

AMOUNT AND LEACHING POTENTIAL OF HEAVY METALS IN BARK MULCH AND COMPOST USED ON THE UNIVERSITY OF BRITISH COLUMBIA GROUNDS

December 15, 2003

University of British Columbia

Supervisor:

Dr. Royann Petrell

Group Members:

Balbir Arora

Nancy Chan

Derek Choy

Jenny Eng

Mehrdad Ghods

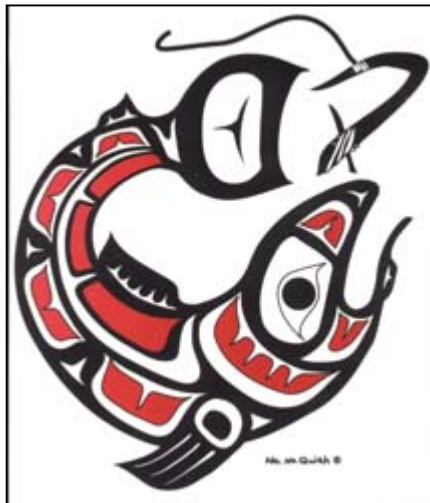
Pablo Gutierrez

Graham Kemp

Alvaro Reyes

Heather Schneider

Crissa Villamayor



Acknowledgements

Members CHBE 465/540 would like to thank the following individuals for their contributions to this project. First, we would like to thank Dr. Petrell (Associate Professor in the Chemical and Biological Engineering Department, the University of British Columbia) for providing us with technical knowledge, inspiration, and guidance. We'd also like to thank the UBC landscape maintenance department and John Metras from the Department of Land and Building Services for providing the opportunity, administrative support and funding for this project. We are indebted to Brenda Sawada, UBC SEEDS coordinator for giving us spiritual guidance and support throughout the term. Lastly, we would like to thank Horace Lam from The Chemical Engineering Store for answering many of our technical questions regarding our project and for providing us with the equipment necessary for carrying out our experiments. Without their help, this project would not have been initiated.

Executive Summary

This project was to ascertain if heavy metals are present in leachate runoff from bark mulch and compost, determine whether or not either of these substances could be significant contributors of metals into aquatic habitat, and to examine alternative strategies to reduce the impact of leachate heavy metals discharge at University of British Columbia (UBC). This research was carried out because aquatic habitat is in continual decline in British Columbia and throughout the world, and all steps must be taken now to preserve and rehabilitate. Exposure to heavy metals in the environment has been linked to adverse effects on aquatic wildlife, including subtle neuro-behavioural effects, chronic kidney damage, sensory or neurological impairments, damage to fetus, swimming performance, changes in biochemistry, such as enzyme activity and blood chemistry, and changes in reproductive potential. UBC's sustainable Development calls for the University to take leadership to work towards a sustainable future through practising sustainable development. This project represents a step in the that direction.

In order to ascertain the presence of heavy metals in fresh bark mulch, soil (used in compost mixtures) and compost being used at UBC campus, several tasks were conducted. Initially duplicate samples were analysed for heavy metal content. Compost and soil samples contained approximately the same amount of heavy metals, and these metals were generally higher in compost/soil than bark mulch. Zinc and chromium were the major metals in the bark mulch. The hemlock-fir mulch mixture had a higher metal content than the fir mulch.

The next major task involved testing the leaching abilities of these heavy metals from various amounts of compost/soil and hemlock/fir mulch into rainwater using a 72-hr shaker flask test. Results from atomic absorption/emission spectrophotometry analysis indicated that aluminium, cadmium and zinc exceeded U.S. Environmental Protection Agency and Canadian water quality guidelines for all bark mulch samples. Arsenic and copper were found to be in excess only in the 30 g bark mulch

sample in 0.35 L rainwater. Soil/compost leachate was above the allowable limits for copper and aluminium. Generally the amount of solid material in the sample did not affect the percent mass leached for aluminium and arsenic. Cadmium and zinc appeared to be affected by the sample amount.

The final experiment consisted of simulated storm runoff events. The target storms (based on UBC's intensity duration frequency curves) were two and five-year storms and 30 and 45 min duration, respectively. Water was manually sprinkled on two existing 2.25 m² plant beds (25% slope) at UBC. The beds consisted of compost/soil over laid with fresh bark mulch. In both beds, the concentration of heavy metals in the leachate collected from the bottom of the beds exceeded the allowable limits for cadmium, zinc and aluminium. The discharge levels in the two beds were, however, distinctive.

Approximately five percent of UBC campus is covered with bark mulch. The contribution of heavy metals from it can be significant as mulch is applied yearly, and requires a metal-free water to dilute the concentration to safe levels. Such runoff is not readily available on campus due to contaminated roadway and parking lots, and the amount of water needed to do this. It was found that even after a 20- fold dilution of sample concentrations, the cadmium level was just at the allowable limit and aluminium was three times above it.

Different alternative strategies to reduce the impact of leachate heavy metals were examined. They include pre-treatment at the source end, and discontinuing the use of bark mulch on Campus. Aquatic habitat is in continual decline in British Columbia, and all remedial steps should be taken now to preserve what is left of it.

It is recommended that the use of bark mulch be discontinued until an effective treatment method is employed to prevent contamination due to leaching of heavy metals.

Table of Contents

<i>Acknowledgements</i>	<i>ii</i>
<i>Executive Summary</i>	<i>iii</i>
<i>Table of Illustrations</i>	<i>vii</i>
List of Tables _____	vii
List of Figures _____	vii
<i>1.0 Introduction</i>	<i>1</i>
<i>2.0 Review of Desorption</i>	<i>3</i>
2.1 Factors that Affect the Desorption of Heavy Metals _____	3
2.2 Conventional Testing Methods _____	4
2.2.1 Chemical Precipitation _____	4
2.2.2 Membrane Filtration _____	5
2.2.3 Ion Exchange _____	5
2.2.4 Sorbents _____	6
<i>3.0 Methodology</i>	<i>6</i>
3.1 Bark Mulch Sampling _____	7
3.2 Soil/Compost Sampling _____	7
3.3 Elemental Analysis _____	8
3.3.1 Pre-treatment of Soil, Compost, and Bark Mulch _____	8
3.4 Shaker Flask Analysis _____	9
3.4.1 Experiment Preparation _____	9

3.4.2 Filtration _____	10
3.5 Storm Simulation Experiment _____	12
3.5.1 Simulated Rain Storm Events _____	12
3.5.2 Test Bed Construction _____	12
3.5.3. Storm Simulation Experimental Procedure _____	13
4.0 Results and Discussion	16
4.1 Elemental Analysis _____	16
4.2 Shaker Flask _____	16
4.3 Storm Simulation _____	21
5.0 Conclusion and Recommendations	25
6.0 References	26
7.0 APPENDICES	28
APPENDIX A - Leachate Test Sample Mass Determination _____	28
APPENDIX B – Shaker Flask Data _____	31
APPENDIX C – Preliminary Calculations for Storm Simulation Experiment _____	32
APPENDIX D - Budget _____	32
APPENDIX E – Rainstorm Simulation Data _____	1
APPENDIX F: Proposal	
APPENDIX G: Water quality results (raw data)	

Table of Illustrations

List of Tables

Table 1.1 Concentration of Heavy Metals in waste derived composts.....	2
Table 3.1 Samples and corresponding dry weights prepared for preliminary analysis.....	8
Table 3.2 Weights of Samples (in g) based on leaching rate and exceedance of water quality criteria.	10
Table 3.3 Final pH values of sample filtrates	11
Table 3.4 Sample volumes and time required for collection	15
Table 4.1 Results of Elemental Analysis.....	16
Table 4.2 Concentrations of Heavy Metals in Run-off and Allowable Limits.....	21
Table 4.3 Overall Discharge Concentration and Allowable Limits	23

List of Figures

Figure 3.1 Experimental test bed apparatus.....	13
Figure 3.2 Saturation of test bed apparatus	14
Figure 4.1 Filtrate Aluminum Concentrations for All Samples	17
Figure 4.2 Filtrate Cadmium Concentrations for All Samples	18
Figure 4.3 Filtrate Zinc Concentrations for All Samples	19
Figure 4.4 Filtrate Arsenic Concentrations for All Samples	20
Figure 4.5 Filtrate Copper Concentrations for All Samples	20
Figure 4.6 Run-off Rate versus Time	22
Figure 4.7 Cadmium Concentration in Overall Discharge	23
Figure 4.8 Aluminium Concentration in Overall Discharge	24
Figure E-1 Arsenic Concentration of Leachate versus Time.....	ii
Figure E-2 Cadmium Concentration of Leachate versus Time	ii

Figure E-3 Calcium Concentration of Leachate versus Time	iii
Figure E-4 Chromium Concentration of Leachate versus Time.....	iii
Figure E-5 Copper Concentration of Leachate versus Time	iv
Figure E-6 Lead Concentration of Leachate versus Time	iv
Figure E-7 Magnesium Concentration of Leachate versus Time	v
Figure E-8 Manganese Concentration of Leachate versus Time.....	v
Figure E-9 Potassium Concentration of Leachate versus Time.....	vi
Figure E-10 Zinc Concentration of Leachate versus Time.....	vii
Figure E-11 Aluminium Concentration of Leachate versus Time.....	vii

1.0 Introduction

Contaminated stormwater is a common problem throughout the world. Modern development has created an impermeable layer of buildings and pavement; a situation that can, during rainstorm events, lead to the dispersion of pollutants from fertilizers, pesticides, concentrated animal and wood waste, and automobile emissions. These contaminants can be transported both into the groundwater, into the storm sewer network, and into aquatic habitat.

Sampling that occurred within the University of British Columbia's (UBC) stormwater outfalls program indicated substances that are harmful to fish or fish habitat are being discharged into the majority of stormwater outfalls, and they commonly exceeded the British Columbian Provincial Approved Water Quality Guidelines. Students in the previous Aquatic Habitat Design course (Authors Various, 2002) found Arsenic (As), Cadmium (Cd), Copper (Cu), Lead (Pb), and Zinc (Zn), were above Approved British Columbian Water Quality Guidelines in stormwater entering aquatic habitat (B.C. Provincial Government, 1998).

There are many possible contributors of heavy metals into the storm water. Recent research shows that these heavy metals are present in bark mulch (Tanaka and Ichikuni, 1982). Studies testing Japanese bark samples from urban, suburban, and rural locations have shown the presence of heavy metals such as Al, Cr, Fe, Co, Ni, Cu, Cd, and Pb (Tanaka and Ichikuni, 1982). It has been shown that metals can be taken up by trees from soils on which spreading of wood ash from pulp and paper industries has been applied. The metal contents have increased within not only the old wood, but the metal content new wood and bark (Osteras and Greger, 2003).

Tests on chromated copper arsenate (CCA) treated wood subsequently turned into mulch, have shown the leaching of Cu, Cd, and As into the runoff (Townsend *et al.*, 2003). Metals are leached from CCA treated wood during rainfall events (Cooper and Ung, 1997; Stilwell and Gorny, 1997;

Hingston *et al.*, 2001) which could mean that naturally occurring metals could also be leached from bark mulch, as it presents more surface area for leaching.

Long-term studies of metal content in bark compost have shown no accumulation of heavy metals (Pinamonti *et al.*, 1997), meaning that the metals are either degraded or leached out. Leachable soluble fraction from municipal solid waste compost varied between 6 to 10% of the metal content for lead, cadmium, copper and zinc, and was much higher for nickel (11-56%). The exchangeable fraction of cadmium was high with magnesium chloride as the extraction fluid (Tisdell *et al.* 1995). Studies have shown that cadmium persists within green waste compost due to its binding properties and its abilities to displace bound Zn (Whittle and Dyson, 2002).

Mulch consisting of a hemlock and fir bark mixture and local compost is widely used on UBC campus grounds for landscaping purposes, providing moisture retention and weed suppression. Approximately three to four inches of bark mulch is applied to each newly formed landscape site, with the re-application of one to two inches every two years thereafter. This totals approximately 1900 cubic yards of bark mulch, and an average of \$20,000 spent on the application annually (John Metras, personal communication).

Composts are rarely tested for the presence of heavy metals due to cost and lack of clarity over testing parameters (Watson, 2002). The results obtained from one study conducted by Whittle and Dyson, 2002 are presented in Table 1.1 showing the heavy metal content found in waste from green waste.

Table 1.1 Concentration of Heavy Metals in waste derived composts.

Element	Green Waste Collected at Civic Amenity Sites (mg/kg)
Zinc	214
Lead	87
Cadmium	0.075
Chromium	20
Copper	37

Source: <http://www.environmental-centre.com/magazine/kluwer/envr/art3.pdf>

In conjunction with UBC SEEDS (Social, Ecological, Economic Development Studies), the main objective of this project was to assess the presence of heavy metals in leachate from bark mulch and to examine alternative strategies to reduce the toxicity of surface water discharges into storm drains at UBC.

2.0 Review of Desorption

Desorption of heavy metals is dependant on many factors. In the industry there are various methods that can be used to remove these heavy metals based on those factors.

2.1 Factors that Affect the Desorption of Heavy Metals

The rate of adsorption and desorption of metals to and from a medium is controlled by water chemistry and the structure of the medium. Desorption returns the metals to the water column. The various factors that control the solubility of trace metals include pH of water, type and concentration of ligand on which the metal could adsorb, the oxidation state of the mineral component and the redox environment of the system.

Due to increase in salinity, decrease in redox potential or decrease in pH, metals may be desorbed from the medium (e.g.sediment). A lower pH increases the competition between the metal and hydrogen ions for the binding sites. A decrease in pH may also dissolve metal carbonate complexes, releasing free metal ions into the water column. Composition of metal complexes changes with decrease in redox potential under oxygen deficit conditions and results in release of metal ions into the water. Competition between cations and metals for binding sites gets increased at elevated salt concentrations. Often, metals will be driven off into the overlying water (Connell *et al.*, 1984).

2.2 Conventional Testing Methods

There are various methods that can be used to treat heavy metal contaminated waste streams.

The methods used in the industry consists of the following:

2.2.1 Chemical Precipitation

Chemical Precipitation is amongst the most common technology used to remove dissolved (ionic) metals from solutions, such as process wastewaters containing toxic metals. “Precipitation is a method of causing contaminants that are either dissolved or suspended in solution to settle out of solution as a solid precipitate, which can then be filtered, centrifuged, or otherwise separated from the liquid portion. A voluminous precipitate can capture ions and particles during formation and settling, in effect “sweeping” ions and particles from the wastewater (Veera and Edgar, 2002).

The most widely used chemical precipitation process is hydroxide precipitation. This precipitation process forms metal hydroxides by using calcium hydroxide (lime) or sodium hydroxide (caustic) as the precipitant. Each dissolved metal has a distinct pH value at which the optimum hydroxide precipitation occurs. Metal hydroxides are increasingly soluble at both low and high pH values. Therefore, the optimum pH for precipitation of one metal may cause another metal to solubilize, or start to go back into solution. Most process wastewaters contain mixed metals and so precipitating these different metals as hydroxides can be a tricky process.

The ionic metals are converted to an insoluble form (particle) by the chemical reaction between the soluble metal compounds and the precipitating reagent. The particles formed by this reaction are removed from solution by settling and/or filtration. The unit operations typically required in this technology include neutralization, precipitation, coagulation/ flocculation, solids/liquid separation and dewatering.

