

**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**

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**Dec 2002**

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CHBE 465:  
Aquatic Design and Rehabilitation

**EFFECTIVNESS OF SOME LOW-COST SORBENTS  
FOR TREATING MIXTURES OF HEAVY METALS  
IN RUNOFF FROM THE FIRST MAJOR STORM  
EVENT AFTER THE EXTENDED DRY PERIOD**

**Final Report Due December 20<sup>th</sup>, 2002  
Final Report Submitted To Eric Mazzi  
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## **Acknowledgments**

There are many people to thank for this report. The authors are indebted to Dr. Royann Petrell for her faith, guidance and input, all crucial in shaping this report. The authors also thank Mr. Eric Mazzi, Manager of UBC's Mechanical Utilities, for graciously providing the opportunity, administrative support and funding to work on this project. They also extend their gratitude towards Mr. Nick Page of Coast Environmental Services Limited for providing storm-water sampling results and recorded storm data.

Finally, the authors acknowledge the project facilitation and spiritual advising generously provided by Brenda Sawada of the University of British Columbia's Social, Ecological, Economic Development Studies (UBC SEEDS) Program to this project.

## **Executive Summary**

The effectiveness of a number of reportedly low cost sorbents at removing arsenic (0.0045 mg/L), copper (0.13 mg/L), cadmium (0.0002mg/L), lead (0.003mg/L), and zinc (0.120 mg/L) from UBC storm-water to below discharge limits as defined by guidelines issued by the federal and provincial governments, was examined as a preliminary step towards the design of a stand-alone storm-water filtration system, within budget.

Two different kinds of tests were carried out to evaluate the sorbents; the first set of tests was used to identify appropriate sorbents, whereas the second test provided error analysis.

The results of these tests showed that most of the low cost sorbents tested (Peat, Yeast, Coffee, Compost, and Fe-oxide coated sand) were incapable of treating the University of British Columbia storm water discharge at the Booming Grounds outfall alone. Industrial grade chitosan from Vanson Halosource was the most effective treatment sorbent for heavy metals. It reduced Cu (almost to compliance level) and Zn (below compliance level) at a highest efficiency of 0.0070 mg/mg chitosan and 0.006 mg/mg chitosan respectively. It somewhat treated lead to below compliance and instrumentation sensitivity of 0.0001mg/L. It also reduced the cadmium concentration to below the detection limit of 0.0002mg/L and the compliance level of 0.017mg/L.

Based on the study conducted, treatment of the storm water runoff at the Booming Grounds outfall would require a cost of between \$150 and \$1200 based on the flow rate and load of Zn during the rainfall event.

Before this sorbent is implemented in a design, further testing over a broader range of metals concentrations must be conducted. The life of the chitosan media must be

determined as well as possible recharging and reusing techniques. The effectiveness over a variation of solution chemistries (such as concentration  $\text{Ca}^{2+}$  and pH) must be examined as well, along with the kinetics of the sorption to optimize sorbent concentration and time requirements for storm-water treatment.

The impact of discharging the untreated storm-water onto a coastal habitat must also be investigated in the future as well, since aquatic life is highly sensitive to these metals being over-compliance.

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## **1.0 INTRODUCTION**

The University of British Columbia (UBC) is situated on an ocean peninsula, surrounded by Pacific Spirit Park and a public beach on the outer perimeter. Typically, after a few months dry summer, it starts to rain in October, and continues raining intermittently until early May. During a given storm (rain) event, water is collected into the storm sewer network, and then removed through a number of discharge points, known as outfalls, which either discharge directly into the ocean or into creeks that run through the park down into the ocean. The quality of the storm-water discharged through these outfalls is of concern due to the negative effects it may have on organisms in both the park and the receiving marine environment.

The quality of UBC's storm-water was routinely assessed at the major outfalls over the past year, and the preliminary results (Coast River Environmental Services, 2002) indicated that the concentration of a number of metals, namely arsenic, copper, iron, lead, and zinc, are above that recommended by both the provincially and federally recommended guidelines for the protection of freshwater aquatic life, respectively the British Columbia Water Quality (BC WQ) and the Canadian Council of the Ministers of the Environment (CCME). These guidelines are enforceable by law, because the metal composition of this storm-water affects coastal aquatic life.

Therefore, as a result of these high metals concentrations in the storm-water, UBC may be in contravention of a number of laws including the Fisheries Act, the Waste Management Act and the Canadian Environmental Protection Act. Fish are not present in the outfalls streams themselves, but the water does discharge in coastal aquatic habitat (for more details, please refer to Appendix E – Laws).

The presence of metals in fresh water streams and the marine environment poses a significant health threat the aquatic (and surrounding) community. At very low concentrations, some of these metals are considered micro-nutrients; however, at higher levels – such as are seen in UBC’s storm-water run-off, many metals cause disease and death in not only higher organisms such as fish, but also on their food supply. For example, zinc causes the epithelial cells of gills to become swollen and eventually slough off, causing the fish to die of asphyxiation (Lloyd, 1960; Skidmore, 1970; Skidmore and Tovell, 1972); copper salts cause extensive breakdown of the gills (Pequignot, Labat and Chantelet, 1975) as well as detrimental enzyme alterations in hepatic and liver metabolism (Baker, 1969; Gardner and La Roche, 1973; Jackim, Hamlin and Sonis, 1970); cadmium causes, among other things, hyperplasia, breakdown of the secondary lamellae of the gills (Ministry of Technology, 1970), extensive gill degeneration (Bilinski and Jonas, 1973), pathological changes in kidney and intestinal tract, leading to impairment of respiratory and extrarenal function through reduction in respiratory surface (Gardner and Yevich, 1970). The combined effects of just these three metals was at worst, several-fold more than additive on a response and concentration basis (Eisler and Gardner, 1973), at best, depending on the relative concentrations, the effect was additive (Eisler and Gardner, 1973). A similar interaction is found between humans exposed to higher concentrations of metals (especially cadmium, arsenic and lead). (For more information on the health effects caused by the exposure of high concentrations of these metals on both fish and humans, please refer to Appendix G – Metals for a brief summary).

In order to assist UBC in addressing storm-water quality, the students of CHBE 465 (the chemical and biological engineering project-based course focussed on rehabilitation of aquatic habitats), with support from the UBC Social, Ecological, Economic Development Studies (SEEDS) program undertook an investigation on how to clean up the storm-water.

After a literature search, it was discovered that contaminated storm-water is a common problem in the western civilization due to a combination of coverage of the earth's surface with an impermeable layer of buildings and pavement, and the dispersion of pollutants (from non-point pollution sources such as fertilizers, parking lots, herbicides, pesticides, fungicides, concentrated animal waste, concentrated wood waste, construction and automobiles) that are transported during rainstorm events into the storm sewer network. (Refer to Appendix G – Metals for a description of possible sources and effects that each individual metal poses on the environment.)

Urban storm-water problems can be dealt with in two ways. First, source control is necessary to reduce the quantity of flow, and to reduce/eliminate the pollutant load to both the groundwater and the storm sewer network. This is an integral part of building a sustainable campus. Secondly, pollutants may be immediately removed from the storm-water using a treatment system.

Initially, many biologically based treatment systems were evaluated (such as wetlands and grass swales; see Appendix F for more information); however, they were discounted due to the large land area necessary (but unavailable) for their implementation, operating cost and ineffectiveness. Therefore a more compact and economic treatment method using sorbents was sought.

## 2.0 OBJECTIVES

The main objective of this project was to examine the effectiveness of a number of sorbents at removing Arsenic, Cadmium, Lead, Copper and Zinc from UBC storm-water to below discharge limits, intended as a preliminary step towards the design of a stand-alone storm-water filtration system.

An additional objective that was stated in the project proposal relating scale up and pilot testing was not addressed due to the complexity and limitations of the sorbents that were tested. This objective did not have a budget implication.

Testing was essential because of the very nature of the UBC storm-water runoff; testing was used to determine whether the sorbent could adsorb the maximum heavy metal concentration found in UBC's storm water. Some values have been found in the literature for maximum adsorption capacity of the adsorbents, but it is necessary to conduct on-site tests because:

- The storm water is contaminated with a cocktail of heavy metals, which may interact with each other or with the adsorbent differently than if the water were only contaminated with one metal species.
- The adsorption characteristics of the adsorbents may depend on the water characteristics. It would be best to test the adsorbents using samples of storm water from the proposed site.

The selection of the above mentioned metals to be targeted in the biological filtration system was determined by assessing both their actual concentration and relative toxicity in the storm-water. The substances identified in the preliminary sampling that superseded regulations were arsenic, cadmium, chromium, copper, iron, lead, magnesium, mercury, zinc and fecal coliform bacteria. Due to apparent low frequency of

guideline transgression or inherent toxicity, chromium, iron, magnesium and mercury were dropped from our focus (research time and sampling costs would be increased if these metals were kept as a reduction target). The focus will be on heavy metals, not fecal coliform, as heavy metals were considered to represent a more serious issue due to their ability to harm aquatic life.

### **3.0 BACKGROUND ON SORBENTS**

Methods for treating heavy metal contaminated waste streams include chemical precipitation, membrane filtration, ion exchange, carbon adsorption and coprecipitation/adsorption by sorbents (Bailey et al, 1999). Precipitation requires chemical reagents, and results in the formation of a sludge which is difficult to dispose of (Sharma and Foster, 1995). Membrane filtration, ion exchange and carbon adsorption systems require a high capital investment; additionally, on-site regeneration and reuse of the required materials has many problems associated with it (Sharma and Foster, 1995).

Cost effective strategies need to be employed in treating large volumes of water. Thus sorbents were selected as a possible basis to treat UBC's storm-water, with cost identified as a dominant factor in the selection of a suitable sorbent in water treatment. Another important factor which was considered is the adsorptive capacity of the material; if the material was expensive on a per mass basis but is far more effective than any other method, the overall cost of the sorbent would actually be lower than that of an ineffective sorbent with poor adsorptive capacity.

Natural materials or waste products from industrial or agricultural processes with large adsorptive capacities can be ideal sorbents, since they are abundant in nature, require little processing, and can be disposed of in a sustainable manner if necessary (Bailey et al, 1999). These sorbents are referred to as 'low cost' sorbents, and are the largely the subject of this investigation.

Six main sorbents were tested in this investigation; this section details why they were chosen out of the many available sorbents for testing.

### **3.1 Leaf Compost**

Leaf compost was tested as a suitable sorbent since there are studies that show certain kinds of leaves and bark provide a surface for heavy metals to adsorb onto (Adeyiga et al, 1998; Sharma and Forster, 1994). Unfortunately, since the composition of the leaf compost is not known, there are variable ranges of adsorption available for the different leaves or wood species that could be in the compost (Adeyiga et al, 1998). This means the effectiveness of the leaf compost will be quite variable as well, depending on the seasonal species found in the compost at any given time in any given part of the compost.

The mechanism that compost leaves remove heavy metals with is not clearly understood; a significant contribution is presumed to come from the leaf mold found growing on composted leaves. Leaf mold has been studied to have favourable kinetics and the adsorbance capacity to reduce heavy metals in solution, such as chromium, nickel, copper, zinc and cadmium (Sharma and Forster, 1994). The chemi-sorbant adsorption has a second order reaction rate, which means that at low heavy metal concentrations, leaf mold efficiently and speedily reduces the soluble heavy metal content. Leaf compost also has bark in it, which can be an effective sorbent because of its high tannin content. Ion exchange takes place as metal cations displace adjacent phenolic hydroxyl groups on the tannin, forming a chelate (Randal et al, 1974). One problem with tannin-containing materials, however, is the discoloration of the water from the phenols, which can interfere with the metal analysis instrument readings. Overall, leaf based wastewater treatment methods are fast, with absorption reaching equilibrium in less than 30 minutes (Adeyiga et al, 1998).

