates that a large amount of zinc exists as ionic and weakly complexed forms in the stormwater.
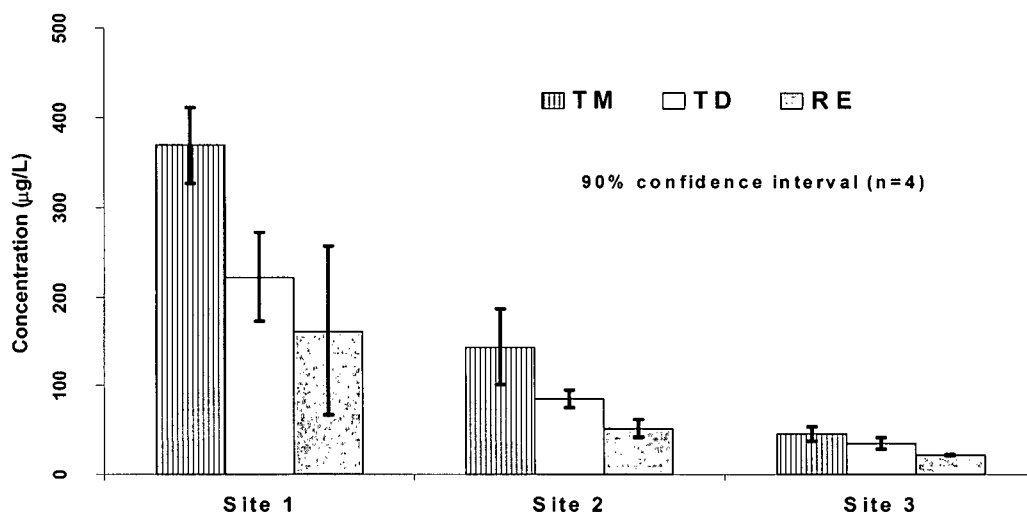
Figure 4- 2 Partitioning of Zn in stomwater sampled at three sites

Manganese

The partitioning of manganese among TM, TD and RE fractions in the stormwater, shown in Fig. 4-3, demonstrates that the total manganese (TM-Mn) concentration was quite high in the street runoff (Site #1), with the average value of 214.3 µg/L. At the stream sites, the mean TM-Mn concentration was 82.4 µg/L in the upstream (Site #2), and 61.8 µg/L in the downstream location (Site 3). The total dissolved manganese (TD-Mn) in the street runoff (Site #1) was not significantly higher than that at the stream sites, which shows a similar pattern to that of copper. The resin removable manganese (RE-Mn) fraction also accounted for a large proportion of the total dissolved manganese, which was found between 65-80% of the TD-Mn at all three sites.
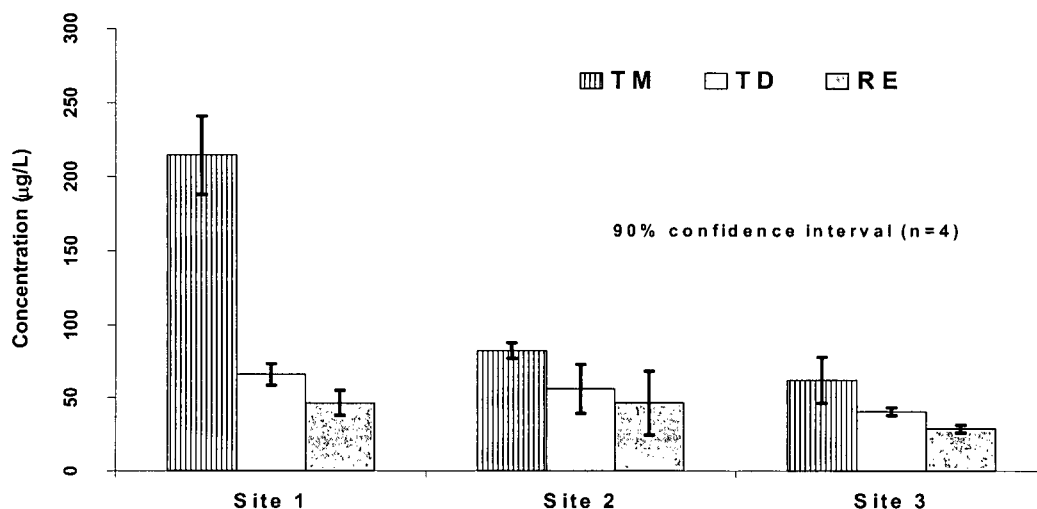
Figure 4- 3 Partitioning of Mn in stormwater sampled at three sites

Iron

The partitioning of metal iron between TM, TD and RE fractions is shown in Fig. 4-4. It clearly indicates that iron exists mainly in the particulate forms in the stormwater throughout the watershed. Although the mean TM-Fe concentration in street runoff (Site #1) was as high as 11.0 mg/L, only 1.1 mg/L of dissolved iron was detected. It was ten times less than the total concentration (TM-Fe) at the same site. TM-Fe concentrations at the two stream sites were significantly lower than that from the street samples. The mean concentration was measured 1.1 mg/L in Still Creek and 0.9 mg/L in Brunette River, respectively. The corresponding TD-Fe concentration was also very low in the stream, less than 0.3 mg/L at the two stream sites was observed. The extremely low concentrations of RE-Fe fraction were found at all the three sites, with the highest concentration of 0.5 mg/L at Site #1, and less than 0.02 mg/L at the two stream sites.
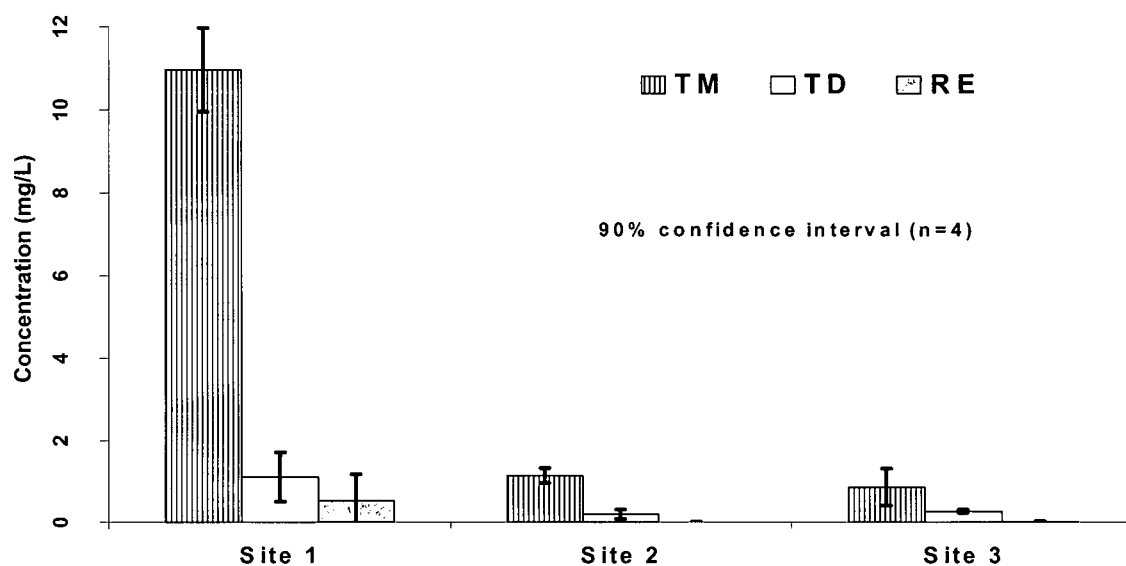
Figure 4- 4 Partitioning of Fe in stormwater sampled at three sites

b. Resin extractable metals in baseflow

The grab sampling was conducted only once under baseflow condition at three sites in August 1998. Only the metals in bioavailable fraction - RE form were measured. The total and total dissolved metals were not analyzed because of their very low concentrations in the baseflow. The RE fractions of Cu, Zn, Mn, and Fe in the baseflow samples are listed in Table 4-1.

Table 4- 2 Resin exchangeable metal (RE) (ug/L) in baseflow

	Cu ($\mu g / L$)	Zn ($\mu g / L$)	Mn ($\mu g / L$)	Fe ($\mu g / L$)
Site #1	3.9	44	50	3.77
Site #2	0.8	79	53	0.29
Site #3	0.2	16	10	0.28

A similar distribution of the RE fraction of Cu and Fe was found at all three sites, where the concentrations were very similar at each site. Although the RE concentrations of these two metals were at very low levels at all three sites, considerably higher concentrations of Cu and Fe were found in the sediment trap (Site #1) than at the stream sites (#2 and #3).

Regarding to the RE fractions of Zn and Mn, RE fraction of Zn was found higher in streams, but lower in street runoff (site #1). However, the maximum concentrations of these two metals were not found at the street site, but in Still Creek. Much lower RE levels of these two metals were found in the Brunette River – downstream of the lake.

From the above results it is obvious that while the total concentration of Fe is always much higher than that of the other three metals in the water system, its RE fraction is at a very low level in both stormwater and baseflow samples.

4.1.1.2 Intensive stormwater samples

The partitioning of trace metals in stormwater samples was carried out over a storm event. It covered each of the four metals at each sampling site. The results of this analysis demonstrate the variations of the trace metal components over a rain event. This indicates the transport characteristics of trace metal contaminants through urban waterways, as well as the distribution of bioavailable trace metal species over a storm period. The data on the partitioning of Cu, Zn, Mn and Fe, the suspended sediment, and pH of the target storm event are given in Appendix C.

Copper

The partitioning of copper in samples at the three sites is shown in Fig. 4-5. The corresponding rainfall intensity (I_{60}) is provided with the street runoff at Site #1 in Fig. 4-5(a). For the two stream sites, the corresponding flow rates over the same period in Still Creek and Brunette River are also included in Figs. 4-5(b) and 4-5(c).

Figure 4-5(a) demonstrates that the TM-Cu increased from 33 µg/L in the early stage of the storm to 113 µg/L in the later period of the rain event in the street runoff. TD-Cu concentration, on the contrary, decreased from 20 µg/L to 5 µg/L during the same period. The RE-Cu concentration of 9 µg/L was only observed in the early storm, and decreased to the undetectable level later. This clearly indicates that the dissolved copper was washed out early in the rainfall event. The increase of TM-Cu with the storm development implies the increase of particulate copper (expressed as TP=TM-TD) discharge with the progress of the rain event. This might be due to the discharge characteristics of metals associated with suspended sediment (SS) from the impervious surfaces (Solo and Perkins 1997, Jarvis 1992, Yuan et al. 1999), and will be presented section 4.3.

Totally different Cu partitioning patterns were observed at the two stream sites (Site #2 and Site #3). At Site #2 (Fig.4-9(b)), TM-Cu, TD-Cu and RE-Cu were all at low levels of 10-17 µg/L through the whole rain event, except one sample at 11:30. The reason of the big change at this time is unknown. Even lower copper levels were measured at Site #3 (Fig.4-9(C)). The concentrations of TM-Cu and TD-Cu were in the range of 3-10 µg/L, and RE-Cu only ranged from 0.6-3.0 µg/L in this site. The low Cu in the down stream site was expected to be due to the sedimentation of Cu in Burnaby Lake. There were no obvious relationships between the copper concentrations and its partitioning and the flow rates of the two stream sites.

Zinc

Zinc partitioning over one storm at the three sampling sites is shown in Figure 4-6. It shows very similar pattern to that of the copper at street runoff (Fig. 4-6(a)). At this site, TM-Zn concentration increased from 151 µg/L to 613 µg/L during the rain event. TD-Zn, on the other hand, kept relatively constant concentration through the sampling period (78-135 µg/L). RE-Zn was closely related to the TD-Zn and showed a similar trend to that of TD-Zn over the whole storm event. The early wash-off of the dissolved phase was not so obvious for zinc. The dissolved phase accounted for a large part of the zinc in the street runoff during most of the rainfall event.
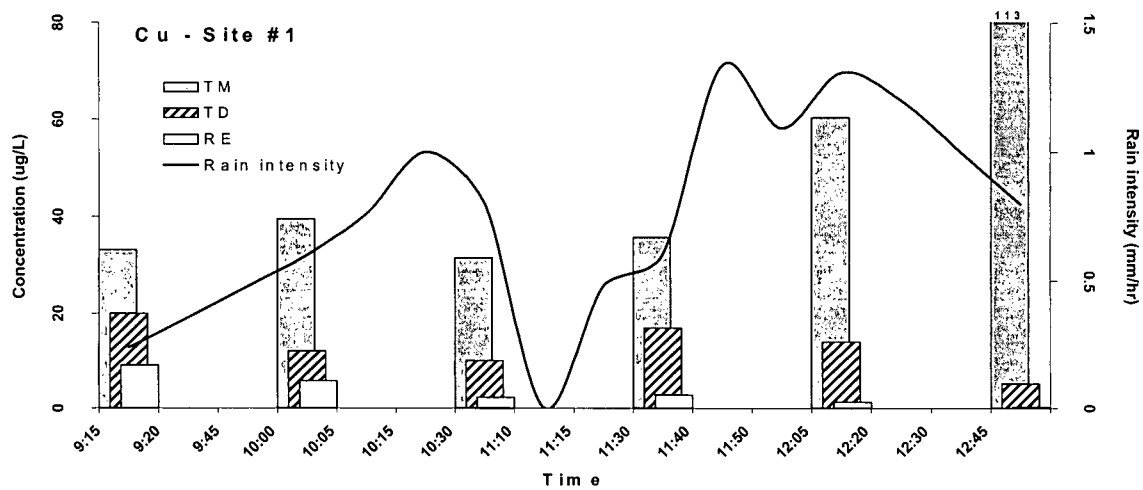
(a) Site #1.
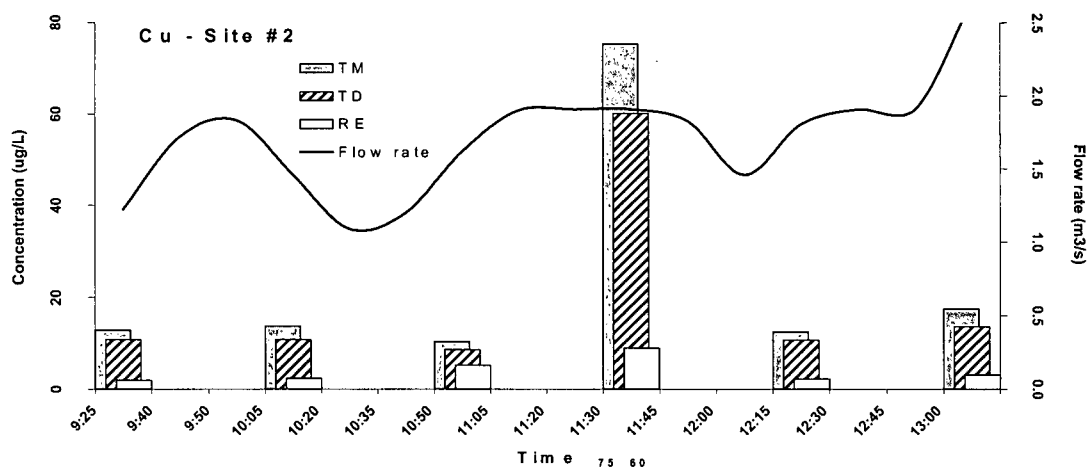
(b) Site #2.
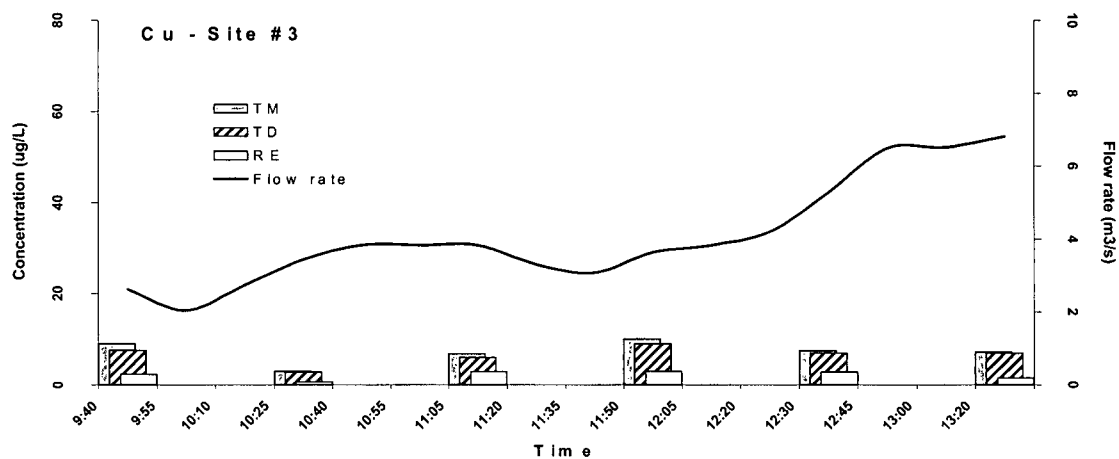
(c) Site #3.

Figure 4- 5 Copper partitioning over one storm event (Nov. 19, 1999)
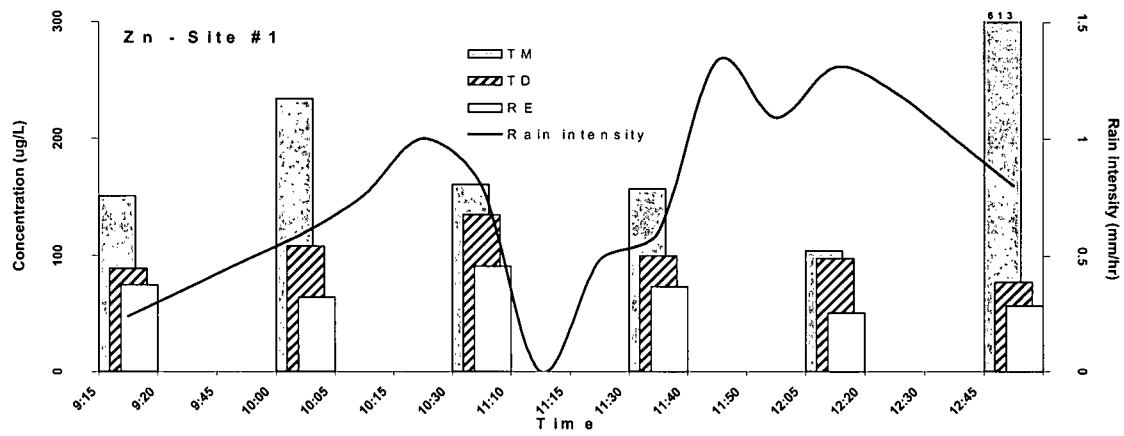
(a) Site #1.
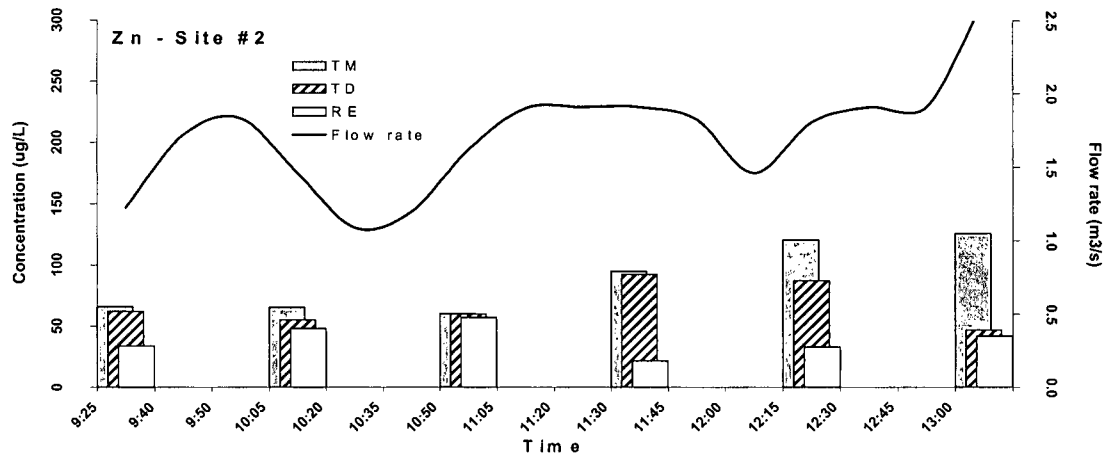
(b) Site #2.
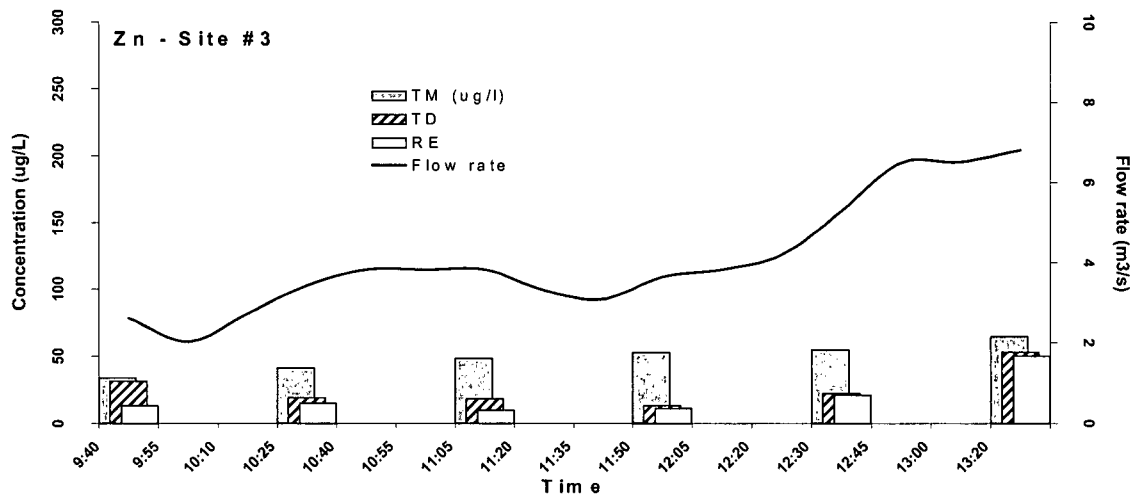
(c) Site #3

Figure 4- 6 Zinc partitioning over one storm event (Nov. 19, 1999)

At the stream sites, unlike copper, the increasing TM-Zn was observed with the progress of the storm, which increased from 66 µg/L to 126 µg/L at Still Creek (Fig. 4-6(b)) and from 34 µg/L to 65 µg/L in the Brunette River (Fig. 4-6(c)). The first flush effect for TD-Zinc seemed also to occur at Site #2, where TD-Zn decreased to its minimum at the end of the rain event even though the flow was still increasing. At site #3, lower TD-Zn and RE-Zn were observed early in the rain period. Later increase of TD-Zn and RE-Zn might be due to the time-delay of the flow at downstream sites. High ratio of RE-Zn over TD-Zn was also observed at all three sites for most of the samples. This observation agrees with the grab sample results, and demonstrates that the dissolved zinc in the stormwater is mostly in the bioavailable form (42 - 94 %).

Manganese

The total manganese (TM-Mn) concentration in street runoff (shown in Fig. 4-7(a)) increased from 62 µg/L to 345 µg/L during the rain event. Similar to the grab samples, a large portion (>70%) of manganese in street runoff was found to be associated with the particulate form. The maximum TM-Mn concentration shown at the end of the rain might be also due to the discharge characteristics of metals associated with SS. The dissolved and resin removable manganese fractions over the sampling period remained at low and consistent levels (14-25 µg/L for TD-Mn and 9-25 µg/L for RE-Mn). The total manganese (TM) concentration was found to be higher at Site #2 in Still Creek (Figure 4-7(b)), with a range of 116-155 µg/L throughout the sampling period. A high ratio of TD-Mn was observed in most of the samples at Site #2, which was similar to that found in the grab samples. It might be concluded that a large proportion of manganese was in the soluble form in the upper region of the watershed. At Site #3 (Figure 4-7(c)) in the Brunette River, TM-Mn concentration was between 57-98 µg/L. The low TD-Mn and associated RE-Mn at Site #3 indicate that manganese exists largely in the particulate form in the downstream region of the Brunette River system. This is supported by the observation of Mattu and Hall in this watershed (1999).
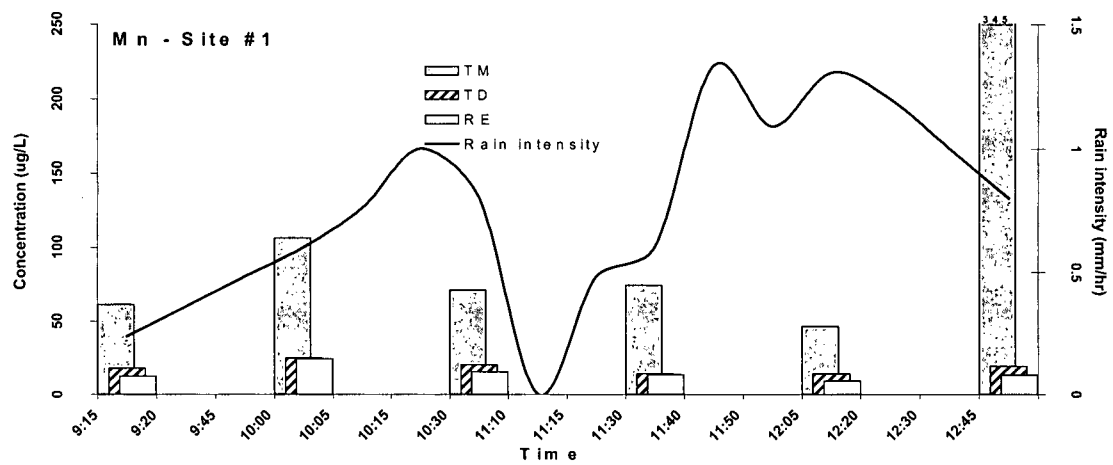
(a) Site #1
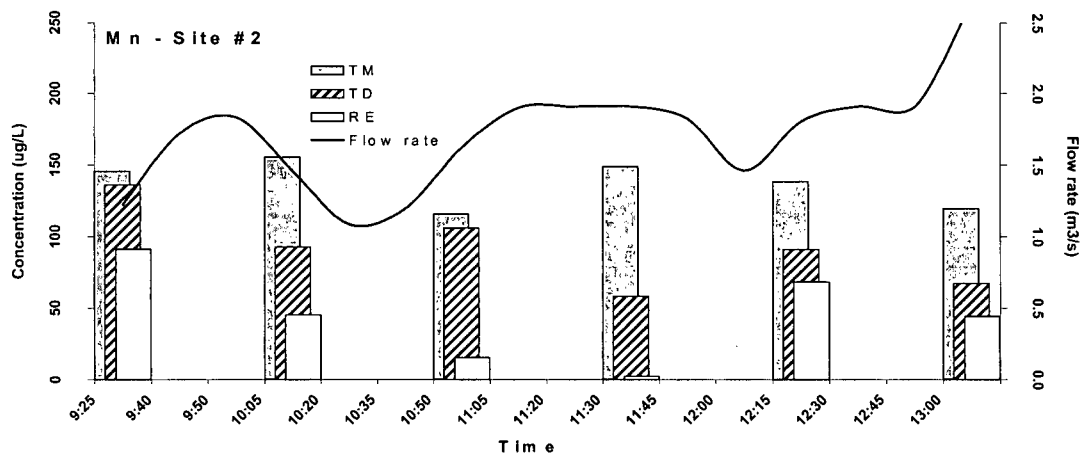
(b) Site #2.
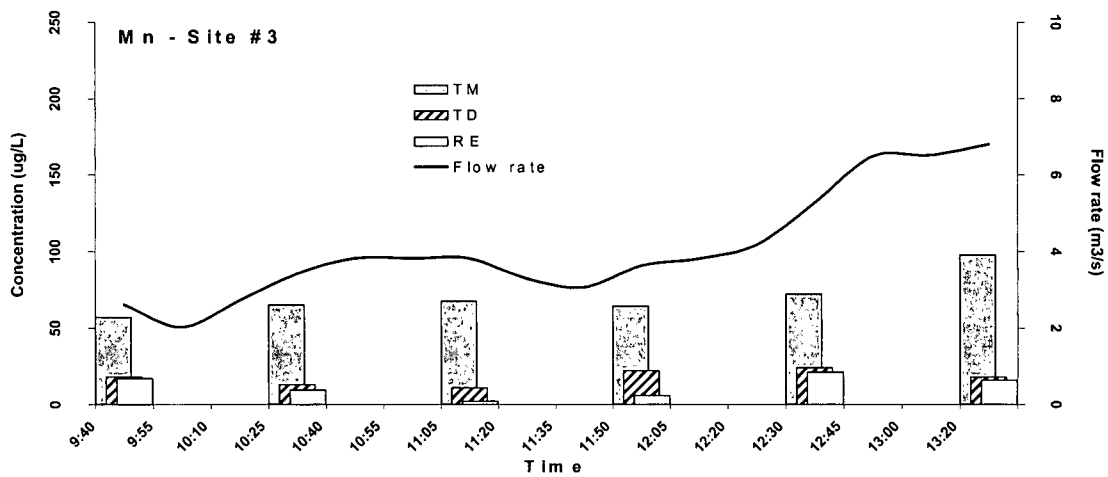
(c) Site #3.