2.2.2 Membrane Filtration

Membrane filtration is the process of separating particles by passing them through a physical barrier. The membrane consists of tiny pores which allows entry to the desired particles. Pressure is added to the membrane in order to force the liquid through the pores. Membrane filtration can be divided into four categories, defined on the basis of the size of the material they are required to separate from the liquid suspending it. These categories are known as reverse osmosis, nanofiltration, ultrafiltration and microfiltration, in order of increasing pore size.

2.2.3 Ion Exchange

Ion exchange is an adsorption process in which charged molecules, called ions, in a solution are exchanged for other ions on the surface of a resin. Ion exchange only removes compounds that ionize. The phenomenon of ion exchange occurs in special synthetic resins and in many natural solids.

The separation of these metals from a waste stream may be accomplished by using an ion exchange resin bed. An ion exchange resin bed is composed of high-molecular-weight polyelectrolytes that can exchange their mobile ions for ions of similar charge from the surrounding medium. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchanges per unit of resin.

The metals are ionized in water and are removed by contact the metals with the ion exchange resins. In a water de-ionization process, the resins exchange hydrogen ions (H^+) for the positively charged ions (such as nickel, copper, and sodium). The hydroxyl ions (OH^-) are exchanged for negatively charged sulphates, chromates, and chlorides. The resin bed then undergoes a regeneration cycle in order to remove the ionized metals.

2.2.4 Sorbents

Sorbents are natural materials from the industry with large adsorptive capacities. Sorbents are abundant in nature, require little processing, and can be disposed of in a sustainable manner. There are many sorbents that can be used for removing heavy metals from waste streams.

Olin *et al.* (1996) and Bailey *et al.* (1999, 1997) have conducted a literature survey to identify low cost sorbents with potential for treatment of heavy metal contaminated water and waste streams. They have identified 12 potential sorbents for lead, cadmium, copper, zinc and mercury. Among the sorbents identified, chitosan has the highest sorption capacity for several metal ions (Masri *et al.* 1974). Chitosan is obtained by deacetylation of chitin, which is extracted from the shells of shrimps, crabs, and other crustaceans and some fungi. Chitosan chelates five to six times greater amounts of metals than chitin. This is attributed to the free amino groups exposed in chitosan because of deacetylation of chitin (Yang and Zall, 1984).

3.0 Methodology

In order to ascertain the presence of heavy metals in bark mulch, soil and compost being used at UBC campus, the project was done in three phases. For the first phase, samples of bark mulch and compost were collected from their respective sources. The samples were then prepared and sent for elemental analysis to find out the concentration of heavy metals present. For phase 2, a shaker flask experiment was conducted to determine whether or not the heavy metals would leach from the samples. Atomic absorption/emission spectrophotometry analysis was conducted on the shaker flask samples and the results were analyzed. Finally, an experiment involving a simulated rainstorm event on a plant bed at UBC was conducted from which the concentration of heavy metals in the run-off was measured.

3.1 Bark Mulch Sampling

Samples of the bark mulch were collected from Fraser Richmond Biocycle in Richmond BC, which supplies the mulch purchased by UBC. The mulch type was dependant on whatever type of tree was processed recently by their suppliers. Typically, the mulch comes from either hemlock or fir or is some mixture of the two. There was no system to identify and record the species of mulch in piles on the plant. However, since the hemlock/fir mixture is distinguishable from pure fir mulch due to its red colour. The site manager identified the contents of the piles and samples of fir mulch and hemlock/fir mulch were collected using garbage bags. For each of the fir and the hemlock fir mixture, two bags of ground mulch and one of course mulch were collected. Each bag contained approximately 7 – 10kg of mulch. The largest particle size present in the course bark mulch was approximately 5cm.

3.2 Soil/Compost Sampling

Soil and compost samples were collected from the soil and mature yard waste compost piles on the UBC campus; three samples were collected from each pile for a total of six samples. The samples were collected from different locations of each pile to ensure that the samples were an accurate representation of the contents of the site; all samples were collected from approximately 30cm below the surface of the pile because material on the surface have been exposed to the environment and any possible heavy metals may have already leached out. The compost was dark in colour and moist to touch. It also contained a few earthworms, centipedes, spiders, and other bugs. The soil consisted of fine particles and contained some rocks. A nail was also found in the soil. Three samples of both soil and compost were collected, each weighing approximately 3 – 4kg.

3.3 Elemental Analysis

Elemental Analysis was required before proceeding with the project in order to determine the heavy metal content of the soil, compost and bark mulch used at UBC. Pre-treatment of the samples was required prior to submitting to SGS Laboratories for elemental analysis. SGS Laboratories was chosen due to the fact that they are able to detect metal concentrations in samples to the nearest 0.1ppm.

3.3.1 Pre-treatment of Soil, Compost, and Bark Mulch

An initial amount of soil, compost, and bark mulch were placed in crucibles to be dried. Due to different estimated moisture content different quantities were used for the different types of material. The quantities taken from each of the bags were 450g, 360g, 400g, and 400g for soil, compost, fir bark mulch, and the hemlock-fir bark mulch respectively. The 12 samples were then dried in a convection oven at approx. 80 °C for 24 hr. After 24 hr, the samples were removed from the oven and allowed to cool. The crucibles containing the same type of material were then combined into composite samples. Two 200g samples (dry weight) were taken from each of the composite samples and placed into glass containers capped with plastic lids. The amounts of each sample sent for analysis is conveyed in Table 3.1.

Table 3.1 Samples and corresponding dry weights prepared for preliminary analysis

Type of Sample	Sample #	Dried Weight (g)
Hemlock/ Fir	1	203.2
	2	200.3
Compost	1	203.4
	2	203.7
Fir Mulch	1	210.8
	2	214.5
Soil	1	200
	2	200

3.4 Shaker Flask Analysis

The elemental analysis yielded data on the amount and types of heavy metals contained in the soil/compost and bark mulch samples. Because the samples contained significant amounts of heavy metals they were also analyzed in the shaker flask experiments. The experiments followed the US EPA Method 1312, the Synthetic Precipitation Leaching Procedure (SPLP) described in “Impact of Chromated Copper Arsenate (CCA) in Wood Mulch” by Timothy G. Townsend *et al.* 2003. Its purpose is to determine whether these heavy metals would leach out of the soil/compost and bark mulch.

3.4.1 Experiment Preparation

First all glassware was acid washed in a bath consisting of 20% HNO₃ Acid. The acid was composed of two litres of concentrated nitric acid in eight litres of distilled water. The samples were then dried in one L beakers for approximately 15 hr. The wet weight of the samples were 250g, 450g, and 400g for soil, compost and bark mulch respectively.

The dried compost and soil samples were combined at a 1:1 ratio in order to form one sample. Due to information obtained from John Metras⁴, they were combined at equal ratios due to the fact that this is the mixture combination typically used at UBC. The hemlock/fir mulch mixture was tested because it is used on Campus. Three duplicate weight samples of dried bark mulch and three duplicate weight samples of compost/soil mixture were weighed into 500mL Erlenmeyer flasks. Sample weights were based on a hypothetical metal leaching rates of 10%, 15%, and 20% and water quality guidelines. See Table 3.3 below. An additional two control samples containing only the acidified rainwater. For more information on selection of sample weights see Appendix A.

Table 3.2 Weights of Samples (in g) based on leaching rate and exceedance of water quality criteria

	10 % Leaching	15 % Leaching	20 % Leaching
Bark Mulch	30	15	7.5
Soil/Compost Mix	20	10	5

Ten litres of rainwater was collected from the rainwater catchment barrel from the landscape architecture farm at UBC. Rainwater water was acidified from a pH level of 6.0 to a pH level of 4.0 using a concentrated acid mixture composed of 40 g of HNO₃ and 60 g of H₂S. 0.350 L of acidified rainwater was added to each sample. 2 control samples containing only 0.350 L of acidified rainwater were also prepared. The rainwater was acidified due to the fact that flower beds at UBC are acidic.

Fourteen flasks were placed onto a shaker table and shaken for 72 hr at moderate speed. This was done in order to assure that the heavy metals had an adequate amount of mixing and time to leach.

3.4.2 Filtration

A water-activated vacuum filtration system was set up using a 1000 mL filter flask, 90 mm diameter Büchner funnel, funnel adaptor, and fast-flow filter paper to remove debris. Filters were replaced in between each sample, and the filter flask and funnel were acid washed in between bark mulch and control sample 1, and in between soil/compost and control sample 2.

All samples were passed through the vacuum filter starting with the low concentration bark mulch samples. After all bark much samples were filtered, one control was filtered, and then all soil/compost samples were filtered starting with the lowest concentration. The second control was passed through the filter at the end. For each sample, 0.250 L of filtrate was transferred into acid-washed Erlenmeyer flasks that were subsequently stoppered, and stored in a refrigerator for 24 hr. PH was recorded for each sample and is summarized below in Table 3.3.

Table 3.3 Final pH values of sample filtrates

Bark Mulch (g)	Soil/Com post (g)	Final Volume of Water (ml)	Final pH
7.5	0	342.5	4.0
7.5	0	342.5	3.0
15	0	335	3.5
15	0	335	4.2
30	0	320	4.0
30	0	320	4.2
0	5	345	5.7
0	5	345	5.6
0	10	340	5.8
0	10	340	6.1
0	20	330	6.2
0	20	330	6.0
0	0	350	2.9
0	0	350	3.7

* initial sample pH normalized to 4.0

All samples were taken to the ALS Environmental Analytical Lab, Vancouver, BC. Sample preservation was not recommended, because ALS were to filter each sample once more through 0.45 µm filter paper to remove particulate matter and to isolate only dissolved metals.

The concentrations of heavy metals were obtained by ALS using procedures adapted from “Standard Methods for the Examination of Water and Wastewater” 20th edition 1998 published by the American Public Health Association, and with procedures adapted from “Test Methods for Evaluating Solid Waste” SW-846 published by the United States Environmental Protection Agency (EPA). The instrumental analysis that was carried out in this experiment was atomic absorption/emission spectrophotometry (EPA Method 7000 series).

3.5 Storm Simulation Experiment

The final experiment was a simulated storm-runoff event. The samples of the leachate resulting from duplicate flowerbeds were analyzed for Arsenic, Cadmium, Zinc, Chromium, Copper, Lead, Magnesium, Manganese, Calcium and Potassium. This analysis was conducted to determine the concentration of these metals in the leachate samples and assess the leaching potential of bark mulch. The leachate values from test beds were compared with respective fresh water allowable limits for these metals (B.C. Provincial Approved Water Quality Guidelines, 1998; Chromium limit: www.state.vt.us/wtrboard/docs/appendixc.pdf). Two year and five year frequency storms were selected because of high probability of occurrence and therefore will most likely contribute to the leachate on a regular basis.

3.5.1 Simulated Rain Storm Events

The amount of water required to simulate the storm water event (2-5 year storm) was estimated by the rational method and intensity duration frequency curves of UBC (this assuming that the time of concentration is reached). For the rational method, the following were assumed;

Runoff coefficient = 0.9

Intensity of rainfall = 19 mm/hr.

The rational method indicated that 0.6 litre/min application rate was required, for up to 45 minutes (see Appendix C).

3.5.2 Test Bed Construction

Two 2.25m² adjacent beds were modified (in front of Microbiology). The area contained a bark mulch cover that had been applied within 3 months prior to the day of the experiment, and represented one of the freshest mulch beds on campus, according to landscape maintenance manager, David Smith.

The sides of each bed (Figure 3.1) were lined with plastic to keep runoff and simulated runoff confined to its respective bed. Approximately 3" of fresh bark mulch was spread over the entire area overlaying the existing soil/compost and bark mulch layer.

Ditches were dug into the soil to a depth of approximately 30 cm at the ends of each bed.

Plastic troughs were placed with the top edge aligned with the bottom of the mulch/compost layer to allow for collection of runoff.



Figure 3.1 Experimental test bed apparatus outside of Microbiology



Figure 3.2 Saturation of test bed apparatus

3.5.3 Storm Simulation Experimental Procedure

Prior to carrying out the experiment, the dry mulch was moistened with tap water (Figure 3.2). Due to the unavailability of rainwater, tap water from a nearby outside tap was used for this purpose. Water was added to the beds until roughly uniform seepage was observed at the collecting troughs.

Following moistening of the beds, 600 mL/min of water was manually sprayed evenly over each bed for a total of 45 minutes using graduated spray bottles. The amount of water at the 30 min

point represented a 2-year storm event while the 45 minute storm represented the 5-year storm event.

The heavy metal analysis required a sample size of 0.25 L.

During the experiment when 0.25 L of runoff water was collected in the troughs, it was transferred to plastic sample containers and the time of sample collection was recorded (Table 3.4). All samples were then filtered through 0.45 μm and sent to ALS Environmental for dissolved heavy metal analysis using the appropriate analysis for the expected concentration.

Table 3.4 Sample volumes and time required for collection

Bed	Sample	Runoff collection time (min)	Sample volume (mL)
1	1	14	235
	2	10.8	260
	3	10	255
	4	7	236
	5	9	260
2	1	28	229
	2	19	235
Control	1	N/A	218
	2	N/A	255

4.0 Results and Discussion

4.1 Elemental Analysis

The Soil/Compost and Bark Mulch samples were taken to SGS for heavy metals analysis. The results obtained are shown in Table 4.1.

Table 4.1 Results of Elemental Analysis

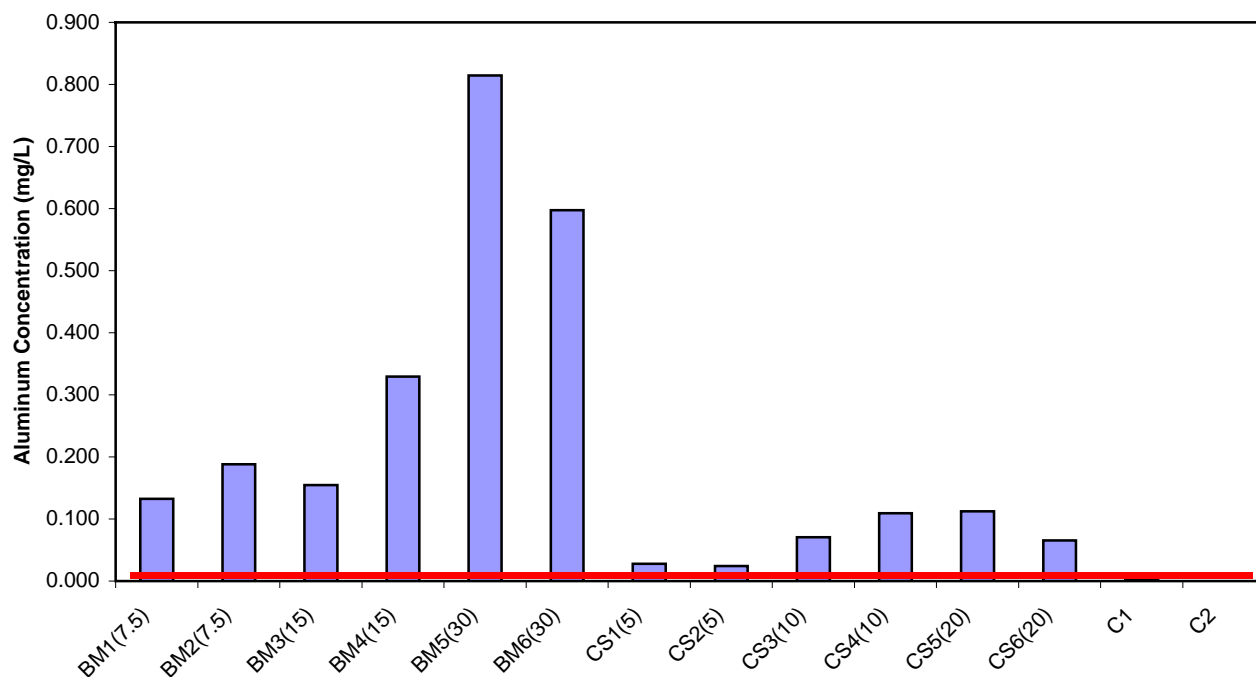
Metal	Compost		Soil		Fir Mulch		Fir/Hemlock Mulch	
	1	2	1	2	1	2	1	2
Zinc (Zn)	79	77	76	88	15	13	25	23
Chromium (Cr)	22	24	15	19	3	1	6	7
Arsenic (As)	2	0.8	1.2	2	< 0.1	< 0.1	< 0.1	< 0.1
Cadmium (Cd)	0.3	0.3	0.3	0.3	0.1	< 0.1	0.1	< 0.1
Mercury (Hg)	< 0.1	< 0.1	0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1
Lead (Pb)	15	9	11	10	< 1	< 1	< 1	< 1

The compost and soil samples had nearly the same heavy metal content. Zinc and Chromium were the major metals in the bark mulch. The hemlock-fir mixture samples have a higher metal content than the fir. Although these results depict compost and soil to contain a larger percentage of heavy metals than bark mulch, the metals could leach out of bark mulch at a higher rate. Further experiments were required in order to determine whether or not heavy metals would actually leach out from the samples.