Leaf compost would be a sustainable, low-cost sorbent if the compost originating from the UBC compost facility on average had appropriate absorbance capacity to treat the UBC storm-water cocktail.

### **3.2 Peat Moss**

Peat moss is a relatively inexpensive and widely available sorbent, with adsorption capabilities for a number of different metals (Bailey et al, 1999), which is why it was tested as a possible sorbent for the UBC storm-water system.

Peat is a complex soil material with organic matter at various stages of decomposition. It contains lignin and cellulose as major constituents; these constituents have a variety of different polar functional groups that can be involved in chemical bonding (Bailey et al, 1999). Because of these functional groups, peat moss has a high cation exchange surface capacity, making it an effective adsorbent for the removal of heavy metals. Initially, these functional groups are charged with calcium, magnesium and iron (III) ions as well as a small concentration of heavy metals, in raw peat; these are exchanged for the more stable heavy metal ion complexes that form instead (Chen et al., 1990) Isotherms show the cation exchange nature of peat is limited but the complexation sites cannot be saturated.

Additionally, peat moss regeneration can be carried out by passing large amounts of 1M sodium hydroxide solution (NaOH) over the spent peat. This regeneration, however, has a poor efficiency (less than 40%) (Sharma and Forster, 1995).

Metal adsorption on peat moss has been quite well studied (Bailey et al, 1999; Kertman et al, 1993; McClland and Rock, 1988; Sharma and Forster, 1995; Tummavuori and Aho, 1980), and the literature values for metal adsorption are provided in Table 1 at the end of this section.



### **3.3 Iron Oxide Coated Sand**

Iron oxide coated sand (IOCS) is a typical regenerable sorbent used for wastewater and storm-water in traditional treatment methods; wastewater is shunted through IOCS beds, as it often controls free metals by adsorption. Depending on the pH, IOCS has a charged surface, which allows soluble metals to adsorb onto it. Once the IOCS bed is completely saturated with metals, it can be flushed with acid at a pH of 3.0 to resorb these metals and effectively regenerate the adsorption sites for further use (Lai et al, 1994).

Literature values available for the five metals this report is documenting were unavailable (Bose et al, 2000). However, since traditional storm-water treatment involves the use of iron oxide coated sand beds, this sorbent was selected for testing in order to check its applicability to this system.

### **3.4 Coffee Grounds**

There is little literature available on the use of coffee ground as sorbents. Extensive investigations have been carried out on the adsorbent capacity of coffee grounds of aluminum ions. Coffee grounds are documented to adsorb large amounts of aluminum ions as well as other miscellaneous heavy metals; unfortunately, metals that this particular report is concerned with were not quoted (Adeyiga et al). Since aluminum is a typical heavy metal, this sorbent was tested for its applicability, as the metals this investigation focuses on are of similar higher end molecular weights. Additionally, coffee grounds are a typical waste product, so reusing them to treat storm-water would be more sustainable than simply disposing of them.

### **3.5 Chitosan**

Chitosan is the de-acetylated derivative of chitin, a polysaccharide layer that forms part of the hard outer shell of crustaceans. Chitin is second only to cellulose in terms of abundance in nature, and is a waste product of the crab meat canning industry (Bailey et al, 1999; Berkeley, 1979).

Chitosan possesses an exceptional affinity for adsorbing metal ions, with a capacity greater than 1 mmol of metal/g for most metals, including arsenic (Bailey et al, 1999). Chitosan can be classified as a coagulant, as it forms agglomerates comprising of its long chainlike molecules and charged impurities in storm-water (Muzzarelli, 1977). Chitosan is soluble in acidic solutions; it is however, non-porous, so it doesn't provide a large surface area for adsorption to occur. The literature values found for adsorption are provided in Table 1, given at the end of this section. The arsenic values could not be found in literature; however, derivatives of chitosan are being investigated as arsenic adsorbents. 'Raw' chitosan must have some of the properties of its derivatives; therefore, arsenic should adsorb onto it as well.

### **3.6 Brewery waste**

Brewery waste is the spent yeast remaining from the fermentation in the beer-making process. Literature shows that brewery waste is capable of allowing the adsorption of copper, cadmium and lead, depending on the pH of the storm-water (Marques et al, 1999). The literature values for a moderate pH level are given in Table 1. Inactive brewery waste is preferred over active brewery waste, as non-viable brewery waste has reportedly had better metal binding capacities (Marques et al, 1999). Additionally, non-viable cultures do not require nutrition; they do not develop a

resistance to the hostile storm-water environment, and they present a reduced health hazard than viable brewery cultures (Marques et al, 1999).

Table 1: Reported adsorption efficiencies

	<b>Arsenic</b>	<b>Cadmium</b>	<b>Copper</b>	<b>Lead</b>	<b>Zinc</b>
chitosan	n/a	559 mg metal / g sorbent <sup>1</sup>	n/a	796 mg/g <sup>1</sup>	n/a
brewery waste	n/a	0.112 mg metal / g sorbent dry weight <sup>2</sup>	0.0381 mg/gdw <sup>2</sup>	2.072 mg/gdw <sup>2</sup>	n/a
peat moss	n/a	5.8 mg/g <sup>1</sup>	19.6 mg/g <sup>1</sup>	230 mg/g <sup>1</sup>	0.0111 mg/g <sub>1</sub>

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<sup>1</sup>Bailey, S.E., Olin, T.J., Bricka, R.M. and Adrian, D.D. (1999) A review of potentially low-cost sorbents for heavy metals, *Wat. Res.* 33-11: pp 2469-2479.

<sup>2</sup>Marques, P.A., Pinheiro, H. M., Teixeira, J. A. and Rosa, M.F. (1999). Removal efficiency of Cu<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> by waste brewery biomass: pH and cation association effects, *Desalination* 124: 137-144

## **4.0 METHODS AND MATERIALS**

From a literature review, several adsorbents were chosen for testing; these were: leaf compost, peat moss, iron oxide coated sand, coffee grounds, chitosan and brewery waste. The leaf compost came from UBC's compost facility in October. The peat moss came from Home Depot. The iron oxide coated sand was bought from Target Play Sand Incorporated. Coffee grounds were obtained from the Pendulum, an UBC on-campus restaurant. The chitosan was standard industrial grade, ordered in from Vanson Halosource in Redmond Washington. Brewery waste was provided by Granville Island Brewery. All sorbents except chitosan were dried at 102°C for greater than 24 hours, and their moisture contents are calculated against their air-dry weight. Each sorbent was tested in distilled water obtained from the booming grounds creek sampling site. Samples were prepared in UBC Chemical and Biological Engineering facilities, while an outside analytical laboratory performed heavy metal analysis. Details on specific methods follow.

### **4.1 Sampling**

It was important to collect a sample of highly contaminated water for testing and design purposes. Preferably, a maximally contaminated sample would be obtained, such that design could be based on a worse case scenario. Due to the action of rain, heavy metal contamination of runoff water occurred in baselines and peaks, with peaks corresponding to the beginning of a storm (the first wash of contaminated surfaces), and intense periods of the rain. The peaks in the runoff experienced a time delay from point of contamination to point of sampling.

In order to obtain representative results, storm water samples were collected at the Booming Grounds Creek Outfalls, shown in Figure 1, on November 5, 2002, during the first flush rain event of a storm. This storm occurred after approximately two dry months,

ensuring that the storm would wash out a large concentration of heavy metals that had accumulated over the dry period.

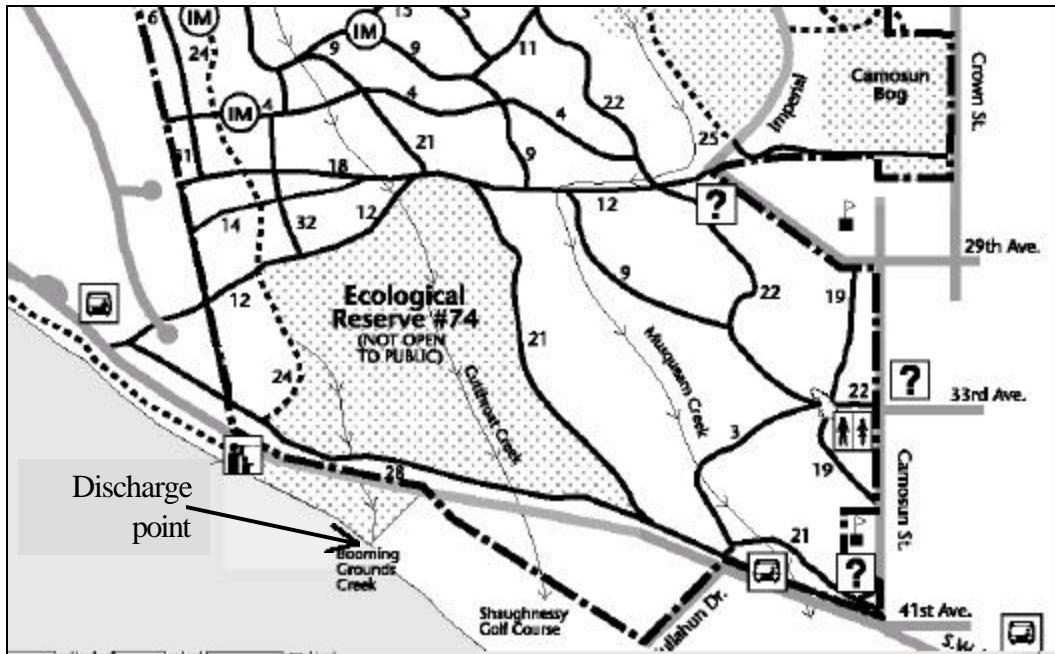


Figure 1: Booming Grounds Creek and surrounding area<sup>1</sup>. The arrow points to the outfalls where sampling took place.

The storm water samples were then used for the various sorbent tests.

Because of the unpredictable nature of rain and its intensity, it was impossible to predict when heavy metal contaminants would peak in concentration. Thus LaMotte metal detection method (a portable water quality meter) was used to determine when zinc concentration (and thus, the overall metal concentration) would peak. In LaMotte detection, reagents are added to a sample to complex with zinc, and light spectroscopy is used to determine the concentration of the complex, and subsequently the zinc concentration. Zinc was the metal tested because LaMotte metal detection was not

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<sup>1</sup> Greater Vancouver Regional District. (2002). *Greater Vancouver Regional District Regional Parks: Pacific Spirit Regional Park*. <http://www.gvrd.bc.ca/services/parks/pdf/webmaps/Pacificspiritmap.pdf>

sufficiently sensitive for the other metals. We assumed by testing only zinc that the other metals' concentrations would peak at the same time.

The strategy for sample collection included performing LaMotte analyses at approximately 15-minute intervals, from the start of the storm until a peak was detected and had passed. The overall 20 L sample was a collection of small 500 ml samples obtained over a span of approximately 30 minutes.

During the first testing and collection period, a peak was detected, thus only one sample collection was required. The peak lasted for a brief period of time, with much of the runoff collected during increasing and decreasing periods of concentration.

Suitability of the collected sample was later confirmed by offsite analysis for heavy metals contamination by ICP scans.

The sample water was allowed to sit in the lab, until all the particulate and sediment had settled. Only the clear supernatant at the top of the storage container was obtained for testing; (excess particulate can interfere with the instruments that are used to analyze the metal content of the storm-water.

## **4.2 Sorbent Testing**

The adsorptive capacity of each sorbent was tested using a 24-hour shake-flask test where an amount of sorbent is mixed into a set volume of contaminated sample and shaken for 24-, presumably long enough for the sorbent to either reach its adsorption capacity or completely remove all heavy metals. Then the sorbent was removed and the cleared sample was analyzed.

The adsorptive capacity of the sorbent was determined by comparing the heavy metal concentration of the liquid sample before and after the test.