Figure 4- 7 Manganese partitioning over one storm event (Nov. 19, 1999)

Iron

A clear partitioning pattern was observed at all three sampling sites (Figure 4-8) during the storm event - most of the iron was in the particulate phase. The highest TM-Fe concentration was found in the street runoff (Site #1), which increased from 13 mg/L in the early stage to 70 mg/L at the end of the rain event. TM-Fe in Still Creek (Site #2) also showed the increasing trend, starting from 7 mg/L to the end of 10 mg/L. Low TM-Fe concentration was found in Brunette River (Site #3), with the concentration of 0.7-1.0 mg/L. The possible reason for this big concentration difference at the two stream sites is the regulation of the Burnaby Lake. Lower TD-Fe was observed at all three sites. The maximum TD-Fe was found at Site #2 with the range of 0.4-0.9 mg/L, which was less than ten times that of TM-Fe at the same site. Very low TD-Fe level of 0.2-0.5 mg/L was at Site #1 and 0.3-0.4 mg/L at Site #3. RE-Fe levels were also very low at all three sites, with the maximum value of 3-25 µg/L.
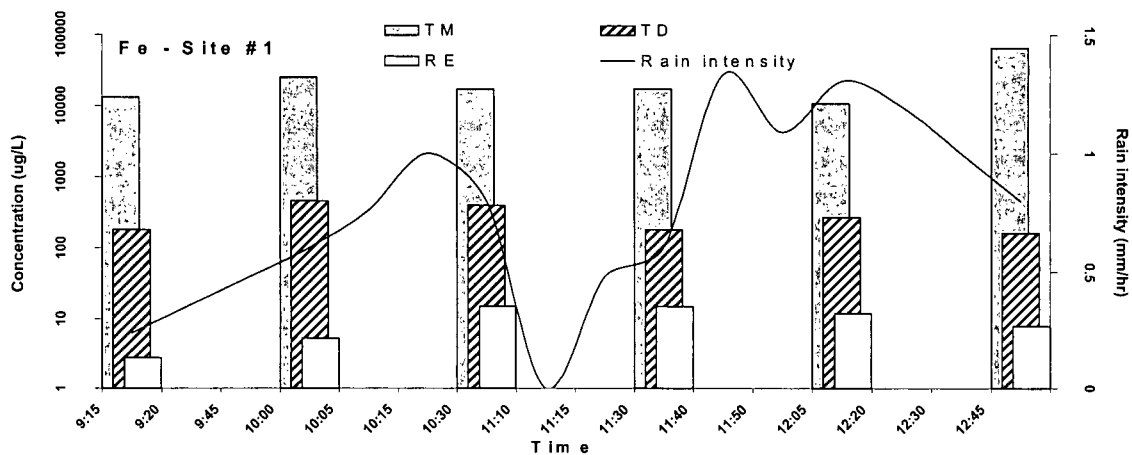
(a) Site #1.
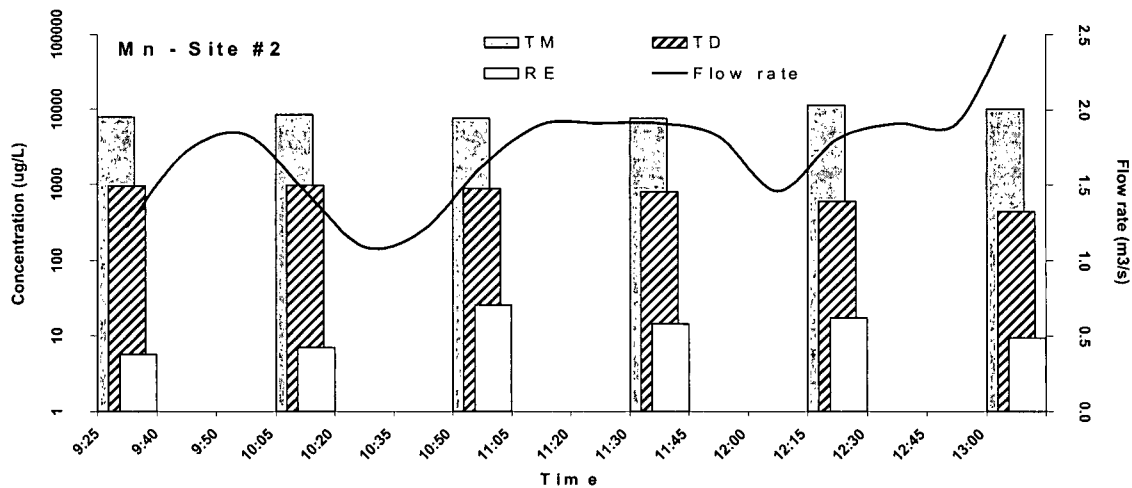
(b) Site #2.
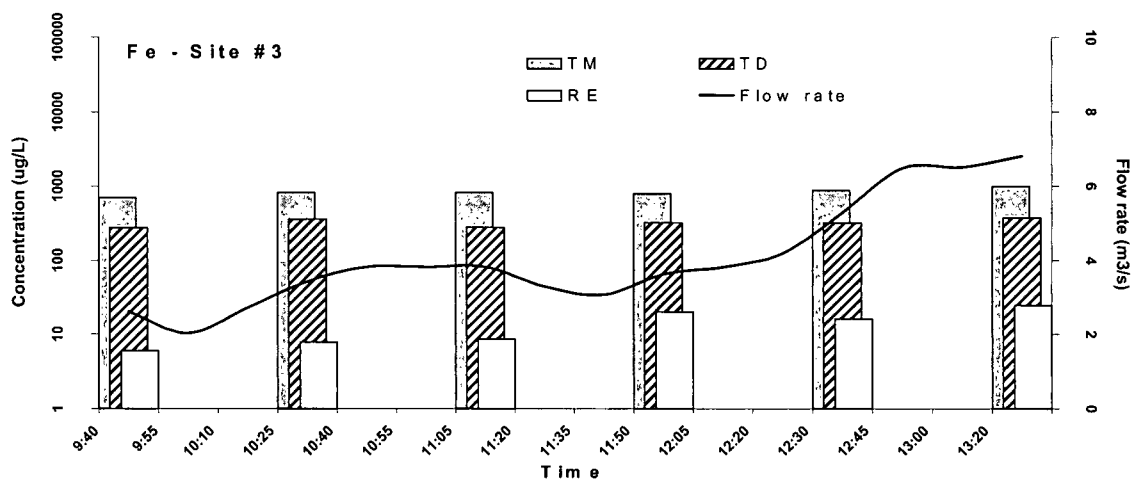
(c) Site #3.

Figure 4- 8 Iron partitioning over one storm event (Nov. 19, 1999)

4.1.1.3 Discussion on the dissolved metal components

The toxicity of trace metal pollutants on aquatic organisms was found to be directly related to the dissolved trace metal species in the water system. Metal in the ionic form or weakly complexed forms with small particle size (RE-fraction) was recognized as the most direct contributor of this toxic effects (Macdonald et. al. 1997, Morrison 1985, Mance and O'Donnell 1983). In the following discussion, we will look at how much the dissolved phase accounts for in the total metals (TD/TM), and then the percentage of dissolved bioavailable metals in the total dissolved phase (RE/TD). Lastly, the fraction of dissolved bioavailable metals in the total trace metals can be summarized (RE/TM).

a. TD/TM

The TD/TM ratio of four metals, Cu, Zn, Mn and Fe, at three sites along the urban hydrological gradient in the Brunette watershed is presented in Fig. 4-9. The results of this study (designated as 99') are the average of three grab stormwater samples collected in Nov. 1999, Jan. 3 and Jan. 10, 2000. The previous monitoring results (Macdonald et al. 1997) at these three sites are also plotted for comparison, which are the average of 18 storms for street runoff at Site #1 and the average of 12 storms in Still Creek (Site #2), respectively. No data for the Brunette River (Site #3) and no data about Fe were collected in the 1997 monitoring program.

(a)

60
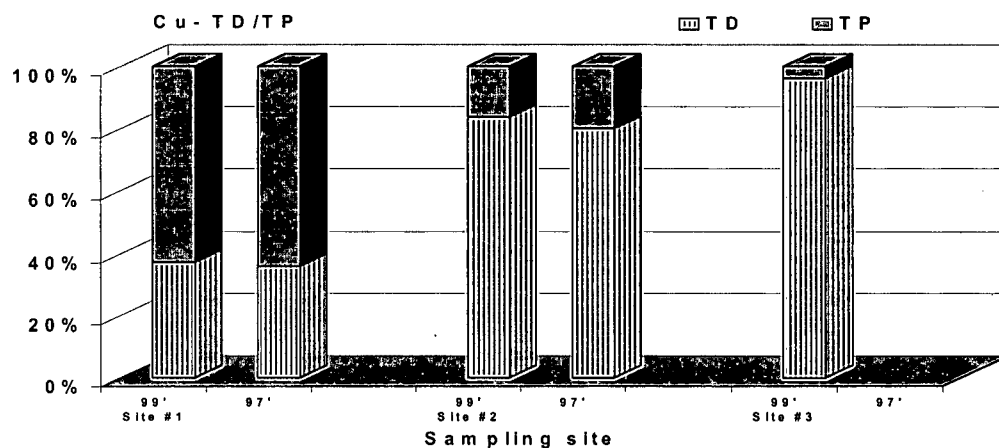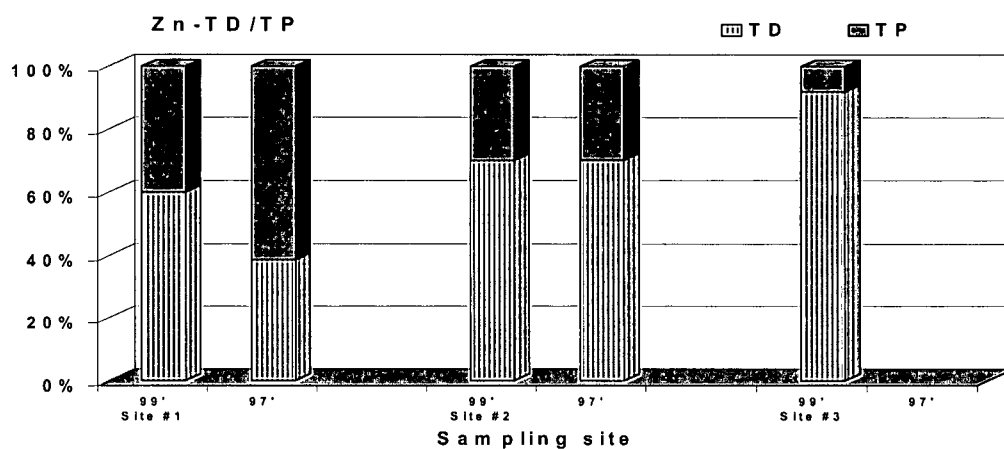
(b)
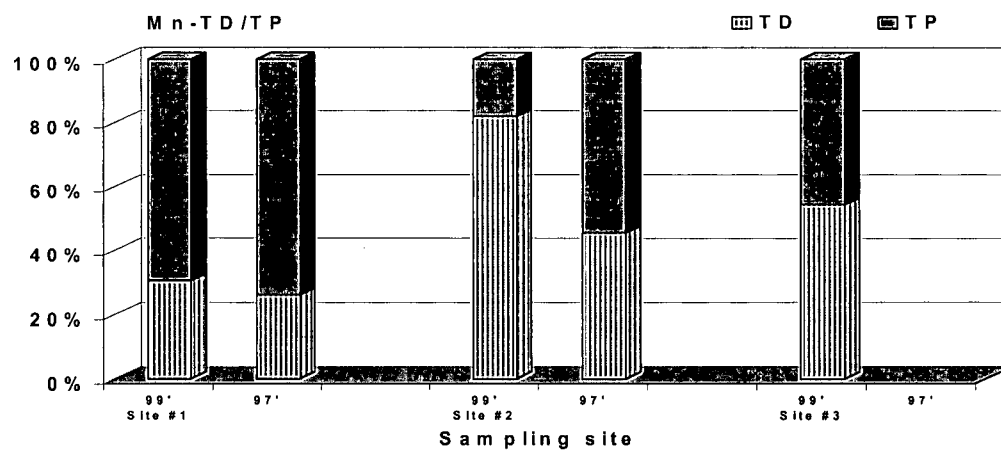
(c)
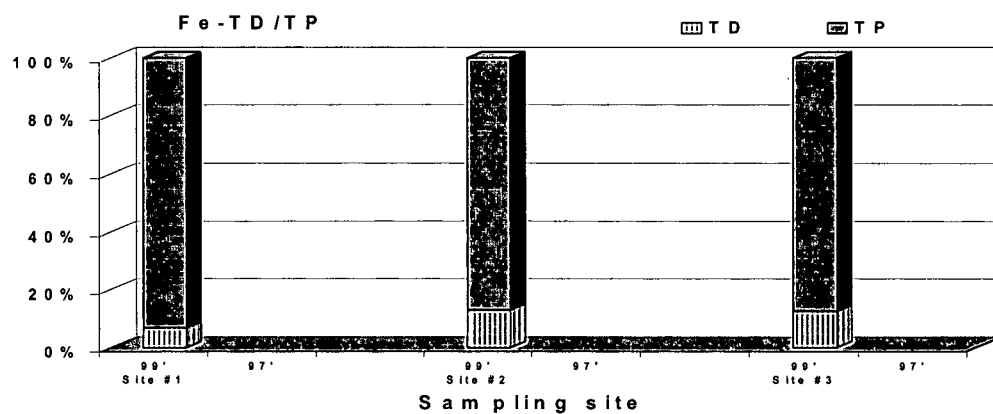
(d)

Figure 4- 9 Ratio of TD/ TM for Cu, Zn, Mn and Fe

61

TD/TM ratio in the street surface runoff

Figure 4-9(a) indicates that the dissolved copper (TD-Cu) in the street runoff (Site #1) accounts for approximately 37% of the total Cu concentration in both studies. It means that more than 60% of copper was in the particulate form when it was washed off from urban impervious surfaces. It has been reported that the high copper concentration in street runoff was due to the high traffic densities - as the results of wear of break linings (McCallum 1995). However, the potential sources of soluble copper may be also from house and garden pesticides containing copper sulfate and copper chromate, and from household plumbing that is commonly solubilised by the relatively corrosive water supply. The metals from all these sources could be deposited on the lawn and roadway, and then washed off during a storm (Macdonald et al. 1997).

Much higher ratio of dissolved Zn was found in this study (approximately 60%) than in the 1997 study (about 40%) in street runoff (Site #1) (Fig.4-9(b)). The high soluble zinc in urban runoff might be contributed by the specific uses of Zn including corrosion of galvanized parts, zinc oxides in paints, zinc chloride in antifreeze as a rust inhibitor, tire wear, and even lubricating oils containing zinc dialkyl (Atlins and Hawley 1978).

Relatively low ratio of dissolved Mn (approximately 30%) was found in street runoff samples in both studies (Fig. 4-9(c)). However, as the concentration of total manganese discharged from surface runoff was very high (as high as 241 µg/L), the dissolved manganese component was also at a relatively high concentration. Macdonald et al (1997) reported that, in addition to natural manganese sources such as erosion of mineral soils in the watershed, the major suspected anthropogenic source was the gasoline additive MMT (methylcyclopentadienyl manganese tricabonyl) used in Canada since 1970s. The combustion products of MMT, thought to be Mn-phosphates, Mn-oxides and Mn-sulfates (Ethyl 1997), may be the major sources of dissolved Mn in stormwater (Mattu and Hall 1999).

Figure 4-9(d) shows that dissolved Fe observed in street runoff had the lowest ratio of 7%, which implied that iron washed out from urban impervious area was mostly bound to the suspended sediment. Shuman (1977) noted that hydrous oxides of Fe are found to some extent in all soils, and this hydrous ferric hydroxide is strongly attached to clay minerals as part of the particulate phase.

TD/TM ratio in streams

At stream sites, a large portion of Cu was found in the dissolved forms in the early stage of the storm. Over 80% of dissolved Cu was found in Still Creek (Site #2) and over 90% was found in Brunette river (Site #3), respectively. A relatively high ratio of dissolved Zn was also observed in the stream sites. The dissolved Zn accounted for approximately 70% at Still Creek and nearly 92% at Brunette River, respectively. The total dissolved ratios of these two metals agreed well in the two studies, and both had larger or narrower ratios of the dissolved fraction in downstream than in upstream portion of the waterway.

The TD/TM ratio of Mn in streams showed an opposite pattern to those of copper and zinc, where the higher percentage of dissolved Mn was observed in the upstream portion. About 82% of dissolved Mn was measured in Still Creek (Site #2), and around 54% was measured in the Brunette River (Site #3). A similar pattern was also reported by Mattu and Hall (1999) in early storm samples, in which they measured TD/TM ratio of 90% in the upstream and 20-40% in the downstream sections. The TD/TM ratio of iron maintained a low level in both upstream and downstream – less than 15%. The low percentage of dissolved iron implied that iron was mainly associated with the particulate phase in streams.

The TD/TM ratio is regulated by many factors such as the type of metal compounds accumulated in the urban surface, the aquatic physical-chemical environment, and the urban hydrological flow regime. It was reported that the high ratio of dissolved metals in the upstream can be either due to the direct response of first flush effect between the street runoff and the connected receiving water (Jarvis 1992, Solo and Perkins 1997), or due to the flow regime in the watershed. The flow rates at two stream sites and the corresponding rainfall intensity recorded over a rainfall event were presented in Figure 4-32. It can be seen that the

flow rate in Still Creek (Site #2) is relatively low. During rainfall, the particulate metals transported through this section may deposit into the streambed (Hall et. al. 1976), which leads to the high ratio of the metal in the dissolved phase. However, the flow rate at Site #3, a downstream site in the Brunette River, was relatively higher. The high proportion of dissolved metals at this site, on the other hand, is attributed to the sedimentation function of the Burnaby Lake located upstream. The possible mechanism of sedimentation is that when the metals are washed into the Burnaby Lake, large amount of particulate associated metals from upper stream (Still Creek) was deposited in the lake due to the slower flow in the lake area. This sedimentation process leads to the decrease of both particulate and total metal concentrations downstream. As a result, a higher ratio of dissolved metal in the down stream is observed.

The higher TD/TM ratio of manganese upstream can be explained as follows: The high soluble manganese found in the Still Creek was related to the MMT combustion products directly flushed from street runoff. This dissolved Mn is apparently oxidized as it passes through Burnaby Lake, resulting in the lower soluble manganese downstream of the lake - Brunette River (Mattu and Hall 1999).

Low ratio of soluble Fe in streams was mostly due to the fact that Fe that originated from the urban storm runoff was largely in the particulate associated form (clay mineral associated Fe-hydrous oxide or Fe phosphate). Another possible explanation is that when the ionic Fe enters the receiving water, the oxidation process of Fe^{2+} to Fe^{3+} takes place in a few minutes under freshwater pH conditions, and then the great affinity between hydroxide ions and Fe^{3+} quickly forms the insoluble ferric hydroxide (Stumm and Morgan 1970). Aquatic pH seems to be the most important influencing factor in the precipitation (oxidation) of iron and manganese. Stumm and Lee (1960) reported that iron is readily oxidized by dissolved oxygen to the ferric form in the alkaline-neutral to slightly acid pH range; while manganese requires a much higher pH for equivalent rates of oxidation.

b. RE/TD

The resin extractable fraction of dissolved trace metals has been found to be more toxic as it can be assimilated directly by the aquatic organisms, which is also regarded as a bioavailable fraction of the dissolved trace metals (Florence and Batley 1980, Morrison 1985 and 1989). Table 4-3 lists the percentage of resin extractable fraction over the total dissolved copper, zinc, manganese and iron.

Table 4- 3 RE / TD for Cu, Zn, Mn and Fe (Averaged over three stormwater samples)

(%)	Metal	Site #1	Site #2	Site #3
RE/TD	Cu	31	13	7
	Zn	75	60	56
	Mn	70	73	75
	Fe	44	1	5

Although the dissolved Cu accounted for quite a large proportion of the total metal Cu in urban receiving water, the resin removable fraction of Cu, on the contrary, was only a smaller percentage. It was reported that Cu in the dissolved phase was largely in the inorganic or organic colloidal forms, such as $Cu-Fe(OH)_3$–humic acid, which were regarded as non-bioavailable forms due to their larger molecular size (Florence and Batley 1980, Morrison 1989). As suggested in the literature, Cu is more likely associated with organic matter in the aquatic system (Allard et al. 1987). In the Brunette watershed, high concentration of organic matter and the initial high color (1500-2000 mg Pt/L) in the storm water indicate that the runoff could contain high concentration of humic substances and/or lignins and tannins - the main characteristics of the leaf degradation products from the watershed area (Macdonald et al. 1997).

The resin removable fraction of metal Zn (RE-Zn), on the other hand, accounted for a larger proportion of the dissolved phase in stormwater. The ratio of RE/TD was around 60% at the two stream sites and over 70% in the street runoff. High portion of RE-Zn was also observed in the urban stormwater by Morrison (1985). He suggested that these soluble forms were free and weakly complexed Zn coming from the soluble chloride complexes of Zn in the urban contributing area.

Manganese also showed a high percentage of bioavailable fraction in dissolved form at all the sites, where over 70% of the dissolved manganese was potentially bioavailable – leaving only 20 - 30% in the colloidal fraction. High ratio of manganese in resin removable form indicates the divalent state of Mn in the water system, which is extremely soluble and was also the common manganese form observed during stormflow in this aquatic environment (McCallum 1995)

High ratio of RE fraction of iron in street runoff implies that large amount of dissolved iron may be in the ionic forms when it was released form trap under reducing conditions. However ionic form of iron was rarely found in the streams, where the RE/TD ratio was only 3-6%. It has been found that metal iron in the stream is mainly in the particulate phase such as Fe oxides or bound to the organic matters and clay minerals (Shuman 1977, Stecko and Bendell-Young 1999). It can be concluded that very little iron in streams was bioavailable.

c. RE/TM

The proportion of the dissolved bioavailable metals (RE) over the total trace metals is summarized in Table 4-4. It gives the percentage of trace metals from the watershed that will potentially contribute to the toxicity of organisms through cell uptake. Also shown in the Table 4-4 is the RE/TM ratio obtained from Morrison's study in Bergsjon - a small urban watershed in Sweden (Morrison 1985).

Table 4- 4   RE / TM for Cu, Zn, Mn and Fe

Ratio (%)	Metal	Site #1	Site #2	Site #3	Morrison (1985)
RE/TM	Cu	11	11	7	18
	Zn	45	42	51	19
	Mn	21	60	41	--
	Fe	3	0.2	1	--

Low ratio of RE-Cu (resin removable fraction of Cu) over its total concentration was measured in a range of 7%-11% at three sites, which was even lower than that observed in storm runoff in Bergsjon watershed. Low ratio of RE-Cu indicates the low ionic form of copper in the water, which is largely affected by pH of the water environment. Allard et al. (1987) pointed out that the partitioning of hydrolysable transition elements such as Cu, Zn, Cd and Pb between dissolved and particulate phase is very strongly related to pH of the aqueous environment. It was suggested that the pH in the stream greater than 5.5 led to the trend of Cu adsorption into the solid phase (Morrison 1987). An adsorption curve obtained from laboratory experiment showed that Cu mostly existed in the particulate phase in normal freshwater pH condition, which jumped from 60% to 90% when the pH increased from 5.5 to 7. The particulate Zn, on the other hand, increased from 10% to 70% with pH change in the same range (Allard et.al. 1987).

The pH range of Brunette watershed was measured as 6.2-6.8, a range when low ionic Cu and high ionic zinc was expected. However, the formation of the particulate Zn was also expected in this pH range. Alloway and Ayres (1993) pointed out that in general, Cu tended to be adsorbed by sediments very strongly, while Zn was usually held weakly. This implies that Zn is likely to be more labile and bioavailable. The transfer coefficients of trace metals in the soil–plant system also supported this conclusion (Kloke et al. 1984). The transfer coefficient – the concentration of metal in the aerial portion of the plant relative to total concentration in the soil – was 0.01-0.1 for Cu and 1-10 for Zn, which indicates that Cu is more strongly bound to the soil colloids and less available to the plant than Zn. Resin extractable zinc (RE-Zn), as expected, accounted for much higher portion, which made up approximately 50% of the total Zn (TM-Zn) in the urban water.

The RE/TM ratio of manganese indicated that approximately 21% of Mn was in the dissolved bioavailable form when washed off from the urban street. The higher ratio of 60% at up stream and 41% at down stream sites showed a similar pattern to that of the TD/TM. As described before, the elevated manganese was from storm runoff, of which a considerable amount of Mn was in the soluble form (due to its sources possibly the combustion products of MMT). Therefore, the high ratio of RE/TM indicated the existence of ionic manganese in

the street (Site #1) and in Still Creek (Site #2). The lower RE/TM ratio at the downstream site might be attributable to the oxidation process when manganese is transported through Burnaby Lake (Mattu and Hall 1999). It was reported that the high concentration of organic matter or bacteria in the lake could play a role in this oxidation, where Mn^{2+} was loosing electrons and being oxidized to the more insoluble Mn^{4+} form (Chapnick et al. 1982, Sunda and Kleber 1994).

Very low RE/TM ratio of 3% for iron in the street runoff demonstrated that only a small portion of iron was in the ionic form from surface runoff. Even lower ratio of RE/TM in streams indicated that most of iron was in the particulate forms when entering the urban receiving water.

4.1.2 Metal partitioning in suspended sediment

4.1.2.1 Partitioning results

Three fractions of particulate metals in suspended sediments - exchangeable fraction (EX), easily reducible Mn-oxide bound fraction (ER), and residue fraction (RES) - were measured for metals Cu, Zn, Mn, and Fe. The detailed results of the speciation are provided in Appendix B.

Figure 4-10 shows the copper partitioning in the particulate phase in both baseflow (BF) (August 1998) and stormwater (SF) samples (November 1999 and January 2000). It can be seen that under baseflow conditions, quite similar distributions of copper in three fractions were observed at all three sites, with the percentage of each fraction of 28-36% in EX, 27-37% in ER, and 21-43% in RES.