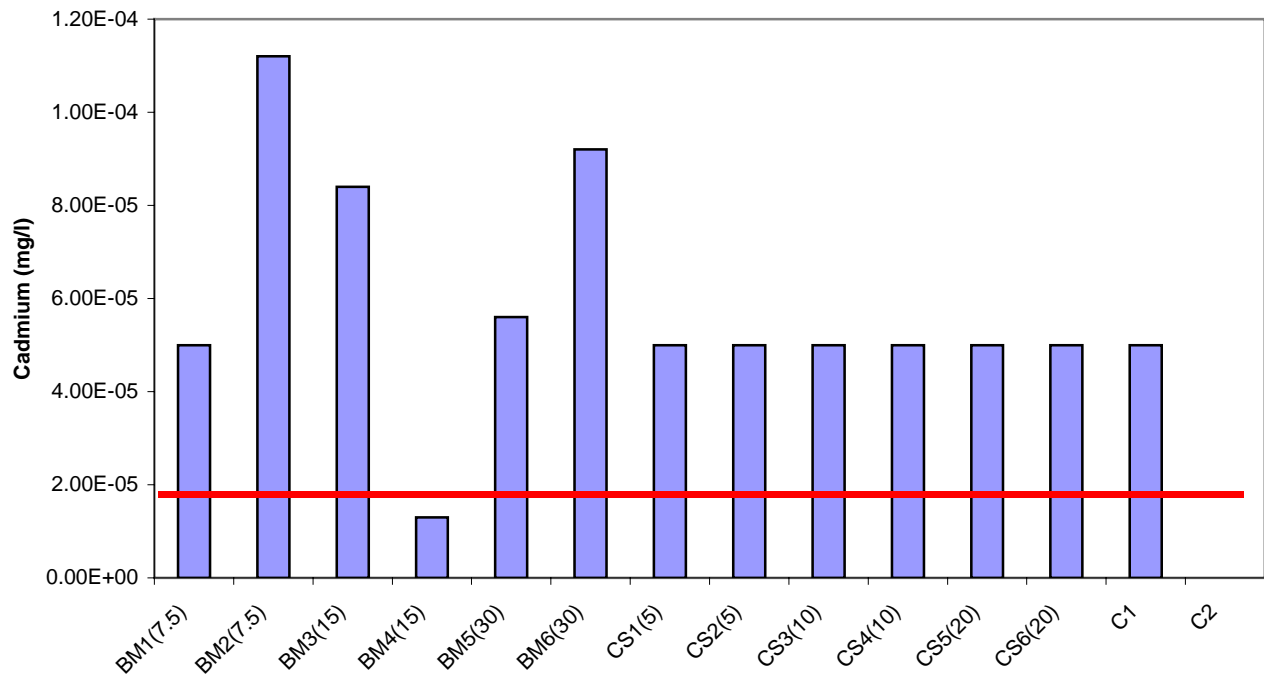
4.2 Shaker Flask

Average metal concentration from the rainwater was subtracted from all obtained filtrate values. Full results can be seen in Appendix B. Of the heavy metal scan over Al, As, Cd, Cr, Cu, Pb, and Zn, all heavy metals except for Cr leached above Canadian limits. It must be noted that Zn in the rain water exceeded water quality criteria (its source in the rain water collection barrel should be investigated as a means of source control). In most cases the concentrations of metals leached was

higher from the bark mulch samples than the soil/compost samples. Figures 4.1 – 4.5 illustrate the concentration of the metals for various samples.



**Figure 4.1 Filtrate Aluminum Concentrations for All Samples
(Red line Indicates Water Quality Limits)**



**Figure 4.2 Filtrate Cadmium Concentrations for All Samples
(Red line Indicates Water Quality Limits)**

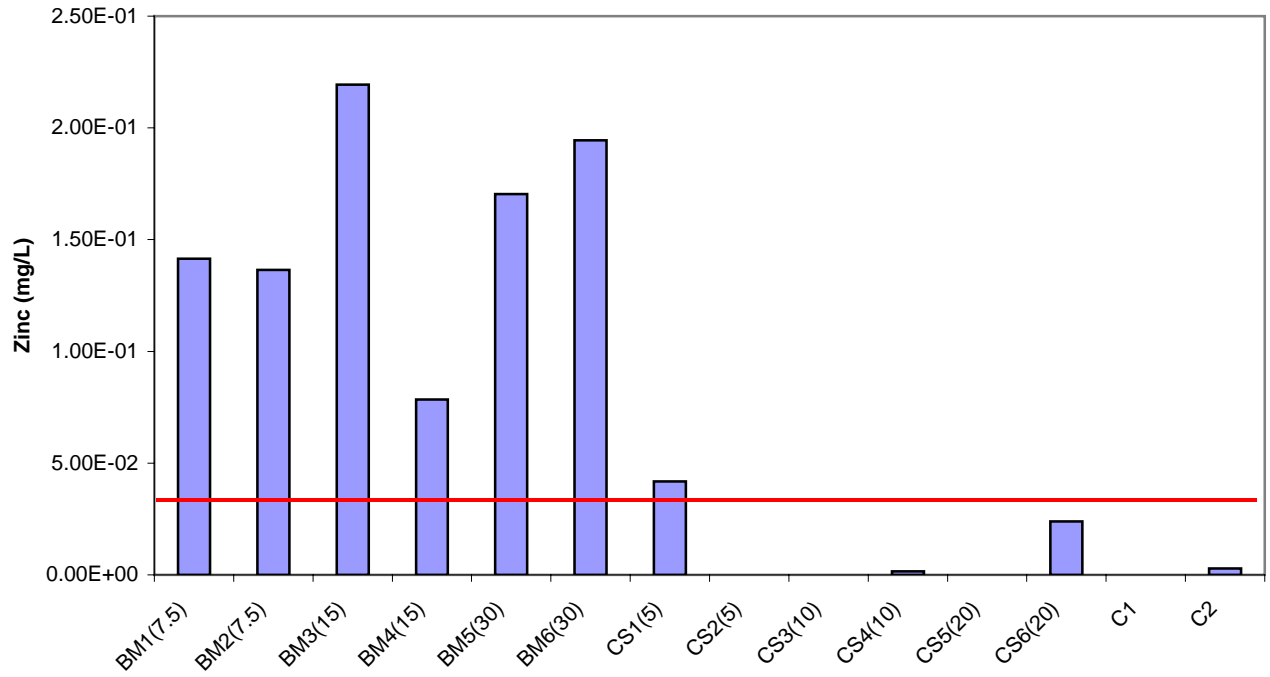
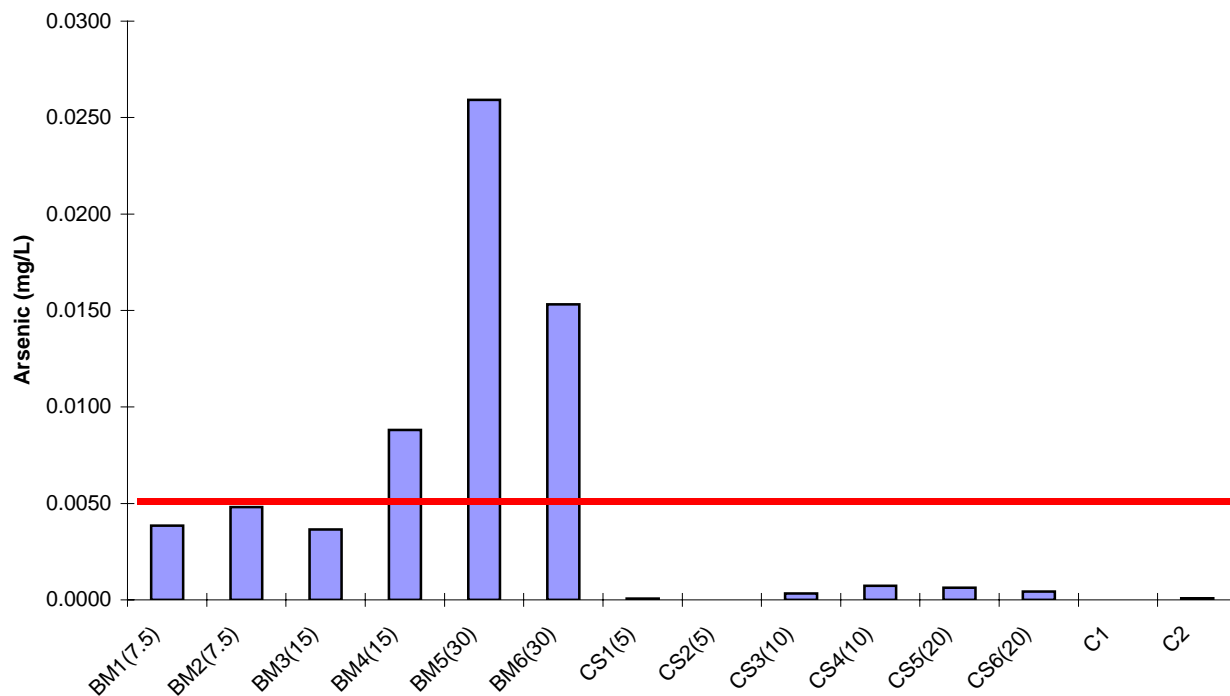
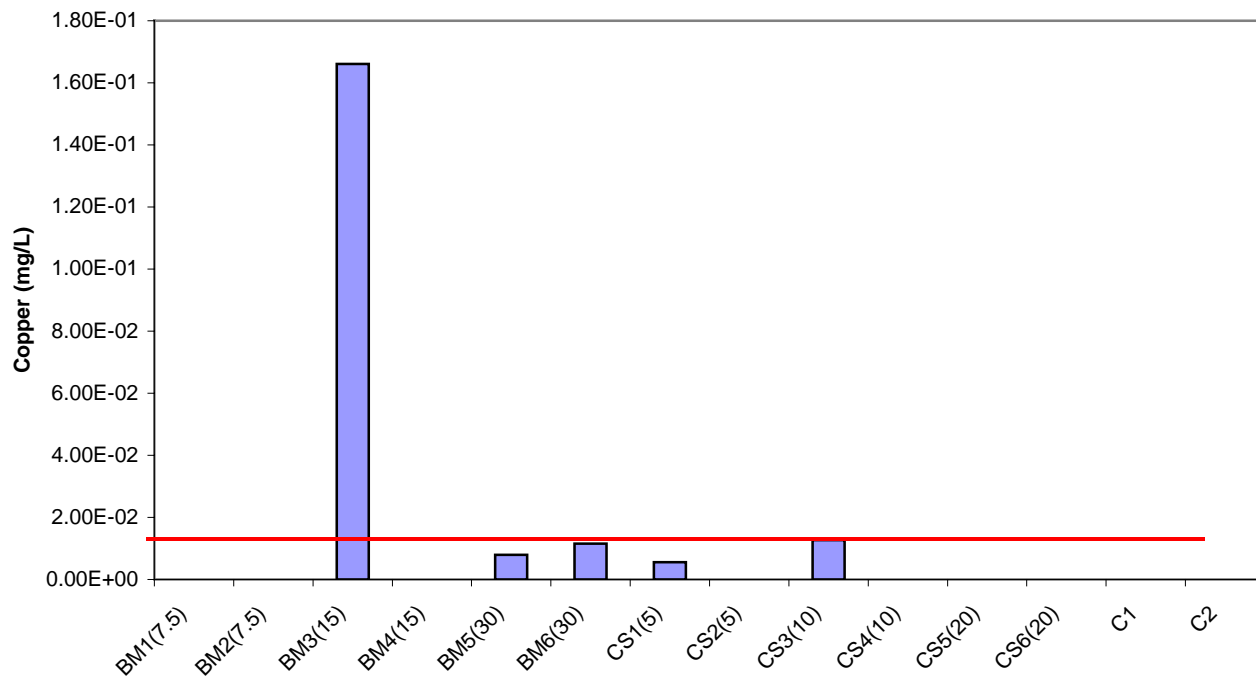


Figure 4.3 Filtrate Zinc Concentrations for All Samples (Red line indicates water quality limits)



**Figure 4.4 Filtrate Arsenic Concentrations for All Samples
(Red line Indicates Water Quality Limits)**



**Figure 4.5 Filtrate Copper Concentrations for All Samples
(Red line Indicates Water Quality Limits)**

Aluminium, Cadmium and Zinc were found to be in excess of water quality guidelines for all bark mulch samples (Figures 4.1-4.3). Arsenic and Copper were found to be in excess only for higher mass samples of bark mulch (Figures 4.4-4.5). Soil/compost leachate was above the allowable aluminium limits for Cadmium and Aluminium.

It was observed that the percent mass leached remained consistent for Aluminium and Arsenic, as seen by the higher concentrations released from the higher mass samples. For zinc, concentrations released remained relatively constant, meaning that the percent mass leached decreased with increasing sample weight. Thus, for zinc the leaching of metals seems to be diffusion-limited.

4.3 Storm Simulation

Allowable water quality limits for aquatic life and the results of leachate analysis for the two beds are presented in Table 4.2. The limits were obtained from the Canadian Council of Ministers of the Environment (CCME) Water Quality Index⁸. It was found that Cadmium, Aluminum and Zinc were 20, 75 and 1.7 times the allowable limits, respectively in one bed, and slightly above the limit in another bed for both simulated rain storm events.

Table 4.2 Concentrations of Heavy Metals in Run-off and Allowable Limits

	Test bed	As	Cd	Zn	Cr	Cu	Pb	Mg	Mn	Ca	K	Al
Sample Concentration (mg/L)	#1	0.0016	0.00034	0.052	0.0021	-0.1069	0.00085	6.93	1.07	20.15	17.33	0.37
	#2	0.0016	0.00020	0.035	0.0026	-0.1067	0.00037	4.87	0.63	15.72	15.83	0.30
Allowable Limits (mg/L)		0.00500	0.000017	0.030	0.6478	0.0020	0.00100	N/A	0.800	N/A	N/A	0.005

Figure 4.3 shows the runoff rate over the 45-minute simulated storm experiment. Much more runoff was observed in bed 1 as compared to bed 2. When the soil and compost layers were made, it was apparent that gravel was below the beds in some areas. Bed 2 might have contained more gravel,

and, thereby increasing infiltration in bed 2. The runoff rate in bed 1 reached a maximum at around 40 minutes after the start of the simulated 45-min storm event. This represents the time of concentration (TC) for the bed, or the time for simulated rainfall at the top of the bed to reach the bottom of the bed where samples were being collected. Due to the little runoff in bed 2, only two samples were able to be collected; thus the time of concentration in bed 2 was not determined.