#### 4.2.1 Sample Preparation

Samples were prepared in the Chemical and Biological Engineering laboratories.

The first set of shake flask adsorbent-experiments (Set I), were conducted in order to assess the efficient-range of sorbent concentrations at which removal of heavy metals from the storm-water sample. A range of sorbent-concentrations, were chosen based on literature reports. The lowest concentration of sorbent required (as reported) or the ‘sorbent capacity’ was interpolated on a log scale over a 3-sample range (for example 87, 260, and 780 g/L for Fe-oxide coated sand), as generally, the relationship between concentration and absorption is hyperbolic.

The second set of shake flask adsorbent-experiments (Set II) was conducted to examine measurement error. Not all the sorbents were tested, but only the ones that showed the most promise or the most scattered results (See Appendix D for detailed results). The sorbent samples at the highest concentration were assessed as multiple replicates ( $n = 1-5$ ) except for chitosan, as it did not arrive in time.

Sample preparation consisted of 4 major steps:

- 1) Mixing of sorbent and runoff
- 2) pH determination (for Set II)
- 3) shaking; and
- 4) filtration

In sorbent and runoff mixing, a set mass of sorbent was weighed and added to 150 ml of runoff in a 250 ml Erlenmeyer flask. In Set II, the pH of the sample was determined before and after sorbent addition to check for major changes, because pH has an effect on sorbent heavy metal uptake.

Samples were covered with a piece of parafilm to prevent exterior contaminant effects. (Sample preparation is examined in more detail in Appendix C)

Shaking was performed on a standard Bellco® Orbital laboratory shaker at a speed setting of 5.

After the 24 hour shake period, samples were filtered and centrifuged, where necessary, to remove all solid particles. A standard millipore filter was used to clear all samples. For Set II, a final pH measurement was carried out before filtration. Filtered or centrifuged solids were discarded and the supernatant was then sent for heavy metals analysis.

As a control on both sets of experiments, blank shake flasks filled with just storm-water were also subjected to the respective procedure, in order to quantify any changes that occur due to the shaking in the storm-water alone.

#### **4.2.2 Desorption**

Along with the sorbent samples prepared for testing, desorption in water was also examined, consisting of runoff water alone were put through the same procedure as sorbent samples. Sorbent samples were prepared with distilled water at the highest sorbent concentration in the Set I of experiments, and at the highest concentration in SET II, primarily as a check for sorbent heavy metals emission. Additionally, in Set II, a pure distilled water sample was prepared to test cleanliness of glassware, catch errors in procedure, and to catch unaccounted for factors.

#### **4.3 Heavy Metals Analysis**

Heavy metals analysis is performed offsite at ALS Laboratories using an ICP for the Set I of experiments. Initially, five metals were tested Arsenic, Cadmium, Copper, Lead, and Zinc. After Set I results, Arsenic and Cadmium were removed from testing, as



the concentration was too close to the detection limit of the ICP instrument. Hardness and alkalinity were also tested because of their effects on the toxicity of heavy metals.

For the Set II, Atomic Adsorption Spectroscopy (AAS) in flame ionization mode was used for analysis.

## 5.0 RESULTS

### 5.1 Storm Water Runoff Sampling

Figure 2 contains the measured flow-rate, conductivity and concentration of zinc during the first major storm event. The peak concentration of Zn was taken at 8 pm on November 5<sup>th</sup>, 2002. Sample water used in all sets of experiments in this report was derived from water collected after this point.

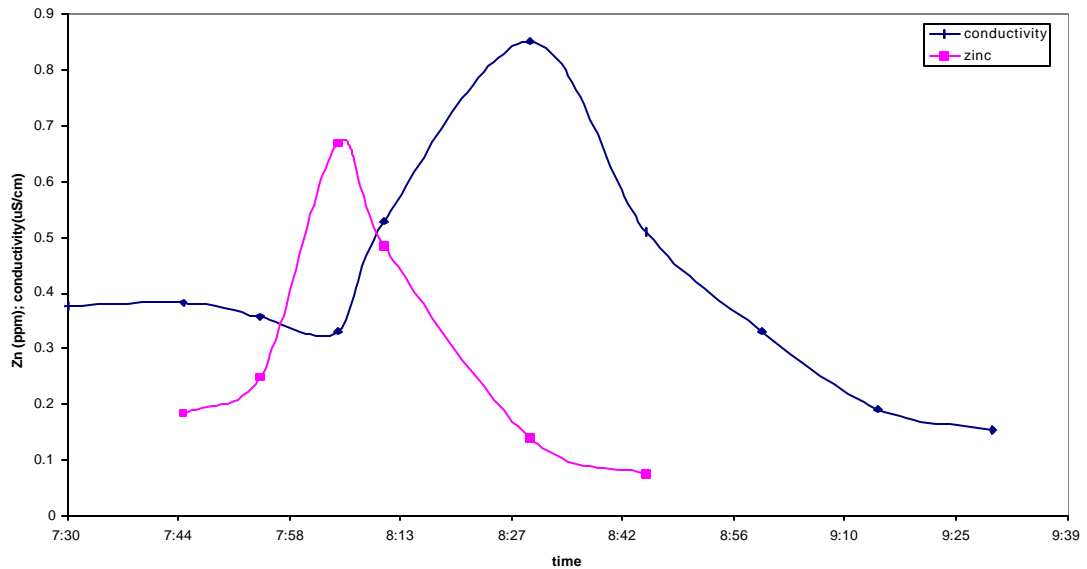


Figure 2: Monitoring UBC storm event for Zinc and Conductivity. (Conductivity data was supplied by Nick Page of Coast River Environmental Services.)

### 5.2 Testing of Storm Water Sample for Metals

Appendix D contains all the data. Previous storm water monitoring results at U.B.C. outfalls indicated concentrations of Arsenic (As), Cadmium (Cd), Copper (Cu), Lead (Pb), and Zinc (Zn), to be above the water quality guidelines. Of these metals, in our sample water, Copper and Zinc, at concentrations of 0.130 and 0.120 mg/L respectively, were found to be above water quality limits. The concentrations of As, Cd, and Pb, were below the detection limits of the ICP-AES instrument used for the analysis,

and thus could not be detected. For all subsequent tests, Atomic Adsorption Spectroscopy (AAS) in flame ionization mode was then used (as described in the Methods) in order to meet the low detection limits for metals As, Cd, and Pb.

### 5.3 Efficiency of Removal from Set I of Experiments

Detailed results from the testing are in Appendix D.

#### 5.3.1 Fe-oxide Coated Sand

The efficiency of sorption is expressed as amount adsorbed in mg for amount of sorbent (in mg), as shown in Figure 3. Fe-oxide coated sand adsorbed  $1.65 \times 10^{-5}$  mg Zn per mg sand. Over an increased concentration of sand, the efficiency of the sorbent to remove Zn from solution decreased. Fe-oxide coated sand did not sorb As, Cu or Pb. Cu was desorbed at high concentrations of sand.

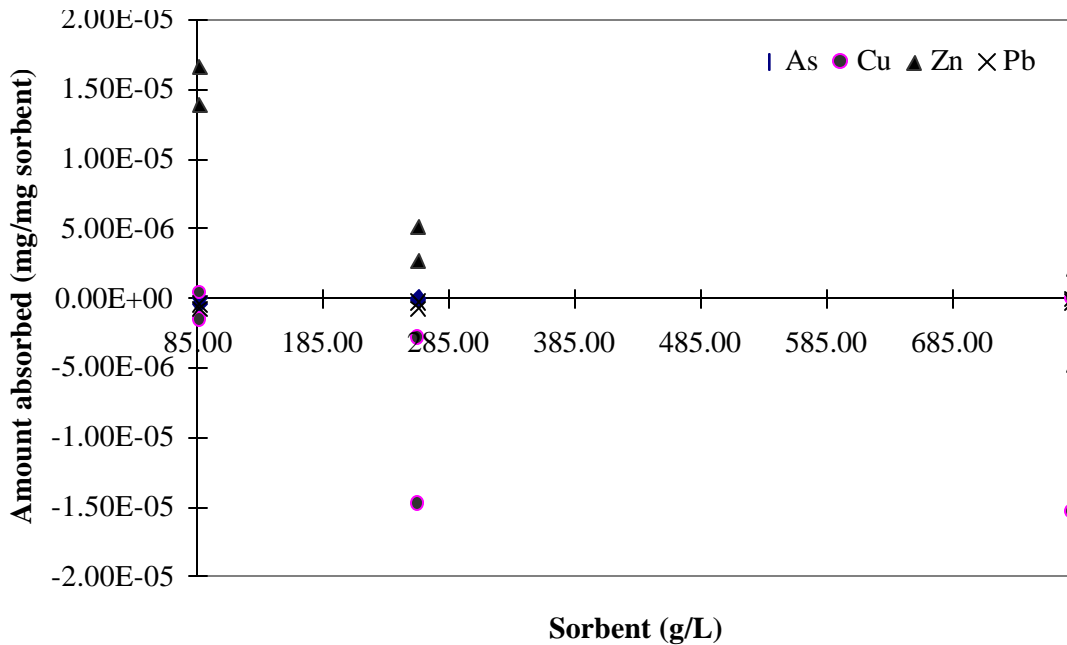


Figure 3: Effect of iron oxide sand on water from one storm-water event

#### 5.3.2 Industrial Chitosan

The industrial chitosan adsorbed Cu and Zn at efficiencies of 0.007mg/mg and 0.006mg/mg chitosan respectively at the lowest concentration of sorbent used. Sorption

efficiency exhibited a linear decrease for Cu. Removal efficiency for Zn, did not follow a linear decrease over the concentration range from 0.025 g/L to 0.25 g/L chitosan (0.006mg/mg), however at a concentration of 2.5g/L, the removal efficiency lowered from 0.006mg/mg (at 0.025 and 0.25g/L chitosan) to 0.0007 mg/mg. A logarithmic decrease in sorption efficiency was observed for removal of As from solution. Industrial chitosan removed Pb from an initial concentration of 0.003 mg/L to a concentration below the detection limits of the AAS instrument (0.001mg/L), which is incidentally the compliance concentration of Pb. As an exact final concentration of Pb is not known (due to the limitations of the testing instrument), removal efficiency could not be shown on this curve. The concentration of Cd was below the detection limits of the AAS instrument and consequently Cd was not reported or tested further.

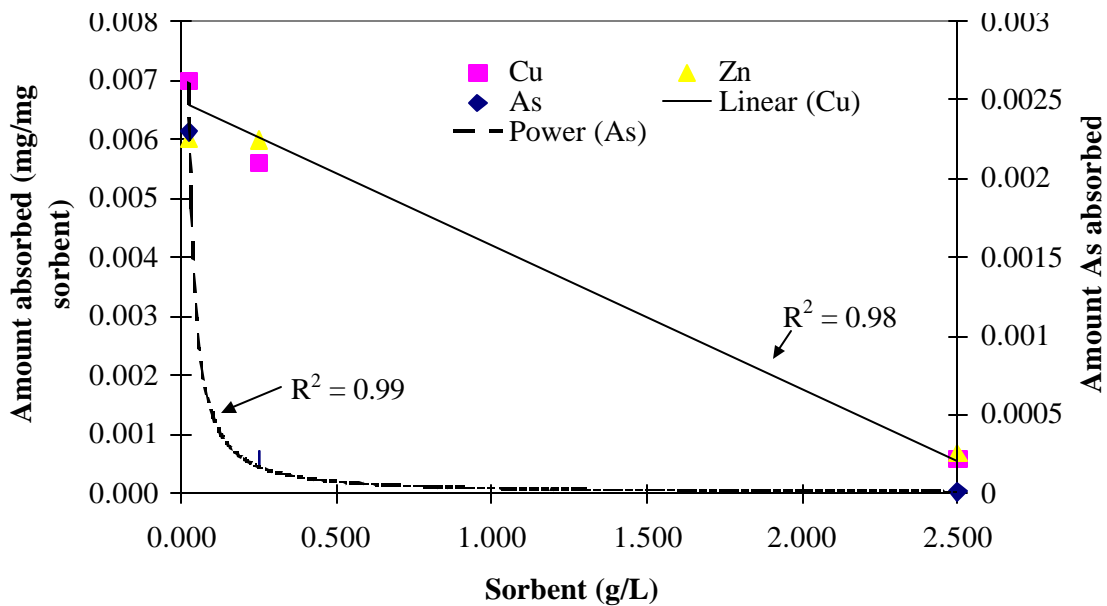


Figure 4: Effect of industrial chitosan on water from one storm-water event.