The variation of copper partitioning in stormwater was also observed in Fig. 4-10. Three particulate Cu fractions in street runoff (Site #1) showed a consistent ratio among EX/ER/RES as 1/1.9/4 (averaged over all stormwater samples). At stream sites, relatively higher ER-Cu was observed in the November samples in both Still Creek (Site #2) and Brunette River (Site #3). The ratio of ER-Cu over RES-Cu as 1.5-2.7/1 was obtained. In

January samples, however, ER-Cu and RES-Cu were only recorded at Site #2, and the average ratio of ER-Cu/RES-Cu was found to be 1/1.3. It should be noted that, due to low SS collection, exchangeable fraction (EX fraction) was not measured in the suspended sediment of stormwater at these two stream sites. As such, the EX fraction was calculated as a component of ER-Cu fraction.
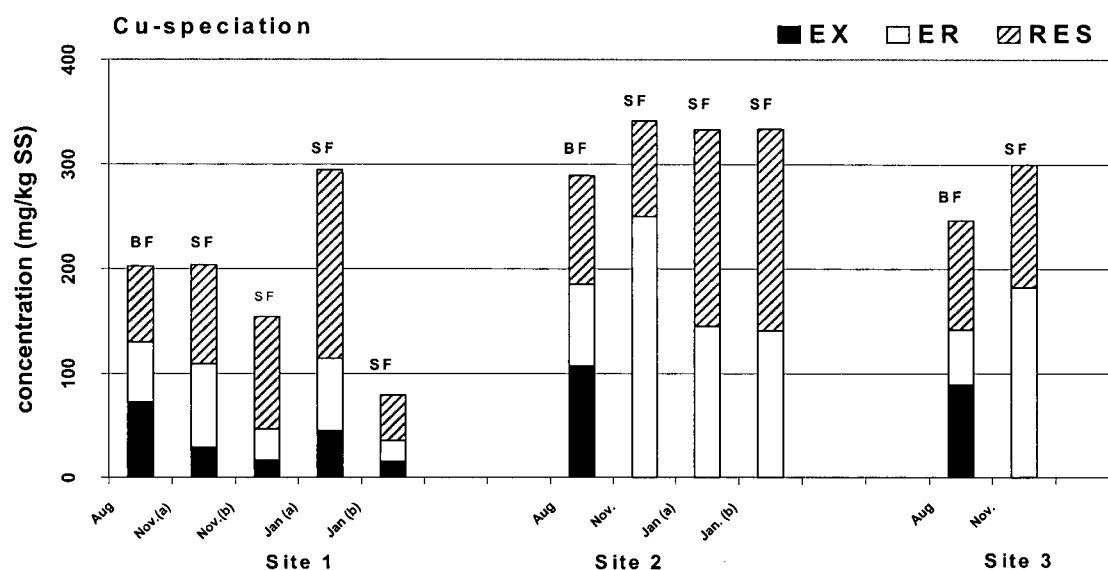
Figure 4- 10 Distribution of copper in three particulate fractions
(BF-- baseflow, SF-- stormflow)

Zinc partitioning in the particulate phase is given in Fig. 4-11. The residual zinc fraction (RES) was found prominent in the baseflow samples, which ranges from 56% - 80% in the SS collected both in the sediment trap and in streams. For the stormwater, the partitioning of EX-Zn, ER-Zn and RES-Zn in street runoff (Site #1) was quite similar over four samples, with the average ratio among these three fractions of 1/1.57/2. At the two stream sites, a similar partitioning pattern was observed, of which the ER-Zn fraction (averaged over two samples) was 58% at Site #2 and 53% at Site #3. This implied the existence of potentially bioavailable zinc associated with the suspended sediment in the water streams.
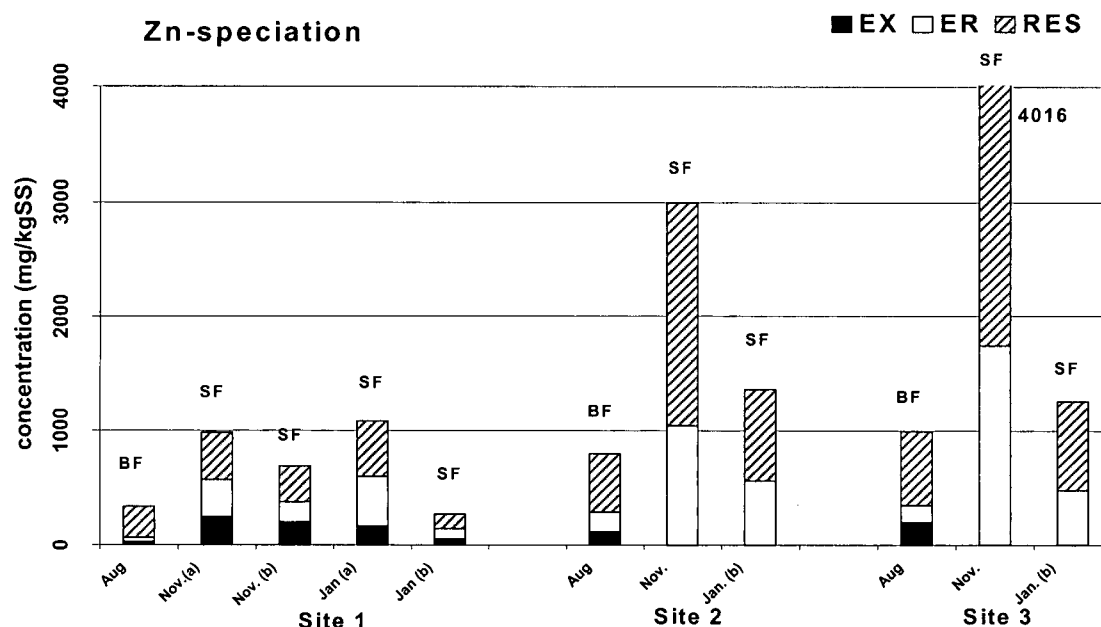
Figure 4- 11 Partitioning of zinc in three particulate fractions at three sites
(BF-- baseflow, SF-- stormflow)

Figure 4-12 shows the results of manganese partitioning in the matrix of the suspended sediment (SS) at the three sampling sites. A consistent high ER-Mn fraction was observed at the two stream sites, in which higher concentration of ER-Mn was found in the Brunette River (Site #3) than that in Still Creek (Site #2) under all flow conditions. The highest concentration of ER-Mn was found at Site #3 (stormwater in November), which was as high as 7508 mg/kg SS. In the sediment trap (Site #1), ratios of the three particulate fractions EX/ER/RES was 1/0.5/1.03 in baseflow and 1/1.1/2.7 during stormflow (averaged over four stormwater samples).
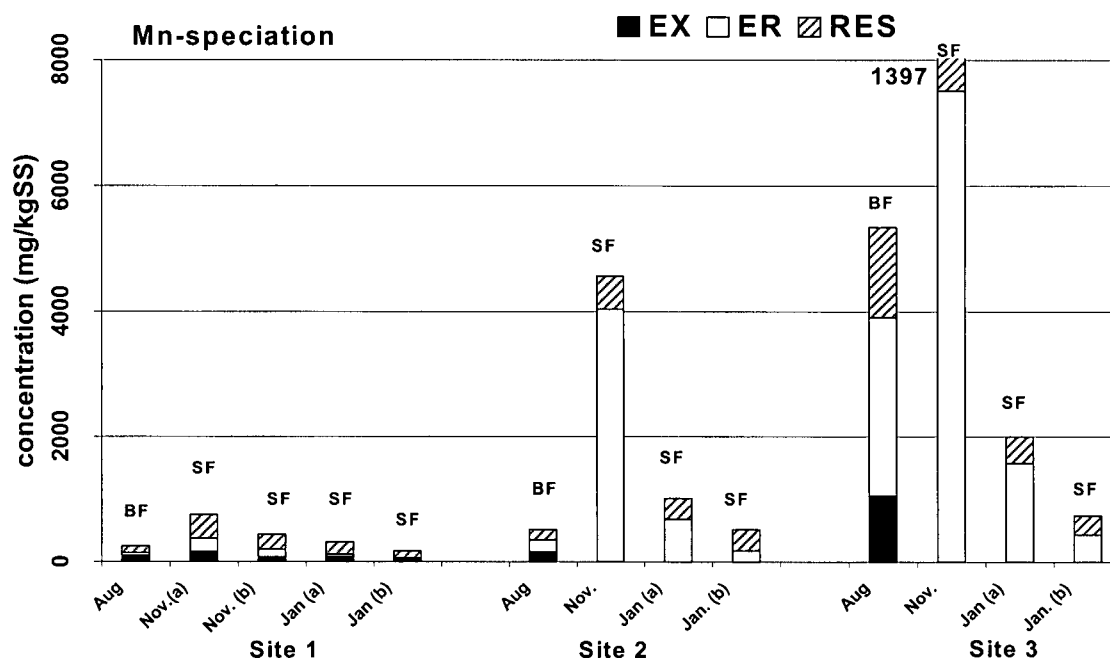
Figure 4- 12 Distribution of manganese in three particulate fractions
(BF-- baseflow, SF-- stormflow)

The predominant component of particulate iron was found in the residue fraction in both baseflow (80-90%) and stormwater (70-80%) except for November samples, as shown in Fig. 4-13. In the stormwater, relatively higher concentrations of iron in ER-Mn fraction were observed at the two stream sites, with the value of 4.5-116 g/kg SS. In baseflow samples, iron in ER-Mn fraction among three sampling sites ranges from 0.6-1.3 g/kg SS. The iron in exchangeable fraction (EX-Fe) was lower in both baseflow (0.2-0.4 g/kg SS) and stormwater (0.06-0.6 g/kg SS).
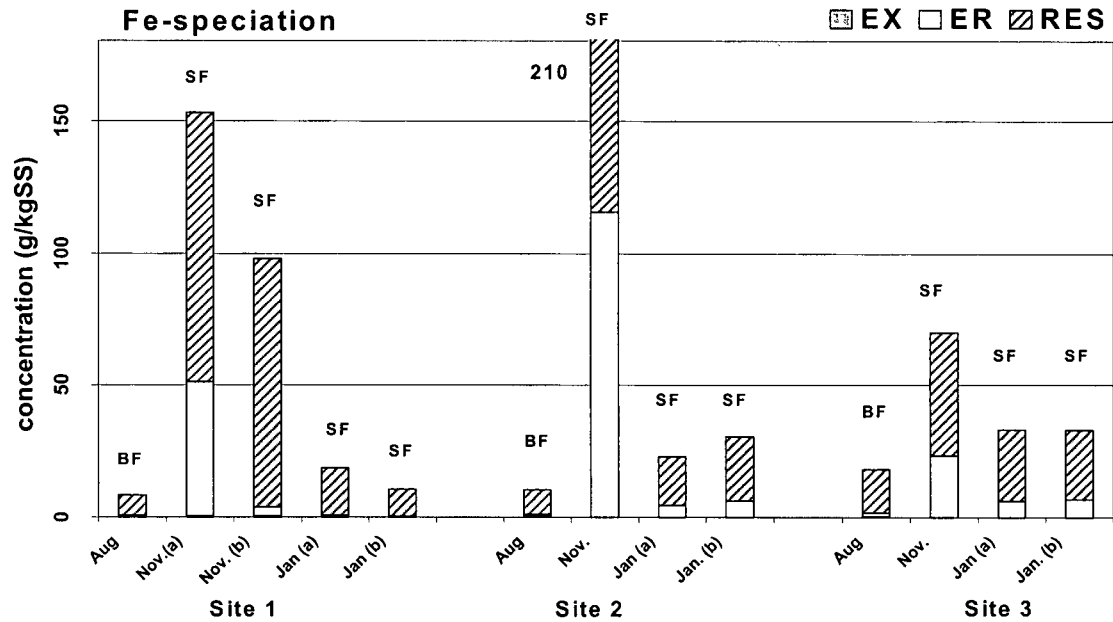
Figure 4- 13 Distribution of iron in three particulate fractions at three sites.
(BF-- baseflow, SF-- stormflow)

4.1.2.2 Discussion on particulate metal components

Of the three metal particulate forms in suspended sediments, exchangeable (EX) and easily reduceable (ER) metal froms are regarded as potentially bioavailable. The bioavailable components of the particulate trace metals at the three sites, as well as their seasonal variations, will be discussed below. Due to the fact that most of the particulate iron is in RES form, and also it is a less toxic metal in the water system, the particulate bioavailable iron is not discussed here.

a. Bioavailable Cu in suspended sediment

The partitioning of particulate Cu in suspended sediment (SS) in four stormflow and one baseflow conditions is shown in Fig. 4-14. It indicates that SS generally contains a large portion of the potentially bioavailable copper, namely EX-Cu and ER-Cu (bound to Mn-oxides). EX-Cu and ER-Cu accounted for approximately 60% of the total particulate Cu in baseflow samples at all three sampling sites. Of which EX-Cu along accounted for about

38% of the total particulate copper, which was similar to the result of EX-Cu=35.2% from a Swedish catchment study (Morrison 1985). ER-Cu contributed a relatively small portion (20%) during baseflow, which was probably due to the manganese oxide formation in water column.
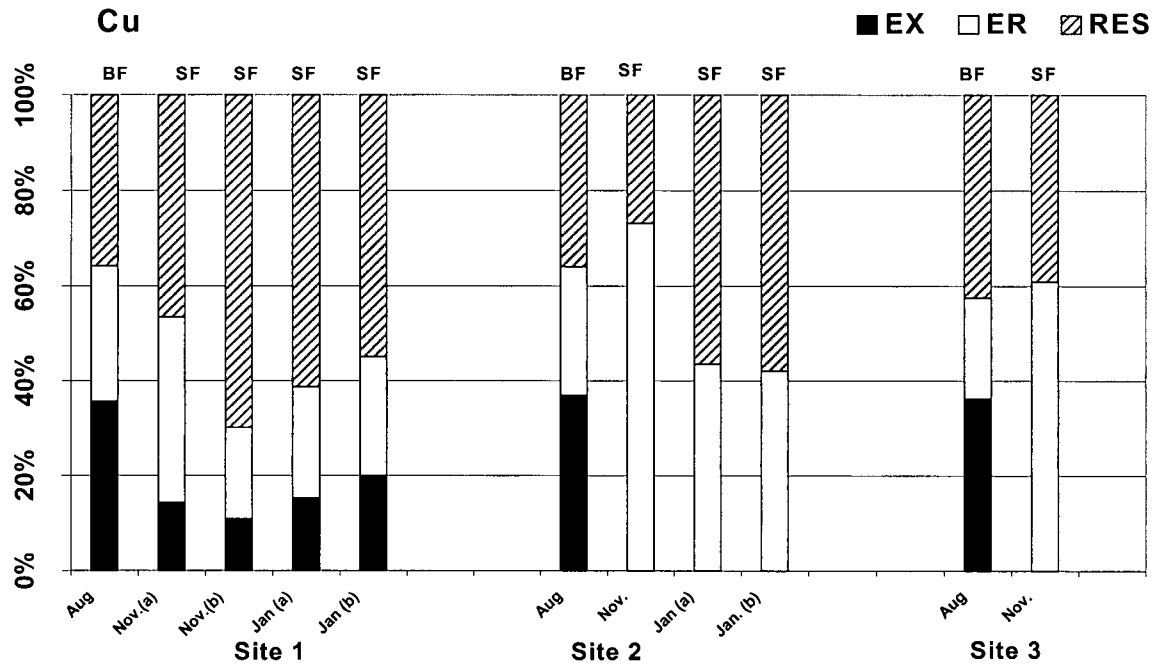
Figure 4- 14 Fractions of particulate Cu in SS at three sites
(BF – baseflow; SF - stormflow)

During the rainfall event the residual fractions were >50% from the street runoff samples, while in the stream sites, a great proportions of the Cu was bound to Mn in the ER-Cu phase of the suspended sediments. A similar pattern was also reported by Stecko and Bendell-Young (1999). Their results from SS collected in the Fraser River Estuary showed that the great proportions of ER-Cu was found during the winter months in the wet weather.

b. Bioavailable Zn in suspended sediment

The percentage of the bioavailable components of Zn in SS (Fig. 4-15) varied significantly from baseflow to stormflow at Site #1 (sediment trap), where bioavailable fractions (EX-Zn

and ER-Zn) accounted for only 20% of the total particulate Zn in baseflow, but increased dramatically to 60% in stormflow. A similar ratio of 22.3% in baseflow was also reported by Morrison (1985) in his study of two urban catchments. He reported that the EX-Zn is derived mostly from road runoff solids and gully pot basal sediments.
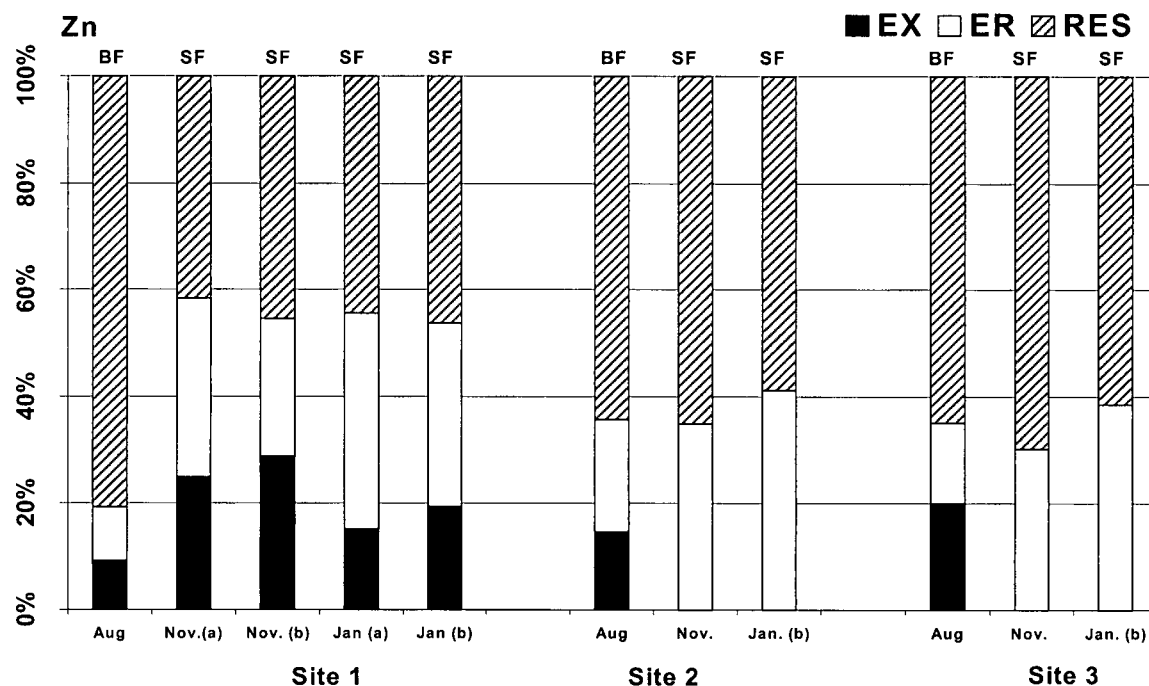
Figure 4- 15 Fractions of particulate Zn in SS at three sites
(BF – baseflow; SF - stormflow)

The bioavailable components of Zn at two stream sites, on the other hand, accounted for a stable but relatively low portion in both baseflow and stormflow conditions, ranging from 30-40%. This may be attributed to the binding of Zn to Fe-oxides and other organic and inorganic materials existing in the water column, as a high level of particulate Fe and color was observed in the watershed streams. However, EX+ER fractions still provide an important potentially bioavailable Zn pool within suspended sediment, which may be released into the soluble phase under normal pH conditions or into the water column with the significant drop in pH or redox conditions (Morrison 1985).

c. Bioavailable Mn in suspended sediment

Figure 4-16 demonstrates three component of particulate manganese in SS among the three sampling sites under different flow conditions. It can be seen that the partitioning pattern of Mn varied significantly from site to site and under different flow conditions. High variability of ER-Mn proportion in SS was also observed in previous studies (Stecko and Bendell-Young 1999). They suggested that the high variability in concentrations of ER-Mn in the suspended sediment could be related to many interactions between biota and Mn oxide.
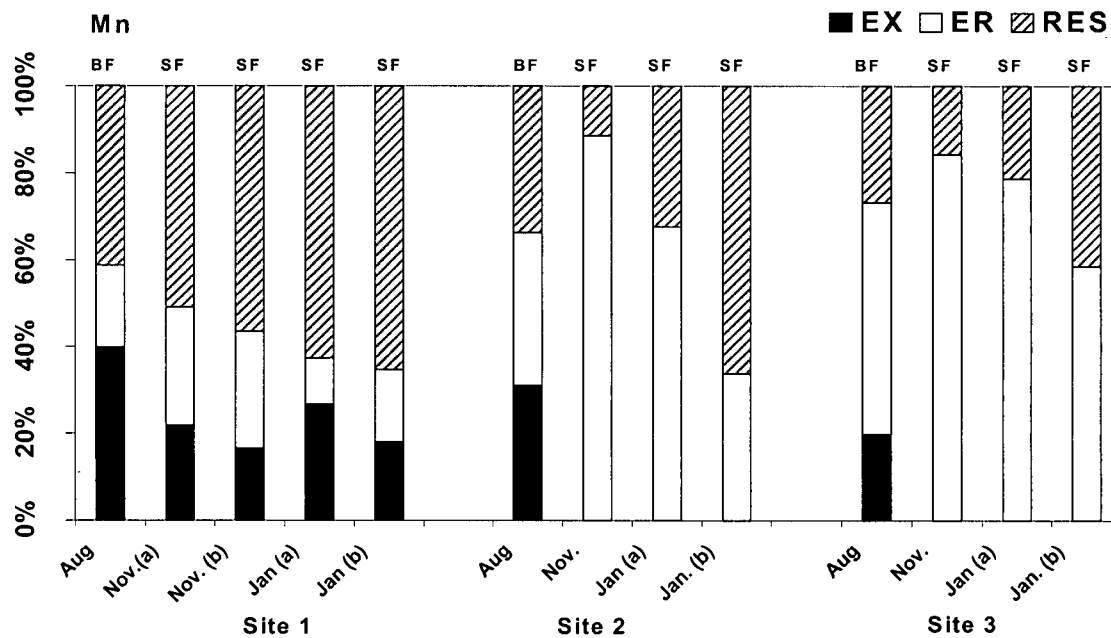
Figure 4- 16 Fractions of particulate Mn in SS at three sites
(BF – baseflow; SF - stormflow)

However, much higher ER-Mn proportion was generally found in the streams than in street runoff, which caused the ratio of particulate bioavailable Mn to be higher in streams than in street runoff.

4.1.3 Bioavailable Copper and Zinc in the Watershed

Copper and zinc are two of the most important and toxic trace metals in the Brunette water system. The concentrations and distributions of these two metals and their bioavailable components are discussed below.

4.1.3.1 Fractionation of Cu and Zn

Five major fractions of Cu and Zn, namely RE for resin extractable and STR-B for strongly bound (colloid form) in the dissolved phase and EX for exchangeable, ER for easily removable and RES for strongly bound in particulate phase, in stormflow at three sites are summarized in Fig. 4-17. It should be noted that due to the limited SS samples collected at Site #2 and Site #3, the particulate metals were only partitioned into ER and RES fraction, and no further partitioning for EX was done at these two sites. ER fraction at these two sites can then be treated as EX+ER – the total potentially bioavailable metal in particulate phase.

Figure 4-17 demonstrates that a significantly high proportion (80-90%) of total dissolved Cu was observed at stream sites. However the RE fraction was only a small portion (7-11%), indicating that copper in the dissolved phase is largely in colloidal form. The dissolved Cu in street runoff (Site #1), on the other hand, was only approximately 30% of the total Cu, of which about two thirds were in the colloid form (STR-B). This indicates that most of Cu discharged from the urban impervious surface was in particulate and non-bioavailable forms.

Of the high percentage of particulate Cu in street runoff, about 25% was associated with the Mn-oxide fraction, which may imply that Mn compounds on the urban street play important role in the transport of Cu. The EX+ER Cu in the particulate phase accounted for about 30% of the TM-Cu, indicating the potential move of the bioavailable Cu fraction from urban non-point source to the receiving water. The lower percentage of particulate Cu found at stream sites is possibly due to the deposition of large amount of metal associated particles onto the bed sediment of stream and lake (Macdonald et al 1997).

The partitioning pattern of Zn was quite similar at all sampling sites. Relatively higher dissolved Zn was found both in street runoff and in streams, which was similar to Morrison's study (1985). The RE-Zn fraction made up 42 – 51 % of TM-Zn at all three sites, indicating a

high level of Zn in ionic and weakly complexed forms. It was believed that the high level of
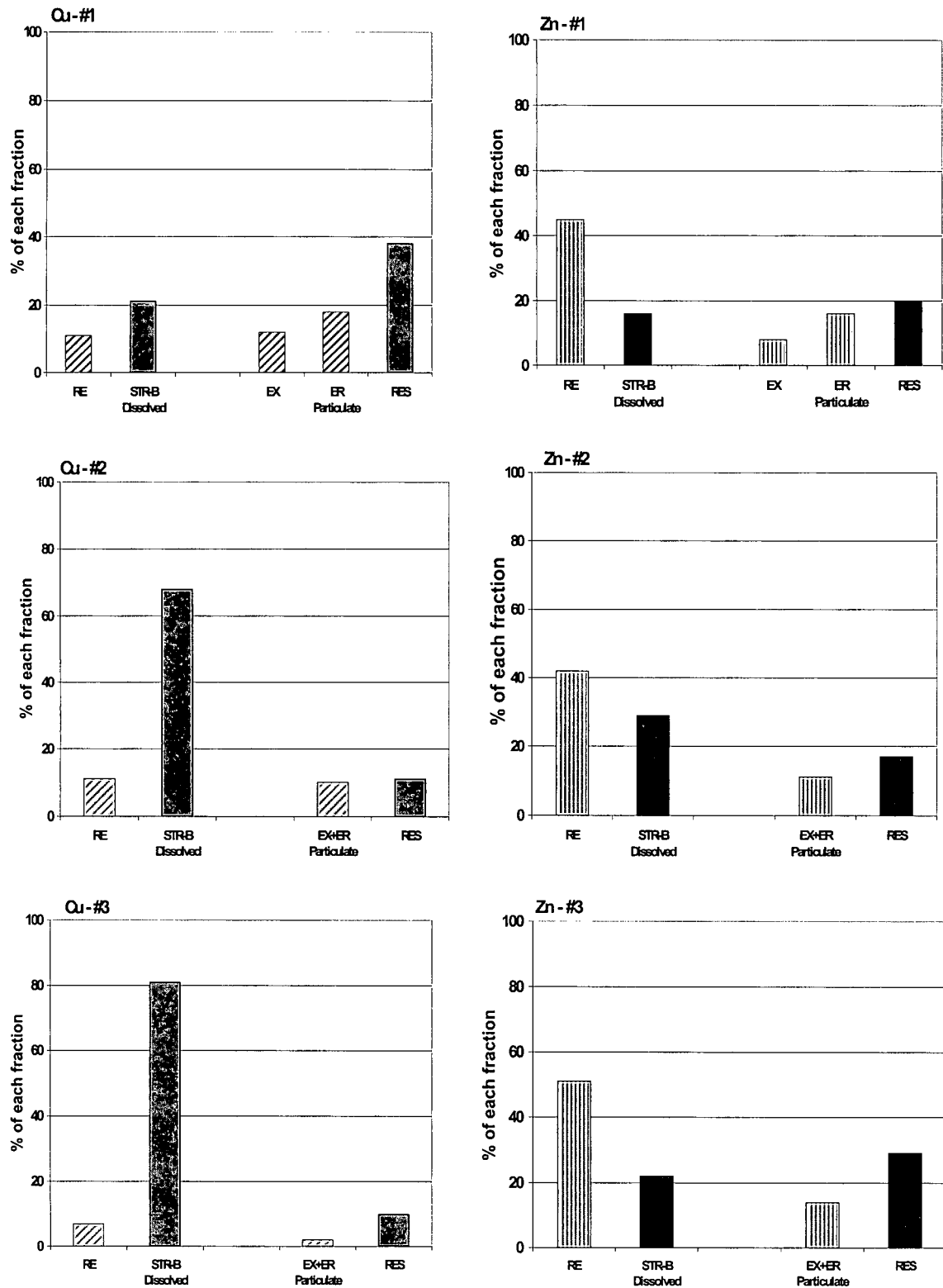
Figure 4- 17 Copper and Zinc partitioning in five fractions among the sampling sites

ER-Zn in stormwater was attributed by the soluble Zn compounds from urban impervious surface (Macdonald et al. 1997) and the behavior of Zn in the freshwater system (Florence an Batley 1980). Particulate Zn accounted for approximately 30-40% of total zinc at all sites, while one of its bioavailable fractions, EX-Zn, made up only 8% of the total Zn in the surface runoff – much less than that of 22.3% in Morrison's study (1985). The other bioavailable particulate fraction ER-Zn was in the range of 11%-16% at all three sites.

4.1.3.2 Concentrations of bioavailable Cu and Zn in the watershed

The concentrations of bioavailable Cu and Zn, i.e. the resin extractable fraction (RE) in dissolved phase and the exchangeable and easily removable fractions (EX and ER) in particulate phase, are shown in Fig. 4-18. The results reflect three flow conditions at three sites. It can be seen that the concentration of Zn is much higher than that of Cu, in every fraction of the three bioavailable forms, at all three sites.

Fig. 4-18 illustrates that the concentrations of bioavailable Cu in both dissolved and particulate phases were mostly in the range of ND-10 µg/L (ND - non-detectable). The maximum concentration of the bioavailable Cu was always found at Site #1 - the street runoff site. This indicates that the street runoff is one of the major sources of copper to the watershed streams. The concentrations of the bioavailable Cu at the two stream sites were significantly lower, and the concentration at downstream site (Site #3) was further lower. The regulating and sedimentation function of the Burnaby Lake lying between Site #2 and Site #3 is quite obvious.