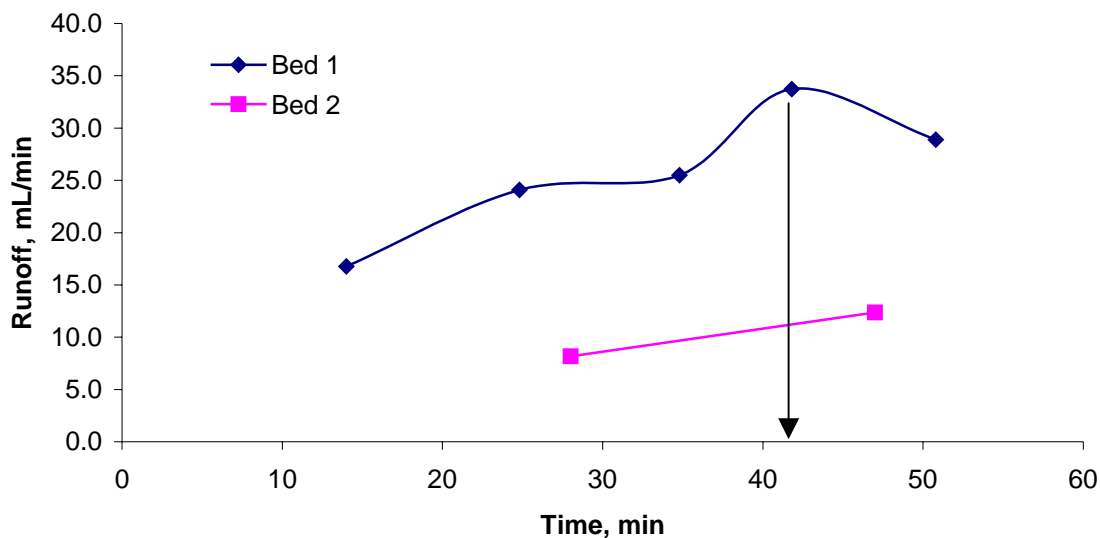


Figure 4.6 Runoff Discharge rate versus Time. Arrow indicates end of simulated rain event for the 45-min 5-yr rain storm event.

Five percent of UBC campus is covered with bark mulch as indicated by one of the campus utility authorities⁴. The best-case scenario, assuming metal-free rainwater, is then a 20-fold dilution of the runoff from mulch beds across campus when discharged into the environment. Thus for comparison purposes, the leachate results from the test beds were multiplied by 0.05% to represent the overall discharge concentration in the environment. This was then compared with allowable limits to determine whether runoff from bark mulch exceeds the water quality criteria as demonstrated in the following Table 4.3. It was found that even after the dilution of sample concentrations, Cadmium was

at the allowable limit, and Aluminium was three times the allowable limit. This is shown in Table 4.3 and graphically in Figures 4.7 and 4.8.

Table 4.3 Overall Discharge Concentration and Allowable Limits

	Test bed	As	Cd	Zn	Cr	Cu	Pb	Mg	Mn	Ca	K	Al
Overall Discharge Concentration (mg/L)	#1	0.00008	0.000017	0.0026	0.00011	-0.0053	0.000043	0.35	0.053	1.01	0.87	0.018
	#2	0.00008	0.000010	0.0017	0.00013	-0.0053	0.000019	0.24	0.031	0.79	0.79	0.015
Allowable Limits (mg/L)		0.00500	0.000017	0.0300	0.64780	0.0020	0.001000	N/A	0.800	N/A	N/A	0.005

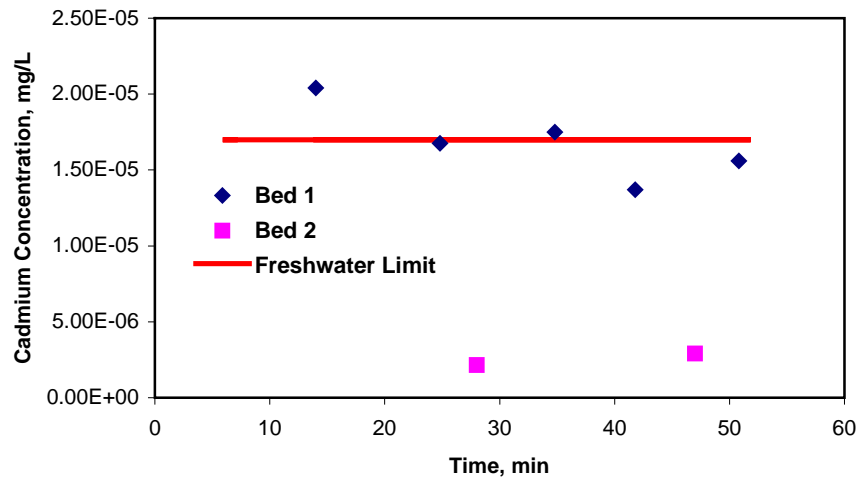


Figure 4.7 Cadmium Concentration in Overall Discharge

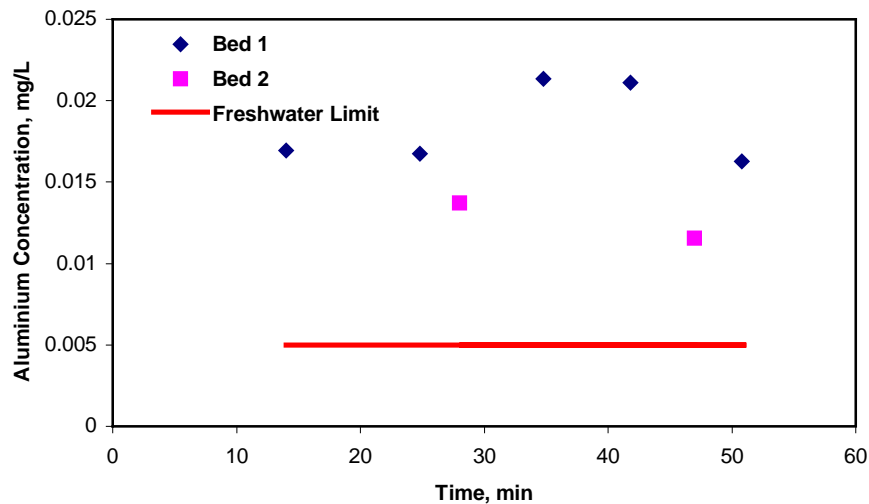


Figure 4.8 Aluminium Concentration in Overall Discharge

It should be noted that although some of the metals did not exceed the water quality criteria, it is evident that bark mulch is a contributor to the heavy metal concentration in the stormwater discharge. **Copper was absorbed by the mulch; this is indicated by negative values in Table 4.3 (it was exceedingly high in the tap water).**

Appendix E shows the leached concentrations of aluminium, arsenic, cadmium, calcium, chromium, copper, lead, magnesium, manganese, potassium, and zinc, without the effect of the control water. There appears to be no statistically significant relationship between concentration and time for the heavy metals, although there is a slight decrease in concentration with time for calcium, magnesium, manganese and potassium. This suggests that these four metals are more quickly leached out than the other heavy metals, which remain adsorbed to the bark mulch and/or compost for more than 45 minutes.

5.0 Conclusion and Recommendations

The main objectives of this project were to assess the presence of heavy metals in leachate from bark mulch and compost, and to examine alternative strategies to reduce the toxicity of surface water discharges into storm drains at UBC.

Hemlock/fir mulch and compost contain heavy metals, and compost contains more than hemlock/fir. The soil and compost contained nearly equivalent amounts, and this could have been due to cross contamination at the UBC yard waste collection facility. Results from 72 hr shaker flask tests indicated that fewer heavy metals leach out of the compost than bark mulch.

In simulated rainstorms representing two and five year storm events, fresh bark mulch contributed to campus heavy metal loadings. From the point of discharge of surface run off from bark mulch beds, experimental results showed that concentration of cadmium, aluminium and zinc in exceeded allowable limits for aquatic life. Even after taking into account the dilution, cadmium and aluminium remained at or above the limits.

One possible solution to reduce the concentration of cadmium and aluminium within bark mulch is precipitation. Precipitation causes the cadmium and aluminium contaminants to dissolve in the solution as a solid precipitate, which can then be filtered, centrifuged, or otherwise separated from the liquid portion. This method of pre-treatment of bark mulch should be performed before the bark mulch is spread over the UBC grounds in order to conform the EPA standards. Another method is use low-cost sorbents as mentioned in a previous report (CHBE 465, 2002 report).

However, the problem of heavy metal leaching from bark mulch can be avoided altogether if other ways to suppress weeds can be found. By removing these unwanted weeds manually, the use of bark mulch can become obsolete.

6.0 References

- Authors (various), 2002. Effectiveness of some low-cost sorbents for treating mixtures of heavy metals in runoff from the first major storm event after the extended dry period. Aquatic Habitat Design (CHBE 465) Report.
- Bailey, SE., Olin, TJ., and Bricka, RM., 1997. Low- Cost Sorbents, “Literature Summary,” Technical Report SERDP – 97-1.
- Bailey, SE; Olin, TJ; Bricka, RM; Adrian, DD., 1999. Review of Potentially Low- Cost Sorbents for Heavy Metals. Water Research [Water Res.], vol.33, no.11, pp 2469-2479.
- British Columbia Provincial Approved Water Quality Guidelines, 1998. (<http://wlapwww.gov.bc.ca/wat/wq/#guidelines>).
- Connell, D.W and G.J. Miller., 1984. Chemistry and Ecotoxicology of Pollution. John Wiley & Sons, NY.
- Cooper P. and Ung Y., 1997. Environmental impact of CCA poles in service. Paper no. IRG/WP 97-50087. Stockholm, Sweden: International Research Group.
- Hingston J., Collins C., Murphy R., and Lester J., 2001. Leaching of chromated copper arsenate wood preservatives: a review. Environ Pollut .111: 53-66.
http://www.epa.gov/owm/mtb/chemical_precipitation.pdf
- Manganese Limit: Ambient Water Quality Guidelines for Manganese (Overview Report) 2001. <http://wlapwww.gov.bc.ca/wat/wq/BCguidelines/manganese.html>
- Masri M.S., Reuter F.W., and Friedman M., 1974. Binding Metal Cations by natural substances. J. Appl Polymer Sci., 18 pp 675-681.
- Metras, John - Associate Director of Municipal & Bus Serv Central Shops, Land & Building Services of the University of British Columbia: Personal Interview: Sept 17, 2003.

- Olin T.J., Rosado J.M., Bailey S.E., and Bricka R.M., 1996. Low- Cost Sorbents Screening and Engineering Analysis of Zeolite for Treatment of Metals, Contaminated Water & Soil Extracts- final report SERDP 96-387, prepared for USEPA and SERDP.<http://www.asc2002.com/manuscripts/E/EP-01Standby.pdf>
- Osteras, A.N. and Greger, M., 2003. Accumulation of, and interactions between, calcium and heavy metals in wood and bark of *Picea abies*. *J. Plant Nut. Soil Sci.*, 166, 246-253.
- Pinamonti, F., Stringari, G., Gasperi, F. and Zorzi, G., 1997. The use of Compost, its effects on heavy metal levels in soil and plant. *Resources, conservation and Recycling*, vol. 21, no. 2, pp 129-143.
- Stilwell DE, Gorny K.D., 1997. Contamination of soil with copper, chromium and arsenic under decks built from pressure treated wood. *Bull Environ Contam Toxicol*, 58(1):22-29.
- Tanaka, J. and Ichikuni, M., 1982. Monitoring of heavy metals in airborne particles by using bark samples of Japanese cedar collected from the metropolitan region of Japan. *Atmospheric Environment*, vol 16, no.8 pp. 2015-2018.
- Tisdell, S.E. and Breslin, V.T., 1995. Characterization and leaching of elements from municipal solid waste compost. *Journal of Environmental Quality*, vol 24, no. 5., pp 827-833.
- ***Townsend, T.G. et al. (2003): Impact of chromated copper arsenate (CCA) in wood mulch; *The Science of the Total Environment* 309, (2003) 173-185
- Veera M. Boddu and Edgar D. Smith., 2002. A composite Chitosan Biosorbent for Adsorption of Heavy Metals from Wastewater. <http://www.asc2002.com/manuscripts/E/EP01Standby.pdf>
- Watson M.E . Fact Sheet., 2002. (<http://ohioline.osu.edu/anr-fact/0015.html>).
- Whittle, A.J. and Dyson, A.J., 2002. The fate of heavy metal in green waste Composting. *Environmentalist* vol 22, no. 1 pp 13-21.
- Yang, TC and Zall, RR., 1984. Adsorption of metals by natural polymers generated from sea food processing wastes. *Ind. Eng. Chem. Prod Res. Dev* 23 pp 168-172.

7.0 APPENDICES

APPENDIX A - Leachate Test Sample Mass Determination

Storm Water Hardness:	45.6
Avg. Allowable Chronic limits:	
As	190 ug/L
Cr(VI)	11 ug/L
Hg	0.012 ug/L
Cd = EXP(0.7852*LN(hardness)-3.49)	
=	0.6 ug/L
Pb = EXP(1.273*(LN(hardness)-4.705))	
=	0.3 ug/L
Zn = EXP(0.8473*(LN(hardness))+0.7614)	
=	54.5 ug/L

The objective was to obtain metal concentrations above detectable limits, as well as near chronic limits. If this degree of leaching could not be obtained in the shaker-flask experiment, it would not be advisable to continue with testing. The objective was to produce metal concentrations near the allowable chronic limits.

To get the predicted concentration, we must use the data from the elemental analysis, in ppm or ug/g, multiply by the grams of sample proposed to obtain ug of heavy metal. Multiply by a leaching factor, to account for what % of the heavy metal in the sample actually leaches, and then divide by the sample volume to obtain the predicted sample concentration.

For this example, we will use Cd because its chronic limit is low, and its concentration in the bark mulch and soil/compost was also low.

Elemental Analysis:

	BM sample	Soil/compost sample
ug/L Cd	0.1	0.3

Going by the bark mulch for this example, multiplying by a leaching factor, assumed to be 10 % of the Cd leaching, we obtain:

$$\text{ug Cd leached} = 0.1 * 0.1 \text{ ppm} = 0.01 \text{ ppm}$$

Pick a sample mass to use, and check if it will be sufficient to produce a high enough concentration

sample mass		30 g dry
sample volume = 350 mL - 50% moisture * BM sample mass / 100		
=		335 mL
	=	0.335 L

*takes into account 50 % moisture of BM at end of experiment

Multiply sample mass by expected ug of Cd leached, and divide by sample volume to obtain final concentration in ug/L.

$$\text{ug Cd leached} = 0.1 * 0.1 \text{ ppm} = 0.01 \text{ ppm}$$

Pick a sample mass to use, and check if it will be sufficient to produce a high enough concentration

sample mass		30 g dry
sample volume = 350 mL - 50% moisture * BM sample mass / 100		
=		335 mL
	=	0.335 L

*takes into account 50 % moisture of BM at end of experiment

Multiply sample mass by expected ug of Cd leached, and divide by sample volume to obtain final concentration in ug/L.

$$\text{final concentration} = (30 \text{ g sample}) * (.01 \text{ ug Cd / g sample}) / (.335 \text{ L}) = 0.896 \text{ ug/L}$$

This is greater than our allowable limit of 0.6 ug/L. It was found that no feasible sample weight would produce detectable concentrations for As, so Cd was the next on the list in terms of low metal concentration in the elemental analysis. Performing the same set of calculations, but for soil/compost, it was seen that assuming 10 % leaching, 20 g of dry sample could be used.