### 5.3.3 Compost

Compost removed Zn and Cu at sorption efficiencies of 0.008 and 0.007 mg/mg respectively. The decrease in efficiency over increased concentration followed was

similar to a logarithmic decrease. Compost did not remove As or Pb from the storm water solution.

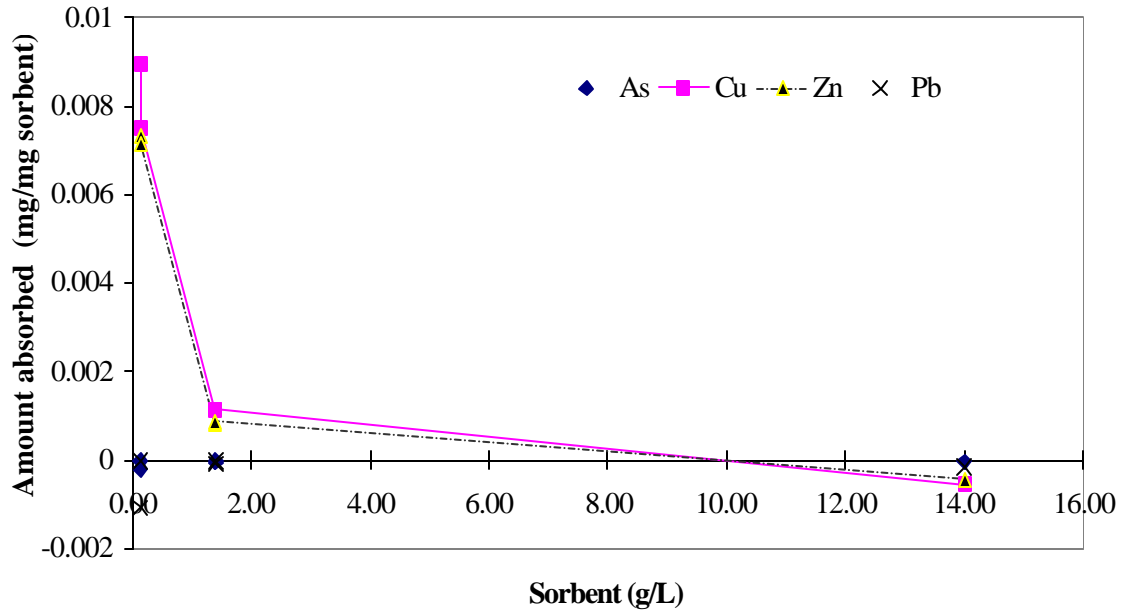


Figure 5: Effect of compost on water from one storm-water event

### 5.3.4 Peat

Peat removed Cu and Zn at efficiencies of 0.005 and 0.002 mg/mg peat respectively at the lowest concentration of peat used (0.32 g/L). Sorption efficiency of Cu followed a logarithmic decrease over increased concentration range. Pb was removed at an efficiency of 0.00008 mg/mg peat (only at the lowest concentration peat 0.32g/L).

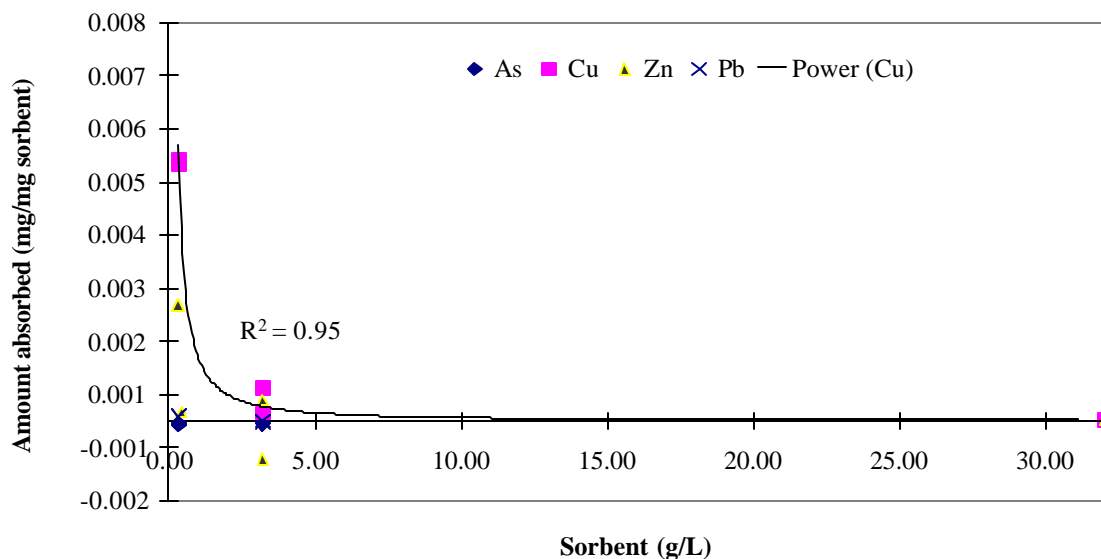


Figure 6: Effect of peat on water from one storm-water event.

#### 5.4 Assessment of mg Metal Absorbed or Released by Sorbents (Set II experiments)

As mentioned in methods, for this analysis, the removal or desorption of the metals Cu, Zn, and Pb by compost, peat, waste coffee grounds, and yeast samples at high concentration was assessed in multiple replicate ( $n = 1-5$ ). Chitosan and Fe-oxide coated sand were excluded from the analysis (chitosan did not arrive in time, while sand was deemed effective at its given concentration). The average amount of a given metal absorbed/desorbed in one storm-water event are shown below, from Figures 6 to 9. These results were quite scattered, and thus had very high standard deviations (much higher than the mg metal/mg sorbent itself), which is why the standard deviation has not been illustrated.

Figure 7 shows the average copper absorbed or desorbed in one storm water event; peat was the only effective sorbent in this set, as copper was desorbed by all the others. Figure 8 shows that all the sorbents desorbed Pb. Figure 9 shows that yeast was the only sorbent desorbing zinc, whereas all the others absorbed zinc.

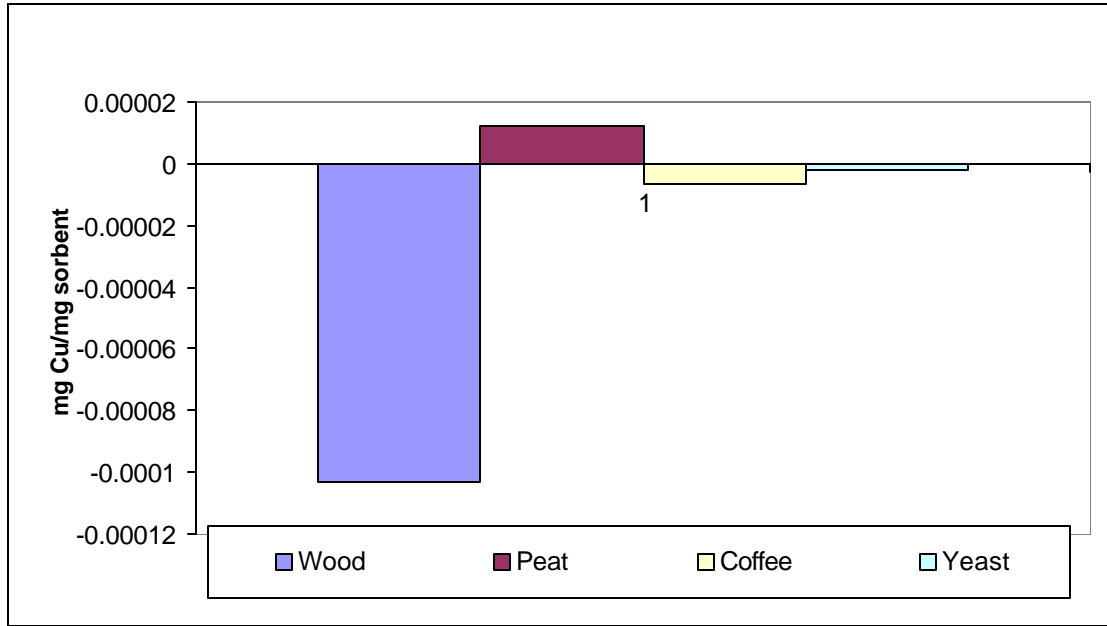


Figure 7: Average copper absorbed/desorbed in one storm-water event ( $n=3-5$ , except for chitosan, where  $n = 1$ )

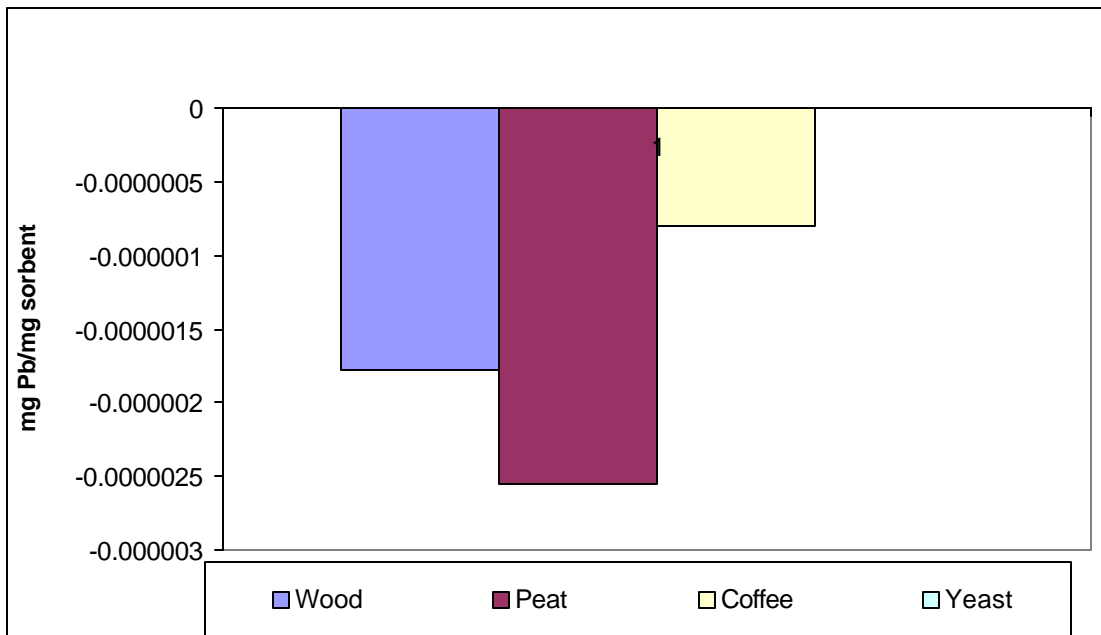


Figure 8: Average lead absorbed/desorbed in one storm-water event ( $n=3-5$ )