Figure 4-18 also indicates that the concentration of the bioavailable Cu is higher in stormflow than in baseflow, for all the three sites. The concentration of dissolved Cu (RE) was always lower than that of the particulate Cu (EX+ER) in street runoff at Site #1, especially in stormflow. However, this difference was not so obvious in streams, where the sedimentation of the particulate metals occurred.
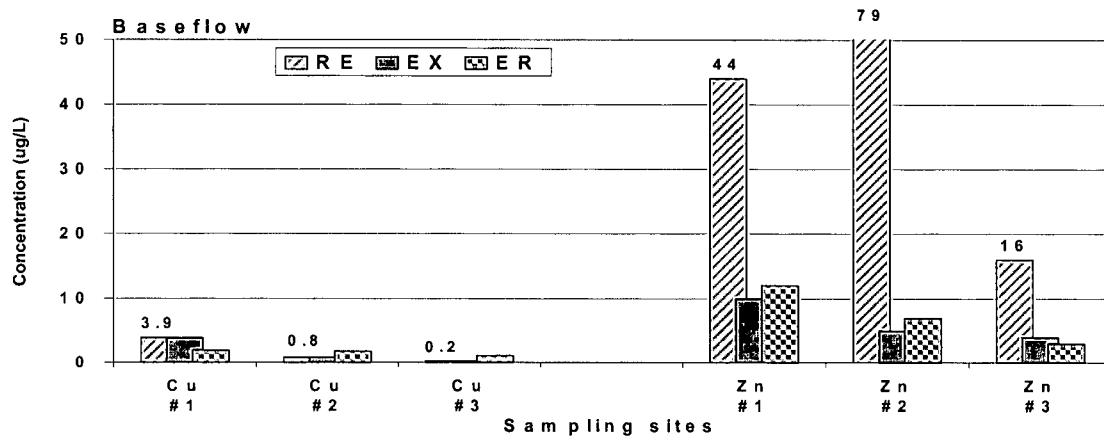
(a)
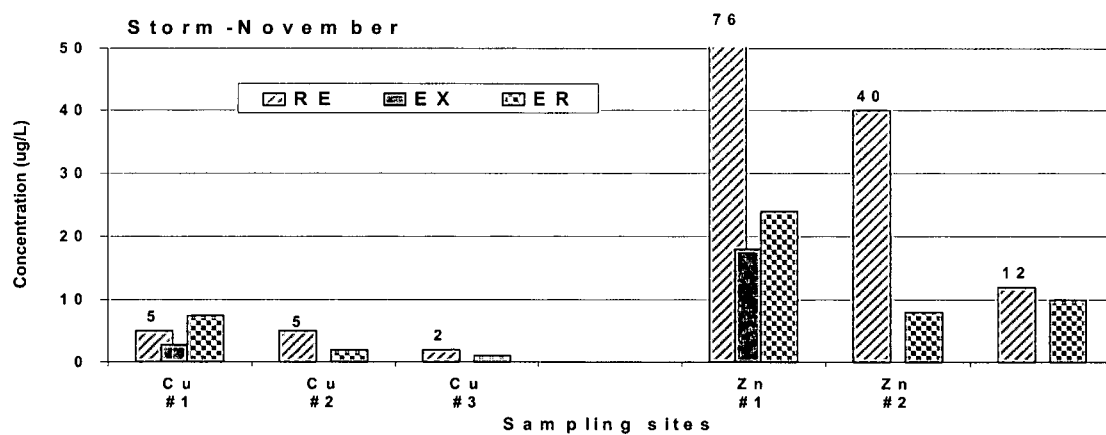
(b)
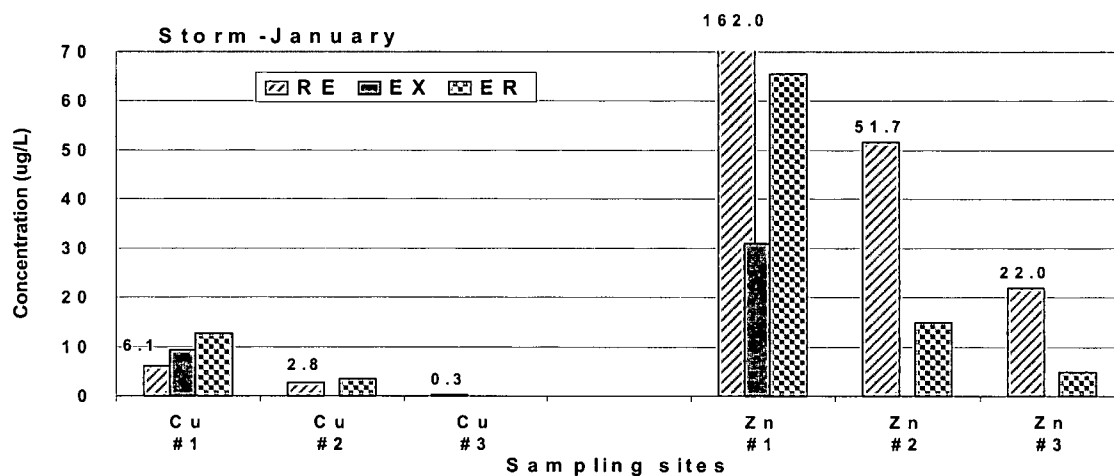
(c)

Figure 4- 18 Bioavailable Cu and Zn levels in the watershed
under baseflow (a) and under stormflow (b) and (c)

Much higher concentrations of both dissolved and particulate Zn were also found in street runoff than in streams during rainfall – they were about two times higher than those in upstream (Site #2) and six times higher than those in downstream site (Site #3). This implies that street runoff was also the major source of Zn to the water system. The concentrations of both dissolved and particulate Zn were also significantly higher in stormflow than in baseflow in street runoff. However, this difference is not so obvious in streams, where most components of the bioavailable Zn showed comparable levels in both baseflow and stormflow.

4.1.4 Regulating Effects of Mn on Cu and Zn

It has been recognized that the manganese bound Cu or Zn is produced when the dissolved Cu or Zn interacts with particulate Mn. If sedimentation occurs during the interaction, this decreases the concentration of Cu and Zn in the dissolved phase and consequently reduces the bioavailable Cu and Zn in the water system. It can be expected that the amount of Mn bound trace metals is determined by both the concentration of particulate Mn and the concentration of dissolved Cu or Zn.

4.1.4.1 Regulating effect on Cu

As presented in this chapter, Mn-bound Cu (ER-Cu) accounted for a large proportion of the particulate Cu - over 25% in most of the samples. The relationship between total particulate Mn and the Mn bound Cu, or specifically the relationship between total particulate Mn and the ratio of Mn bound Cu over all Cu contributed to ER-Cu (TD-Cu + ER-Cu) were analyzed. It was found that no clear trends of manganese regulating copper in the stormwater was observed. The variation between ER-Mn and TD-Cu could be caused by various physical and chemical conditions in the water system.

4.1.4.2 Regulating effect on Zn

The same relationship was analyzed for Zn. A positive relationship between ER-Mn and the ratio of ER-Zn/TD-Zn + ER-Zn is evident in Fig. 4-19 (R=0.56). However, considerable

variability in this relationship makes it difficult to draw a firm conclusion of the regulating effect of manganese on the bioavailable Zn in the stormwater.

As mentioned before, the regulating effect of Mn on Cu and Zn in the water column is determined by the particulate fraction of the metal Mn. However, it has been found that the partitioning of Mn changes significantly in the Brunette water system. A monitoring program over a rain event in Brunette watershed showed that in Still Creek, Mn in the soluble form was approximately 90% at the beginning of the storm, and decreased to less than 20% with increasing flow (Mattu and Hall 1999).
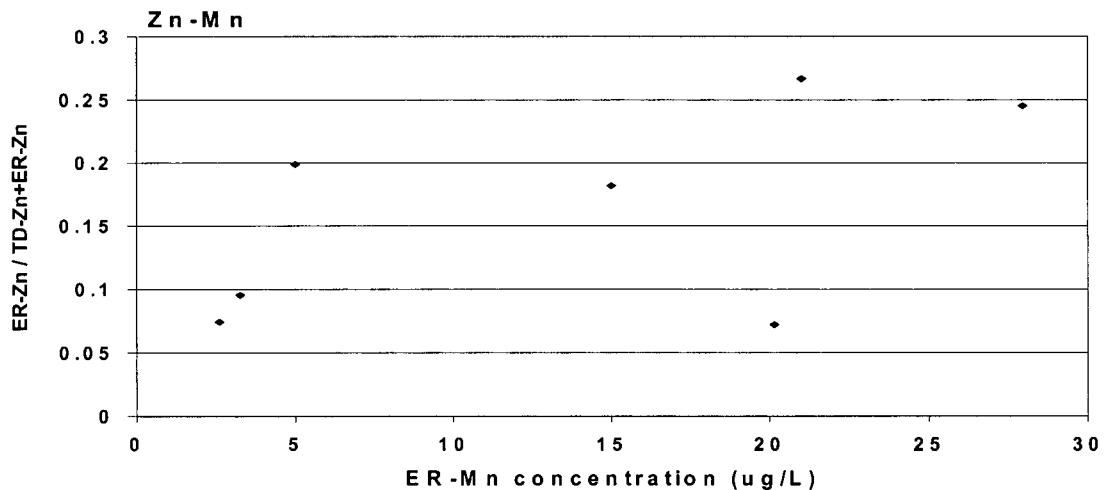
Figure 4- 19 Effect of Mn on Zn bioavailability

At the Brunette River site, the dissolved Mn fraction made 20-40% of the total Mn. However, this suggests that the Mn seemed to be oxidized as it traveled down into the lake, since Mn was mostly in the soluble form when entering Burnaby Lake, and mostly in the particulate form when leaving the lake. Therefore, it can be expected that the change of particulate Mn in the watershed waterways is likely to help regulate particle associated Cu and Zn in the water system, which will reduce the dissolved Cu and Zn phases especially downstream of Burnaby Lake. This is confirmed by the higher levels of Mn and associated Zn and Cu that precipitate on the resin membranes during storm events at the Brunette River site.

4.2 Bioavailable metal study by dialysis with resin receiver in situ

The field experiments using dialysis with resin receiver were conducted with both long time (1-2 weeks) and short time (24 hours) exposures to simulate the uptake of trace metal species by the aquatic organisms in the urban stream. The uptake rates for all targeted metals were measured in the sediment trap and at the two stream sites. The experiments were conducted seasonally based on the flow pattern in the urban streams (two in baseflow and four in stormflow and snowmelt conditions). A complete data set for the metal uptake is listed in Appendix D.

4.2.1 Trace metal uptake under baseflow condition

Trace metals taken up by receiver resin and membrane in baseflow condition were examined in two exposure periods in 1998. One was conducted for 7 days in July, and the other was for 15 days in August.

4.2.1.1 Copper uptake

The copper taken up by receiver resin and membrane at the three sites is shown in Fig. 4-20. The lowest resin uptake rate was found in the sediment trap at Site #1, with the range of 1.95 -2.89 pg/mm^2.h. The uptake rates at Site #2 and Site #3 were found higher, ranging from 5.4 to 5.9 pg/mm^2.h at Site #2 and 4.9 to 5.4 pg/mm^2.h at Site #3, respectively. It was noted that although the resin uptake rates of the copper varied from site to site, they were relatively consistent in July and August during baseflow at all three sites. This may imply that the bioavailable copper species in the watershed during the drier summer period is low but at consistent levels.
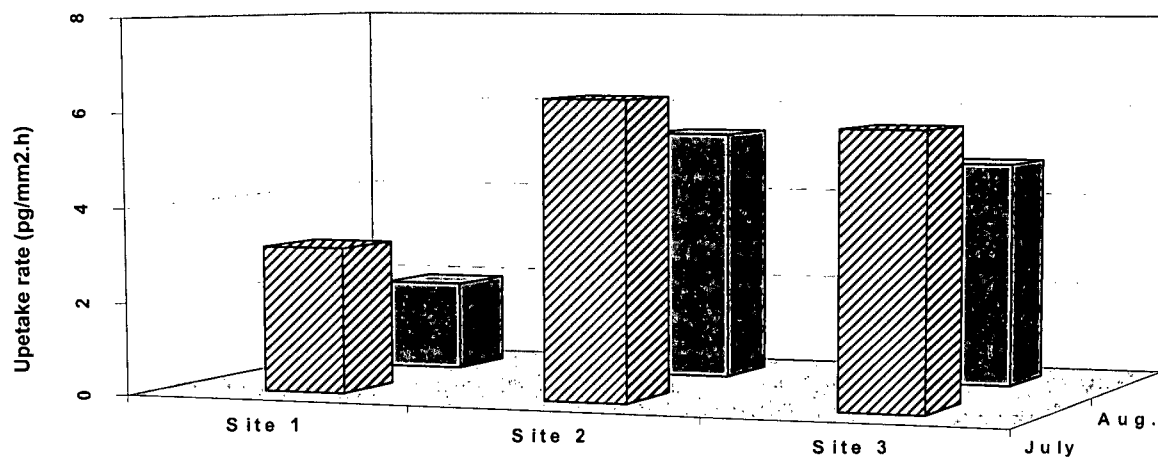
(a) Resin uptake
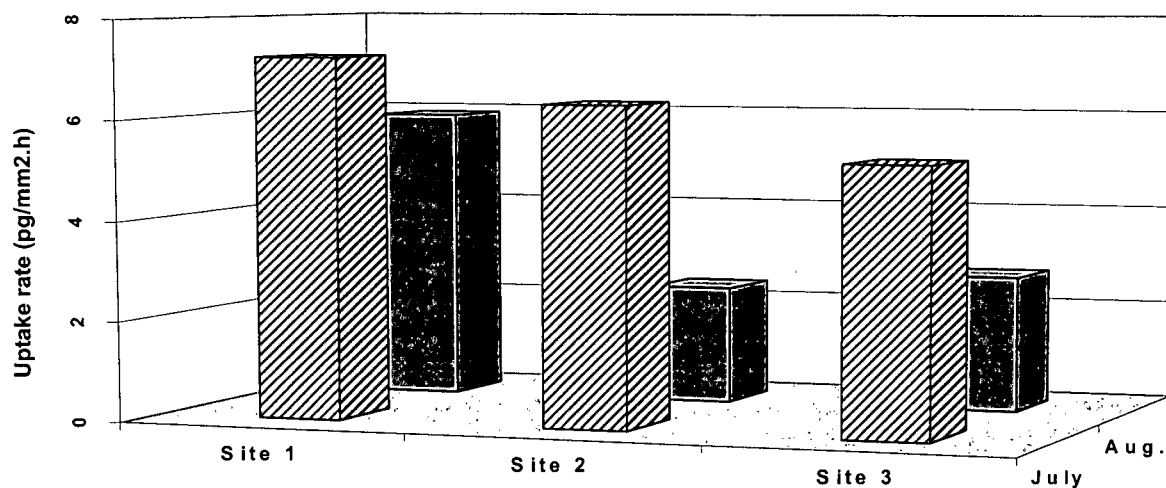
(b) Membrane uptake

Figure 4- 20 Copper taken up in baseflow by (a) resin and (b) membrane

The membrane uptake rate for copper, on the other hand, varied not only from site to site, but also from time to time (Fig. 4-20 (b)). Relatively higher uptake was found in the sediment trap than at the stream sites. The range of uptake rate of 5.9 -6.7 $pg/mm^2.h$ was found at Site #1, whereas the range of uptake rate of 2.4-5.8 $pg/mm^2.h$ and 2.7-4.9 $pg/mm^2.h$ was observed at Site #2 and Site #3, respectively.

4.2.1.2 Zinc uptake

The receiver uptake for zinc was quite variable between the two experiments (Figure 4-21).
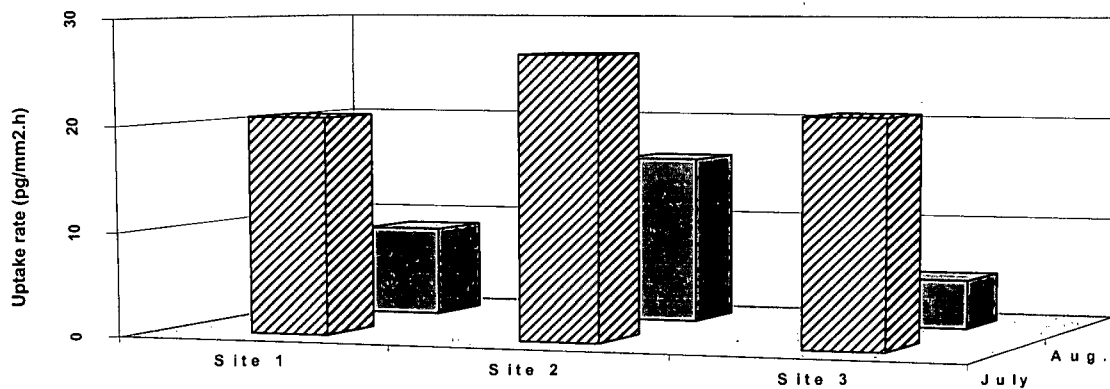
(a) Resin uptake
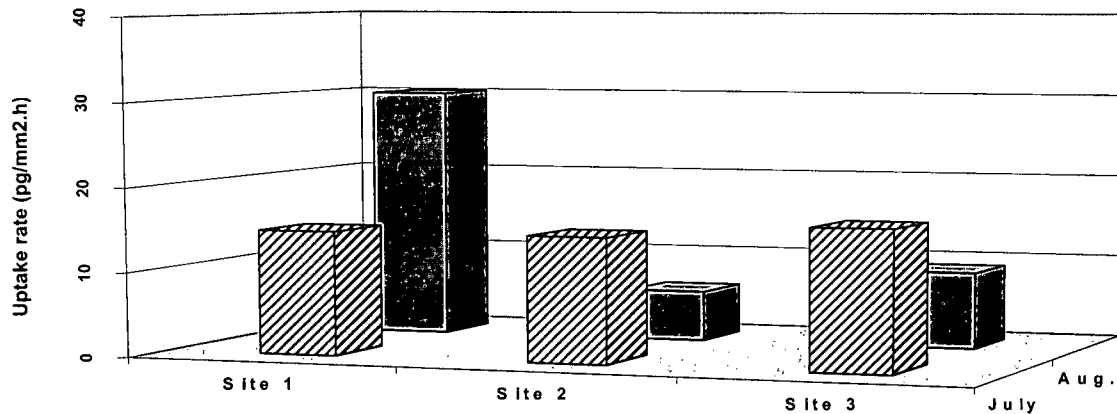
(b) Membrane uptake

Figure 4- 21 Zinc taken up in baseflow by (a) resin and (b) membrane

In July, the uptake rates by resin at all three sites were quite similar (with the range between 19-25 pg/mm^2.h), and so were the uptake rates by membrane (13.5-15 pg/mm^2.h). However, the differences between the uptake rates by resin and by membrane were quite significant at the sampling sites. In the two experiments, the maximum resin uptake rate was found at Site #2, while the highest membrane uptake was found at Site #1 and Site #3, respectively. These results might be due to the different physical and chemical conditions that affect the uptake of zinc at these three sites. For instance, a water condition appropriate for membrane adsorption or precipitation may prevent the transmission of metal species inside the dialysis bag, and allow uptake by the resin.

4.2.1.3 Manganese uptake

Manganese taken up by the receiver is shown in Fig. 4-22. The high resin uptake rates were found in the sediment trap (Site #1) in both experiments, which was 265 pg/mm^{2}h in July and 124 pg/mm^{2}h in August. Significantly low resin uptake rates were measured at the two stream sites - 24-35 pg/mm^{2}h in Still Creek (Site #2) and 15-16 pg/mm^{2}h at Brunette River (Site #3). A totally opposite pattern of the membrane uptake was observed at these three experimental locations, where the lowest uptake rate of 3-7 pg/mm^{2}h was at Site #1, and highest rate of 344-486 pg/mm^{2}h was at Site #3. However, membrane uptake was also low at Site #2 with the range of 35-58 pg/mm^{2}h.
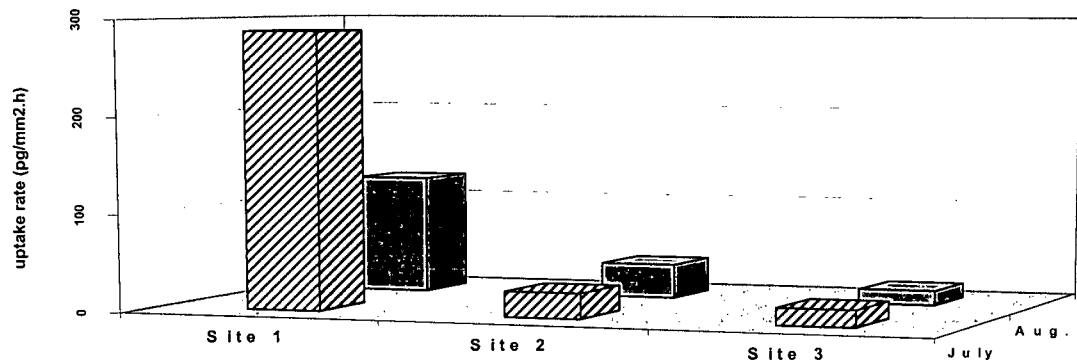
(a) Resin uptake
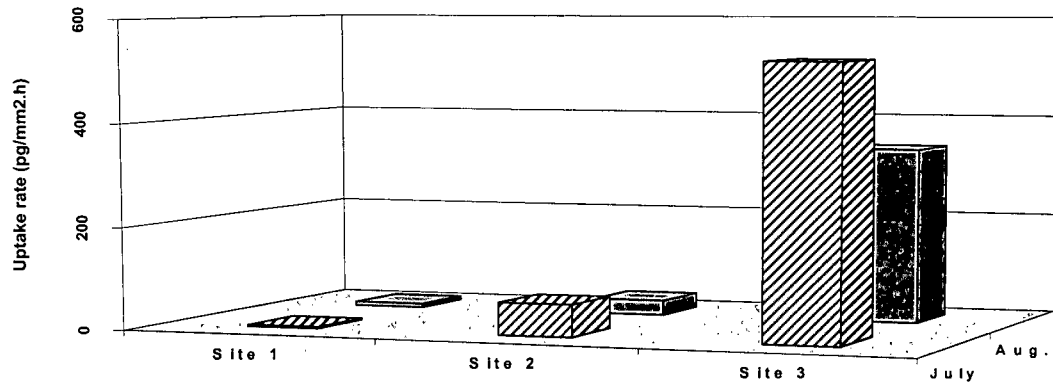
(b) Membrane uptake

Figure 4- 22 Manganese taken up in baseflow by (a) resin and (b) membrane

4.2.1.4 Iron uptake

The distribution of iron uptake at the three experimental sites was quite similar to that of the manganese, as shown in Fig. 4-23. Very high resin uptake rate (6962 pg/mm^2h) was found at Site #1 in July's experiment. The rates at the two stream sites were also significantly low - 98 pg/mm^2h at Site #2 and 65 pg/mm^2h at Site #3. Similarly, the highest iron uptake rate by the membrane was also found in Brunette River (Site #3) - with the value of 1234 pg/mm^2h in July. The rates of iron taken up by the membrane at the two other sites were similar, which was 398 pg/mm^2h at Site #1 and 355 pg/mm^2h at Site #2 in July's experiment.
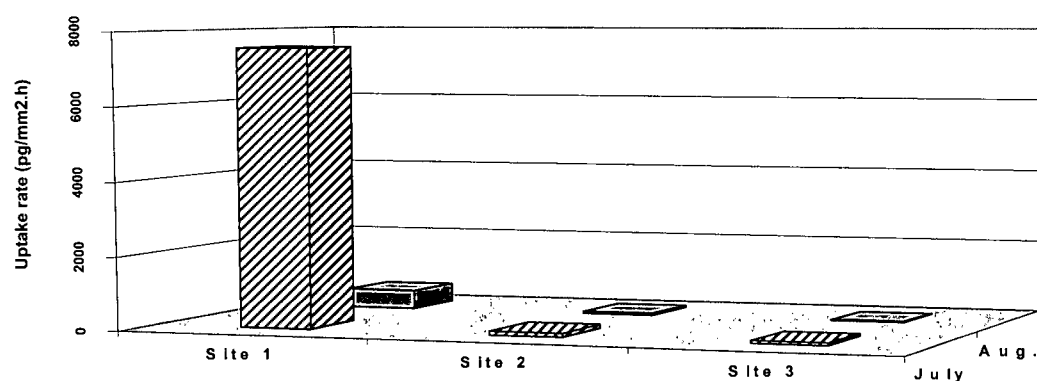
(a) Resin uptake
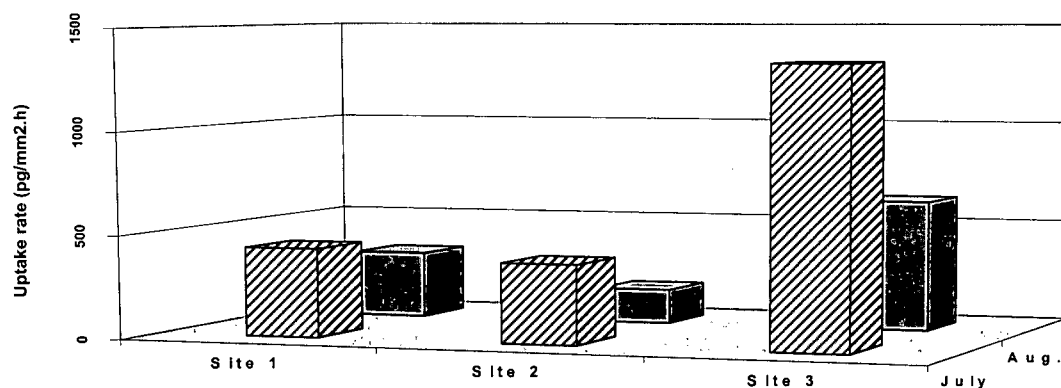
(b) Membrane uptake

Figure 4- 23 Iron taken up in baseflow by (a) resin and (b) membrane

4.2.2 Uptake of trace metal in stormflow and snowmelt in the field

Four one-week-exposure experiments were conducted during stormflow and snowmelt conditions. They were snowmelt condition in February 1999, stormwater conditions in October and November 1999, and January 2000, respectively. It should be noted that the uptake data are not available for the experiment in October 1999 at Site #2, as the receiver was lost during the experiment. The results of trace metal uptake study over one rain event are also presented in this section.

4.2.2.1 Copper uptake

Although the copper uptake rates by resin were quite variable in the four experiments, they showed little difference at the three experimental sites, as shown in Fig. 4-24(a).
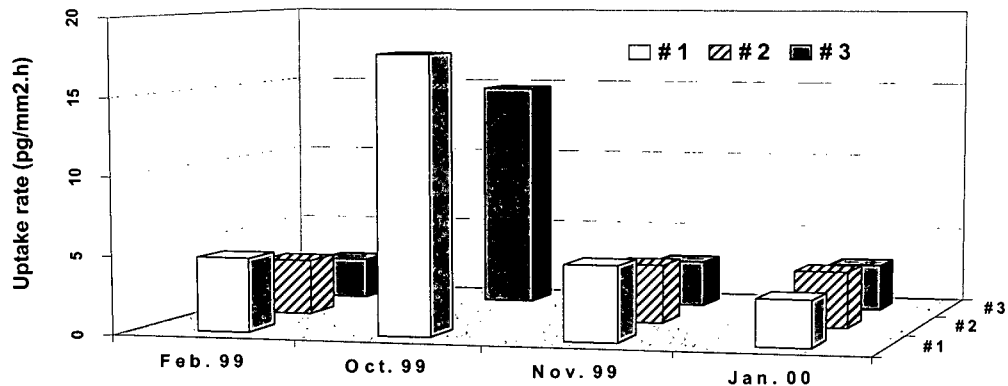
(a) Resin uptake
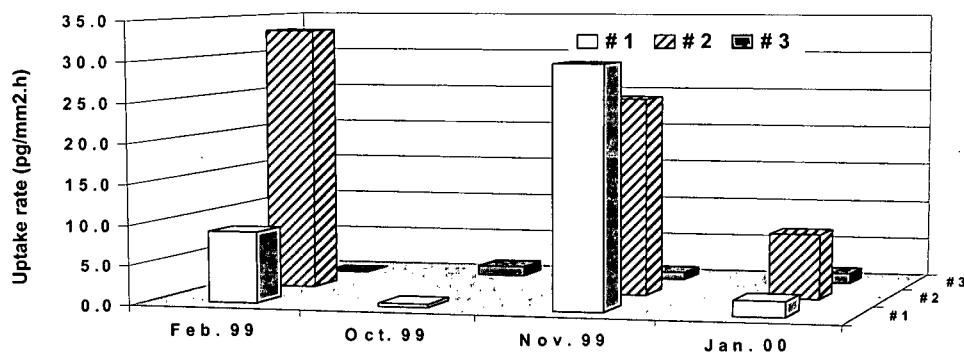
(b) Membrane uptake

Figure 4- 24 Copper taken up in stormwater by (a) resin and (b) membrane

The maximum uptake was recorded in a stormflow in October 1999, which was at least three times higher than those in other three stormflow or snowmelt.