Assuming different leaching percentages (10 %, 20 %, 40 %), we just need to divide our sample mass by 2, thus the sample masses to be used were 30 g, 15 g, and 7.5 g for bark mulch, and 20 g, 10 g, and 5 g for soil/compost.

APPENDIX B – Shaker Flask Data

Average	N/A	N/A	N/A		0.19	0.000857202		0.0086991	0.0020205	0.0783472
Bark Mulch 1	7.5	0	4	0.142	0.004	<5E-5	0.001	0.009	0.000	0.198
Bark Mulch 2	7.5	0	3	0.198	0.005	0.000	0.001	0.014	0.001	0.193
Bark Mulch 3	15	0	3.5	0.164	0.004	0.000	0.001	0.183	0.014	0.276
Bark Mulch 4	15	0	4.2	0.339	0.009	0.000	0.002	0.008	0.001	0.135
Bark Mulch 5	30	0	4	0.824	0.027	0.000	0.003	0.025	0.001	0.227
Bark Mulch 6	30	0	4.15	0.607	0.016	0.000	0.003	0.028	0.003	0.251
Compost/Soil 1	0	5	5.72	0.037	0.001	<5E-5	<5E-5	0.023	0.000	0.098
Compost/Soil 2	0	5	5.6	0.034	0.001	<5E-5	<5E-5	0.013	<5E-5	0.046
Compost/Soil 3	0	10	5.75	0.080	0.001	<5E-5	0.000	0.030	0.000	0.046
Compost/Soil 4	0	10	6.11	0.119	0.001	<5E-5	0.001	0.015	0.000	0.058
Compost/Soil 5	0	20	6.17	0.122	0.001	<5E-5	0.001	0.015	0.001	0.046
Compost/Soil 6	0	20	5.97	0.075	0.001	<5E-5	<5E-5	0.013	0.000	0.081
Rain Water 1	0	0	2.89	0.014	0.001	<5E-5	<5E-5	0.020	0.001	0.054
Rain wWater 2	0	0	3.68	0.005	0.001	0.000	<5E-5	0.014	0.000	0.060

Hardness 70 EPA Chromium Limit = $\exp(0.8190(\ln(\text{hardness}))+3.688)$ = 0.665135

For As, Cd, Cu, Pb, and Zn, Canadian Water Quality Guidelines value are given

Values Subtracted from Average of Control Rain Water

Sample ID	Bark Mulch (g)	Soil / Compost (g)	Final pH	Aluminum	Arsenic	Cadmium	Chromium	Copper	Lead	Zinc
Limits				0.005	0.005	1.70E-05	0.64779912	0.002	0.001	0.03
Average	N/A	N/A	N/A	0.1876	0.1900	0.0009	0.0013	0.0087	0.0020	0.0783
Bark Mulch (7.5)	7.5	0	4	0.132	0.004	<5E-5	0.001	-0.007	0.000	0.141
Bark Mulch (7.5)	7.5	0	3	0.188	0.005	0.000	0.001	-0.003	0.001	0.136
Bark Mulch (15)	15	0	3.5	0.154	0.004	0.000	0.001	0.166	0.014	0.219
Bark Mulch (15)	15	0	4.2	0.329	0.009	0.000	0.002	-0.009	0.000	0.078
Bark Mulch (30)	30	0	4	0.814	0.026	0.000	0.003	0.008	0.001	0.170
Bark Mulch (30)	30	0	4.15	0.597	0.015	0.000	0.003	0.012	0.003	0.194
Compost/Soil (5)	0	5	5.72	0.028	0.000	<5E-5	<5E-5	0.006	0.000	0.042
Compost/Soil (5)	0	5	5.6	0.024	0.000	<5E-5	<5E-5	-0.004	<5E-5	-0.011
Compost/Soil (10)	0	10	5.75	0.070	0.000	<5E-5	0.000	0.013	0.000	-0.011
Compost/Soil (10)	0	10	6.11	0.109	0.001	<5E-5	0.001	-0.002	0.000	0.002
Compost/Soil (20)	0	20	6.17	0.112	0.001	<5E-5	0.001	-0.002	0.000	-0.011
Compost/Soil (20)	0	20	5.97	0.066	0.000	<5E-5	<5E-5	-0.004	0.000	0.024
Rain Water	0	0	2.89	0.004	0.000	<5E-5	<5E-5	0.003	0.000	-0.003
Rain Water	0	0	3.68	-0.004	0.000	0.000	<5E-5	-0.003	0.000	0.003

APPENDIX C – Preliminary Calculations for Storm Simulation Experiment

If	L=	3 m
	Width=	0.75 m
	Area=	2.25 m ²
	Estimated Runoff	
	Coefficient=	0.9
	Intensity=	16 mm/hr
Then		
	Qp=	0.00054 m ³ /min 0.540 L/min
	Flow rate used=	0.6 L/min

APPENDIX D - Budget

Budget (Updated Dec 15th)

* This is the current budget

Revenue	\$ 5,000.00	
Expenses:		
Sampling Costs (Experiment #1)	\$ 1,184.00	Cost for Sampling 8 containers (Experiment #1)
	-\$ 118.40	10% Discount
SGS Laboratories	\$ 1,065.60	
	\$ 74.59	Taxes
	\$ 1,140.19	
Sampling Costs (Experiment #2)	\$ 1,755.00	Cost for Sampling 13 containers (Experiment #2)
	-\$ 267.50	15% Discount
ALS Environmental	\$ 1,487.50	
	\$ 104.13	Taxes
	\$ 1,591.63	
Sampling Costs (Experiment #3)	\$ 720.00	Cost for 9 samples (Experiment #3)
	\$ -	0% Discount
ALS Environmental	\$ 720.00	
	\$ 60.00	Taxes
	\$ 780.00	
From chemistry store	\$ 327.25	(funnels, powder, etc) - Order 313818
	\$ 6.25	Order 313996
	\$ 62.16	Order 313995
	\$ 106.00	Rental Fees - Order 313996
Re-imbursements	\$ 96.97	(Set up for Experiment #3)
Miscellaneous	\$ 236.90	
Total Expenses:	\$ 4,347.35	
Net Income	\$ 652.65	Money still left over (as of December 15/2003)

APPENDIX E – Rainstorm Simulation Data

Concentrations of Elements Detected in Runoff Samples (mg/L)

	Q (ml/min.)	Time (min.)	As	Cd	Ca	Cr	Cu	Pb	Mg	Mn	K	Zn	Al
Bed 1	16.8	14.0	0.00173	0.000458	22.6	0.00242	0.00917	0.00349	7.29	1.14	17.4	0.0685	0.391
	24.1	24.8	0.00176	0.000385	22.6	0.00137	0.00711	0.00236	7.68	1.17	18.3	0.0606	0.387
	25.5	34.8	0.00183	0.000400	22.5	0.00318	0.00818	0.00355	7.24	1.09	17.8	0.0712	0.479
	33.7	41.8	0.00177	0.000324	21.6	0.00194	0.0064	0.00238	6.95	1.04	17.6	0.0540	0.474
	28.9	50.8	0.00186	0.000362	20.0	0.00172	0.00721	0.00287	6.26	0.927	16.9	0.0634	0.377
Bed 2	8.2	28.0	0.00185	0.000093	13.3	0.00129	0.00854	0.000802	2.76	0.203	14.0	0.0269	0.326
	12.4	47.0	0.00176	0.000108	13.0	0.00307	0.00792	0.00197	2.96	0.188	14.6	0.0286	0.283
Control 1	N/A	N/A	0.00018	0.00005	1.73	bd*	0.108	0.0019	0.156	0.00445	0.268	0.0111	0.0508
Control 2	N/A	N/A	0.00016	0.00005	1.70	bd*	0.121	0.00226	0.154	0.00415	0.263	0.0113	0.0528

*bd: below detection limit

Concentrations of Elements Detected in Runoff Samples After Subtracting Control (mg/L)

	As	Cd	Ca	Cr	Cu	Pb	Mg	Mn	K	Zn	Al
Bed 1	0.0016	0.00041	0.057	0.0024	-0.105	0.00141	7.14	1.14	20.9	17.1	0.339
	0.0016	0.00034	0.049	0.0014	-0.107	0.00028	7.53	1.17	20.9	18.0	0.335
	0.0017	0.00035	0.060	0.0032	-0.106	0.00147	7.09	1.09	20.8	17.5	0.427
	0.0016	0.00027	0.043	0.0019	-0.108	0.00030	6.80	1.04	19.9	17.3	0.422
	0.0017	0.00031	0.052	0.0017	-0.107	0.00079	6.11	0.92	18.3	16.6	0.325
Bed 2	0.0017	0.00004	0.016	0.0013	-0.106	-0.00128	2.61	0.20	11.6	13.7	0.274
	0.0016	0.00006	0.017	0.0031	-0.107	-0.00011	2.81	0.18	11.3	14.3	0.231