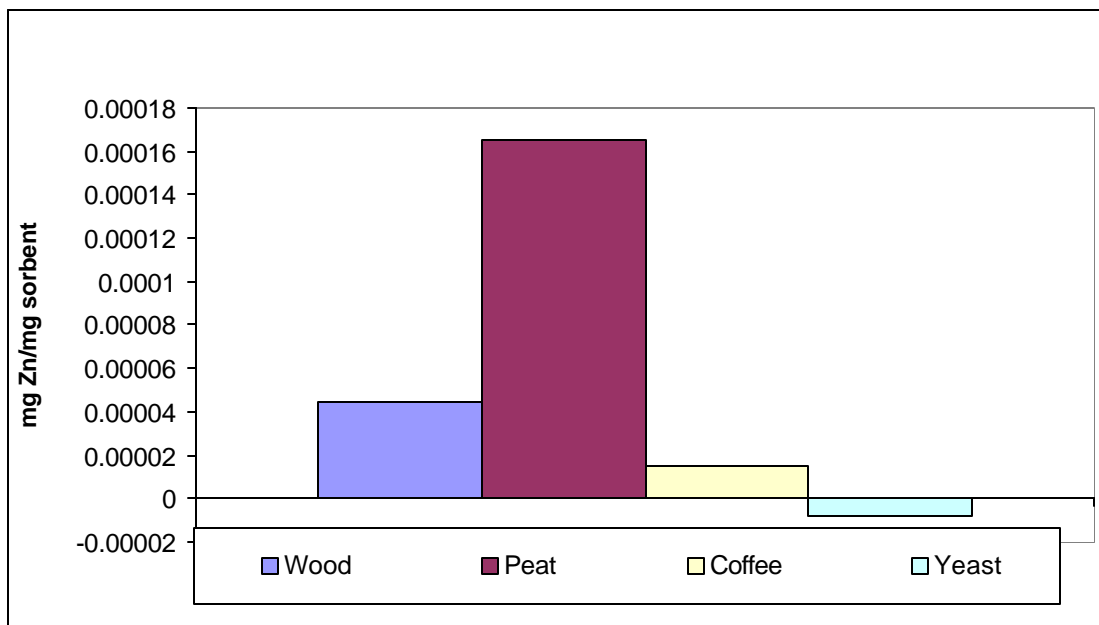


Figure 9: Average zinc absorbed/ desorbed in one storm-water event ( $n=3-5$ )

### 5.5 Desorption of Metals from Sorbents in Distilled Water (Set I of Experiments)

Some of the sorbents released in water only. For example, the concentration of Zn in the yeast flask increased after the shake flask experiment. Figure 10 shows the release profile for Zn at the highest concentration of the sorbents: peat, Fe-oxide coated sand, compost, yeast, and industrial chitosan. Yeast, compost and peat all released Zn in distilled water. Lead, copper and arsenic are similarly shown in Figures 11, 12 and 13, respectively. Chitosan released a very low level of arsenic, as shown in Figure 13.



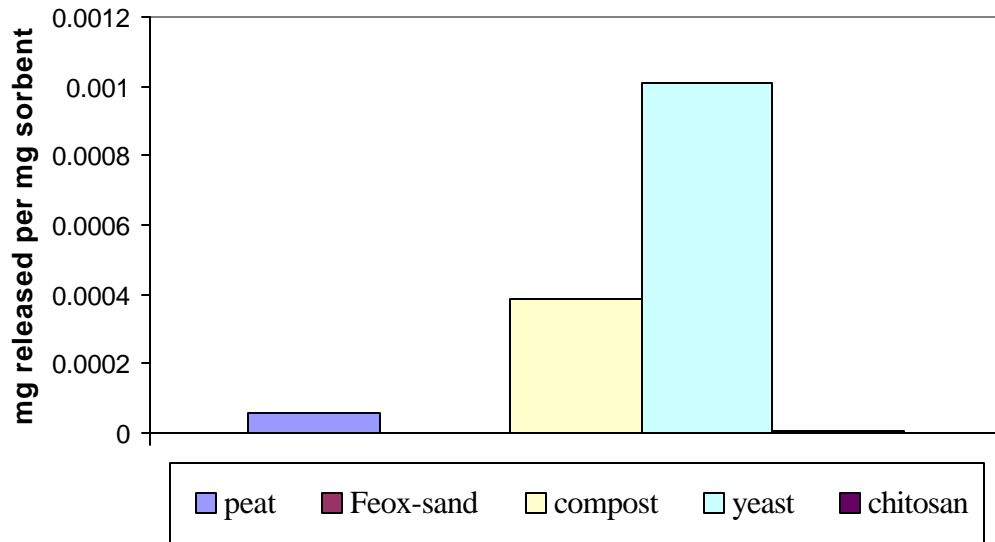


Figure 10: Desorption of zinc in distilled water at high sorbent concentration ( $n=1$ )

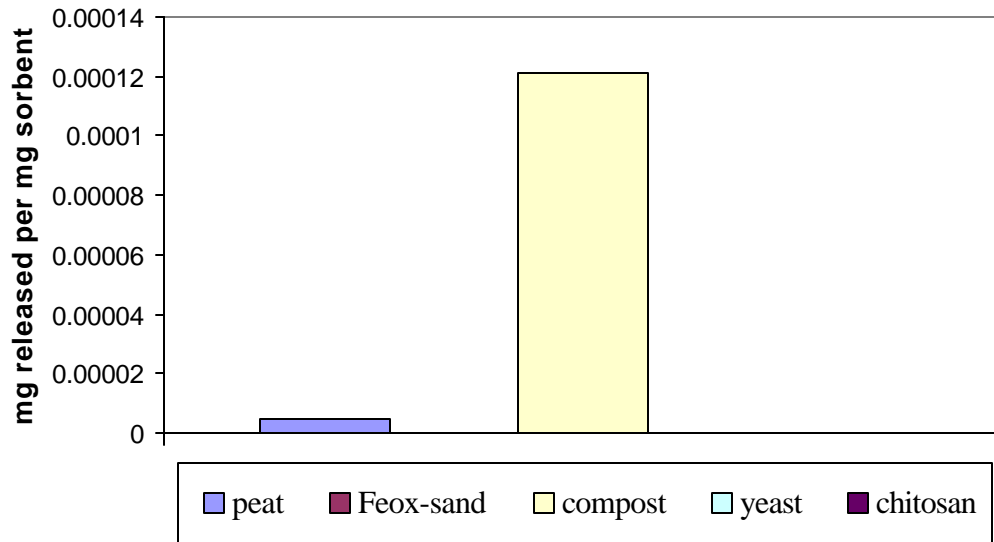


Figure 11: Desorption of lead in distilled water at high sorbent concentration ( $n=1$ )

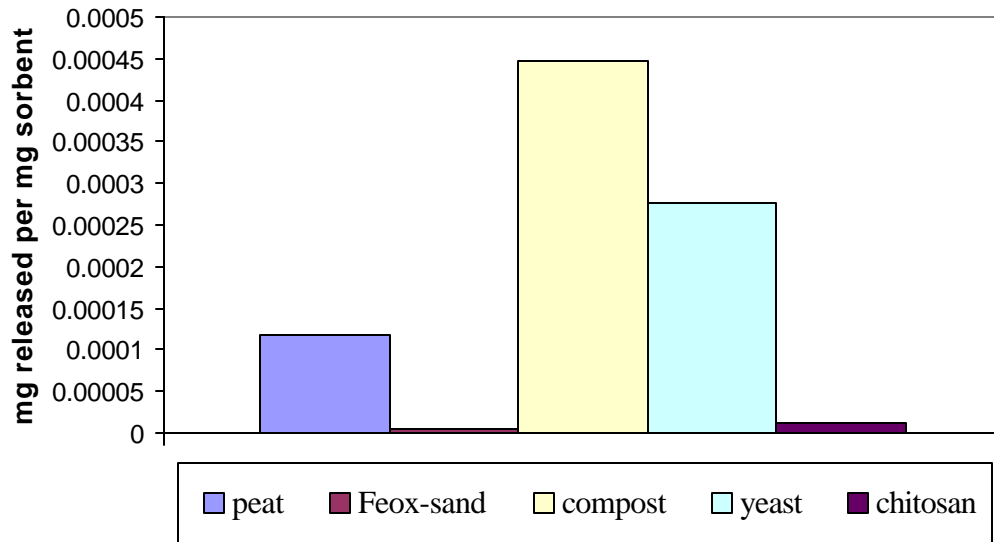


Figure 12: Desorption of copper in distilled water at high sorbent concentration (n=1)

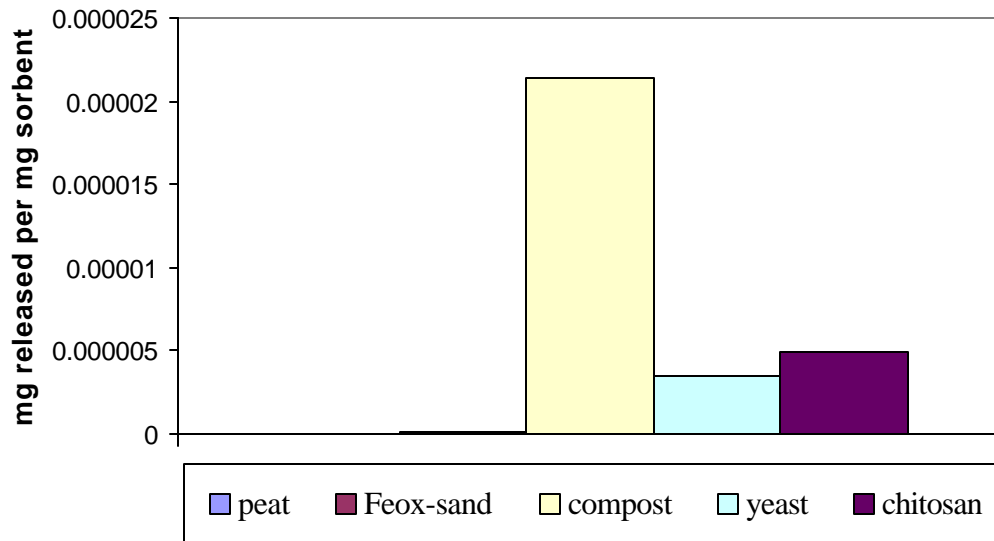


Figure 13: Desorption of arsenic in distilled water at high sorbent concentration (n=1)

### 5.6 Overall Treatment Results of Storm Water

The final concentration after treatment (using the most effective treatment method) and the initial concentration are shown in Figures 14 through 16, relative to compliance levels for copper, lead and zinc respectively.

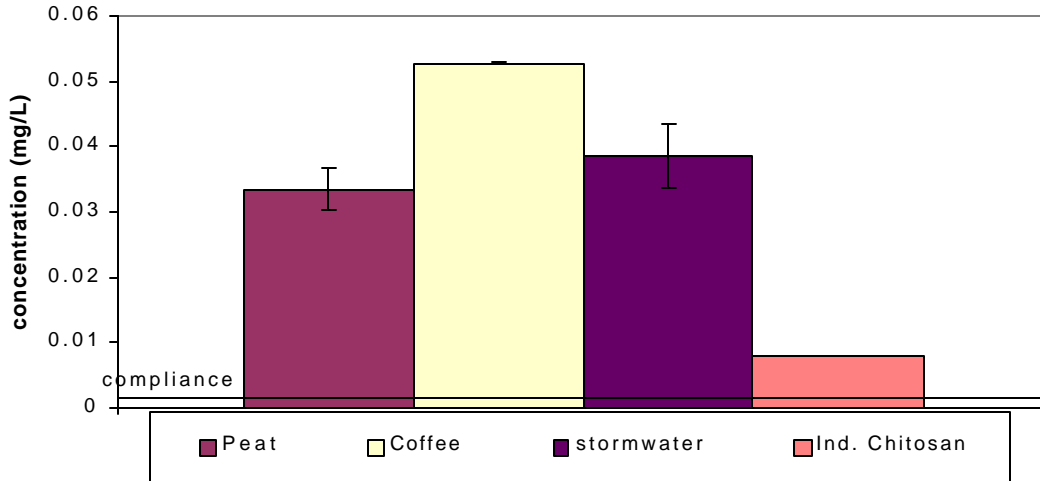


Figure 14: Copper concentration in the storm-water after treatment ( $n = 3-5$ ,  $n = 1$  for chitosan). Bars indicate one standard deviation..