The membrane uptake of Cu also varied greatly in the four experiments, as shown in Fig. 4-24(b). However, very low rates were recorded in October 1999 at all sites, which corresponded to the maximum resin uptake rate of the four experiments. Higher membrane uptakes were observed in February and November 1999. The highest rate was in February at Site #2 of 33.3 pg/mm^2.h.

4.2.2.2 Zinc uptake

The maximum resin uptake of Zn was also found in October 1999, especially in the sediment trap (115 pg/mm^2·h) (Fig. 4-25). The uptake rates from the other experimental periods were significantly lower - ranging from 20 to 40 pg/mm^2·h. Membrane uptake of Zn, on the contrary, was also lower in October's experiment. High membrane uptake was detected in February and November at both Site #1 and Site #2. Also like the case for copper, the zinc uptake rates by membrane were considerable low for all the experiments at Site #3.

4.2.2.3 Manganese uptake

Manganese uptake by resin was found much higher at the two stream sites than that at the sediment trap, as shown in Figure 4-26(a). It ranged from 52-88 pg/mm^2.h at Site #2, and 60-82 pg/mm^2.h at Site #3. While at Site #1, the manganese uptake rate was only 8-35 pg/mm^2·h of the four experiments.

Manganese uptake by membrane showed the opposite pattern to the uptake by resin at site #1 and site #3 (Fig. 4-26(b)), i.e., the higher resin uptake corresponded to the lower membrane uptake. However, high membrane uptake of manganese was also found at Site #2, with the rates ranging from 45-147 pg/mm^2·h. It may imply the high manganese concentration in the Still Creek. Figure 4-26 also demonstrates that the relatively low manganese uptake rates were found at Site #1, the sediment trap, both by resin and by membrane.
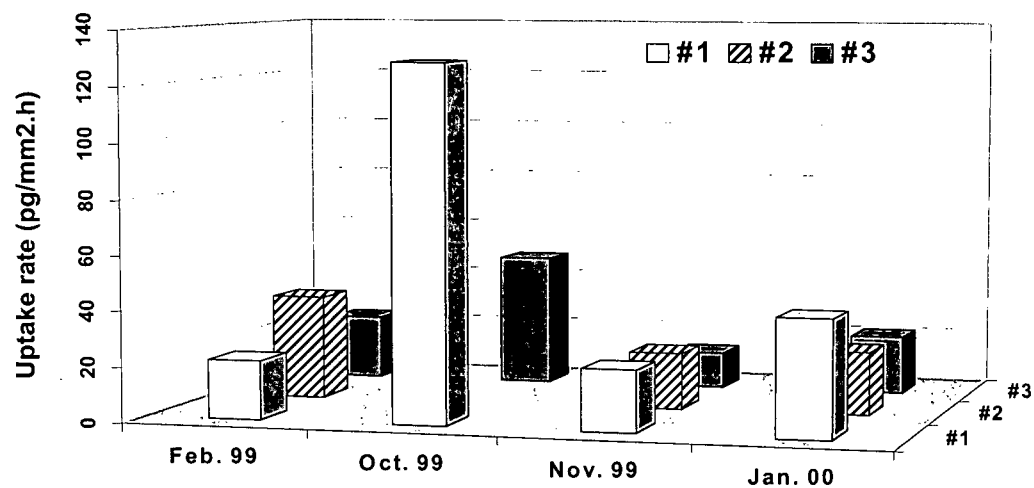
(a) Resin uptake
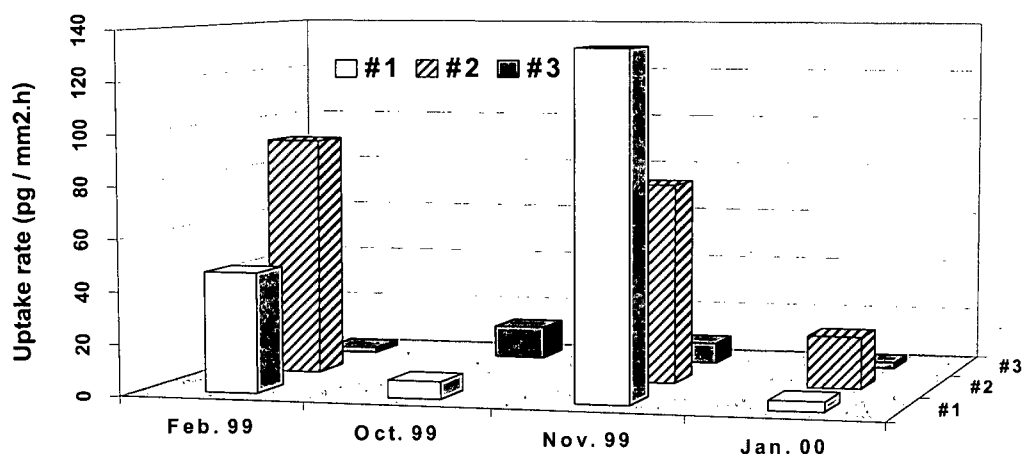
(b) Membrane uptake

Figure 4- 25 Zinc taken up in stormwater by (a) resin and (b) membrane
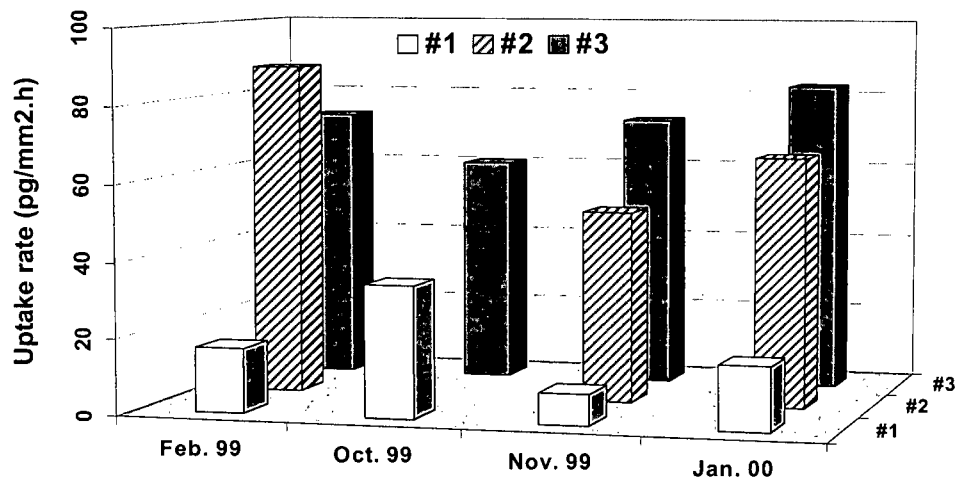
(a) Resin uptake
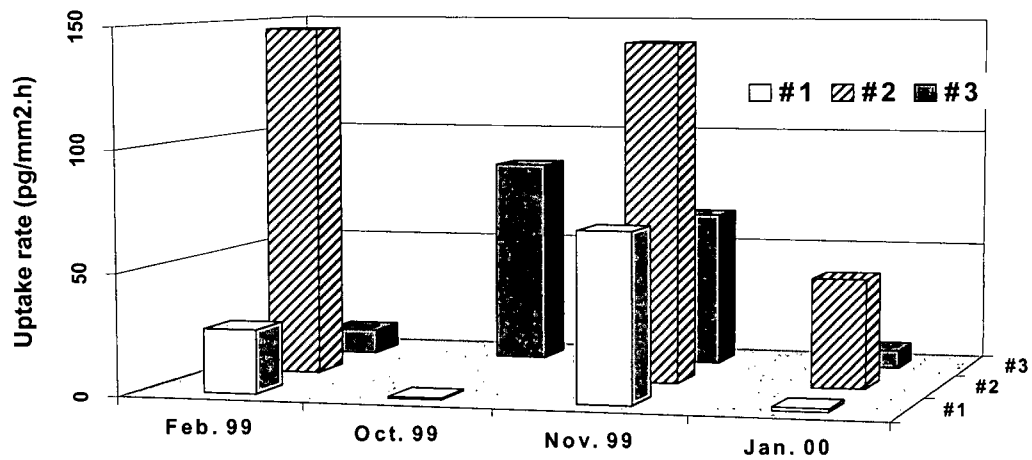
(b) Membrane uptake

Figure 4- 26 Manganese taken up in stormwater by (a) resin and (b) membrane

4.2.2.4 Iron uptake

Iron taken up by resin was at low levels compared to their precipitation onto the membrane, as shown in Fig 4-27(a) and (b).
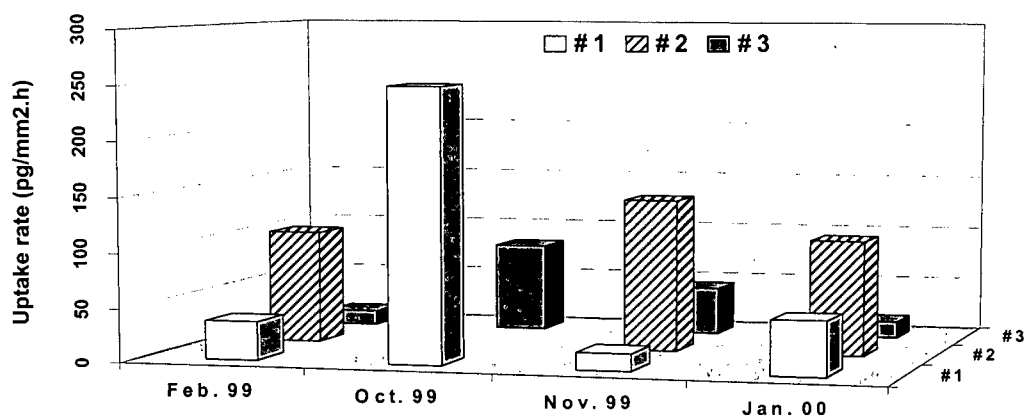
(a) Resin uptake
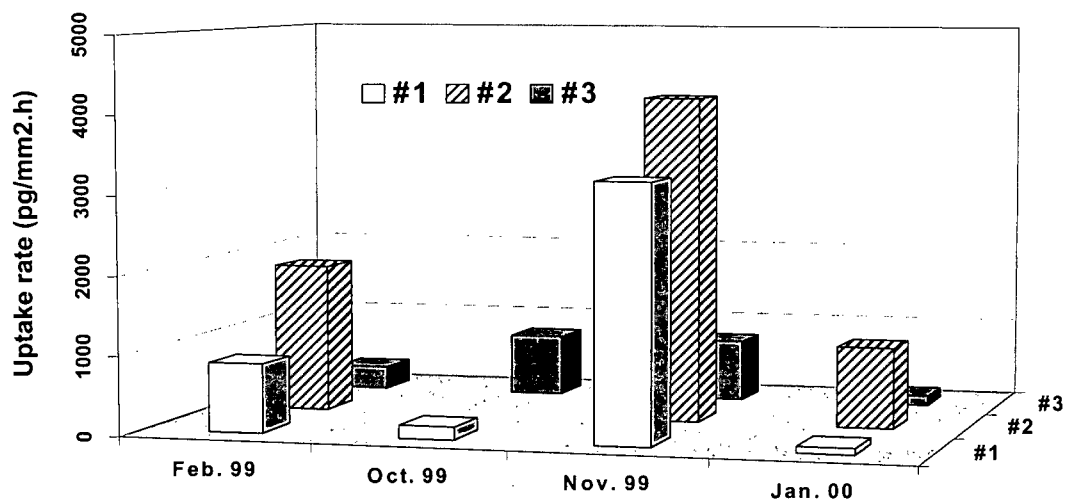
(b) Membrane uptake

Figure 4- 27 Iron taken up in stormwater by (a) resin and (b) membrane

In the sediment trap, the uptake rate by resin was quiet variable, ranging from 16-250 $pg/mm^2 \cdot h$ in stormflow and snowmelt. The relatively constant high uptake was measured in Still Creek at Site #2, where the rates were from 105-141 $pg/mm^2.h$. Lower uptake was recorded at Site #3 at 14-83 $pg/mm^2 \cdot h$. The membrane uptake rate also varied significantly from one experiment to another, with the highest rate of 3188 $pg/mm^2.h$ in November and lower than 100 $pg/mm^2.h$ in January. It can be seen clearly that the higher membrane uptake

91

rate corresponded to lower resin uptake rate at this site. High rates were also occurred at Site #2 in all experiments, ranging from 1020-4112 pg/mm^2.h. Membrane uptake of iron at Site #3 was at the rate of 125-785 pg/mm^2.h, where the relatively higher rates were found in October and November.

4.2.2.5 Trace metal uptake over one rain event

One storm metal uptake experiment was conducted in November 1999. During this experiment, the receivers were installed before the rainfall at the three sites, and collected after the rainfall. The rain lasted for about four hours in this experiment (See Fig. 4-32 for the detailed rain and flow). The total exposure time of the receiver was about 24 hours. The resin uptake results of the four metals are shown in Figure 4-28, and the membrane uptake results are shown in Figure 4-29.

It is evident from Fig.4-28 that the bioavailable copper and zinc in the stormwater quickly penetrated the dialysis membrane and complexed with resin inside the bag. The uptake rates were as high as 6.8-11.4 pg/mm^2.h for copper, and 13-25 pg/mm^2.h for zinc at all three sites. The high uptake rate indicates that the receiver is highly sensitive to the available metal species in the stormwater. Much higher uptake of manganese by resin was found at the two stream sites. It was at 194 pg/mm^2.h at Site #2 and 174 pg/mm^2.h at Site #3. This finding may imply that with the effects of the storm runoff, manganese is largely in the bioavilable form (ionic or weakly complexed form) in transport through Brunette River waterways.

For the membrane uptake (Figure 4-29), only iron demonstrated a high uptake rate in the stormwater. The rate of iron taken up by membrane was 128 pg/mm^2.h at Site #1, 646 pg/mm^2.h at Site #2, and 160 pg/mm^2.h at Site #3. Copper taken up by membrane was not detected at all three sites over this four-hour rainfall exposure period. Zinc taken up by the membrane was measured as 7-12 pg/mm^2.h. The rate of membrane uptake for manganese was 2 pg/mm^2.h at Site #1, 12 pg/mm^2.h at Site #2, and 28 pg/mm^2.h at Site #3.
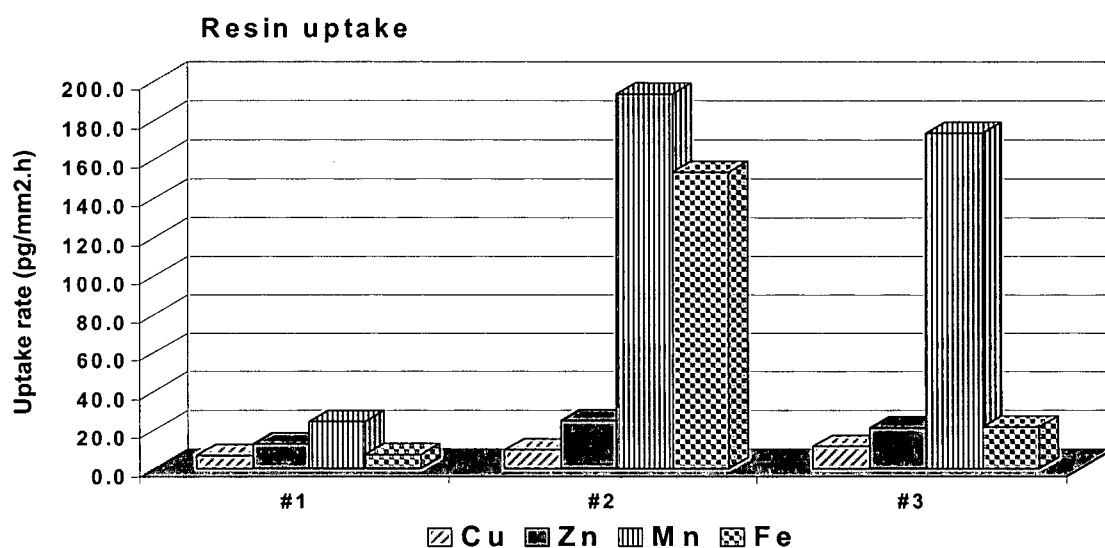
Resin uptake

Figure 4- 28 Metal uptake by resin - over one storm
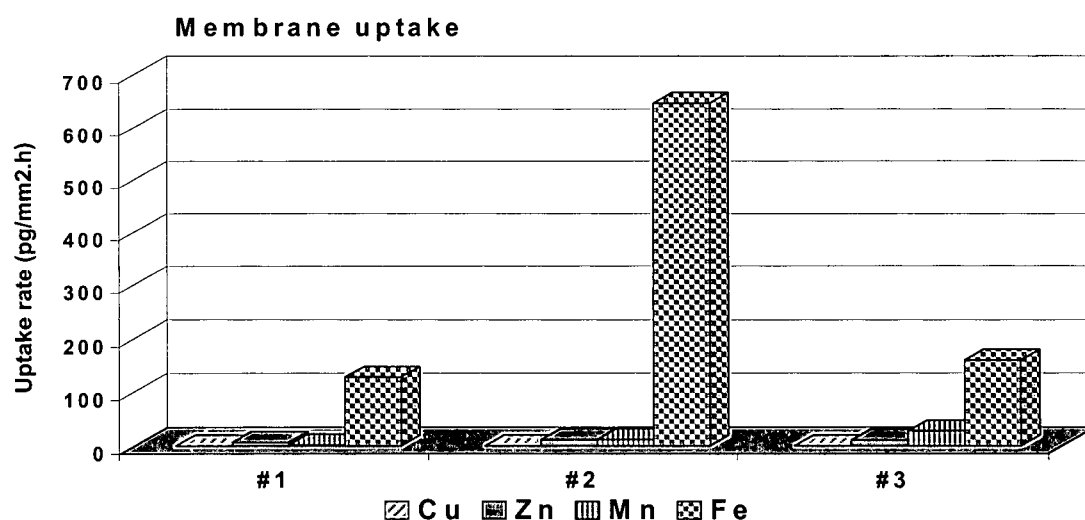
Membrane uptake

Figure 4- 29 Metal uptake by membrane - over one storm

4.2.3 Resin uptake of trace metals in the watershed

Figure 4-30 presents the receiver resin uptake rates of copper(a), zinc(b), manganese(c) and iron(d) from the experiments at three sites at difference flow conditions over the study periods. Their distributions and variation will be discussed.
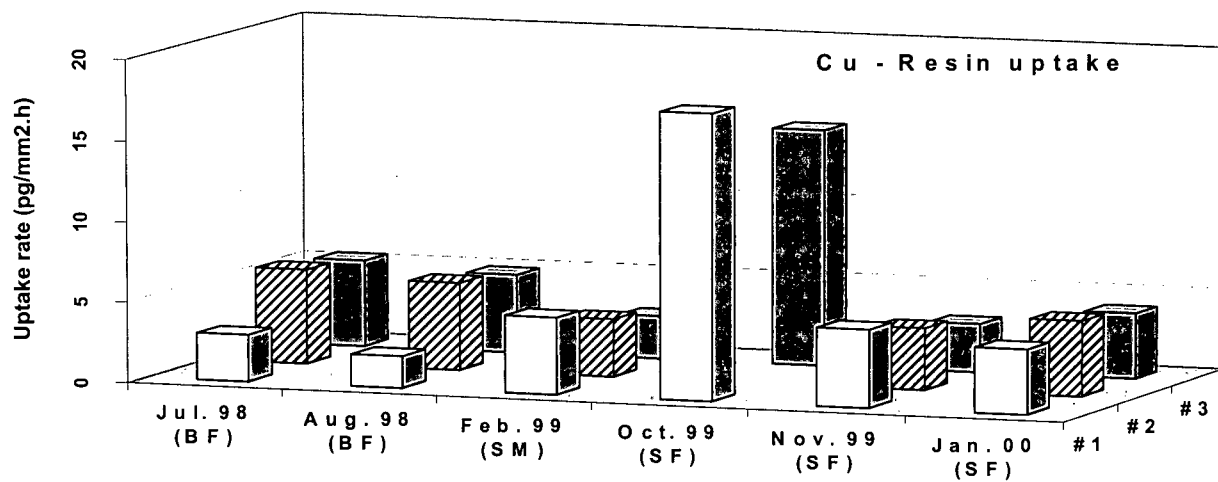
(a)
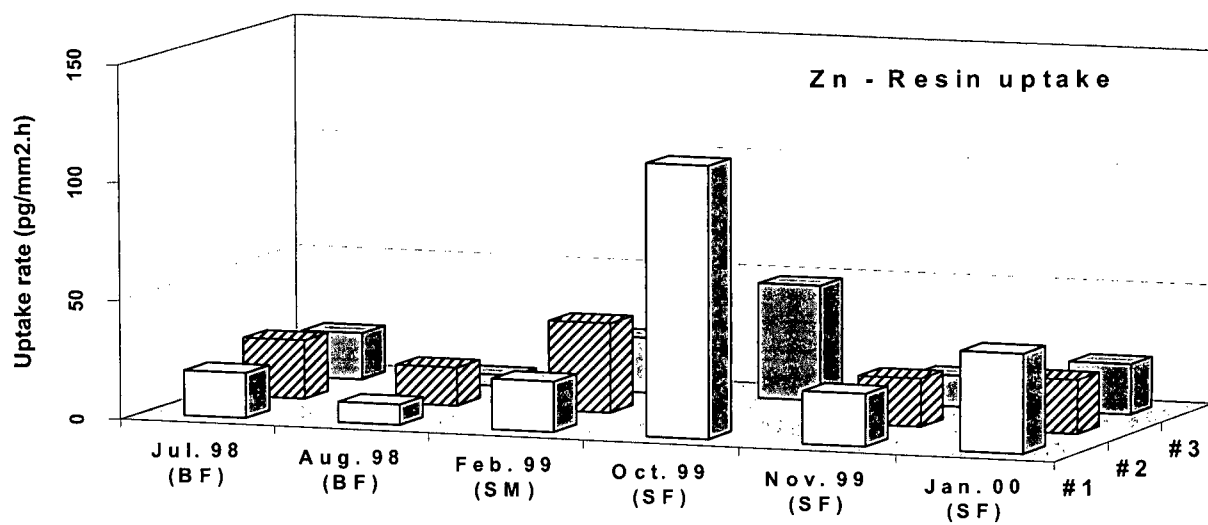
(b)
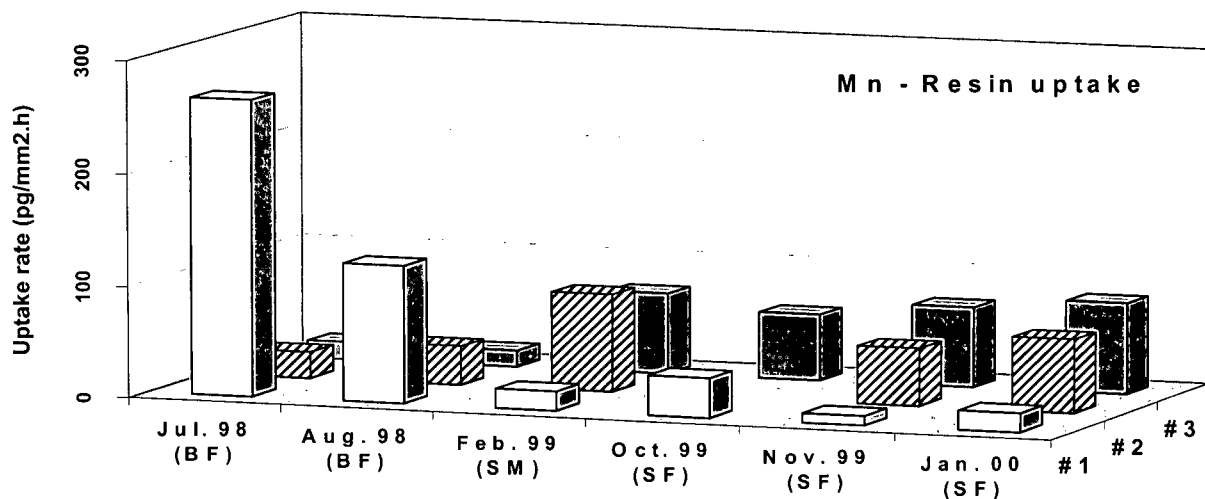
(c)
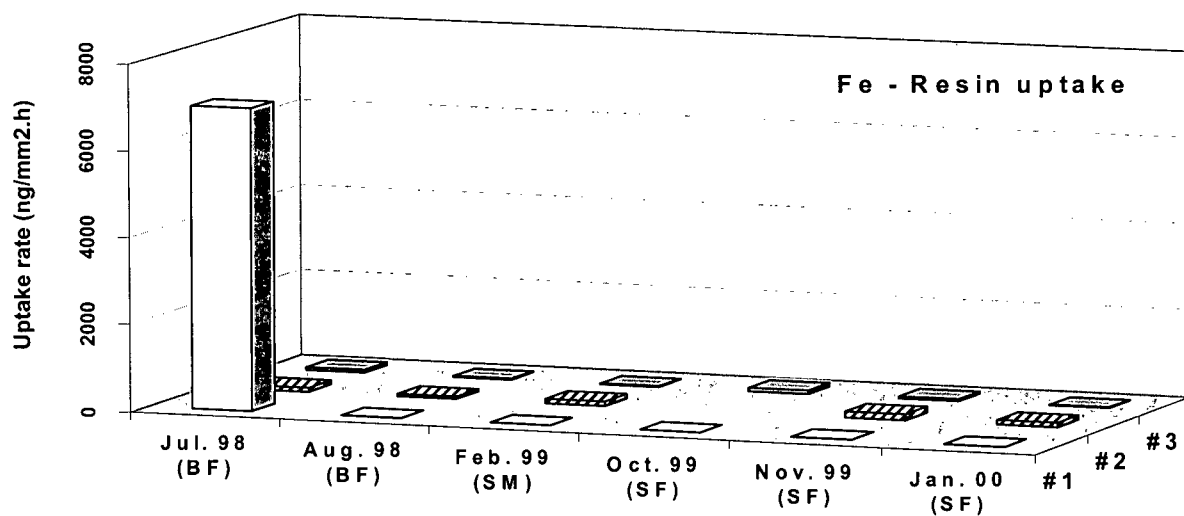
(d)

Figure 4- 30 Spatial and seasonal variation of Cu, Zn, Mn and Fe uptake by resin
(BF – baseflow, SM – snowmelt, and SF – stormflow)

4.2.3.1 Seasonal variation of resin uptake

A similar pattern of resin uptake was observed for both Cu and Zn (Fig. 4-30 (a) and (b)).
During summer baseflow (July and August 1998), the uptake of copper and zinc by receiver
was relatively consistent. However, the uptake rates of these two metals varied considerably
from storm to storm in the wet season. A much higher uptake rates for both Cu and Zn were

observed in stormwater in October – the beginning of the wet season of the year. The significant variation through different storms was also observed in Morrison's study (1985). The reason for this uptake variation is expected to be due to the variation of bioavailable trace metal levels in the stormwater and the flow regime in the urban waterway, possibly the dilution factor. There is no significant difference of Cu and Zn uptakes between stormflow in January and snowmelt in February at all three sampling sites, which differs from Morrison's conclusion that higher uptake was detected during a snowmelt period. This may be due to the climate difference of the two watersheds. In the Brunette watershed, rainfall events usually follow soon after a snow, which makes the snow melt very fast. The accumulation of metal pollutants in the snow does not usually have time to occur.

The manganese uptake was totally different from those of Cu and Zn as shown in Fig. 4-30(c). The maximum uptake rate was measured in baseflow in the sediment trap, which was much higher than the others. This is possibly due to the release of manganese from the reducing environment of the bottom sediment caused by the organic matter degradation under quiescent conditions in the trap, since the manganese is a redox sensitive species (Stecko and Bendell-Young 1999). In stormflow conditions, higher uptake rates occurred mostly in streams.