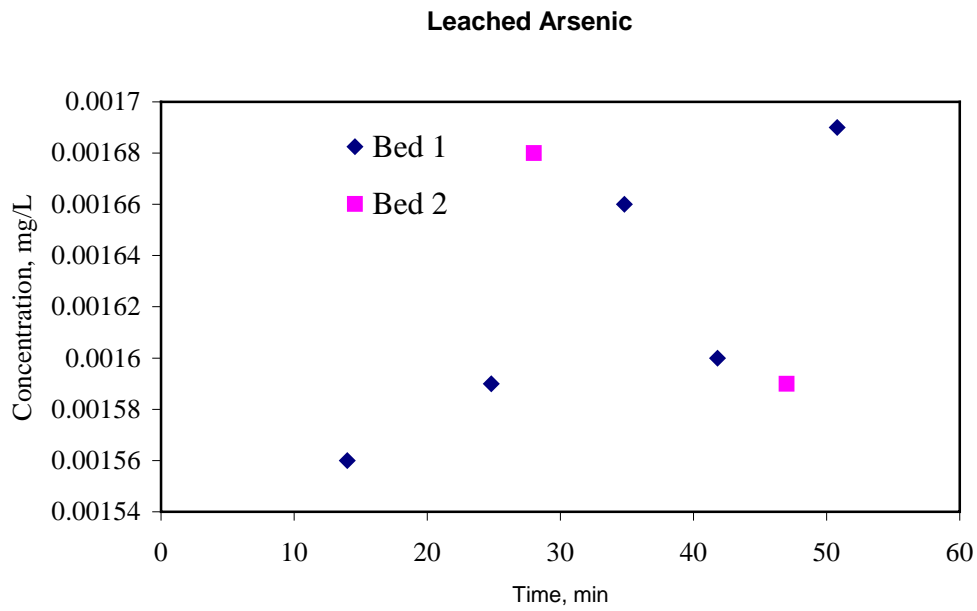


Figure E-1 Arsenic Concentration of Leachate versus Time

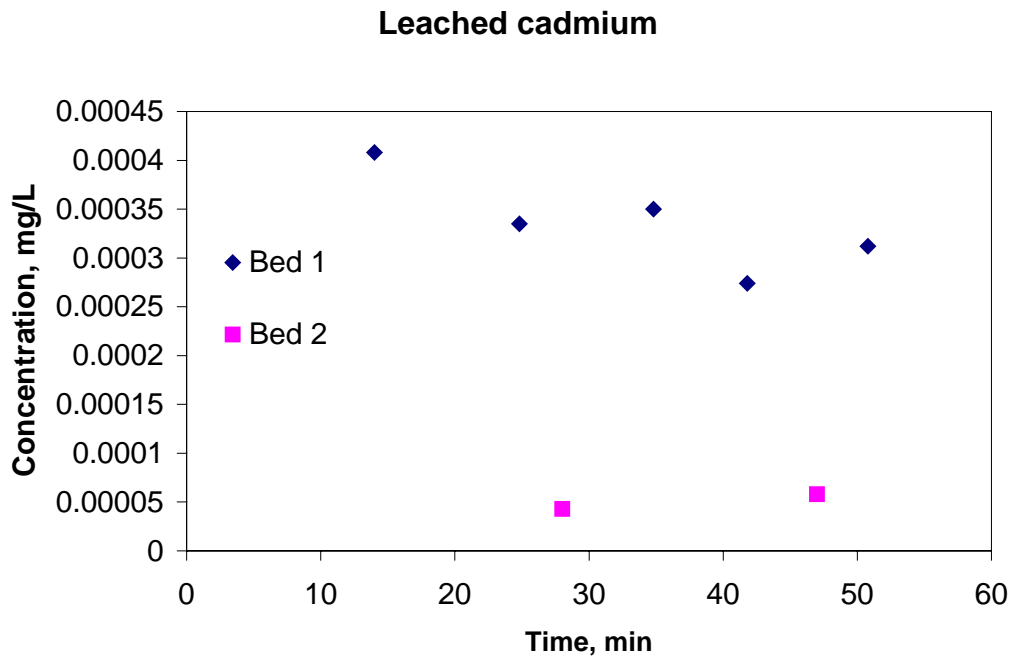


Figure E-2 Cadmium Concentration of Leachate versus Time

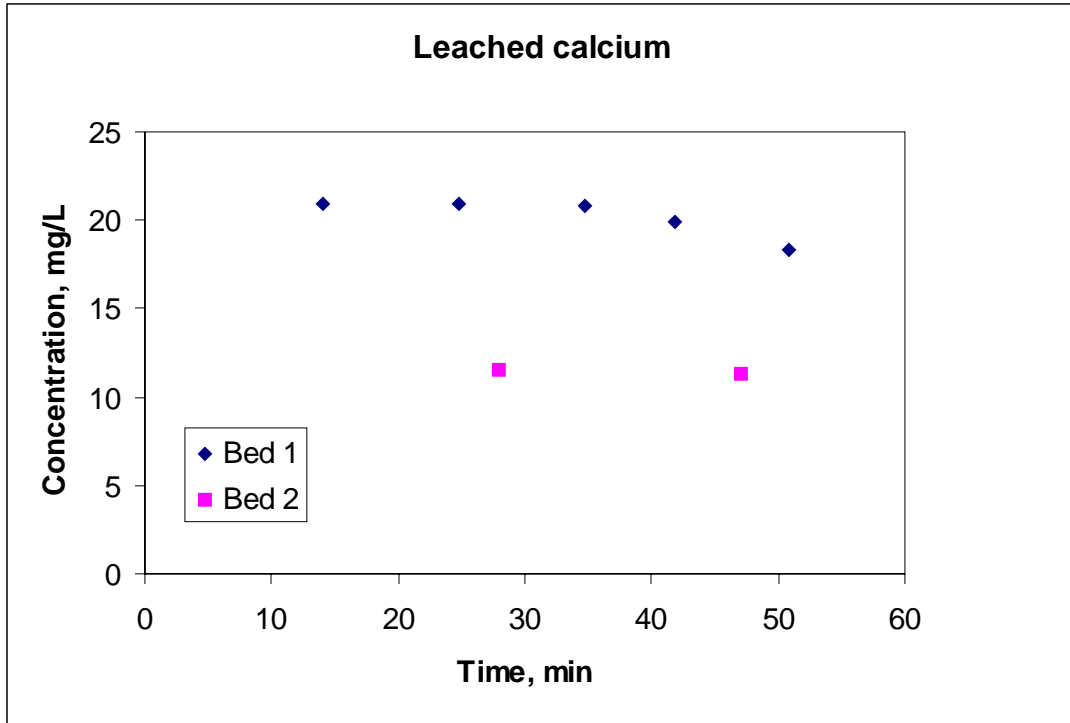


Figure E-3 Calcium Concentration of Leachate versus Time

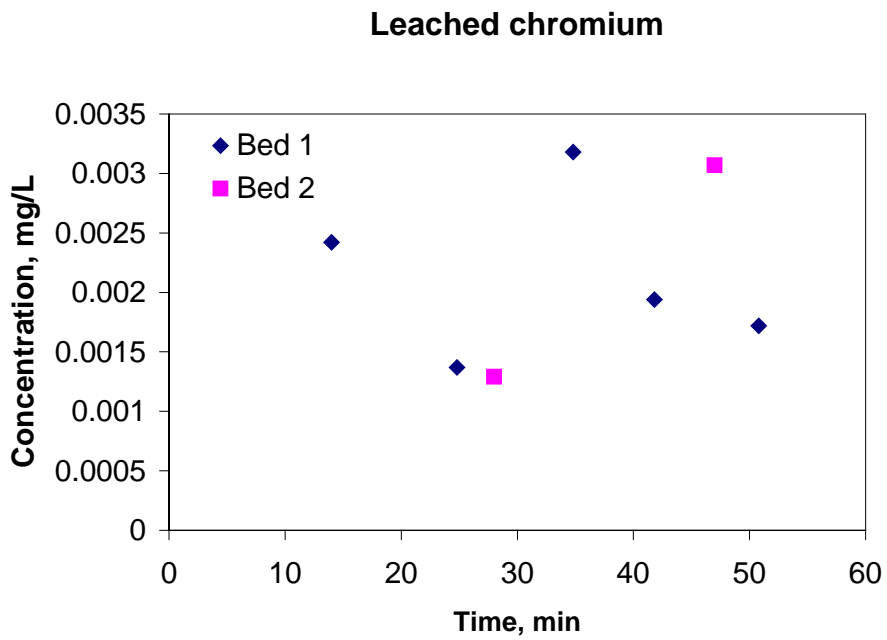


Figure E-4 Chromium Concentration of Leachate versus Time

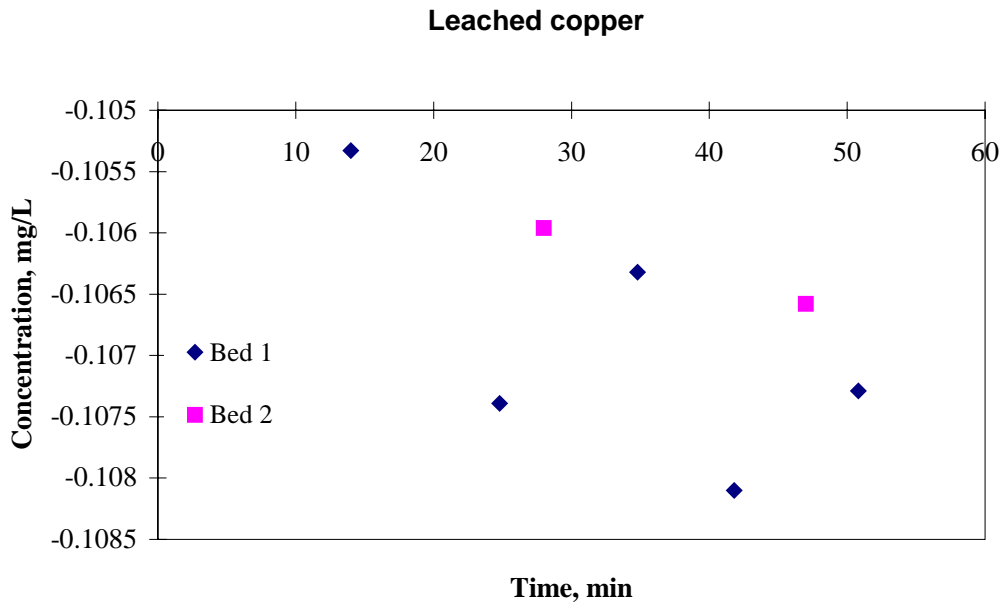


Figure E-5 Copper Concentration of Leachate versus Time

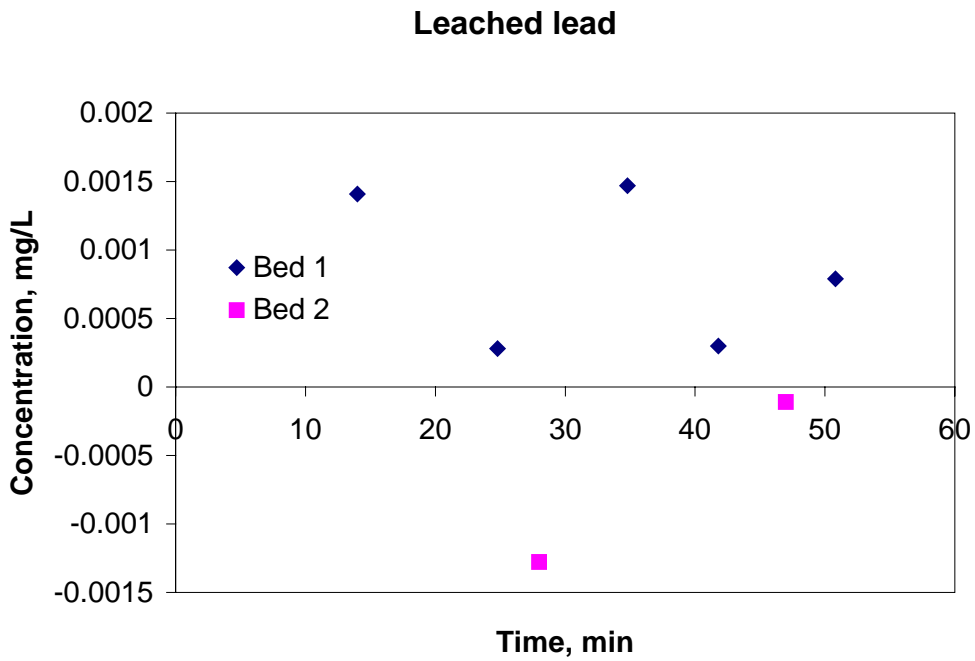


Figure E-6 Lead Concentration of Leachate versus Time

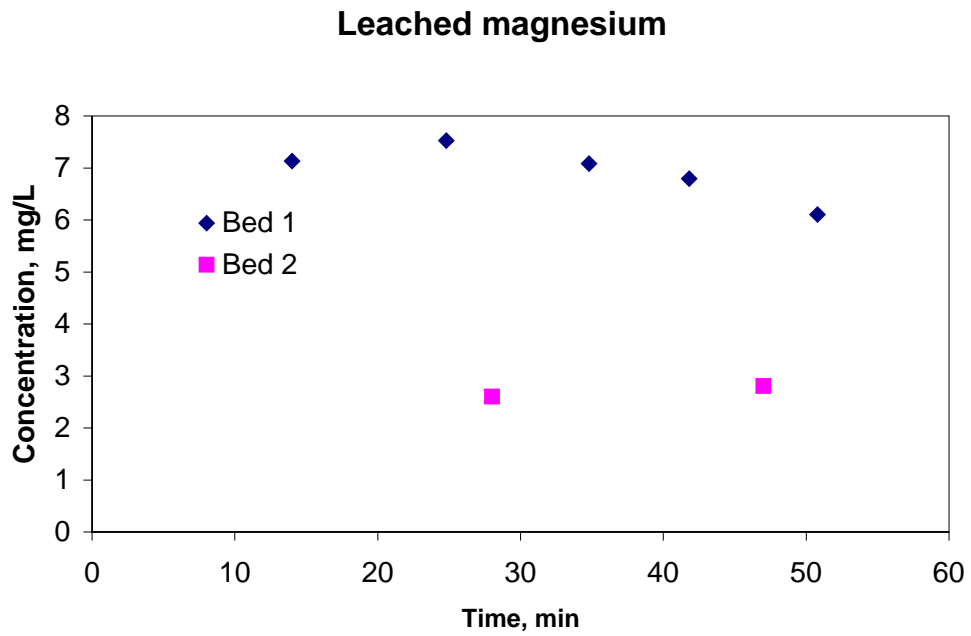


Figure E-7 Magnesium Concentration of Leachate versus Time

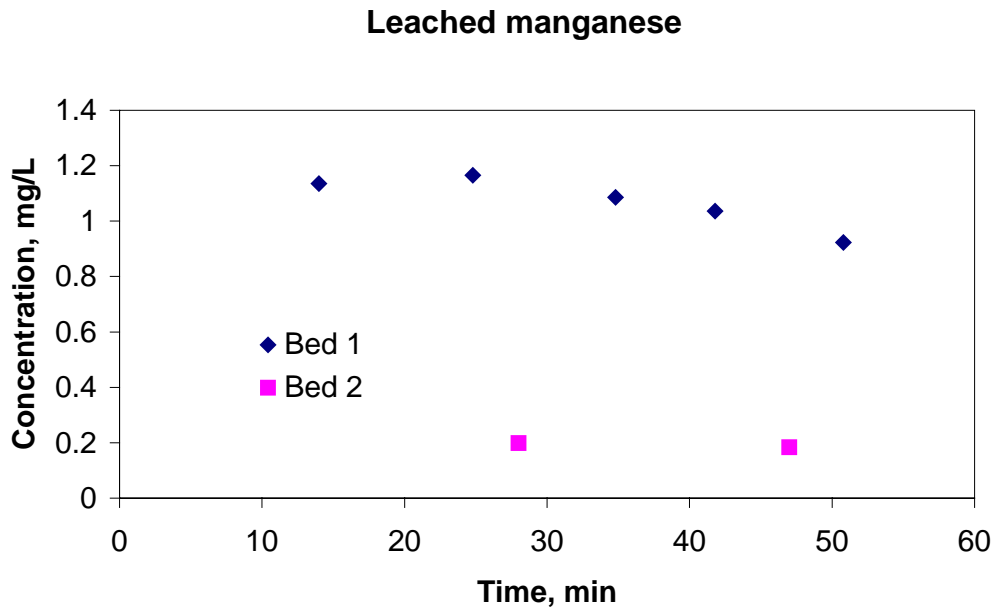


Figure E-8 Manganese Concentration of Leachate versus Time

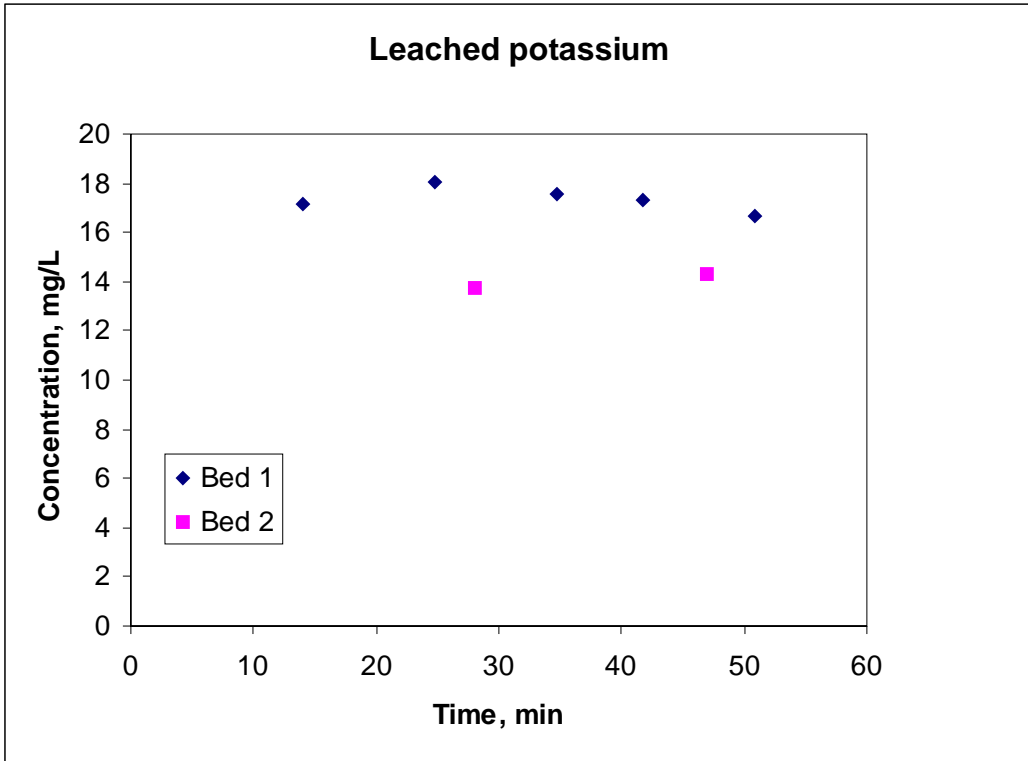


Figure E-9 Potassium Concentration of Leachate versus Time

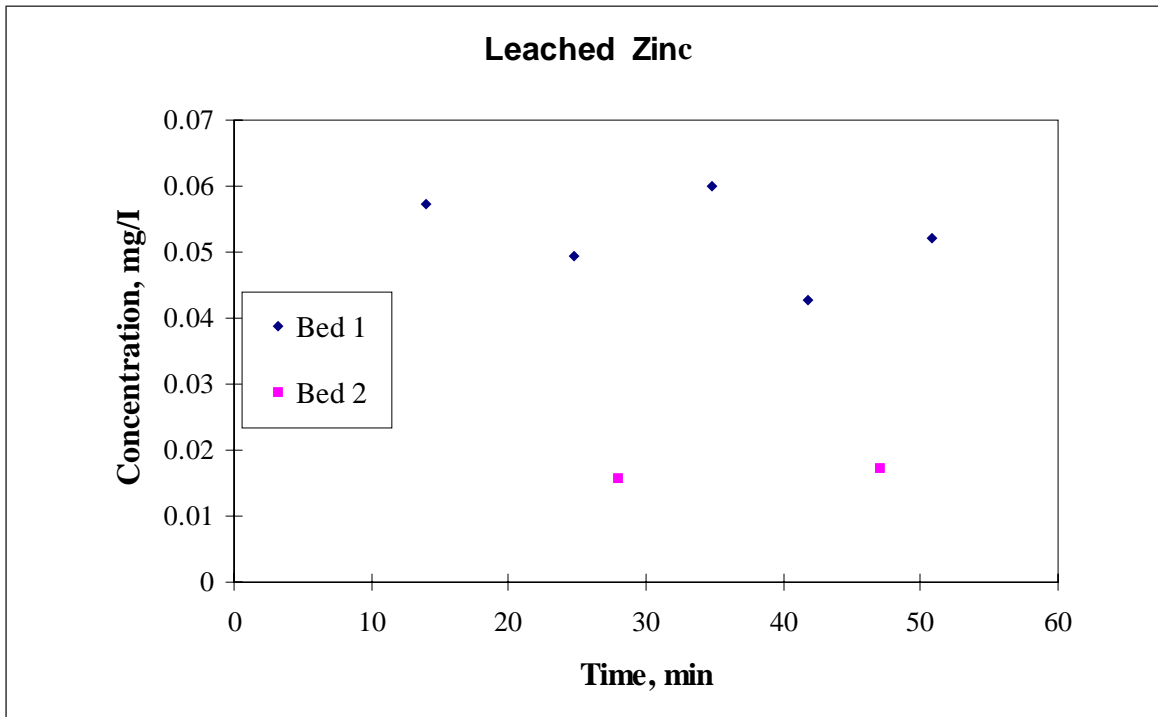


Figure E-10 Zinc Concentration of Leachate versus Time

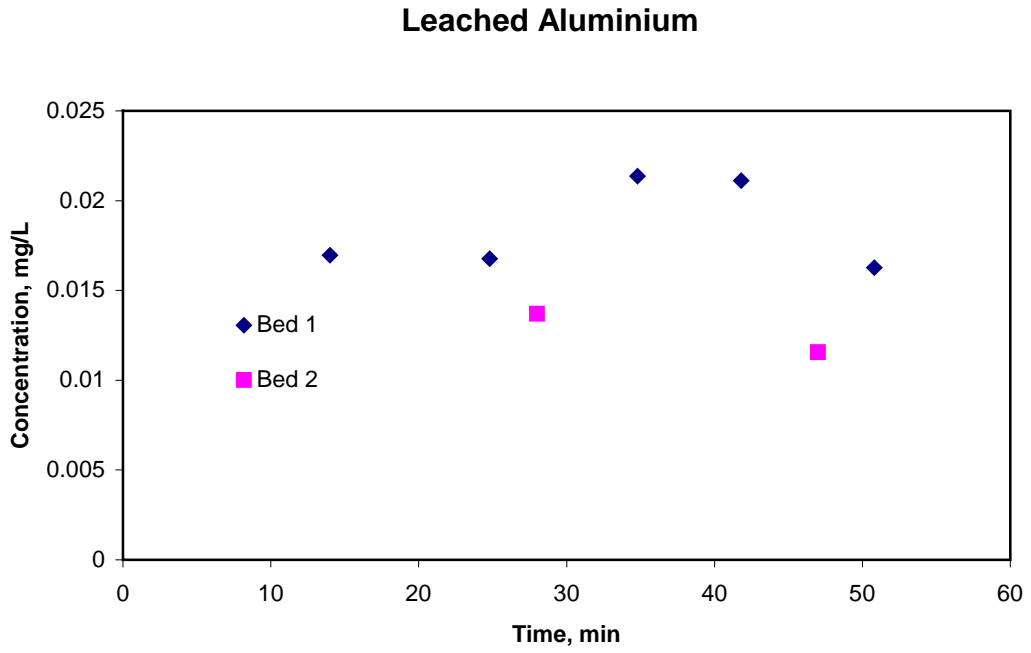


Figure E-11 Aluminium Concentration of Leachate versus Time

**Appendix. F Proposal Investigation of Heavy Metals in Bark Mulch and
Compost present on UBC Campous Grounds and Contributions to the
Contamination of Stormwater Run-off**

CHBE 465

Class of 2003

Dr. Royann Petrell

Balbir Arora

Nancy Chan

Derek Choy

Jenny Eng

Mehrdad Ghods

Pablo Gutierrez

Graham Kemp

Alvaro Reyes

Heather Schneider

Crissa Villamayor

November 5, 2003

University of British Columbia

Table of Contents

Summary	iii
1.0 Introduction	1
2.0 Methodology	4
2.1 Soil/Compost Sampling	4
2.2 Soil/Compost Characterization	4
2.3 Bark Mulch Sampling	4
2.4 Bark Mulch Characterization	5
2.5 Shaker Flask Analyses	5
2.6 Rainstorm-Leaching Test	5
3.0 Budget	7
4.0 Deliverables	7
5.0 Timeline	7
6.0 References	8
Appendix A: General Effects of Heavy Metals on Aquatic Life	11

Summary

The idea of this project was initiated by the research completed by the class of 2002 of CHBE 465, in which results suggested that bark mulch currently used on the University of British Columbia campus may be releasing toxic heavy metals through runoff during rainstorm events into sensitive aquatic habitats in the area. The purpose of this project is to determine whether the bark mulch/compost mixture current used on the UBC campus is capable of releasing heavy metals during rainstorm events. If this is found to be true, the amounts of metals released will be quantified. Samples of bark mulch and compost that are similar to the types used by UBC will be tested for their heavy metals content, then they will be subjected to conditions similar to those during a rainstorm event and it will be determined whether they will release any heavy metals.

It is expected that this project will operate on a budget of approximately \$5000. In September 2003, team members, students enrolled in the CHBE 465 class, will be introduced to the project and be allowed to familiarize themselves with any related background materials. The students will be divided into two main groups, focusing on different aspects of the project. Procedures for sample collection and testing will be drafted by the end of September. In early October, samples of bark mulch and compost will be collected; these samples will be prepared and shipped to external testing facilities for various types of analysis. By December 2003, quantified results will have been obtained and analyzed, leading to a formal report that evaluates the impact of the use of bark mulch on aquatic habitats, and suggest possible solutions.

1.0 Introduction

Urban development has created an impermeable layer of buildings and pavement, and altered natural drainage systems to accommodate the resulting increase in flows. During storm events, pollutants from fertilizers, pesticides, concentrated animal waste, wood residues and automobile emissions can be carried via runoff into streams. The change in flow patterns and the contaminated waters have destroyed or endangered aquatic habitat. On the University of British Columbia, these contaminants are transported during rainstorm events into the storm sewer network (old stream system) and, ultimately, into the nearby ocean.

Students of the Aquatic Habitat Design course in 2002 studied low-cost sorbents that may be used to absorb heavy metals from stormwater. Preliminary sampling of UBC's stormwater outfalls indicated that the discharge of substances harmful to fish or other marine organisms at the majority of stormwater outfalls commonly exceeded both the Provincial Approved Water Quality Guidelines as well as the Federal Environmental Quality Guidelines (<http://wlapwww.gov.bc.ca/wat/wq/#guidelines>). The results indicated that concentrations of arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn), were all above the levels stated in the Provincial Approved Water Quality Guidelines. Of these metals, copper and zinc were found to be above water quality limits at concentrations of 0.130 and 0.120 mg/L respectively (CHBE 465 Report, 2002). The general effects of heavy metals on aquatic life are described in Appendix A, while the specific effects of arsenic, cadmium, copper, lead and zinc are discussed in Appendix B.

There are many possible contributors responsible for releasing heavy metals into the stormwater. Recent research has shown that these heavy metals are present in bark mulch (Tanaka and Ichikuni, 1982), which leads to the suspicion that bark mulch is a possible source of the heavy metals leachate at

UBC. Mulch consisting of hemlock and fir bark is widely used on the UBC campus grounds for landscaping purposes, providing moisture retention and weed suppression. Approximately three to four inches of bark mulch is applied to each newly formed landscape site, with the re-application of one to two inches every two years thereafter. This amounts to approximately 1900 cubic yards of bark mulch used, at an average cost of \$20,000 annually (John Metras interview).

There is also a possibility that the heavy metals are released by compost that is also laid on the UBC campus (See Table 1). The compost is derived by composting yard waste collected on campus in large open piles on South Campus at UBC. When needed, mature compost is mixed with soil and often laid below the bark mulch. Therefore, it is possible that the compost, or a combination of the compost and bark mulch, is responsible for the release of heavy metals.

This main objective of this project, performed in conjunction with the UBC Social, Ecological, Economic Development Studies (SEEDS), is to assess the presence of heavy metals in leachate from bark mulch and compost, and to examine alternative strategies to reduce the toxicity of surface water discharges into storm drains at UBC. Local rainfall conditions that may cause desorption of heavy metals from the mulch will also be investigated. If the bark mulch and compost prove to be a significant source of pollution, recommendations will be made to UBC concerning them.

Table 1: Chemical Compositions of Compost (Composting Council of Canada)

Parameter	1996	1997	CCME limit for Type A and AA compost
	g Kg⁻¹		
Dry Matter	449	458	
Kjeldahl N	9.9	20.07	
C ^x	253	253	
P ^x	2.23	6.71	
K ^x	3.25	7.55	
Ca ^x	12.78	36.07	
Mg ^x	2.95	3.88	
S ^x	2.69	4.39	
Na ^x	1.03	4.07	