Coffee, Industrial Chitosan and Peat all showed potential to treat copper in the storm-water sample, however at the lowest concentration sorbent used for his treatment experiment, none brought the concentration below the compliance level.

Industrial chitosan and yeast showed potential from the previous experiments to remove lead from the storm water sample.

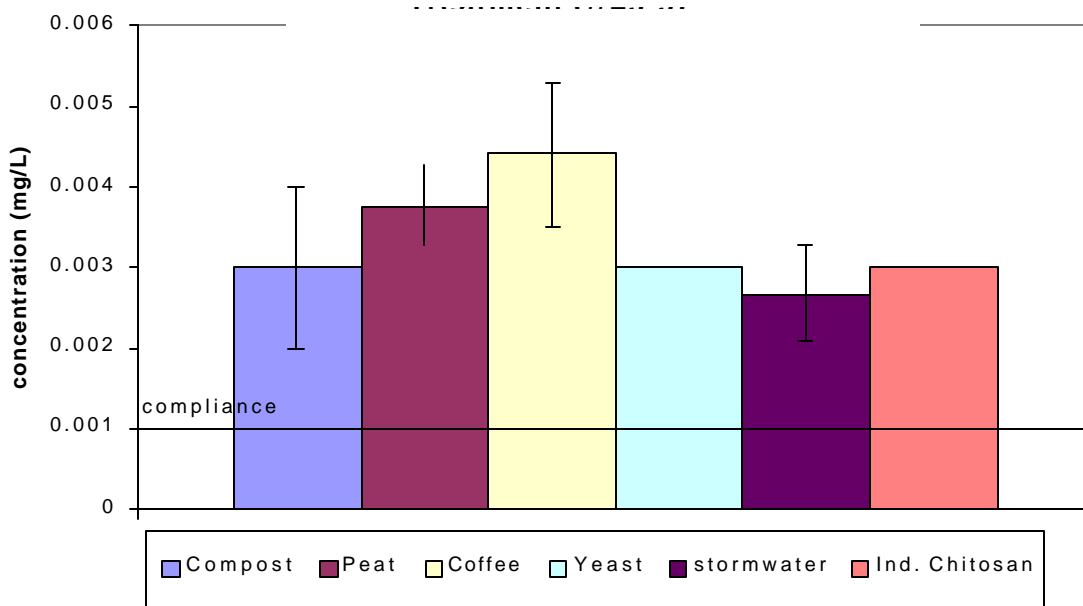


Figure 15: Lead concentration in storm-water after treatment ( $n = 3-5$ )

All of the sorbents showed the capacity to remove Zn from the storm water sample. Nevertheless, at the lowest concentration used, industrial chitosan was the only sorbent to remove zinc to a concentration below the compliance level.

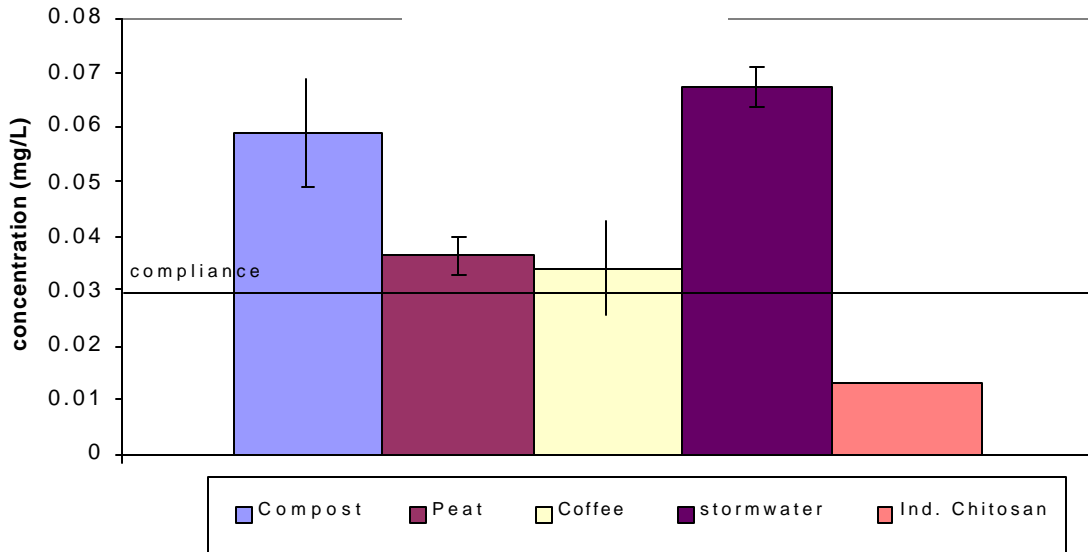


Figure 16: Zinc concentration in the storm-water after treatment (n = 3-5)

### 5.7 pH Observations

The pH recorded before and after sorbents were added stays generally the same, with a change of no more than 0.20. Some of the samples are far more acidic than others, especially the coffee, yeast and distilled water samples, which had pH's of 5.10, 5.50 and 4.41, respectively. Storm water pH increased with time by 0.40; peat had no impact on pH before and after conditioning. Coffee has a stable pH as well, and yeast increased the pH from approximately 0.16 units. The distilled water and sorbent 'blanks' all exhibited a slight increase in pH. (This data is shown in Appendix B)

### 5.8 Design to Treat Zinc with Chitosan During a Typical Storm Event

In order to assess the amount of chitosan required to treat the Zn output in a typical storm, a design calculation was carried out. This design was based on the Zn

concentration observed in our storm-water sample, and water volumetric flow rate ( $Q$ ) from a typical previous storm that had been monitored in February 17<sup>th</sup>, 2002 by Coast River Environmental Services. Figures 17 and 18 show the concentration of zinc and the flow rate during the storm event sampled on November 5<sup>th</sup>, 2002 and a typical storm event flow rate.

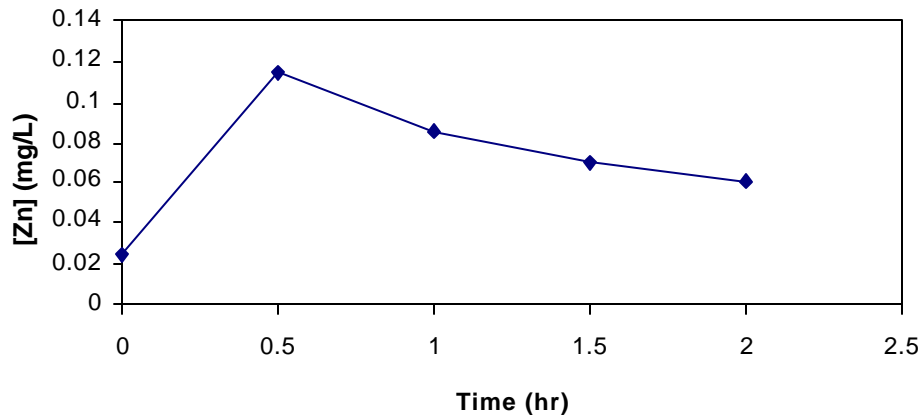


Figure 17: Booming Grounds Creek zinc concentration for one storm-water event

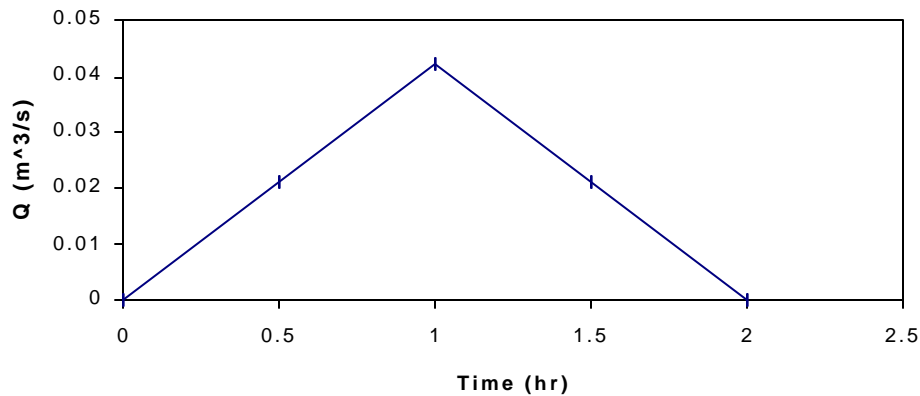


Figure 18: Discharge rate for Booming Grounds Creek for one storm-water event.

The amount of Zn flowing per second in the storm-water, which is the product of these two graphs, is illustrated in Figure 19. In order to determine the total mass of Zn in the storm water, the area under the curve from Figure 19 must be obtained.

Approximating this area using a triangular shape gives the total zinc load of 25 920 mg at a flow of 302.4 m<sup>3</sup>.

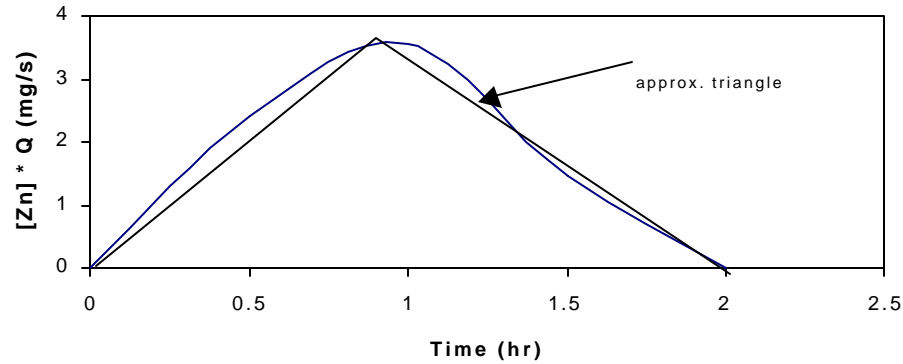


Figure 19: Zinc load for Booming Grounds Creek for one storm-water event.

Based on the total amount of Zn estimated from Figure 19, and using the cost of chitosan as 0.0032 cents/mg, the following design cost for the zinc and water loads of a typical storm event at the Booming Grounds outfall was made per storm.

Table 2: Design cost for zinc and water loads of a typical storm event at the Booming Grounds Creek outfall.

Sorbent per volume (g/L)	mg zinc absorbed / mg sorbent	zinc removal (mg/L)	mg sorbent	Cost (\$)
0.025	0.006	0.006	4320000	138.24
0.250	0.006	0.06	4320000	138.24
2.500	0.00069	0.069	37565217	1202.087

## **6.0 DISCUSSIONS AND CONCLUSIONS**

### **6.1 Storm Water Runoff Sampling**

The concentrations of As (0.0045 mg/L), Cu (0.13 mg/L), Cd (0.0002mg/L), Pb (0.003mg/L), and Zn (0.120 mg/L) are similar to the storm water concentrations obtained by the University of British Columbia Stormwater Sampling Program (Coast River Environmental Services Ltd.). For example a storm monitored on August 21<sup>st</sup>, 2001 gave the following concentrations of heavy metals: As (0.014 mg/L), Cu (0.084 mg/L), Cd (0.0006 mg/L), Pb (0.023 mg/L), and Zn (0.24 mg/L). Typical urban storm water values are As (.013 mg/L), Cu (0.035 mg/L), Cd (0.008 mg/L), Pb (0.150 mg/L), and Zn (0.150 mg/L) (Stanley Associates Engineering, 1992)

### **6.2 Efficient Range of Sorbent Concentration**

From the results of Analysis 1, it was shown that adsorption efficiency for metals is decreased as the concentration of sorbent is increased. An increase in the concentration of sorbent provides more sorption sites for the metals and thus more metals are adsorbed (Bailey et al, 1999). However it was evident from these results, that the increase in the amount of sorbent used was much greater than the kinetics of metals sorption, thus giving a lower efficiency of sorption in mg of metal sorbed/mg sorbent. In several cases the decrease in sorption efficiency showed a linear or logarithmic path. For example, Figure 3 shows the linear decrease in sorption efficiency of industrial chitosan for Cu.