It can be seen in Fig. 4-30(d) that, except for the sediment trap under baseflow, low uptake rates of iron were found in all receiver experiments. This phenomenon clearly demonstrated that iron in the urban water system exists mostly in the non-bioavailable fractions. The extremely high uptake of iron in the sediment trap during baseflow (July 1998) seems due to the release of ionic iron from the iron binding fraction of the sediment under stronger reducing conditions in the trap. There was a very long dry period before and during the experiment, and which leads to the dramatic decrease of dissolved oxygen (DO) (60-80% decrease of the DO saturation level caused by the bacteria activities) in the sediment (Morrison 1985).

4.2.3.2 Spatial distribution of resin uptake

The resin uptake rates of Cu and Zn in baseflow were relatively lower in the sediment trap (Site #1) than in streams (Sites #2 and #3). However, according to the discussions in Section 4.1.3.2 of this chapter, the concentrations of RE-Cu and RE-Zn were found mostly lower in streams than in the trap. One possible explanation of the high metal uptake versus low bioavailable metal concentration in baseflow is the difference of trace metal pools in both sediment trap and streams environment. While the receiver was exposed to a low but consistent level of bioavailable trace metal in streams, limited amount of RE-Cu and RE-Zn were formed in the trap during the dry period. Another possible explanation is the concentration gradient layer that encloses the resin receiver. The uptake rate may be determined by the thickness of this layer, which is inversely proportional to the flow rate. Since there is no flow in the sediment trap during the dry season, the thicker gradient layer slows down the uptake rate at this site. However, this possible impact needs to be investigated further.

During the storm event, on the other hand, the higher uptake amounts of Cu and Zn were generally found in the street runoff than in the streams. The resin uptake rates of Cu and Zn at both street and stream sites were well correlated to the bioavailable copper and zinc measured in stormwater, which will be discussed further in the following section.

Quite high uptake rates of manganese were found in both upstream (Site #2) and downstream site (Site #3) of the water system in the wet season. This is because a large amount of manganese, as the combustion products of MMT, was discharged through urban impervious surfaces and contributed considerable soluble manganese which is potentially available to the organisms in the urban water stream (Mattu and Hall 1999). The reason that less uptake of Mn was measured in the sediment trap during storms is unknown, since the RE-Mn level at this site was found similar to those in streams. No significant difference of iron uptake was observed in the watershed. The possible explanation is that iron exists mostly in the non-bioavailable forms.

4.2.4 Environmental factors affecting the metal uptake

Several factors that may affect the Cu and Zn uptake were examined. They are found functioning in different flow conditions.

4.2.4.1 In stormflow condition

In storm condition, two major factors have been regarded as the contributors for increasing the bioavailable metal uptake rate, namely the rainfall intensity and the antecedent dry period (Morrison 1987, Hall and Anderson 1988). Previous work found that the dry period before the rainfall plays a very important role - the longer dry period causes more trace metal accumulation on the urban impervious surfaces, and leads to more trace metals flushed into the water system during the rain (Yuan et al. 1999). The metal uptake in four rain periods is summarized both for Cu and Zn, and presented in Table 4-5. The analysis between Table 4-1 and Table 4-5 indicates that a 12-day dry period before the rain causes the Cu uptake rate at Site #3 approximately four times as high as that of a 5-day dry period before the rain, and five times as high as that of 0-day dry period. Higher uptake of Zn after a longer dry period was observed in the same experiment, but it was not as significant as that for Cu.

Table 4- 5 Summary of the resin uptake in four rain periods

Resin experimental (7 days exposure)	Resin uptake rate (pg/mm^2.h)			
	Cu		Zn	
	Site #2	Site #3	Site #2	Site #3
Feb.1999	3.6	2.7	38	23
Oct. 1999	--	15	--	49
Nov. 999	4.8	3.8	21	13
Jan. 2000	3.6	3.0	23	21

The other factor affecting the metal uptake rate, the rainfall intensity, is also listed in Table 4-1. However, this factor is not as significant as that of antecedent dry days before the rainfall in affecting the metal uptake.

4.2.4.2 In baseflow condition

High uptake of trace metals in baseflow conditions was expected to be due to the low level of dissolved oxygen (DO) in the water system. It was found that the DO level in Still Creek at Douglas station is consistently less than 5 mg/L during the summer (Macdonald et al. 1997), because Still Creek at this section is deep and slow moving, leading to the minimum re-aeration. The typically low DO level has also been found in the upper reach of the Brunette River, (Cariboo Road Station) with the measured value of 2.6 mg/L in the summer time. The ecological effects in Burnaby Lake might also affect the DO level in the lower reach of Brunette, since decomposition of algae and macrophytes could result in decreased DO (Macdonald et al. 1997). Low level of DO may also lead to the release of sediment bound metals (ER-Mn bound or RE-Fe bound) into the water column as the dissolved phase that can be assimilated by the Chelex resin.

The uptake of metal in the sediment trap during the dry season might be also affected by the same factor, where the reducing conditions in the trap cause the release of particulate Mn and Fe to the dissolved phase and further liberate Cu and Zn bound to them. The release of Mn and Fe was indicated by the higher uptake of Mn and Fe by the receiver resin, as described above.

Flow rate might be another factor that influences the metal uptake rate, as stated in 4.2.3.2 in this chapter. However, this needs to be studied in future research.

4.3 Suspended sediment and trace metal transportation

4.3.1 Suspended sediment

Suspended sediments were measured for total suspended sediment (TSS) over a rain event (Nov.19, 1999), and the results are given in Appendix C. The changes of the TSS concentration over a rain event at three sampling sites was shown in Figure 4-31. The

corresponding rainfall intensity in the region and the flow rates at the two stream sites during the rain event are shown in Fig. 4-32.
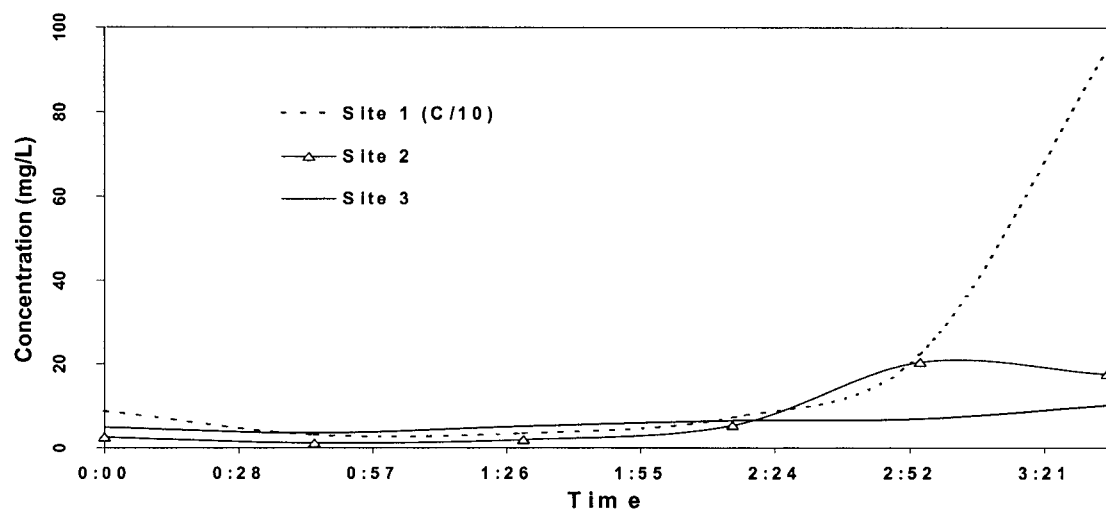
Figure 4- 31 Variation of *TSS* concentration over one storm at three sites
(Nov.19, 1999, sampling time refer to Appendix C)
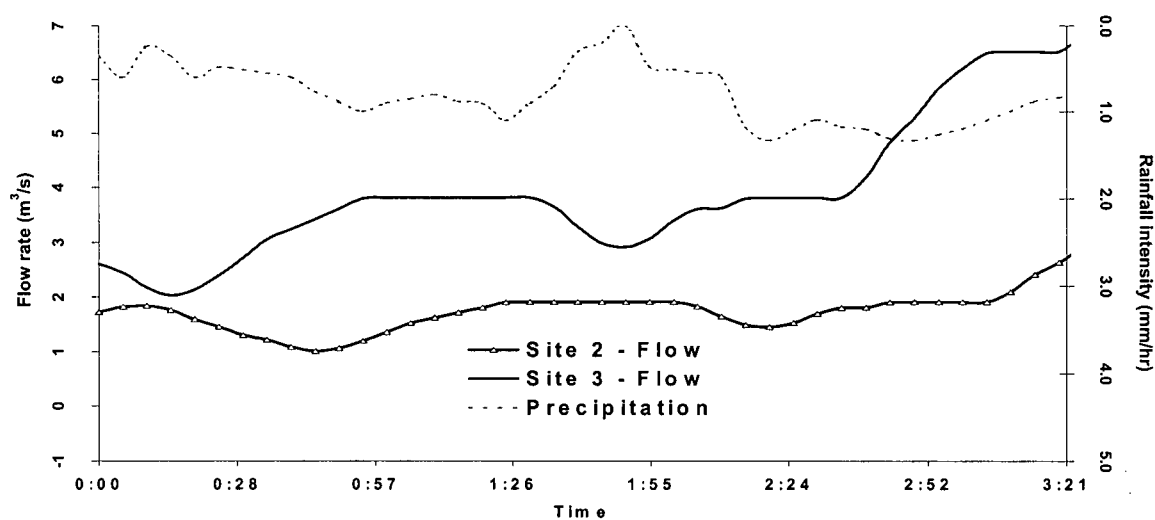
Figure 4- 32 Corresponding rainfall intensity and stream discharge
at sites #2 and #3 (Nov.19, 1999)

The significant increase of TSS concentration in the surface runoff with the rainfall development is indicated at Site #1 (Fig. 4-31). This phenomenon agrees with the previous studies on the SS discharge pattern under stormflow that, the TSS increases with the storm

development (Jarvis 1992, Solo and Perkins 1997, Hall, unpublished data). The slight increase of TSS concentration at Site #2 and Site #3 are also shown in Fig. 4-31. A smaller change at Site #2 in the stream might be due to dilution and the effect of flow regime such as low flow (Fig. 4-32) in Still Creek. However, a smaller change in TSS during the rainfall event at Site #3 was controlled by sedimentation in Burnaby Lake, even though a relatively high flow was observed in this site (2-6 m^3/s). The different TSS concentration trends among these three sites indicate that the direct response of TSS to rainfall intensity was significant in the street runoff from urban impervious surface (Site #1).

4.3.2 Trace metal transport with SS

Trace metal contaminants discharged from urban impervious surface through storm runoff have been regarded as the typical non-point source pollution to the receiving water. Sampling of street runoff (Site #1) is to sample closer to the potential pollutant sources as urban activity generates many of the pollutants in the stormwater (MacDonald et al. 1997). Many previous studies found that trace metals transported through urban impervious surface is largely associated with total suspended sediment (TSS) (Hall and Anderson 1988, Jarvis 1992, Solo-Gabriele and Perkins 1997). In this study, an intensive sampling activity was conducted for street runoff. The TSS and metal Cu, Zn, Mn and Fe were measured through six sequential samples over a rainfall period and the results are presented in Fig. 4-33.

Very good correlation between the total metal (TM) and the total suspended sediment (TSS) has been found for each of the four metals, with the correlation coefficient of R_{Cu}=0.98 for Cu, R_{Zn}= 0.92 for Zn, R_{Mn}= 0.94 for Mn, and R_{Fe}= 0.92 for Fe. This conclusion further demonstrates that trace metals transported through urban impervious surfaces is largely associated with total suspended sediment.

TSS - Cu

TSS - Zn
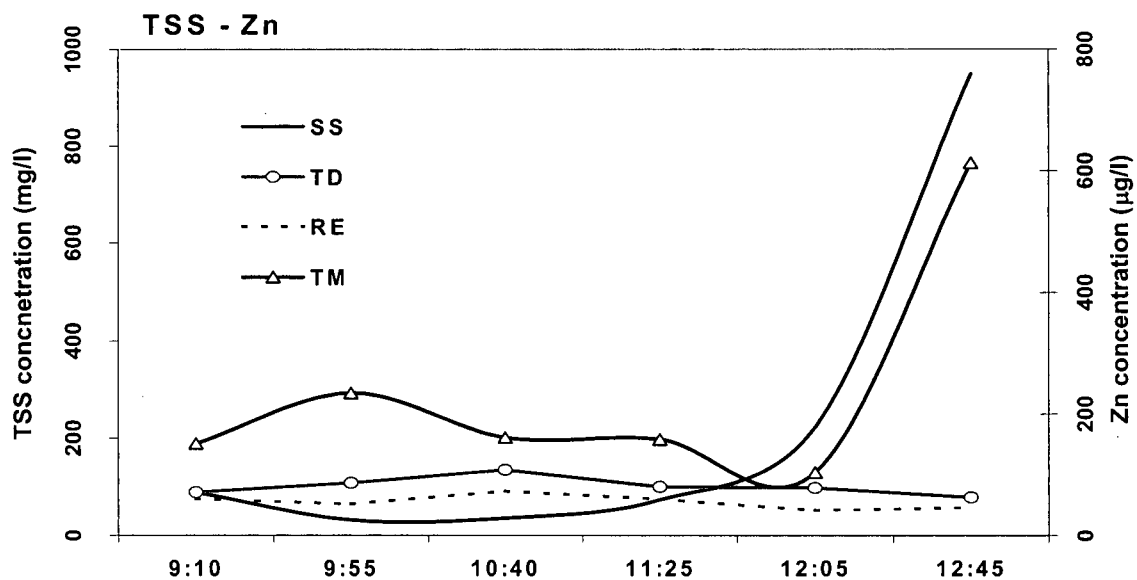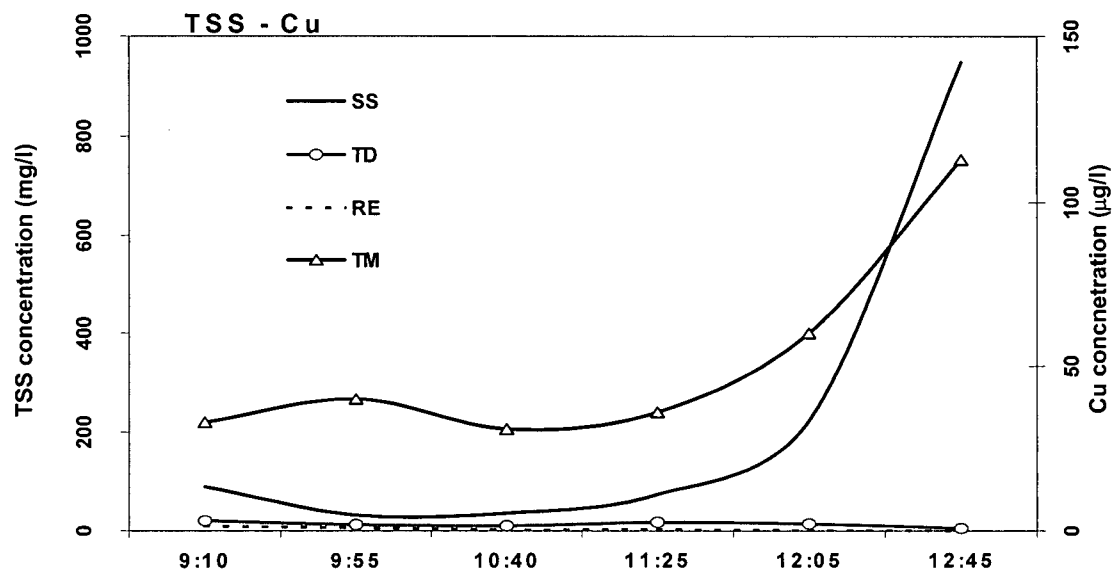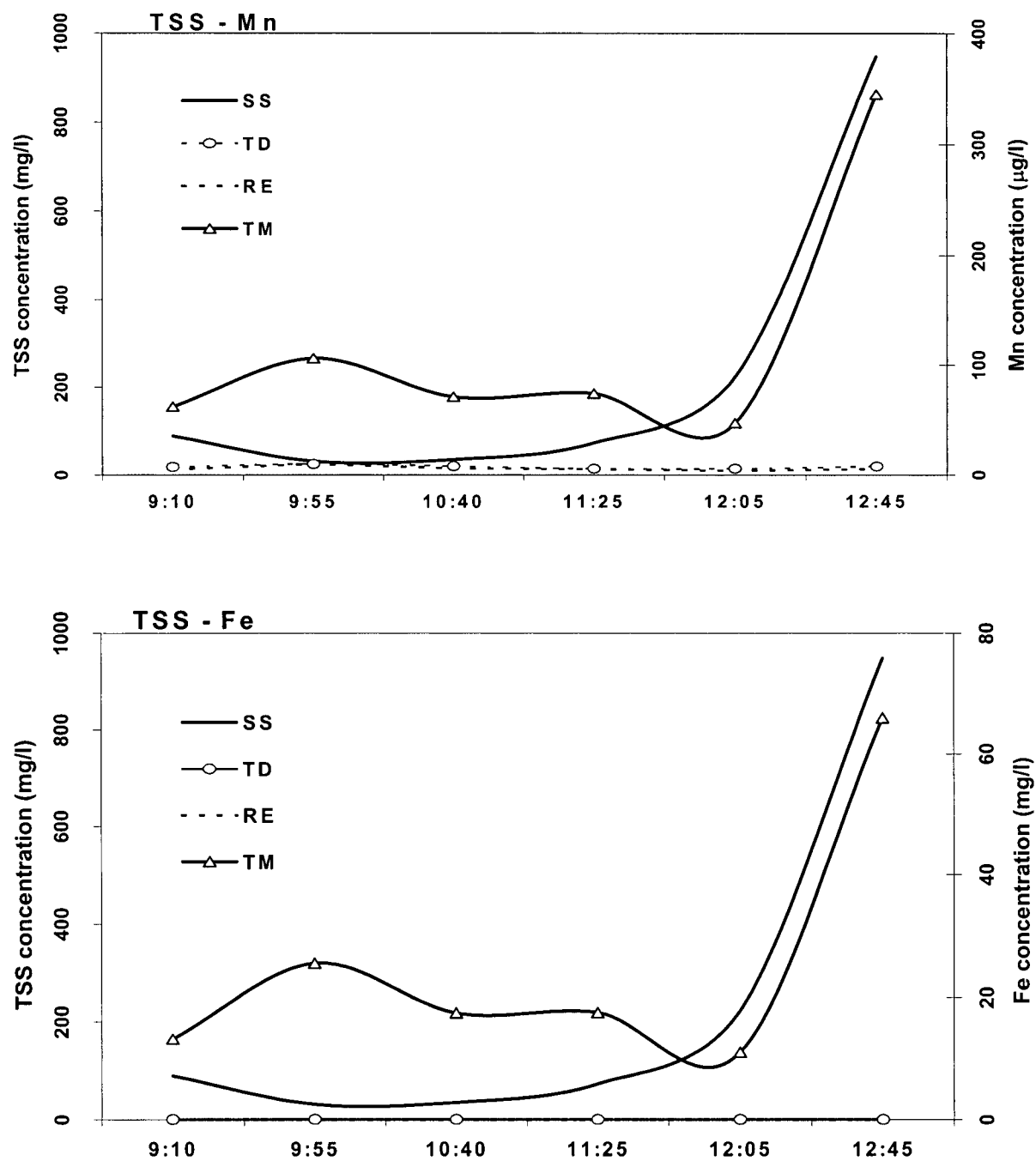
Figure 4- 33 Concentration change of Cu, Zn, Mn and Fe with TSS over a storm event
(Nov. 19, 1999 at street runoff (Site #1))

Figure 4-33 also indicates that TSS has no relationship with either dissolved metals (TD), or
their bioavailable forms (RE) in storm runoff. This pattern was also observed by many other

studies, and the conclusion was drawn that metals in dissolved form are washed off during the early part of a storm event (Jarvis 1992, Solo-Gabriele and Perkins 1997, McDonalds et al. 1997). It can then be concluded that the bioavailable trace metal species that can be directly taken up by the aquatic organisms are mostly washed off at the early stage of the storm event. The storm intensity will also be important regarding the mobilization of street dirt and movement of stream sediments and their associated particulate metals by the higher flow.

4.4 Other relevant data

Listed in the following were the relevant data that were also measured or collected in this study. They correspond to each of the sampling under baseflow and stormflow conditions.

4.4.1 pH

The pH values were only measured in the water samples from the intensive sampling scheme. The results showed that stormwater pH was relatively constant with the value of 6.4 - 6.7 at all three sampling sites, and the data were given in Appendix C in the intensive sampling data set.

4.4.2 Flow data and precipitation data

Precipitation data during the study period, from January 1998 to January 2000, and the flow data at two sampling sites in the watershed streams were collected from GVRD, and are shown in Fig. 4-34.

It is obvious that the rainfall occurs mainly in the winter - from November to February. The rainfall in this wet season is several times more than that in the dry season - from June to October, as are the flow rates in the stream (shown in Fig. 4-34).
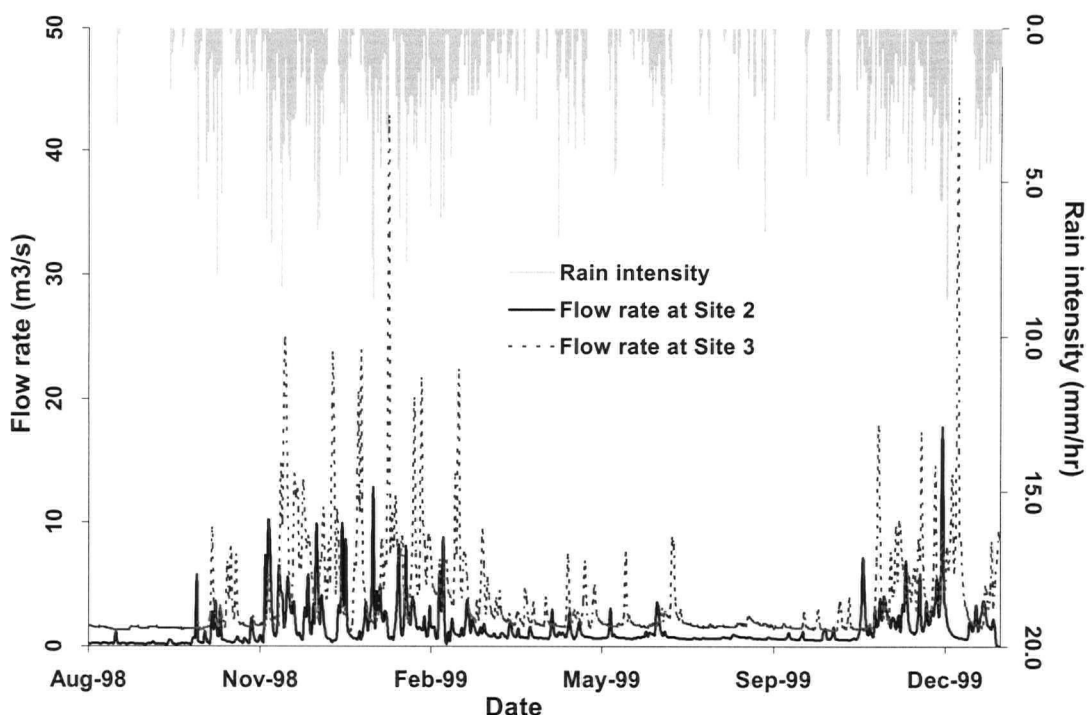
Figure 4- 34 Rainfall and flow data over the study periods in the Brunette River watershed

4.5 Assessment of trace metal toxicity in the watershed

4.5.1 Assessment with relevant water quality criteria

The potential toxicity of trace metals Cu and Zn in the Brunette River water system was assessed according to the existing water quality objectives (Swain 1989, EPA 1983, and EEC 1983). Table 4-6 compares the average total Cu and total Zn in street runoff and streams with the Water Quality Objectives (WQO) for the Brunette Watershed set up by the Ministry of Environment (Swain 1989). This is a long term objective for protection of aquatic life and wildlife.

It can be seen that both total Cu and total Zn are over 10 times higher than those allowed by the Objective in the street runoff. The trace metal concentrations in streams, though are significantly lower than those in street runoff, but are still much higher than those recommended by the Objective. Cu is 5.8 times higher and Zn is 4.4 times higher in Still

Creek (Site #2), and Cu is 3.6 times higher and Zn is 1.3 times higher in the Brunette River (Site #3) than the WQOs.

Table 4- 6 Comparison of total Cu and Zn with Water Quality Objectives (BC Canada)

	Sampling Sites			WQO Standard (BC)
Cu (μg/L)	Site 1	Site 2	Site 3	Cu (μg/L) Hardness >30 mg/L as CaCO$_3$
	76	29	18	5
	Site 1	Site 2	Site 3	Zn (μg/L)
Zn (μg/L)	370	132	39	30

When one compares the concentrations of Cu and Zn at the three sampling sites with the US EPA criteria based on the total metal concentration (EPA 1983), it can be seen that total Cu of this study exceeds the 24-hour average at all three sites, and the maximum for freshwater toxicity at both Sites #1 and #2. The total Cu in street runoff significantly exceeds the threshold of the intermittent discharge criteria, and may create significant mortality. The concentration of total Zn, on the other hand, exceeds both the 24-hour and maximum values for freshwater toxicity only in surface runoff (Site #1). Zn in the Still Creek (Site #2) exceeds the 24-hour criteria for freshwater toxicity, but is lower than the maximum limit. Total Zn at Site #3 is below the criteria listed in Table 4-7.

Table 4- 7 USEPA Water Target Concentrations for total Cu and total Zn

Trace metal	Total hardness (mg/l)	Freshwater toxic criteria (μg/L)		Intermittent discharge criteria (μg/L)	
		24 hour	Maximum	Threshold	Significant mortality
Copper	50	5.6	12	20	50-90
	100	5.6	22	35	90-150

	50	47	180	380	870-3200
Zinc	100	47	321	680	1500-4500

By comparison to EEC's Environmental Quality Objective (EQO), a criterion based on the total dissolved metals (TD), copper does show toxic effects in the Brunette River water system since the dissolved Cu concentrations are much higher than the EQO criteria at all three sites (Table 4-8). For zinc, while the dissolved Zn exceeds the EQO criteria at Site #1, it may also have possible toxic effect at Site #2 depending on water hardness. Again at Site #3, the concentration of dissolved Zn is far below toxic level.

Table 4- 8 Comparison of total dissolved Cu and Zn with EEC water quality criteria

Cu (µg/L)			
Site #1	Site #2	Site #3	EQO standard (EEC)
17-32	24-25	15-20	1-6 Hardness = 0-100 mg/L as $CaCO_3$
Zn (µg/L)			
Site #1	Site #2	Site #3	EQO standard (EEC)
179-266	77-92	30-41	70-170 Hardness = 0-100 mg/L as $CaCO_3$

4.5.2 Assessment with bioassy uptake

There is still no criterion for the trace metal uptake rate by organisms. The trace metal uptake rates measured in the Brunette River watershed are compared with previous work in the Bergsjon catchment (Morrison 1987) - a residential area (15.6 ha) located 10 km northeast of central Goteborg, Sweden. The uptake experiment in that work was conducted in Backebolsmotel of Goteborg – a drainage area of a 600 m section of the heavily used motorway.

4.5.2.1 Uptake in street runoff

Table 4-9 shows that higher Cu and Zn uptake rates both by resin and dialysis membrane were found in Brunette River watershed compared to that of the Backebolsmotel. Both the resin and membrane uptake rates varied considerably in the experiments in both catchments. It can be concluded from the comparison that the bioavailable Cu and Zn from street runoff are significantly higher in the Brunette River watershed than in Backebolmotel.