Fe ^x	12.84	12.80	
Mn ^x	1.00	1.11	
	mg Kg⁻¹		
Cu ^x	170	270	100
Zn ^x	370	610	500
B ^x	10	30	
Pb ^x	99	14	150
Hg ^x	1	1	0.8
As ^x	7	2	13
Se ^x	1	1	2
Mo ^x	12	9	5
Cd ^x	3	2	3
Co ^x	11	6	34
Cr ^x	21	11	210

^xDetermined by Walkley Black Method

^xDetermined from nitric acid digest

2.0 Methodology

This section contains the proposed methods and procedures for sample collection and preparation for the heavy metal tests, such as the elemental analysis, shaker flask experiment and the rainstorm-leaching test. Once these tests are completed, different methods for heavy metals removal appropriate to UBC will be analysed. All chemical analyses will be conducted off-campus at approved testing facilities for environmental investigations at prices ranging from \$80 to \$120 per sample.

2.1 Soil/Compost Sampling

Soil and compost samples will be collected from the soil and mature yard waste compost piles on the UBC campus; three samples will be collected from each pile for a total of six samples. The samples will be collected from different locations of each pile to ensure that the samples are an accurate representation of the contents of the site; all samples will be collected from approximately 30cm below the surface of the pile because material on the surface have been exposed to the environment and any possible heavy metals may have already leached out.

2.2 Soil/Compost Characterization

The samples of soil and compost will be dried in crucibles inside a convection oven at 80°C for at least 24 hours to remove moisture. After sufficiently cooling, 200g of the dried samples will be placed in glass containers and capped with plastic lids. The prepared samples will be sent to an external company for elemental analysis of heavy metals.

2.3 Bark Mulch Sampling

Samples of the bark mulch will be collected at Fraser Richmond Biocycle, which supplies the mulch purchased by UBC. There is no system to identify and record the species of mulch in piles on the plant. However, since the hemlock/fir mixture is distinguishable from pure fir mulch due to its red colour, samples will be collected from fir mulch and hemlock/fir mulch mixture piles using garbage bags.

2.4 Bark Mulch Characterization

The samples of mulch will be placed on a baking sheet and dried in a convection oven at 80°C for at least 24 hours until the moisture is removed. After sufficiently cooling, 200g of the dried samples will be placed in glass containers and capped with plastic lids. The prepared samples will be sent to an external company for elemental analysis.

2.5 Shaker Flask Analyses

The elemental analysis will yield data on the amount and types of heavy metals contained in the soil/compost and bark mulch samples. Samples containing significant amounts of heavy metals will be tested in the shaker flask experiments. The experiments will follow the US EPA Method 1312, the Synthetic Precipitation Leaching Procedure (SPLP) described in “Impact of Chromated Copper Arsenate (CCA) in Wood Mulch” by Timothy G. Townsend et al. Its purpose is to determine whether these heavy metals will leach out of the soil/compost and bark mulch.

2.6 Rainstorm-Leaching Test

If it is found that heavy metals leach out of the samples in the shaker flask analyses, a rainstorm-leaching test will be conducted. A two-year rainstorm event will be simulated in order to determine quality of the runoff. The dimensions of the leachate bed will be similar to typical flowerbeds on the UBC campus.

3.0 Budget

At this point there is limited information on the budget due to the fact that our future courses of action are dependent upon the results of our preliminary tests. The following table shows an estimate of the costs that will be incurred:

Table 2: Estimated Budget

Total Funds	\$5,000.00
-------------	------------

Expenses:		Explanations
		Cost for
Elemental Analysis	\$1140.00	Containers and Analysis
Shaker Flask Analysis	\$1100.00	Chemical Analysis
Rainstorm-Leaching Test	\$100.00	Supplies
	\$2650.00	Chemical Analysis
	<u>\$10.00</u>	Transportation
Cash remaining	\$0.00	

4.0 Deliverables

An oral and written report will be given in return for the funds to support the project.

5.0 Timeline

The actual schedule will be subject to return periods for the chemical analyses. The approximate schedule follows:

Table 3: Proposed Timeline

Elemental Analysis	End of September
Shaker Flask Analysis	End of October
Oral Presentation of Preliminary Results and Discussion of Rainstorm-Leaching Test Design	End of October
Rainstorm-Leaching Test	End of November
Final Report	End of November

6.0 References

Al Asheh, S; Banat, F, Environmental Geology, Vol. 40, no. 6, pp. 693-698. 23 Mar 2001

An H.K., Park B.Y. and Kim D.S. (2001). Crab Shell for the Removal of Heavy Metals from Aqueous Solution. Water Res. 35(15): 3551 – 3556

Bilinski, E. and Jonas, R.E.E. (1973). Effects of cadmium and copper on the oxidation of lactate by rainbow trout (*Salmo gairdneri*) gills. J. Fish. Res. Bd Can 30(10): 1553-1558

BRITISH COLUMBIA APPROVED WATER QUALITY GUIDELINES (CRITERIA) 1998
(<http://wlapwww.gov.bc.ca/wat/wq/BCguidelines/approved.html>)

British Columbia Ministry of Water, Land, Air, and Parks Protection
<http://wlapwww.gov.bc.ca/wat/wq/BCguidelines/approved.html>

Brown P.A., Gill S.A. and Allen S.J. (2000). Metal Removal from Wastewater using Peat. Water Res. 34(16): 3907 – 3916

Buhl K.J. (1997). Relative Sensitivity of Three Endangered Fishes, Colorado Squawfish, Bonytail, and Razorback Sucker, to selected Metal Pollutants. Ecotoxicology and Environmental Safety 37: 186 – 192

C. Kenndy, Fish Respond to Toxic Environments, International Congress of Biology of Fish. July 1998.

Cadmium, Safety and Health Topics, US Department of Labour, Occupational Safety and Health Administration, May 8, 2002 (www.osha.gov)

Connell, D.W., G.J. Miller. 1984. Chemistry and Ecotoxicology of Pollution. John Wiley & Sons, NY.

Dambies, L. 2001. Research Work: Arsenic Removal Technologies. URL:
<http://ldambies.free.fr/arsenictechnologies.html>

Davis A.P., Shokouhian M., Ni S. (2001). Loading Estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. Chemosphere, Vol. 44, pp. 997 – 1009

Gardner, G.R., and La Roche, L.G. (1973). Acute toxicity to an estuarine teleost of mixtures of cadmium, copper and zinc salts. J. Fish. Biol. 5: 131-142

<http://www.chilternkoi.nildram.co.uk/Copper%20and%20koi.htm>

<http://www.epa.gov/opptintr/lead/leadinfo.htm>

<http://www.nrdc.org/water/pollution/storm/chap2.asp>

http://www.stormwaterinc.com/products/pl_media.shtml

Jain S.K. (1999). Protective role of zeolite on short and long term lead toxicity in the teleost fish. Chemosphere 39(2): 247 – 251

Kennish, M.J. 1992. Ecology of Estuaries: Anthropogenic Effects. CRC Press, Inc., Boca Raton, FL.

Lanphear B.P., Roghmann K.J. (1997). Pathways of Lead Exposure in Urban Children. Environ. Res. 74: 67-73

Liu X., Hopke P.K. and Cohen D. (1995). Sources of fine particle lead, bromine, and elemental carbon in southeastern Australia. The Sc. of the Total Environ. 175: 65 – 79

Macdonald A., Silk L., and Schwartz M. (2002) A Lead-gill binding model to predict acute lead toxicity to rainbow trout. *Comparative Biochemistry and Physiology, Part C* 133: 227 – 242

Mandal, B.K. and Suzuki, K.T. 2002. Arsenic around the world: A review. *Talanta* 58:201-235.