### **6.3 Metals Adsorbed or Released by Compost, Peat, Coffee and Yeast**

Set I of the experiment sought to find a useful range of sorbent to remove heavy metals from the storm water. It was determined that the use of the low concentration of sorbent, provided the most efficiency, especially for chitosan and Fe-oxide coated sand. Set II sought to determine the sorption efficiency of compost, peat, coffee, and yeast at

the lowest concentration used in analysis 1 (for compost and peat) and reported in literature (for yeast and waste coffee grinds). Whereas, peat showed a low treatment efficiency for Cu, compost, coffee and yeast increased the concentration Cu in solution (a negative result). Likewise, the sorbents at increased concentrations appeared to increase the amount of Pb in the storm water sample. However, compost, peat and coffee all removed Zn from solution. These results warranted further investigation.

#### **6.4 Metals Release in Distilled Water**

Analysis 3 shows that all of the sorbants (except chitosan and sand) desorbed metals when shaken in distilled water in batch experiments. This is not surprising as in a solution of low ionic strength, such as distilled water, metals and cations with tend to ionize into solution (Lai). Nevertheless, this gives evidence that the use of sorbants as treatment for metals may exacerbate metal loads. In particular, yeast was shown to greatly increase the concentration of Zn in distilled water and in the storm water sample. Compost and peat may be a concern as they are routinely used as a soil amendment on campus.

#### **6.5 Assessment of Treatment Results for Storm Water Sample**

Industrial Chitosan was the sorbent found to be most suitable at removing metals from solution. It removed Cu (almost to compliance level) and Zn (below compliance level) at a highest efficiency of 0.0070 mg/mg chitosan and 0.006 mg/mg chitosan respectively. Only yeast and chitosan tested at low concentrations, somewhat treated Pb. These results were somewhat surprising as according to literature, of the five metals tested, Pb is the one that is most readily adsorbed (0.796mg/mg chitosan). However, for the storm water of interest, the initial lead concentration was very low (0.003mg/L), and the concentration after treatment was even lower (below the detection limit and



compliance level of 0.001mg/L). Chitosan is also known to adsorb cadmium with an efficiency of 0.559mg/mg chitosan. The concentrations of Cd before and after treatment are both below the detection limit of 0.0002mg/L and the compliance level of 0.017mg/L, thus this assessment could not be made.

#### **6.6 Design for Treatment of Zn with Chitosan..**

Based on the study conducted, treatment of the storm water runoff at the Booming Grounds outfall would require a cost of between \$150 and \$1200 based on the flow rate and load of Zn during the rainfall event.

The chitosan can be encased into beads, that can be regenerated by using EDTA (Nghah et. al, 2001; Erosa et al, 2001; Juang and Shao, 2001); these can be encased in a detention pond, such as the one illustrated below in Figure 20 below. The section cut-outs and overflow structure details are given for this pond are given in Figure 21 and Figure 22 below. The maintenance details, dimensions and design equations are all provided in pages 3-29 to 3-40 in Volume III of the Storm Water Management in Western Washington manual.

These designs propose a structure that can trap or 'detain' the storm-water, until more storm-water arrives or the treatment time of the water has been met. Other treatment strategies that can be applied to this system are detention tanks and detention vaults, all which treat the over-compliance storm-water by diverting just the toxic peak based on a conductivity reading over the baseline level, and then letting the under-compliance volume of water in the storm through.

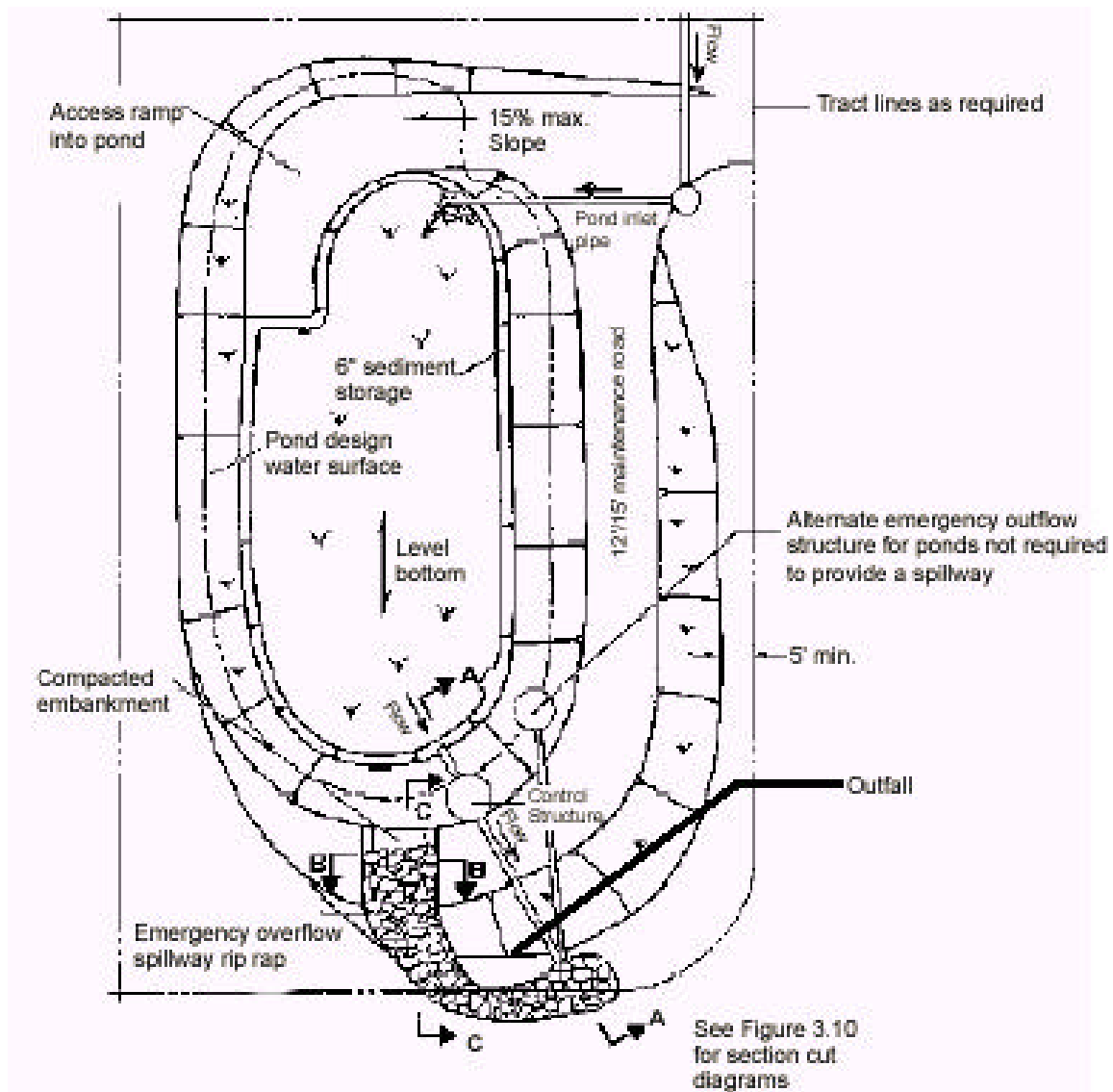


Figure 20: Typical detention pond. Section cut-out diagrams in Figures 21 and 22<sup>2</sup>.

<sup>2</sup> Washington State Department of Ecology and Water Quality (2001): *Storm Water Management for Western Washington Volume III: Hydrologic Analysis and Flow Control BMPs*. <http://www.ecy.wa.gov/programs/wq/stormwater/manual.html>, P. 3-29

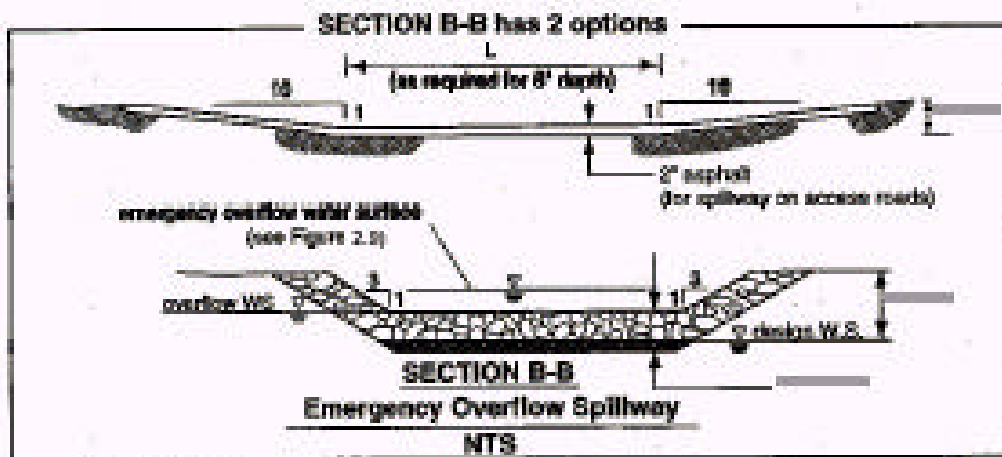
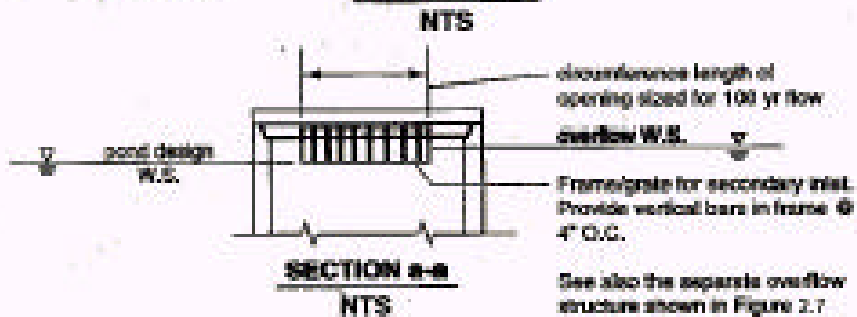
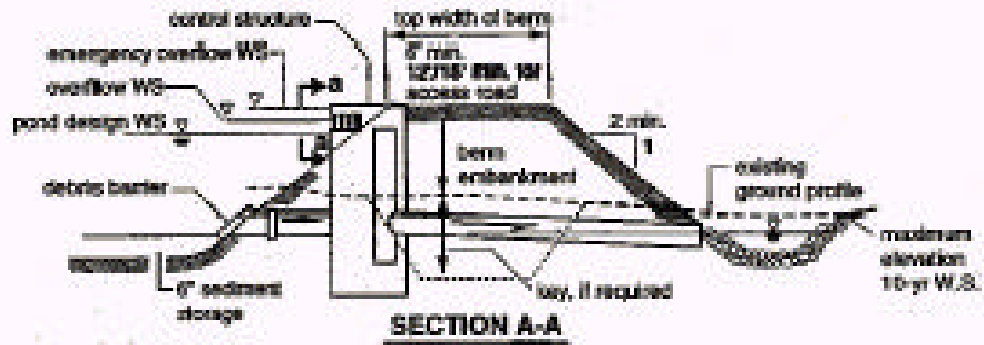


Figure 21: Section cut-outs for detention pond<sup>3</sup>.