Table 4- 9 Trace metal uptake rates in street runoff (pg/mm^2.h)

Street Runoff	Brunette River Watershed (Site #1)		Backebolsmotel	
	Resin	Membrane	Resin	Membrane
Cu	7.9 (0.8-25.0)	10.3 (0.0-39.8)	1.6 (0.6-4.4)	2.6 (0.7-7.5)
Zn	50.2 (16.9-164.0)	47.9 (1.3-194.2)	9.5 (2.5-21.3)	2.9 (0.8-8.3)

4.5.2.2 Uptake in stream

The trace metal uptake in stormwater, on the other hand, is at about the same level in the two studies, as indicated in Table 4-10. Except for a much lower membrane uptake rate of Zn, the Bergsjon Catchment shows quite similar Cu and Zn uptake rates by resin and membrane in the stormwater to those detected in Brunette River Watershed.

Table 4- 10 Trace metal uptake rate in stream (pg/mm^2.h)

Stormwater	Brunette River watershed		Bergsjon catchment	
	Resin	Membrane	Resin	Membrane
Cu	5.3 (0.0-16.0)	10.0 (0.0-37.4)	13.4 (0.6-41.3)	22.4 (4.4-78.7)
Zn	26.8 (10.6-64.0)	31.0 (0.0-124.5)	25.6 (4.0-67.1)	2.4 (0.9-4.5)

4.5.2.3 Uptake in baseflow

Table 4-11 indicates that both studies detected relatively low Cu and Zn uptake rates in baseflow. The uptake rates were quite similar in these two urban watersheds under baseflow conditions. The variable uptake rates in baseflow conditions were explained as the contamination of in-pipe sediment remaining after storm events, which resulted in metals being leached by ground water entering the pipe system (Morrison 1987).

Table 4- 11 Trace metal uptake rate under baseflow (pg/mm^2.h)

Stormwater	Brunette River Watershed		Bergsjon Catchment	
	Resin	Membrane	Resin	Membrane
Cu	5.6 (4.9-6.4)	--	4.3 (2.8-5.9)	--
Zn	17.3 (5-27)	--	11.2 (4.0-14.4)	--

A maximum biological uptake flux was used to assess Zn, i.e. 2.35 pg/mm^2.h - a maximum rate of Zn taken up by the seawater alga *Phaeodactylum cornutum* (Turner 1983). It can be seen that Zn uptake rates in the Brunette River watershed exceed this maximum biological uptake rate even in the dry season. The exceedance is much more serious in the wet season, in which the highest Zn uptake was found to be as high as 177.9 pg/mm^2.h in street runoff and 62.3 pg/mm^2.h in streams. From this comparison it might be concluded that Zn is toxic in the Brunette River watershed, if the Chelex resin can be considered analogous to an aquatic organism, such as algae.

4.6 Discussion on the two approaches

4.6.1 Relationship between the two approaches

Trace metal partitioning and trace metal uptake experiments were the two different approaches to measure metal bioavailability. It is reasonable to believe that these two approaches are correlated. The correlation between the metal uptake and the trace metal partitioning was analyzed in this study. The receiver experiments and the water samplings at three sites in two storm periods, seven days each in Jan.3 and Jan.10 2000, were chosen for this analysis. The results demonstrated a fairly good correlation between the metal uptake and the resin removable fraction (RE fraction) of Cu and Zn.

4.6.1.1 Cu

The correlation between Cu uptake rate and Cu concentration in total dissolve (TD-Cu) and resin removal (RE-Cu) fractions in the water is shown in Fig. 4-35. It can be seen that the uptake rate of copper seems well correlated with resin removable Cu concentration in the water. The correlation coefficient of Cu uptake to the resin removable fraction of Cu (RE-Cu) in stormwater was $R^2 = 0.77$. TD-Cu and copper uptake showed less linear correlation compared to the RE-Cu, with the correlation coefficient of $R^2 = 0.59$. No clear relationship between TM-Cu and Cu uptake was found. It can then be concluded that although the resin removal fraction of Cu accounts for only a small fraction of dissolved Cu, as well as in total Cu, it is the bioavailable portion that determines Cu uptake by the receivers.
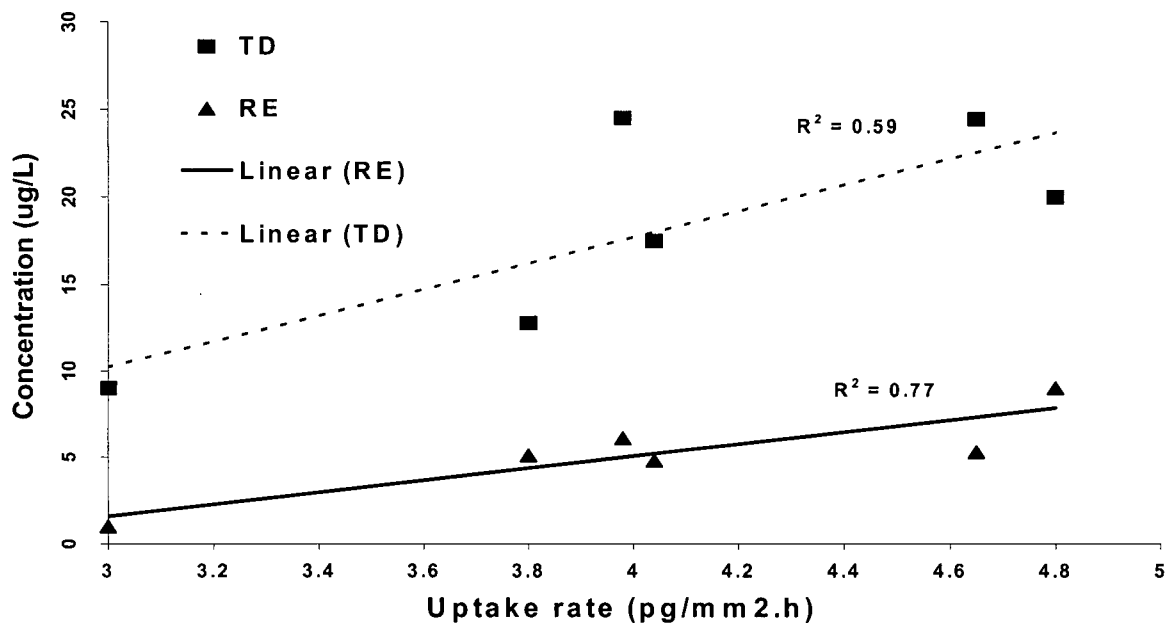
Figure 4- 35 Correlation of Cu uptake rate to TD-Cu and RE-Cu

4.6.1.2 Zn

Positive correlation between receiver uptake rate for Zn and concentrations of three Zn fractions, TM-Zn, TD-Zn, and RE-Zn, is shown in Fig. 4-36, i.e. the higher concentration of the metal in the stormwater, the higher the metal taken up by receiving resin in the dialysis bag. The curve fittings indicate that the best correlation of Zn uptake is to the bioavailable zinc (RE-Zn), with the coefficient of $R^2 = 0.97$. A significant correlation of resin uptake rate with TD-Zn ($R^2 = 0.94$) and TM-Zn ($R^2 = 0.79$) was also observed. However, it should be noted that this is based on a very limited data set and additional texts are needed to confirm these results.
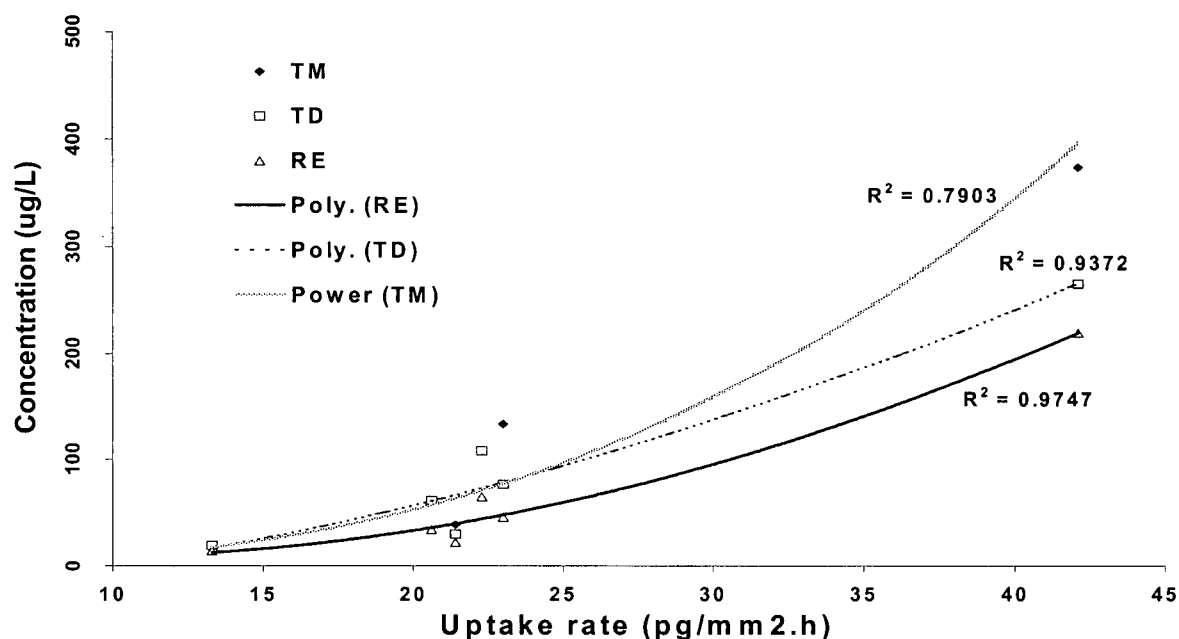
Figure 4- 36 Correlation of Zn uptake rate to TM-Zn, TD-Zn, and RE-Zn

4.6.2 Method suitability and experimental design

4.6.2.1 Partitioning Method

In this study, the grab sample was used to measure bioavailable metal species in the urban runoff. Even though the water was taken in the early rainfall period, the grab samples only represented a snap shot of that rainfall event but might not represent the distribution of bioavailable metal species in the runoff over time. The intensive sampling over a whole rain event is necessary if a more meaningful mean value is desired, especially in the case of heavy storms with highly variable runoff.

Filtration to collect suspended sediment can cause another problem that needs to be addressed. The filter itself may bring contamination to the analysis, especially when several filters are used for one sample. Using a continuous centrifuge in the field may avoid this problem.

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4.6.2.2 Receiver experiment

The study of trace metal bioavailability by using "Dialysis with Resin Receiver" technique is thought to be a more direct and more meaningful method. However, the variability of resin and membrane uptake rates among the experiments was observed. This phenomenon reflects the intermittent and variable nature of bioavailable metal discharge in the stormwater (Morrison 1987).

It should be noted that trace metals assimilated by organisms are expressed as an uptake rate with the unit of $pg / mm^2.h$, which indicates that the uptake rate or flux of the bioavailable metal species through the dialysis membrane is closely correlated to the available metal species in the water, the dialysis membrane exposure area and the exposure time. The uptake rate therefore is a time-averaged value used to describe the available metal species that can penetrate a cell under a certain time period. It was found in this study that the exposure time is a very important factor that influences the uptake rate. This is because the exposure of the receiver in the stream will lead to the adsorption of particulate metal and other substance on the membrane surface (especially during storm period). This may clog the pathway of the metal species to the cell surface and lead to the non-linear uptake. The longer a receiver is exposed in the stream, the greater potential there is for adsorption to occur on the dialysis membrane. As such, the exposure time design for this experiment must be considered, which should be correlated to the rainfall and the flow pattern in the urban receiving water. A comparative experiment with the Chelex resins in dialysis tubes and live organisms held in flow through enclosures needs to be conducted to confirm the use of these resins as surrogate organisms for metal bioavailability studies.

Chapter 5

Summary

Trace metals, their bioavailability, their spatial distributions, and their seasonal changes in the water system, were studied with two techniques, namely metal speciation and dialysis with resin receiver. Both techniques were used to investigate the trace metal bioavailability in the Brunette River watershed from July 1998 to January 2000.

The concentrations of trace metals and their bioavailable forms both in dissolved (total water partitioning) and particulate (sediment geochemistry) phases in both street runoff and streams were measured. Control factors regulating the metal forms in the urban receiving water were analyzed. The potential assimilation of bioavailable trace metals by the aquatic organisms was simulated through dialysis with resin receiver technique. The uptake rate of resin inside the tubing can provide an indication of the bioavailable metal species in the urban receiving water and their potential accumulation and toxic effects on the aquatic organisms.

The spatial distribution of bioavailable trace metals in the Brunette water system was analyzed along a hydrological gradient from street runoff to streams above and below Burnaby Lake. The temporal change of the bioavailable metals was examined with the sampling and analysis under baseflow and stormflow conditions.

5.1 Potentially bioavailable trace metals in Brunette Watershed

The following conclusions can be made of the potential bioavailable trace metals in Brunette water system.

➢ Copper in three bioavailable components, RE-Cu in dissolved phase and EX-Cu and ER-Cu in particulate phase, accounted for 41% in street runoff, 21% in Still Creek and 9% in Brunette River of the total copper concentrations over the period of investigation. Although the dissolved Cu contributed a large portion in the stormwater samples, it was mostly in the non-bioavailable forms. This study found that copper in the dissolved phase was largely in the colloidal fraction - 70% in the street runoff and 85-92% in stream sites. The high colloid Cu in the dissolved phase may be attributable to organic matter from urban runoff that can contain humic-like substances and/or lignins and tannins - the leaf degradation products in the watershed (Macdonald et al. 1997). Thus, the immediate bioavailable Cu (RE-Cu) concentration was relatively low - 5-6 µg/l at street site, 3-5 µg/l in Still Creek and less than 2 µg/l in Brunette River. This represents approximately 10 % of the total Cu concentration (TM-Cu). Cu in the particulate bioavailable fraction (EX+ER) also showed a low proportion of the total Cu in both street runoff (30%) and in streams (<10%). The particulate fraction of Cu (EX+ER) clearly declined from street runoff to Still Creek and then to the Brunette River under all flow conditions. The seasonal change of these two bioavailable particulate fractions was observed only at the street runoff site, where a higher concentration of particulate bioavailable Cu (EX+ER) was found in surface runoff –fall and winter period (10-22 µg/l) than in baseflow (6 µg/l) drier summer period.

➢ Zinc was found largely in bioavailable forms in the Brunette watershed. Three bioavailable Zn fractions accounted for 50-70% of the total Zn concentration at all three sampling sites. The RE-Zn dissolved form was predominant, and accounted for 40-50% of the total Zn. The particulate Zn in the bioavailable fractions (EX+ER), on the other hand, contributed a relatively low percentage (11-24%). This might imply that Zn was mainly in the ionic and weakly complexed bioavailable fractions. A decrease of RE-Zn

concentration following the hydrological gradient was observed during storm runoff, in which the RE-Zn was 119 µg/l in the street runoff, decreased to 46 µg/l in Still Creek and to 17 µg/l in the Brunette River. The concentration of bioavailable Zn in baseflow was relatively low, and there was no significant difference between up and down stream reaches. However, a high level of RE-Zn (79 µg/l) was still measured in Still Creek during the dry season.

➢ In stream trace metal uptake by the receiver resin was highly variable during storm flow. The higher uptake rates were observed in the early part of the rainfall season (October). The analysis showed that major control factors seemed to be the rainfall intensity and the antecedent dry period that determined the accumulation of Cu and Zn and their potential bioavailability to the receiving water organisms. No significant difference of resin uptake rate was found under stormflow and snowmelt conditions, which is attributable to the rapid snow melt that is characteristic of our mild, marine coastal climate. Considerable *in situ* resin uptake of trace metals was also found under baseflow conditions. Low dissolved oxygen in the sediment trap and in the deeper water of Still Creek probably caused the release of ionic metals from sediments to the water column, which then increased the bioavailable trace metals species to the water under baseflow conditions. Membrane uptake rate showed an opposite pattern to the resin uptake rate, i.e., the higher uptake rate by membrane, the lower uptake rate by resin. The oxidation of iron and manganese on the dialysis tubing probably facilitated adsorption of other metals to the tubing.

➢ Trace metal concentration obviously decreased along the urban hydrological gradient. The highest concentrations of Cu and Zn were found in the street runoff – the major non-point source of the trace metals. The concentrations of trace metals were found to be highly correlated to the suspended sediment in surface runoff, indicating the particle-associated characteristic of trace metals from the wash-off. Cu and Zn in the upstream section of the watershed (Still Creek) showed significantly higher concentration than downstream (Brunette River). This difference seemed to be caused by the hydrologic

feature of the watershed, such as the low flow in Still Creek and sedimentation in Burnaby Lake in the middle of the watershed between the two streams.

➢ The effect of manganese on regulating Cu and Zn in the Brunette River water system was not clearly demonstrated in this study, as the concentration of Mn was not well correlated to those of the Mn-bound Cu and Zn. However, considerable particulate ER-Cu and ER-Zn and high concentration of manganese were observed in urban runoff. Since manganese is well recognized as the trace metal scavenger, it is reasonable to believe that the regulating effect of Mn on Cu and Zn does exist in the Brunette River water system, but a more detailed, focused study is needed to elucidate this relationship.

➢ Assessment of Cu and Zn measured in the watershed with the relevant water quality and toxicity criteria indicates that both these trace metals can have potential toxic effects on the organisms in the Brunette River watershed, especially in street runoff and upstream in Still Creek. Comparisons to WQ criteria also demonstrated that copper seemed to have a higher toxic effect to the aquatic life than zinc in this watershed since the criteria for copper toxicity is much lower.

5.2 Methods suitability

5.2.1 Water sampling

In this study, the grab sample was used to measure bioavailable metal species in the urban watershed. The grab samples were normally taken in the early stage of a rainfall event, which only represents a snap shot of that rain period but not really the bioavailable trace metal species in the whole rainfall period. Intensive sampling needs to be done over the whole rain event to measure the mean value and provide more meaningful data.

Filtration to collect suspended sediment in this study might cause problems. Since many filters were used to provide sufficient particulate material for the geochemical fraction, this might lead to contamination of samples for analysis. Continuous flow through centrifugation

should be used in the future work for suspended sediment collection. This would provide enough particulate metal sample for the analysis, and filter blank contamination during the filtration and digestion processes can be avoided.

5.2.2 Receiver technique

The study of trace metals using Dialysis with Resin Receiver technique is thought to be a more direct and more meaningful method of measuring bioavailability. However, the variability of resin and membrane uptake rates during the experiments was observed. This phenomenon reflects the intermittent and variable nature of bioavailable metal discharges in the stormwater (Morrison 1987). It should be noted that trace metals assimilated by organisms is expressed as uptake rate in the unit of $pg / mm^2.h$. The uptake rate or flux of the bioavailable metal species is closely correlated to the available metal species in the water, the dialysis membrane exposure area and the exposure time in water. The uptake rate therefore is an averaged value used to describe the available metal species that can penetrate cell under certain time period. It was found in this study that the exposure time is a very important factor that influences the uptake rate. A too long exposure time will lead to the adsorption of particulate metal and other substance on the membrane surface (especially during storm period), which may clog the pathway of the metal species into the cell surface and lead to the non-linear uptake. Thus the optimal design of the exposure time must be taken into account for the future receiver experiment, which should be correlated to the rainfall and the flow pattern in the urban receiving water.

5.3 Recommendation and further work

Field work (water sampling and receiver experiment) and sample analysis (water and suspended sediment speciation and receiver resin analysis) in this study provided meaningful data on the bioavailability of copper and zinc and their distribution in the Brunette River watershed. This information, in conjunction with the water quality data, precipitation data and flow data in the watershed, provided a more detailed understanding of trace metal contamination and their toxic effects in this typical urban watershed.

Future investigations of the bioavailable trace metal should focus on a more detailed analysis of suspended sediment both spatially and temporally, to provide a better understanding of the bioavailable trace metal in the particulate phases. More baseflow water analysis needs to be done to verify the bioavailable trace metals in watershed in non-rainfall period, since the limited data in this study only provides preliminary conclusions. The water quality measurements need to be conducted at the same time as the water sampling and receiver resin experiments, so that a more accurate explanation of the existing bioavailable trace metal species in the Brunette River watershed can be obtained. Comparative studies with *in situ* receiver resins and bioassay organisms need to be conducted to firm up the use of this technique as a bioavailability assessment tool.

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Appendix

Appendix A *Trace metal speciation in the water samples*

Table A- 1 Speciation for baseflow water

Sampling data	Metal (μg/L)	Sampling site	Total Metal (TM)	Total Dissolved (TD)		Total Particulate (TP)		
				RE	STR-B	EX	ER	RES
Aug. 17, 1998	Cu	#1		3.9		3.9	1.9	2.4
		#2		0.8		0.8	1.7	2.3
		#3		0.2		0.2	1.1	2.1
	Zn	#1		44.0		1.1	1.2	9.6
		#2		79.0		2.5	3.6	11.0
		#3		16.0		4.0	3.0	13.0
	Mn	#1		50.0		3.0	2.0	3.0
		#2		53.0		4.0	4.0	4.0
		#3		10.0		21.0	57.0	29.0
	Fe	#1		3.8		8.0	20.0	255.0
		#2		0.3		8.0	18.0	208.0
		#3		0.3		7.0	26.0	332.0

Table A- 2 Speciation for stormwater (1)

Sampling data	Metal (μg/L)	Sampling site	Total Metal (TM)	Total Dissoved (TD)		Total Particulate (TP)		
				RE	STR-B	EX	ER	RES
Nov. 19, 1999	Cu	#1	35.0	5.0	10.0	2.7	7.5	8.9
		#2	28.0	5.0	18.0	0.0	1.9	0.7
		#3	7.0	2.0	4.0	0.0	1.0	0.7
	Zn	#1	176.0	76.0	32.0	18.0	24.0	30.0
		#2	71.0	40.0	27.0	0.0	8.0	15.0
		#3	44.0	12.0	8.0	0.0	10.0	23.0
	Mn	#1	78.0	16.0	3.0	12.0	15.0	28.0
		#2	141.0	43.0	55.0	0.0	31.0	4.0
		#3	64.0	9.0	8.0	0.0	43.0	8.0
	Fe	#1	10563.0	10.0	297.0	45.0	3700.0	7500.0
		#2	7880.0	13.0	889.0	0.0	890.0	1610.0
		#3	777.0	11.0	297.0	0.0	134.0	268.0

Table A- 3 Speciation for stormwater (2)

Sampling data	Metal (µg/L)	Sampling site	Total Metal (TM)	Total Dissoved (TD)		Total Particulate (TP)		
				RE	STR-B	EX	ER	RES
Jan. 3, 2000	Cu	#1	67.2	4.4	12.8	6.8	10.5	27.3
		#2	29.8	3.1	21.9		3.1	4.0
		#3	15.5	0.6	14.8		0.0	1.9
	Zn	#1	373.8	219.6	46.7	25.0	66.0	73.0
		#2	132.8	45.5	31.4	--	--	--
		#3	39.1	22.3	7.2	--	--	--
	Mn	#1	187.2	51.4	15.7	13.0	5.0	30.0
		#2	76.8	33.0	7.2		15.0	7.0
		#3	78.4	27.0	12.7		19.0	5.0
	Fe	#1	9980.0	920.0	810.0	27.0	79.0	2731.0
		#2	1320.0	5.0	75.0		95.0	395.0
		#3	1330.0	10.0	290.0		75.0	320.0

Table A- 4 Speciation for stormwater (3)

Sampling data	Metal (µg/L)	Sampling Site	Total Metal (TM)	Total Dissoved (TD)		Total Particulate (TP)		
				RE	STR-B	EX	ER	RES
Jan, 10 2000	Cu	#1	85.1	7.8	20.0	12.0	15.0	33.0
		#2	28.8	2.5	21.4	--	4.0	5.5
		#3	19.8	0.0	19.6	--	0.0	2.0
	Zn	#1	364.7	104.4	74.5	37.0	65.0	88.0
		#2	130.3	57.8	34.7	0.0	15.0	21.0
		#3	38.4	21.6	19.1	0.0	5.0	7.0
	Mn	#1	241.4	41.0	23.4	22.0	21.0	83.0
		#2	88.0	59.5	18.1	--	5.0	10.0
		#3	45.0	30.2	10.7	--	4.0	3.0
	Fe	#1	11950.0	130.0	350.0	47.0	274.0	7727.0
		#2	960.0	10.0	280.0	--	176.0	691.0
		#3	380.0	20.0	200.0	--	69.0	268.0

Appendix B   Metal speciation in the suspended sediment (SS)

Table B- 1 Cu Speciation in SS

	mg /KgSS				ug/L		
	EX	ER	RES		EX	ER	RES
Aug#1	72.3	57.4	72.6		2.4	1.9	2.4
Aug#2	107.1	78.0	104.1		2.4	1.7	2.3
Aug#3	89.3	52.2	104.6		1.8	1.1	2.1
Nov#1a	29.2	79.7	94.7		2.7	7.5	8.9
Nov#1b	17.0	29.5	107.7		6.5	11.3	41.2
Nov#2	0.0	249.8	91.6			1.9	0.7
Nov#3	0.0	182.3	117.4			1.0	0.7
3,Jan#1	45.0	69.3	180.5		6.8	10.5	27.3
3,Jan#2		145.1	188.1			3.1	4.0
3,Jan#3		0.0	161.6			0.0	1.9
10,Jan#1	15.8	19.8	43.5		12.0	15.0	33.0
10,Jan#2		140.5	193.1			4.0	5.5
10,Jan#3		0.0	196.3			0.0	2.0

Table B- 2 Zn Speciation in SS

	mg /KgSS				ug/L		
	EX	ER	RES		EX	ER	RES
Aug#1	31.0	34.0	273.0		1.1	1.2	9.6
Aug#2	117.0	168.0	514.0		2.5	3.6	11.0
Aug#3	199.0	149.0	647.0		4.0	3.0	13.0
Nov#1a	245.0	327.0	409.0		18.0	24.0	30.0
Nov#1b	199.0	178.0	314.0		76.0	68.0	120.0
Nov#2	0.0	1043.0	1955.0			8.0	15.0
Nov#3	0.0	1746.0	4016.0			10.0	23.0
3,Jan#1	164.0	436.0	480.0		25.0	66.0	73.0
10,Jan#1	52.0	92.0	124.0		37.0	65.0	88.0
10,Jan#2	0.0	562.0	800.0		0.0	15.0	21.0
10,Jan#3	0.0	482.0	770.0		0.0	5.0	7.0

Table B- 3 Mn Speciation in SS

	mg /KgSS				ug/L		
	EX	ER	RES		EX	ER	RES
Aug#1	99.0	47.0	102.0		3.0	2.0	3.0
Aug#2	160.0	182.0	175.0		4.0	4.0	4.0
Aug#3	1053.0	2856.0	1434.0		21.0	57.0	29.0
Nov#1a	163.0	204.0	381.0		12.0	15.0	28.0
Nov#1b	73.0	118.0	248.0		28.0	45.0	95.0
Nov#2	0.0	4040.0	521.0		0.0	31.0	4.0
Nov#3	0.0	7508.0	1397.0			43.0	8.0
3,Jan#1	84.0	34.0	197.0		13.0	5.0	30.0
3,Jan#2		686.0	328.0			15.0	7.0
3,Jan#3		1575.0	426.0			19.0	5.0
10,Jan#1	30.0	28.0	109.0		22.0	21.0	83.0
10,Jan#2		174.0	341.0			5.0	10.0
10,Jan#3		437.0	309.0			4.0	3.0

Table B- 4 Fe Speciation in SS

	g /KgSS				ug/L		
	EX	ER	RES		EX	ER	RES
Aug#1	0.2	0.6	7.6		8.0	20.0	255.0
Aug#2	0.3	0.8	9.3		8.0	18.0	208.0
Aug#3	0.4	1.3	16.5		7.0	26.0	332.0
Nov#1a	0.6	50.4	102.2		45.0	3700.0	7500.0
Nov#1b	0.6	3.1	94.4		230.0	1200.0	36140.0
Nov#2		116.0	209.8		0.0	890.0	1610.0
Nov#3		23.4	46.8			134.0	268.0
3,Jan#1	0.2	0.5	18.1		27.0	79.0	2731.0
3,Jan#2		4.5	18.6			95.0	395.0
3,Jan#3		6.3	27.0			75.0	320.0
10,Jan#1	0.1	0.4	10.2		47.0	274.0	7727.0
10,Jan#2		6.2	24.5			176.0	691.0
10,Jan#3		6.8	26.3			69.0	268.0

Appendix C   Stormwater Quality (SQ) at Intervals over the Storm Event   (Nov. 19, 1999)