Matlock M.M., Henke K.R., Atwood D.A. (2002) Effectiveness of commercial reagents for heavy metal removal from water with new insights for future chelate designs. *J. Hazardous Mat. B92*: 129 – 142

McKann, K. and Olsen, L. (1994) “Pollutant removal efficiencies of the Greenwood Urban Wetland stormwater treatment system”, *Lake and Reservoir Management*: 9(2): 97.

Metras, John: Personal Interview: Sept 17, 2003.

Ministry of Technology, U.K. (1970). *Water Pollution Research 1969*, p. 62. London, H.M.S.O.

Nriagu, Jerome, *Zinc in the Environment, Part I: Ecological Cycling*

OECD Workshop on Sources of Cadmium in the Environment, Summary of Proceedings, Organization for Economic Co-operation and Development, Sweden, October 16-20, 1995

Provincial Approved Water Quality Guidelines and Federal Environmental Quality Guidelines (<http://wlapwww.gov.bc.ca/wat/wq/#guidelines>).

R. Kelein, *Preventing Damage to 600 miles of Maryland Streams, Etlands, Rivers, & Tidal Waters*. Community & Environmental Defence Services. 1988

Rashed M.N. (2001) Lead removal from contaminated water using mineral adsorbents. *The Environmentalists* 21: 187 – 195 (2001)

Riordan C., McHale A.P. (1998) Removal of lead from solution using no-living residual brewery yeast. *Bioprocess Eng.* 19: 277 – 280

Santa Clara Valley Nonpoint Source Control Program. 1992. Source Identification and Control Report.

Schwuger M.J., Subklew G., Woller N. (2001). New alternatives for wastewater remediation with complexing surfactants. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 186: 229 – 242

Strnadova N., Schejbal P. (1997) The removal of metals by improved chemical precipitation. *European Water Pollution Control* 7(6): 29 – 32

Tanaka, J; Ichikuni, M. 1982. Monitoring of heavy metals in airborne particles by using bark samples of Japanese cedar collected from the metropolitan region of Japan. *Atmospheric Environment*, vol. 16, no.8 pp. 2015-2018.

The Causes of Urban Stormwater Pollution The National Resources Defence Council

Tox FAQ's for Cadmium, Agency for Toxic Substances and Disease Registry,
<http://www.atsdr.cdc.gov/tfacts5.html>

US Environmental Protection Agency

Waste Management Branch and Ministry of Environment, Developing Criteria and Objectives for Managing Contaminated Sites in British Columbia, 1989.

<http://wlapwww.gov.bc.ca/wat/wq/BCguidelines/approved.html>)

Woodward Clyde Consultants

Yin, P. Yu, Q. and Kaewsarn, P. (2001) Biosorption and desorption of cadmium(II) by biomass of *Laminaria japonica*, *Environ. Technol.* 22(5): 509-514.

Appendix A: General Effects of Heavy Metals on Aquatic Life

The following is an excerpt from the CHBE 465 2002 report:

"Heavy Metals" is a quasi-scientific term used to describe a group of toxic metallic elements and their compounds. A few are known to travel long distances through the atmosphere via the Grasshopper Effect. Under certain circumstances, exposure to high levels of these metals in the environment has been linked to adverse effects on aquatic wildlife, including:

- 1) Subtle neuro-behavioural effects (lead)
- 2) Chronic kidney damage (cadmium)
- 3) Sensory or neurological impairments (mercury)
- 4) Damage to fetus (lead and organic mercury)
- 5) Morphological change in tissues
- 6) Changes in physiology, such as suppression of growth and development, poor swimming performance
- 7) Changes in biochemistry, such as enzyme activity and blood chemistry
- 8) Changes in behaviour
- 9) Changes in reproduction

Appendix B: Effects of Specific Heavy Metals on Aquatic Life

Heavy metals that are of particular concern to surface water systems are cadmium, chromium, mercury, lead, arsenic, and antimony (Kennish, 1992). These heavy metals and their effects on the aquatic life are discussed in further detail in the following sections.

Arsenic

Arsenic is an ever-present element that is the 20th most abundant element in the earth's crust, and 12th in the human body. It is widely recognized that even low-level consumption of arsenic can lead to cancerogenesis (Mandal and Suzuki, 2002). The terrestrial abundance of arsenic ranges between 1.5 to 3 mg per kg. Anthropogenic sources exceed natural sources in the environment by at least three times; man-made sources of arsenic include herbicides, insecticides, desiccants, wood preservatives, feed additives, drugs and poison (Mandal and Suzuki). Napoleon is rumoured to have died from arsenic poisoning.

Arsenic toxicity, both long and short term, has various effects on humans; it causes respiratory, pulmonary, cardiovascular, gastrointestinal, hematological, hepatic, renal, dermal, neurological, developmental, reproductive, immunologic, genotoxic, mutagenic, carcinogenic diseases, as well as diabetes mellitus. Arsenic is known to inhibit more than 200 enzymes in human biochemistry. Studies indicate arsenic accumulates in human tissue with age, which is consistent with observations on laboratory animals (Mandal and Suzuki). Studies on laboratory animals have indicated that the toxicity of arsenic is dependent on its form and oxidation state. Soluble inorganic arsenicals are more toxic than organic arsenicals. Clearly, it is very important to maintain very low levels of arsenic in any given water system, since it accumulates to toxic levels within organisms over time.

Traditional methods of reducing arsenic levels in water include precipitation/coagulation and ion exchange (Dambies, 2001). For precipitation/coagulation, the chemistry of the type of arsenic in the water is reduced by oxidizing it into a solid state. Ion exchange is a more applicable water treatment method, and is carried out with commercial resin called Amberlite IRA 900. The results indicated that the process operates best at a pH of approximately 6, where the maximum uptake capacity is about 75 mg/g of resin dry weight. However, this process can be quite expensive when treating a large amount of water, so other treatment methods for arsenic reduction are still in development.

Cadmium

Cadmium can exist in water as a hydrated ion, in inorganic complexes such as carbonates, hydroxides, chlorides or sulphates, or in organic complexes with humic acids. At sufficiently high levels, cadmium is very toxic to both humans and aquatic organisms. The most serious consequence of chronic cadmium poisoning is cancer (lung and prostate); the first observed chronic effect is generally kidney damage. Cadmium is also believed to cause pulmonary emphysema and bone disease (osteomalacia and osteoporosis). Fish are typically more sensitive to cadmium in aquatic habitat than are humans from drinking water. Cadmium causes hyperplasia, the breakdown of the secondary lamellae of the gills (Ministry of Technology, 1970), extensive gill degeneration (Bilinski and Jonas, 1973), and pathological changes in the renal and intestinal tracts. Ultimately, prolonged cadmium exposure leads to the impairment of respiratory and extrarenal function through reduction in respiratory surface (Gardner and Yevich, 1970).

In urban areas, the majority of Cd is released through wear of the rubber of automobile tires on the surface of roads and parking lots. Other possible sources include phosphate fertilizers, manure, insecticides, industrial paints, metal coatings (possibly on buildings), and road salts used for de-icing.

Detention ponds and wetlands may be used to remove cadmium from stormwater run-off. Removal efficiencies of 26% for a detention pond, followed by 33% by a wetland treatment have been reported for stormwater treatment in Orlando (McKann and Olson, 1994). Cadmium can be also be sorbed onto marine algae under specific conditions (Yin, et. al. 2001).

Copper

Copper is a widely used industrial metal whose applications include electrical wiring, plumbing, air conditioning tubing and roofing. The properties of copper, which make it suitable for these applications, include high electrical and thermal conductivity, good corrosion resistance, ease of fabrication and installation, attractive appearance, availability, and high recyclability. Additionally, copper, which is an essential nutrient to humans and other forms of life, is biostatic/biocidal to certain organisms. A common application of the latter is its antifouling properties in seawater. Only a small part of the total copper and, for some sources, dissolved copper is in a toxic form, in which it is extremely toxic to aquatic organisms, killing in the parts per billion range. For juvenile fish, at the temperature of 22°C, a sub-lethal dose of copper at 0.2ppm to 1.2ppm for four weeks will result in lethal accumulation within the fish.

Sources of copper in stormwater runoff include petroleum products, wood products, mining wastes, antifreeze, brake linings, asphalt, concrete and engine wears. Another source of copper in urban stormwater is from copper algacide. (Kelevin, 1998). Possible sources of copper from UBC stormwater may include wood compost leakage, brake linings from parking lots, antifreeze from cars, concrete and engine wears. The copper concentration in the runoff sample collected for the November 5, 2002 was 0.13 mg/L with a hardness of 45.1 mg/L; this is above the 30-day average concentration criteria for freshwater aquatic life, but below the maximum concentration allowed.

A pond can remove about half the copper in stormwater. Recharging stormwater into the soil removes up to 98% of the copper. MDE's proposed recharge requirement and a pond would reduce parking lot copper loads by 62%. Recharging the first 1.5-inches of runoff would reduce copper loads by 90%. While copper loads would remain higher than the forest release rate, with 1.5-inches of recharge the impact would be one-fourth of that resulting from MDE's proposed recharge requirement. The cost and maintenance of this method is relatively low.

At pH below 7.0, the toxicity of copper is greatly enhanced. For this reason, among others, frequent partial water changes, dilution of organics, checking and adjusting pH prior to copper treatment, if necessary, is warranted. Regular, routine maintenance and checking of water chemistry assures that the proper amount of free copper is present, without premature absorption or precipitation. The toxicity of copper decreases as water hardness increases. A significant reduction occurs when the bicarbonate alkalinity exceeds 150ppm as calcium carbonate. Consequently, toxicity to fish decreases as alkalinity increases.

Lead

Lead occurs naturally in the environment as Galena (PbS), it is the 36th most common element on earth. Apart from background levels of lead, and natural sources, lead finds its way into the environment through several human activities. Lead is present in:

- Vehicle exhaust (Liu et al. 1995)
- Emissions from such industries as steel production (Liu et al. 1995)
- Emissions from garbage incinerators (Liu et al. 1995)
- Old paint (Lanphear, et al. 1996)

- Building siding, higher where painted with lead based paint (Davis et al. 2000)
- Automobile brakes (Davis et al. 2000)
- Automobile tires (Davis et al. 2000)
- Used engine oil (Davis et al. 2000)
- Lead Batteries (US EPA)
- Solder in old piping (US EPA)
- Lead Arsenate in Fungicides and Herbicides

In the case of vehicle exhaust and paint, lead levels have dropped drastically with the banning of leaded gasoline and leaded paint, respectively. The majority of sources come from the breakdown of materials used by the automobile. Of the above human-use related sources, UBC may be adding lead through: herbicides and fungicides, old paint, old piping, and through its many automobile users. The lead concentration in the runoff sample collected for the November 5th, 2002 evening storm event was 0.003 mg/L with a hardness of 45.1 mg/L. This is above the 30-day average concentration criteria for freshwater aquatic life, but below the maximum concentration allowed.

The oxidation state of dissolved lead in water is very similar to calcium (Pb^{+2} and Ca^{+2}). Calcium is a beneficial element in fish physiology and is taken up through the gills. Due to its analogous nature, lead is also taken up. High lead concentrations tend to cause acute and chronic effects in fish, but not immediate death. Levels of lead greater than 170000ug/L were required to adversely affect a variety of fish in a mortality experiment (Buhl, K.J. 1996). Lead at levels higher than background tend to adversely affect body weight, digestive enzymes, and lipase (Jain, S.K. 1999) (Macdonald et al. 2002).

There are two basic methods for removing dissolved Lead from water: adsorption and precipitation. The effectiveness of each depends very much on the conditions of the water and the concentration of lead in the water. Adsorption works by adding a sorbent to the contaminated water; lead ions adsorb either onto or into the sorbent. Activated carbon is a widely used sorbent. A large amount of research has been devoted to finding other suitable sorbents for removing lead from water. Some sorbents tested include:

- Non-living brewery yeast (Riordan C. et al. 1998)
- Peat (Brown P.A. et al. 2000)
- Talc, chalcopryrite, and barite (Rashed M.N. 2001)
- Crab shell (An H.K. 2001)

There are expensive and cheap sorbents available for water treatment, all with varying efficacies. Maintenance issues include the removal of spent sorbent, addition of new sorbent, and the regeneration or disposal of spent sorbent. Most spent sorbents can be regenerated by washing in a low pH solution (Rashed M.N. 2001). The percent removal of lead from solution depends on several factors such as pH and hardness. Adsorption is typically an ion-exchange process, with a lead ion taking up a site vacated by another ion (Brown P.A. et al. 2000).

Chemical precipitation works by complexing the lead ion with another chemical and thereby reducing its solubility. There is a large number of complexing agents available for the treatment of lead in solution:

- NTA, EDTA, gluconic acid (Strnadova N. et al. 1997)

- Oil soluble surfactants (Schwuger M.J. et al. 2001)
- TMT, Thio-Red, STC, SDTC (Matlock M.M. et al. 2002)

Complexing agents are manufactured reagents and tend to be expensive. There are potential addition, removal, regeneration and disposal problems. Also, some complexes begin breaking down in a relatively short amount of time (20 hours) (Matlock M.M. et al. 2002).

Zinc

The concentration of zinc is typically 5ug/L to 45ug/L in river water. Concentrations in streams affected by mine drainage are commonly 100ug/L or more. At concentrations above 5mg/L (upper limit by Water Quality Criteria, 1972), humans can begin to detect zinc by taste. Although humans are unlikely to have any health effects from zinc toxicity at this point, some aquatic life have much lower tolerances of zinc and may be affected.

Excess zinc can lead to respiratory incapacitation, as indicated by increased respiratory activity (i.e. breathing rate, volume and frequency of ventilation, coughing, and decrease in oxygen uptake efficiency). Zinc damage enhances lactic acid production/accumulation as temperature and exposure time are increased. Zinc can also kill aquatic life by causing “direct damage to the gill membranes by ionic zinc-separation of epithelium from underlying central pillar cells of the gill lamellae. Such structural damage increases the effective distance that oxygen must diffuse to reach the blood, with death resulting from the eventual collapse of the weakened pillar cell system and consequent restricted blood flow through gill capillaries” (Hem, 1985). Sellers (1975) used a lower level of zinc concentration, which was significant enough to cause accumulation of mucus on the gills from zinc exposure, which caused oxygen tension in the arterial blood of fish. Chronic toxic effects of zinc include:

- Less obvious, but just as hazardous as acutely toxic effects for fish
- Sustained exposure to zinc sulfate can cause damage to development of liver blood vessels, kidney, heart muscles, sexual maturity, vacuoles, nuclei.
- Inhibits normal growth and maturation by inducing stress causing severe hormonal disorder

Effects of zinc depend on zinc concentration, time of exposure, and species. They are further modified by environmental factors, such as water hardness, oxygen and CO₂ concentration, pH, salinity, and temperature. Influences of age, stage in life cycle, behavior, metabolism, acclimation, and selective mortality must also be considered and controlled.

Zinc has only one significant oxidation state (Zn²⁺), which is more soluble in most types of natural water than lead and copper. It is widely used in metallurgy, especially as a constituent of alloys, such as brass and bronze. It is also used in galvanizing, deposited as a protective coating to prevent corrosion of steel or other metals, which are used in building, transportation and appliance industries.

Zinc is one of the three major trace metals found in stormwater runoff, along with lead and copper, which account for 90-98% of total metals observed. Of this amount, zinc accounts for approximately 35% (lead 54% and copper 9%). Peak concentrations of zinc are generally observed shortly after runoff begins, usually within first 30 minutes.

Appendix G. Raw Data