Table C- 1 Stormwater quality data at Site #1

Time	pH	SS (mg/L)	Cu (µg/L)			Zn (µg/L)			Mn (µg/L)			Fe (µg/L)		
			TM	TD	RE	TM	TD	RE	TM	TD	RE	TM	TD	RE
9:10	6.5	89	33	20	9	151	89	75	62	18	12	13154	179	3
9:55	6.4	31	40	12	6	234	108	64	106	25	25	25523	465	5
10:40	6.5	35	31	10	2	161	135	91	71	20	15	17449	401	15
11:25	6.5	73	36	17	3	158	100	74	74	14	13	17528	181	15
12:05	6.4	223	60	14	1	104	98	51	47	14	9	10991	272	12
12:45	6.6	948	113	5	0	613	78	57	345	19	13	65952	163	8

Table C- 2 Stormwater quality data at Site #2

Time	pH	SS (mg/L)	Cu (µg/L)			Zn (µg/L)			Mn (µg/L)			Fe (µg/L)		
			TM	TD	RE	TM	TD	RE	TM	TD	RE	TM	TD	RE
9:25	6.4	3	13	11	2	66	62	34	145	136	92	7830	949	6
10:05	6.5	1	14	11	2	65	55	48	155	93	45	8468	972	7
10:50	6.6	2	10	8	5	60	60	57	116	106	15	7629	882	25
11:30	6.6	5	75	60	9	94	92	22	149	58	2	7591	804	14
12:15	6.7	20	12	11	2	121	87	33	138	91	68	11464	598	17
13:00	6.6	18	17	14	3	126	47	48	119	67	44	10319	444	9

Table C- 3 Stormwater quality data at Site #3

Time	pH	SS (mg/L)	Cu (µg/L)			Zn (µg/L)			Mn (µg/L)			Fe (µg/L)		
			TM	TD	RE	TM	TD	RE	TM	TD	RE	TM	TD	RE
9:40	6.8	5	9	8	2	34	31	13	57	18	17	702	273	6
10:25	6.7	4	3	3	1	41	19	15	65	13	9	812	359	8
11:05	6.7	5	7	6	3	48	18	10	68	11	2	810	278	9
11:50	6.6	7	10	9	3	53	13	11	64	22	6	783	321	20
12:30	6.6	7	8	7	3	55	22	21	72	24	21	875	322	16
13:20	6.7	10	7	7	2	65	53	50	98	18	16	998	376	25

Appendix D   Chelex receiver uptake results

<u>Table D- 1 Results in July (7.23 - 7. 30), 1998</u>

D-1A   Resin uptake

Metal	Site No.	Mean (pg/mm^2.hr)	Range (pg/mm^2.hr)	No. of samples
Cu	#1	2.89	1.41-1.38	4
	#2	5.85	5.36-7.33	4
	#3	5.36	3.38-7.33	4
Zn	#1	19	13-27	4
	#2	25	22-27	4
	#3	20	13-17	4
Mn	#1	265	186-349	4
	#2	24	17-33	4
	#3	16	7-26	4
Fe	#1	6962	5590-8506	4
	#2	98	14-289	4
	#3	65	19-108	4

D-1B   Membrane uptake

Metal	Site No.	Mean (pg/mm^2.hr)	Range (pg/mm^2.hr)	No. of samples
Cu	#1	6.67	5.36-7.33	4
	#2	5.85	3.38-9.30	4
	#3	4.86	3.38-7.33	4
Zn	#1	14	11-16	4
	#2	14	7-27	4
	#3	15	9-25	4
Mn	#1	3	1-6	4
	#2	58	39-82	4
	#3	486	259-814	4
Fe	#1	398	308-512	4
	#2	355	174-617	4
	#3	1234	607-2123	4

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Table D- 2. Results in August (8.17 - 9.2), 1998

D-2A   Resin uptake

Metal	Site No.	Mean (pg/mm².hr)	Range (pg/mm².hr)	No. of samples
Cu	#1	1.95	0.62-3.28	2
	#2	5.41	5.05-5.77	2
	#3	4.85	4.78-4.91	2
Zn	#1	9	5-13	2
	#2	16	10-22	2
	#3	5	4-5	2
Mn	#1	124	79-168	2
	#2	35	13-58	2
	#3	15	12-18	2
Fe	#1	521	379-664	2
	#2	56	31-80	2
	#3	20	14-27	2

D-2B   Membrane uptake

Metal	Site No.	Mean (pg/mm².hr)	Range (pg/mm².hr)	No. of samples
Cu	#1	5.90	4.98-6.81	2
	#2	2.36	2.33-2.40	2
	#3	2.73	2.27-3.19	2
Zn	#1	30	23-37	2
	#2	6	6-7	2
	#3	9	6-12	2
Mn	#1	7	7-8	2
	#2	29	25-34	2
	#3	344	304-385	2
Fe	#1	300	255-344	2
	#2	155	145-166	2
	#3	584	473-695	2

Table D- 3. Results in Febrary (2.11 - 2.18), 1999

D-3A   Resin uptake

Metal	Site No.	Mean (pg/mm^2.hr)	Range (pg/mm^2.hr)	No. of samples
Cu	#1	4.73	0.79-8.75	4
	#2	3.57	0.74-7.65	8
	#3	2.66	0.00-7.25	6
Zn	#1	21	18-25	4
	#2	38	17-62	8
	#3	23	20-26	6
Mn	#1	17	15-18	4
	#2	88	68-109	8
	#3	73	65-80	6
Fe	#1	36	25-50	4
	#2	105	59-174	8
	#3	14	9-32	6

D-3B   Membrane uptake

Metal	Site No.	Mean (pg/mm^2.hr)	Range (pg/mm^2.hr)	No. of samples
Cu	#1	8.98	8.98-8.98	4
	#2	33.31	16.98-22.23	8
	#3	0.00	0	6
Zn	#1	47	41-52	4
	#2	94	70-125	8
	#3	2	0-6	6
Mn	#1	26	24-28	4
	#2	147	111-200	8
	#3	10	4-23	6
Fe	#1	870	820-919	4
	#2	1893	1893-2493	8
	#3	294	148-573	6

Table D- 4. Results in October (10.27 - 11.3), 1999

D-4A   Resin uptake

Metal	Site No.	Mean (pg/mm^2.hr)	Range (pg/mm^2.hr)	No. of samples
Cu	#1	18.00	9.00-25.00	6
	#2	--	--	6
	#3	15.00	9.00-16.00	6
Zn	#1	115	89-164	6
	#2	--	--	6
	#3	49	29-64	6
Mn	#1	35	29-40	6
	#2	--	--	6
	#3	60	45-71	6
Fe	#1	250	226-290	6
	#2	--	--	6
	#3	83	19-194	6

D-4B   Membrane uptake

Metal	Site No.	Mean (pg/mm^2.hr)	Range (pg/mm^2.hr)	No. of samples
Cu	#1	0.45	0.00-1.37	6
	#2			6
	#3	1.25	0.00-2.42	6
Zn	#1	7	3-9	6
	#2			6
	#3	13	8-20	6
Mn	#1	1	0-1	6
	#2			6
	#3	86	60-108	6
Fe	#1	157	71-249	6
	#2			6
	#3	785	548-1064	6

Table D- 5. Results in November (11.19 - 11.25), 1999

D-5A   Resin uptake

Metal	Site No.	Mean (pg/mm^2.hr)	Range (pg/mm^2.hr)	No. of samples
Cu	#1	4.80	4.20-5.30	4
	#2	3.80	1. 70-6.20	4
	#3	3.00	2.60-3.80	4
Zn	#1	22	17-29	4
	#2	21	17-27	4
	#3	13	1-19	4
Mn	#1	8	6-11	4
	#2	51	43-66	4
	#3	73	60-96	4
Fe	#1	16	14-19	4
	#2	141	92-184	4
	#3	45	22-73	4

D-5B Membrane uptake

Metal	Site No.	Mean (pg/mm^2.hr)	Range (pg/mm^2.hr)	No. of samples
Cu	#1	30.00	18.00-40.00	4
	#2	25.00	12.00-37.00	4
	#3	1.00	0.00-1.00	4
Zn	#1	134	93-194	4
	#2	78	38-118	4
	#3	8	7-8	4
Mn	#1	69	55-95	4
	#2	142	92-191	4
	#3	65	53-76	4
Fe	#1	3233	2544-4096	4
	#2	4158	2214-5841	4
	#3	784	740-884	4

Table D- 6. Results in November (11.19), 1999 (One storm)

D-6A   Resin uptake

Metal	Site No.	Mean (pg/mm^2.hr)	Range (pg/mm^2.hr)	No. of samples
Cu	#1	6.80	2.70-10.50	4
	#2	9.60	7.40-12.60	4
	#3	11.40	9.80-13.60	4
Zn	#1	13	8-16	4
	#2	25	14-37	4
	#3	21	11-33	4
Mn	#1	24	22-27	4
	#2	194	176-213	4
	#3	174	133-213	4
Fe	#1	7	0-15	4
	#2	154	134-175	4
	#3	21	14-29	4

D-6B   Membrane uptake

Metal	Site No.	Mean (pg/mm^2.hr)	Range (pg/mm^2.hr)	No. of samples
Cu	#1	0	0	4
	#2	0	0	4
	#3	0	0	4
Zn	#1	7	0-15	4
	#2	12	9-16	4
	#3	11	9-13	4
Mn	#1	2	0-6	4
	#2	12	6-19	4
	#3	28	25-33	4
Fe	#1	128	74-211	4
	#2	646	499-907	4
	#3	160	70-262	4

Table D- 7. Results in January (1.3- 1.10), 2000

D-7A   Resin uptake

Metal	Site No.	Mean (pg/mm^2.hr)	Range (pg/mm^2.hr)	No. of samples
Cu	#1	3.98	3.26-4.47	4
	#2	4.65	3.66-5.02	4
	#3	4.04	2.91-6.90	4
Zn	#1	42	40-44	4
	#2	23	22-24	4
	#3	21	20-24	4
Mn	#1	17	15-19	4
	#2	66	56-72	4
	#3	82	77-92	4
Fe	#1	51	41-72	4
	#2	107	84-142	4
	#3	16	12-21	4

D-7B   Membrane uptake

Metal	Site No.	Mean (pg/mm^2.hr)	Range (pg/mm^2.hr)	No. of samples
Cu	#1	1.90	0.63-3.63	4
	#2	8.30	5.49-11.79	4
	#3	1.30	0.39-3.23	4
Zn	#1	4	1-9	4
	#2	20	15-23	4
	#3	2	2-3	4
Mn	#1	2	0-4	4
	#2	45	28-58	4
	#3	7	5-9	4
Fe	#1	80	28-182	4
	#2	1020	790-1217	4
	#3	125	107-133	4

Appendix E   Resin evaluation for exchange capacity and Ca & Mg interference

E.1 Exchange capacity test.

Chelex-100 chelating resin (BIO-RAD) was used in the Dialysis with Resin Receiver in the field experiments to determine trace metal avilability. When the receiver was contacted with the water, the bioavailable trace metal species in the water will penetrate the dialysis membrane and complex with the Chelex resin. The exchange capacity test conducted herein is to ensure that the resin used inside the dialysis bag is suffucient for the available trace metals it will be complexed when the receiver was kept in contact with trace metal polluted water for a certain time period (exposure time). The test procedure, the results and the conclusion were described below.

A. Procedure:

Two grams of chelex resin were used for the exchange capacity test for trace metal Cu and Zn. The solution concentration for Cu and Zn were prepared as below:

Metal solution

(1) Cu^{++} = 4 meq in 100 ml of water, Cc_u = 1270.8 mg Cu^{++}/ L

(2) Zn^{++} = 4meq in 100 ml of water, Cz_n = 1307.4 mg Zn^{++} / L

The experiment was conducted in the following steps. Ten ml of metal solution were exchanged with Chelex-100 resin (2 g) in a separate column of 25 cm in length and 1.5 cm in diameter, and the solution after exchange was collected in a 50 ml volumetric flask. After each 10 ml solution exchange, 30 ml deionized water were added to the exchange column, and the water was continuous received into the flask. The flow rate was 0.5-1 ml/min. The metal solution in the volumetric flask was diluted to 50 ml and AAS analysis for Cu or Zn concentration. The above procedure was repeated for each 10 ml of trace metal solution to

get the exchange capacity curve. Each metal was tested twice to ensure the results were consistent.

B. Results

The resin capacity curve for trace metal Cu and Zn showing in Figure E-1 below indicated that the exchange capacity of the Chelex-100 resin reaches the saturation at approximately 70 ml of metal solution passing through the column.

Resin exchange capacity test (Cu)

(a)

Resin exchange capacity test (Zn)
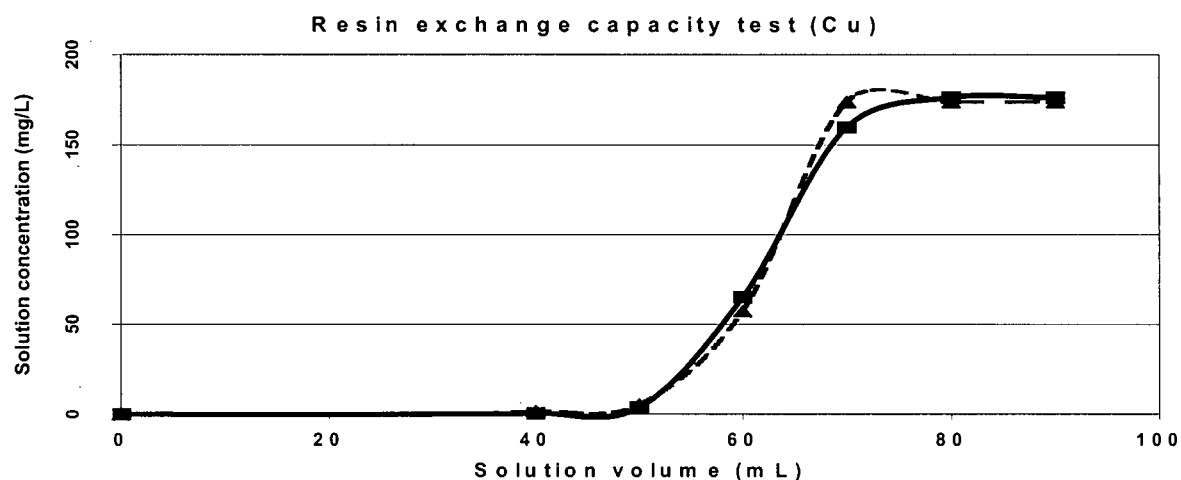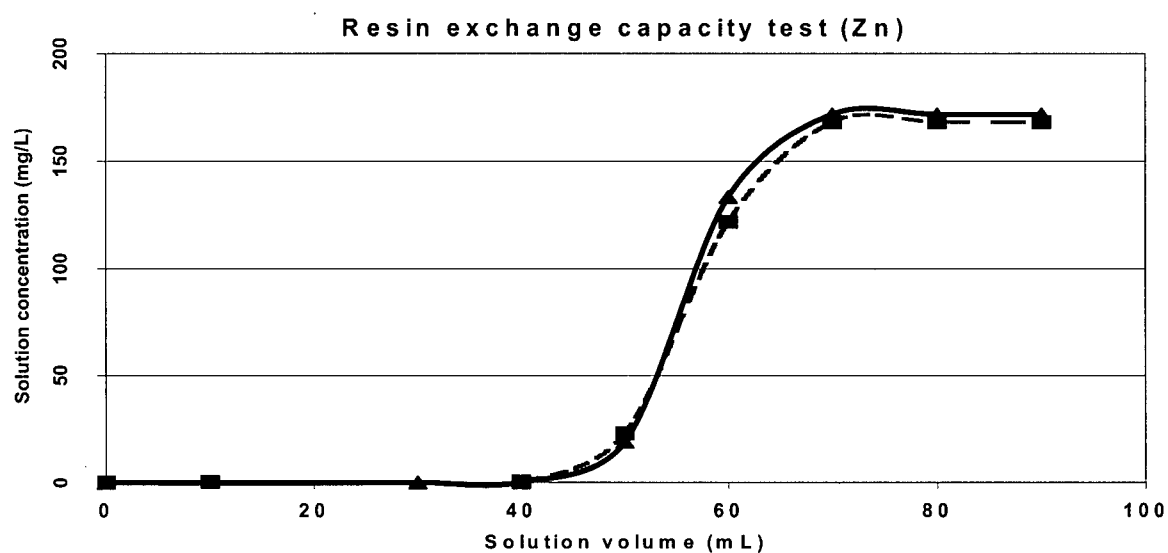
(b)

Figure E- 1 Resin exchange capacity test for Cu (a) and Zn (b)

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The calculation gives that the Chelex-100 resin exchange capacity for metal Cu and Zn in Table E-1.

Table E- 1 Chelex resin exchange capacity

Exchange capacity	Cu	Zn
mg(metal) / g(resin)	44.48	45.76

In the field experiment, the highest metal uptake by Chelex resin was 7.9 mg/g (Fe+Mn+Cu+Zn in July, 1998 experiment), which is approximately 6 times lower than the resin exchange capacity.

C. Conclusion

The use of 1 gram of resin in the receiver is sufficient for the field experiment to test trace metal bioavailability over the exposure periods studied in the Brunette River watershed.

D. Experiment data

Table E- 2 Resin exchange capacity test for Cu solution in 2.3, 1999

Vol. Solution (ml)		abs(nm)	C (mg/l)		abs(nm)	C (mg/l)
Cu concentration for resin exchange capacity test at 2.3, 1999 (solution: Cu only, resin are all old resin)						
10 ml	**n1**	0.00	-0.13	**o1**	0.00	-0.13
20ml	**n2**	0.00	-0.13	**o2**	0.00	-0.13
30ml	**n3**	0.00	-0.13	**o3**	0.00	-0.06
40ml	**n4**	0.03	1.71	**o4**	0.01	0.38
50ml	**n5**	0.08	5.40	**o5**	0.05	3.70
60ml	**n6**	0.52	57.30	**o6**	0.57	65.05
70ml	**n7**	0.73	173.81	**o7**	0.73	159.80
80ml	**n8**	0.73	173.81	**o8**	0.73	176.19
90ml	**n9**	0.73	173.81	**o9**	0.74	176.19
100ml				**o10**	0.74	176.19

Table E- 3 Resin exchange capacity test for Zn solution in 2.3, 1999

Vol. Solution (ml)		abs(nm)	C (mg/l)		abs(nm)	C (mg/l)
Zn concentration for resin exchange capacity test at 2.3, 1999 (solution: Zn only, resin are all old resin)						
10 ml	**n1**	0.03	0.25	**o1**	0.00	-0.16
20ml	**n2**	0.00	-0.12	**o2**	0.00	-0.16
30ml	**n3**	0.01	-0.05	**o3**	0.01	0.00
40ml	**n4**	0.04	0.42	**o4**	0.02	0.12
50ml	**n5**	0.56	22.73	**o5**	0.49	18.86
60ml	**n6**	1.03	121.66	**o6**	1.05	133.26
70ml	**n7**	1.10	168.03	**o7**	1.10	171.60
80ml	**n8**	1.11	168.03	**o8**	1.11	171.60
90ml	**n9**	1.11	168.03	**o9**	1.11	171.60

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E.2 Interference test for Chelex resin

With the consideration that calcium (Ca) and magnesium (Mg) are the most common ionic metals in the urban water, interference of these metal species may affect the complexation of resin with the target trace metals in the water. The interference of Ca and Mg were tested in the laboratory to see that if there will be the interface of these metals on the trace metal copper and zinc complexation with Chelex resin.

A. Procedure:

Two grams of chelex resin were used for the interference test for trace metal Cu. Three solutions were prepared in this test. The first is prepared by Cu, Mg and Ca, second consists of Ca and Cu only and the third is only made by Cu for comparison. The constituents of each solution were described below.

Metal solution

Solution 1: Cu^{++} = 4 meq in 100 ml of water, C_{Cu} = 127.08 mg Cu^{++} / 100 ml

$\qquad$ Ca^{++} = 5 meq in 100 ml of water, C_{Ca} = 100.2 mg Ca^{++} / 100 ml

$\qquad$ Mg^{++} = 2 meq in 100 ml of water, C_{Mg} = 24.31mg Mg^{++} / 100 ml

Solution 2: Cu^{++} = 4 meq in 100 ml of water, C_{Cu} = 127.08 mg Cu^{++} / 100 ml

$\qquad$ Ca^{++} = 10 meq in 100 ml of water, C_{Ca} = 200.4 mg Ca^{++} / 100 ml

Solution 3: Cu^{++} = 4 meq in 100 ml of water, C_{Cu} = 127.08 mg Cu^{++} / 100 ml

The interference experiment was conducted in the following steps. Ten ml of metal solution were eluted through a separate column (25 cm in length and 1.5 cm in diameter) containing Chelex-100 resin (2 g) with flow rate of 0.5-1.0 ml/min. The eluant was collected in a 50 ml volumetric flask. After each 10 ml metal solution , 30 ml deionized water were added to the

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exchange column, and the water was collected in the same volumetric flask. The metal solution in the volumetric flask then was diluted to 50 mL and AAS analysis for the concentration of each element sample. Repeat above procedure for each 10 ml of trace metal solution to get the curves for Ca, Cu and Mg. The elution profiles were conducted in duplicate.

B. Results

Figure E-2 and E-3 showed the interference of Ca and Mg on the trace metal Cu complexation with Chelex resin. For the comparison purpose, the measurement of Cu solution was also drawn in these two figures. It can be seen in the figures that the presence of Ca^{+2} and Mg^{+2} affect the complexation between the chelex resin and metal Cu. The elution profiles of the Cu in the presence of Ca and Mg (Fig. E-2) or only Ca (Fig. E-3) demonstrates different complexation ability when compared to the pure Cu solution (The distinct breakthrough curve). In the early stage, Ca and Mg in the water may compete with Cu for the resin complexation sites, showing in Figure E-2 that Ca and Mg curve increased dramatically after elution of 20 ml solution through the exchange column. Based on this competition, the complexation of Cu in the resin will be delayed. However, it is clear that the priority of resin complexation was with Cu, since Ca or Mg reached saturation on the resin quickly, while Cu kept binding to the Chelex resin. Table E-4 (Freiser, H. and Fernando, Q. 1963) lists the relative stability constant of Ca^{+2}, Mg^{+2}, Cu^{+2} and Zn^{+2} for the Chelex functional group, which ensure that the priority of the Cu and Zn complexed with the Chelex resin than Ca^{+2}, Mg^{+2} in the water system.

Table E- 4 Formation constants of metal complexes of Chelex resin functional group (EDTA)

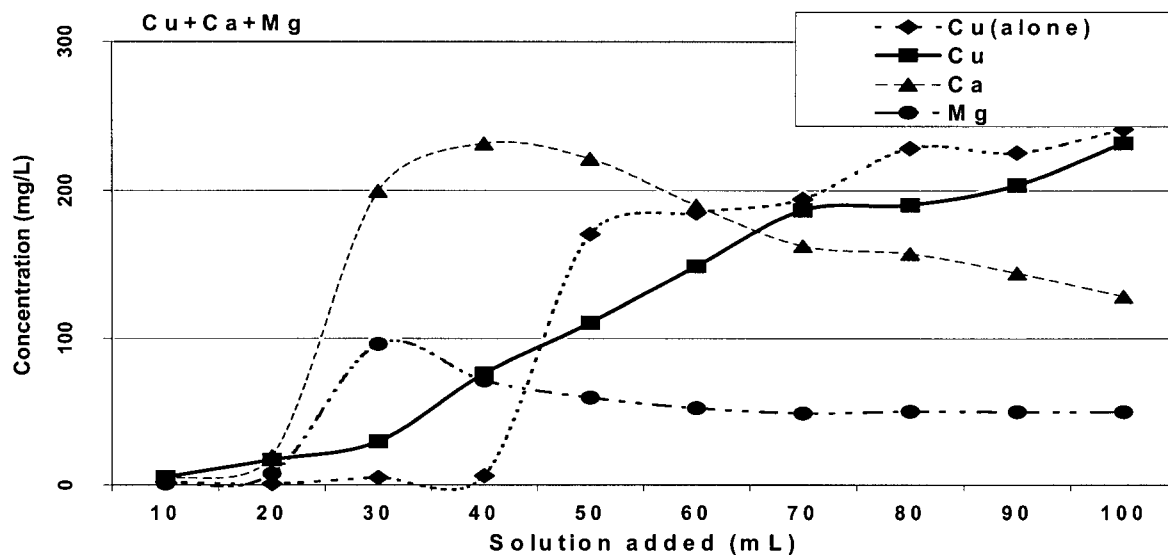| Metal Ion	log k
Cu^{+2}	18.8
Zn^{+2}	16.5
Ca^{+2}	10.7
Mg^{+2}	8.7

Figure E- 2   The effect of calcium and magnesium on the complexation
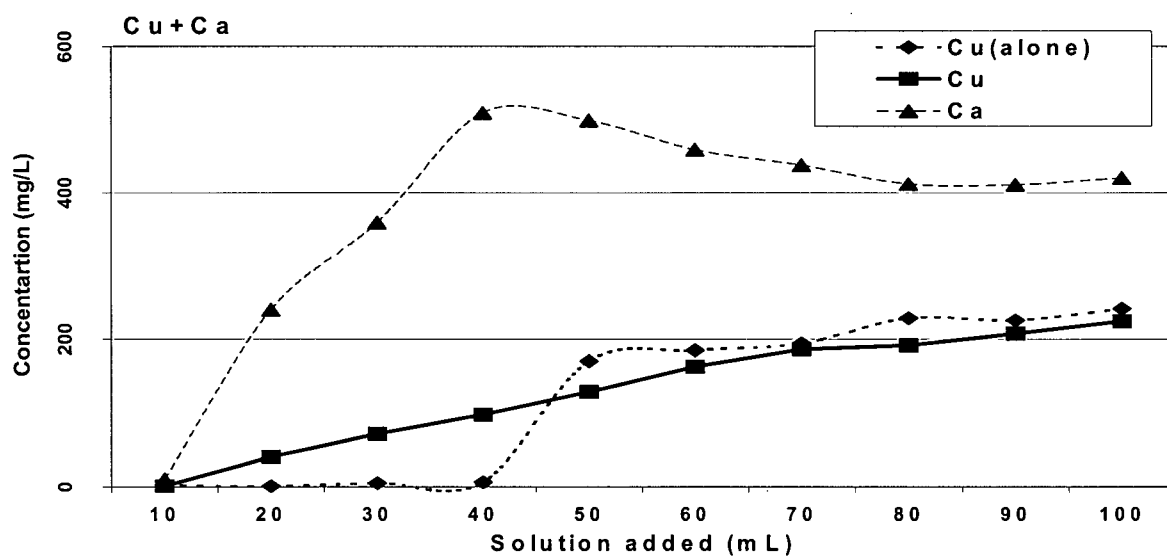of copper on Chelex resin

Figure E- 3   The effect of calcium on the complexation of copper on Chelex resin

C. Conclusion

Ca and Mg in the water column affect the initial complexation profile of Cu with the chelex resin. However, the experimental curve indicates that the chelex resin can continue to bind Cu even when saturated with Ca and Mg. So interference from divalent cations such as Ca^{+2} and mg^{+2} should be small considering their relative concentrations in the field water samples compared to the levels used in the laboratory experiment.

D. Experimental data (Average value of two parallel experiments)

Table E- 5 Solution of Cu+Ca+Mg (mg/L)

Vol.of Cu+Ca+Mg solution (mL)	Cu(alone) (mg/L)	Cu(mg/L)		Ca(mg/L)		Mg(mg/L)	
		run-1	run-2	run-1	run-2	run-1	run-2
10	2	1	10	5	3	1	1
20	1	17	18	19	21	6	9
30	5	24	36	234	165	98	94
40	6	65	87	286	177	71	71
50	170	105	116	272	171	58	61
60	185	136	160	236	144	51	53
70	194	175	198	205	119	48	49
80	228	193	187	195	119	49	51
90	225	198	209	183	105	48	51
100	241	232	232	163	93	49	50

Table E- 6 Solution of Cu-Ca (mg/L)

Vol.of Cu+Ca solution (mL)	Cu(alone) (mg/L)	Cu(mg/L)		Ca(mg/L)	
		run-1	run-2	run-1	run-2
10	2	2	1	7	13
20	1	30	51	163	316
30	5	43	99	214	503
40	6	70	124	513	505
50	170	98	160	505	491
60	185	144	182	456	462
70	194	169	204	434	442
80	228	179	205	379	445
90	225	193	222	393	428
100	241	210	238	397	444

Cu (only) solution for the comparison