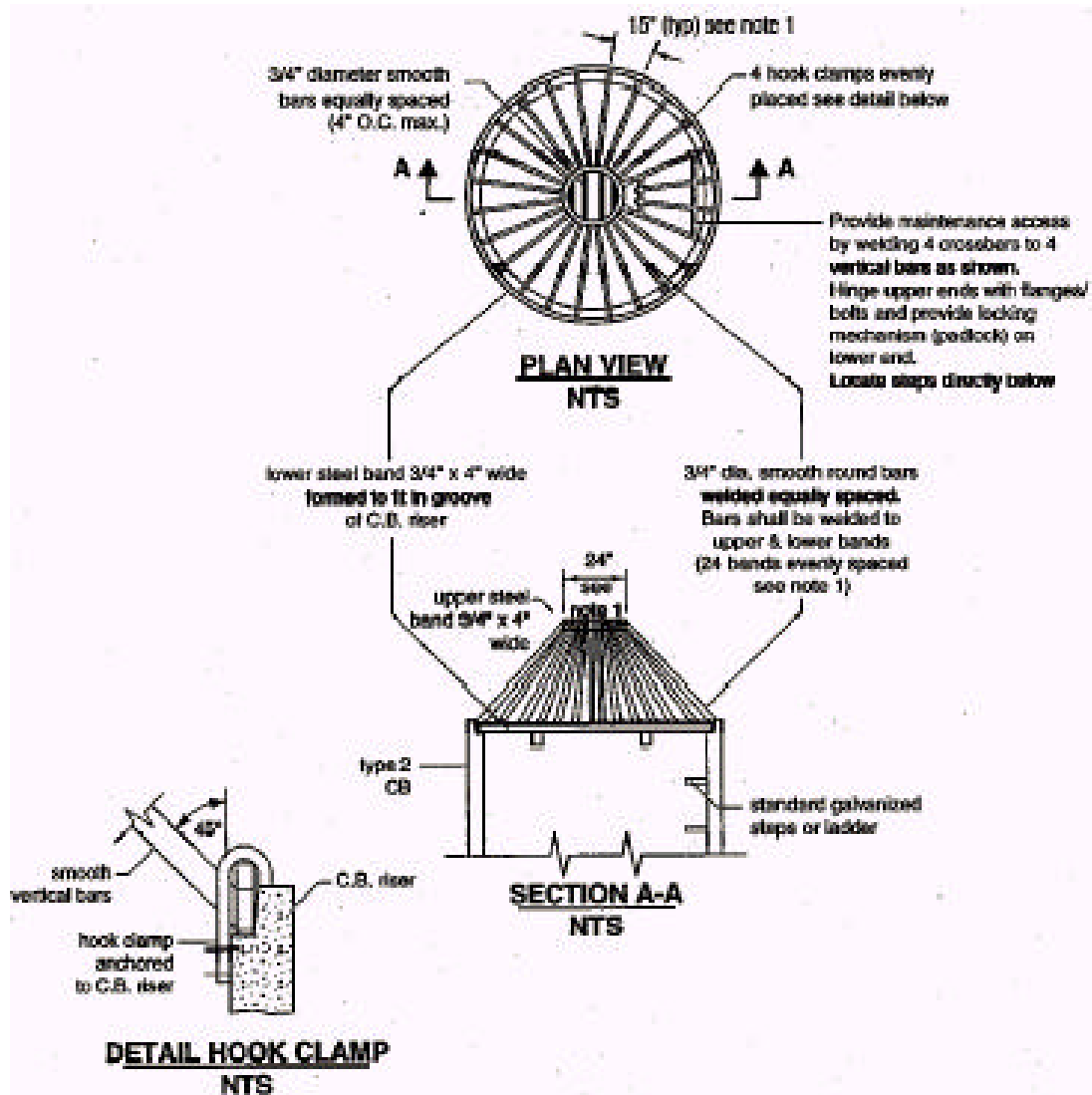


Figure 22: Overflow structure for detention pond<sup>4</sup>.

<sup>3</sup> Washington State Department of Ecology and Water Quality (2001): *Storm Water Management for Western Washington Volume III: Hydrologic Analysis and Flow Control BMPs*. <http://www.ecy.wa.gov/programs/wq/stormwater/manual.html>, P. 3-30

<sup>4</sup> Washington State Department of Ecology and Water Quality (2001): *Storm Water Management for Western Washington Volume III: Hydrologic Analysis and Flow Control BMPs*. <http://www.ecy.wa.gov/programs/wq/stormwater/manual.html>, P. 3-31



## **7.0 FUTURE WORK**

The current study showed that most of the low cost sorbents tested (Peat, Yeast, Coffee, Compost, and Fe-oxide coated sand) were incapable of treating the University of British Columbia storm water discharge at the Booming Grounds outfall. However, industrial grade chitosan from Vanson Halosource shows promise as treatment sorbent for heavy metals. Before this sorbent is implemented in a design, further testing over a broader range of metals concentrations must be conducted. The life of the chitosan media must be determined as well as possible recharge techniques. As well, its effectiveness over a variation of solution chemistries (such as concentration  $\text{Ca}^{2+}$  and pH) must be determined. The kinetics of the sorption must also be studied in detail, in order to determine the most efficient sorbent concentration and time required to treat the storm-water.

Additionally, the impact of discharging the untreated storm-water onto a coastal habitat must also be investigated, since aquatic habitat is highly susceptible to these metals being over compliance..

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## **APPENDIX A: PROPOSAL**

### **Summary**

This is a proposal to discover a viable remediation technology to treat heavy metals from UBC's storm-water runoff. In preliminary testing of UBC's storm-water runoff, several heavy metals (Cadmium, Copper, Lead, Zinc and Arsenic) were found to be above the BC Water Quality (BCWQA) guidelines for marine life. An overabundance of heavy metals can cause harm and often death to the organisms living in and around the water. With regards to UBC's policy towards sustainability and minimal environmental impact, heavy metal contamination is a very important issue that needs to be addressed. In collaboration with UBC Plant Operations, and as part of a SEEDS (Social, Ecological, Economic Development Studies) project, the CHBE 465 – Aquatic Habitat Remediation class will examine a prevalent existing storm-water treatment technology as well as a newer and more innovative method to remove heavy metals from UBC's storm-water.

The existing technology being focussed on is sand filtration, since sand is commonly used to treat storm-water. Aside from that, other low cost adsorbents will be investigated as potential mediums to adsorb the heavy metals out of the storm-water. After checking the available literature on several adsorbents, nonliving organic and inorganic adsorbents were selected for this application, since they are more effective at adsorbing heavy metals over a relatively small land area, than living organic adsorbents are.

Of these adsorbents, the most effective ones will be examined as part of this project. Laboratory tests will be conducted to determine the heavy metal adsorptive rate and capacity from UBC's runoff using algae, solid brewery waste, coffee grounds, chitosan, iron oxide coated sand, peat moss, wood and leaf compost.

After the laboratory tests, the design of a treatment system will be conducted based on a 2-year storm. The specific goal of the treatment system will be to remove arsenic, cadmium, copper, lead and zinc out of storm-water from the Booming Grounds Outfall to below recommended values from the BC Ministry of Water, Land and Air Protections- BC Approved Water Quality Guidelines. The project cost is \$5000 and the deliverables include a report outlining the findings of the laboratory tests, recommendations regarding the applicability of adsorbents that have been tested and a viable treatment system designed specifically for the UBC storm-water system. This project is expected to be completed by the end of the year 2002.

### **A.1 Introduction**

“Water is H<sub>2</sub>O, hydrogen two parts, oxygen one,  
But there is also a third thing, that makes it water  
And nobody knows what that is.”

-DH Lawrence (1885-1930)

The preliminary sampling of UBC’s storm-water runoff program, conducted by the CHBE 465 class of 2001, indicated that the discharge of toxic substances (as defined in the Canadian Environmental Protection Act) at the majority of storm-water runoff outfalls exceeded both the Provincial Approved Water Quality Guidelines as well as the Federal Environmental Quality Guidelines. As a consequence, UBC is in contravention of the federal Fisheries Act, the Waste Management Act, and the Canadian Environmental Protection Act. According to the Fisheries Act, Chapter F14, line 35. (1) “No person shall carry on any work or undertaking that results in the harmful alteration, disruption or destruction of fish habitat”; additionally, the Act states on line 36. (3)

“Subject to subsection (4), no person shall deposit or permit the deposit of a deleterious substance of any type in water frequented by fish or in any place under any conditions”.

Other regulations being refracted include BC Waste Management Act stating that it is against the law to discharge hazardous waste to the environment and onto fish habitat, as well as onto recreational areas, which include primarily the beaches around UBC.

In order to assist UBC in addressing this issue, the students of CHBE 465 (the chemical and biological engineering project-based course focussed on rehabilitation of aquatic habitats) undertook an investigation aimed at alleviating this problem.

Contaminated storm-water is a common problem in the western civilization due to a combination of coverage of the earth’s surface with an impermeable layer of buildings and pavement, and the dispersion of pollutants (from non-point pollution sources such as fertilizers, parking lots, herbicides, pesticides, fungicides, concentrated animal waste, concentrated wood waste, construction and automobiles) that are transported during rainstorm events partially into the groundwater but mostly into the storm sewer network.

Urban storm-water problems can be dealt with in two ways. First, source control is necessary to reduce the quantity of flow, and to reduce/eliminate the pollutant load to both the groundwater and the storm sewer network. This is an integral part of building a sustainable campus. Second, since it takes too much time to reverse the damage done by the existing infrastructure, and also in order to invoke others to change their polluting ways, pollutants should be immediately removed from the storm-water runoff using a treatment system. The latter can be expensive (both the initial investment and on-going operating costs), and will result in potentially another problem with regards to what should be done with the collected contaminants.

As the project team is a group of students in Chemical and Biological Engineering studying aquatic habitat rehabilitation, and since the project timeline is only three months long, only two major treatment systems are being investigated. One is based on a conventional treatment system (sand filtration), and the other is based on using low-cost adsorbents. A review of several treatment systems is attached.

The overall goal of this project, is to develop a stand alone filtration system to reduce the concentration of Arsenic, Cadmium, Copper, Lead and Zinc to below the water quality guidelines of the Canadian Environment Protection Act (Schedule 1). These guidelines are comparatively similar to the British Columbia Approved Water Quality Act and the Canadian Council of Ministers of the Environment.

The selection of the above mentioned metals to be targeted in the biological filtration system was determined by assessing both the actual concentration and relative toxicity of the substance in the storm-water. The substances identified in the preliminary sampling that superceded regulations were Arsenic, Cadmium, Chromium, Copper, Iron, Lead, Magnesium, Mercury, Zinc and Fecal Coliform Bacteria. Due to apparent low frequency of guideline transcendence or inherent toxicity, Chromium, Iron, Magnesium and Mercury were dropped from our focus (research time and sampling costs would be increased if these metals were kept as a reduction target). The focus will be on heavy metals, not Fecal Coliform, as heavy metals were considered to represent a more serious issue due to their ability to harm aquatic life.

The goal of this testing is to determine whether the adsorbent can adsorb the maximum heavy metal concentration found in UBC's storm water. Some values have

been found in the literature for maximum adsorption capacity of the adsorbents, but it is necessary to conduct on-site tests because:

- The storm water is contaminated with a cocktail of heavy metals, which may interact with each other or with the adsorbent differently than if the water were only contaminated with one metal species.
- The adsorption characteristics of the adsorbents may depend on the water characteristics. It would be best to test the adsorbents using samples of storm water from the proposed site.

Samples will be collected in 4L acid-washed containers during the first flush (3 hours) rain event of a storm. All samples and tests will be conducted within one week of sampling in order to avoid microbial alteration of samples and results.

The objective is to assess which adsorbent(s) can effectively treat the maximum metals concentration found in UBC's storm water run-off. Maximum adsorbent-capacities for each adsorbent have been reported previously however it is necessary to conduct our own tests to ensure treatment efficiency before implementing a full-scale treatment system.

In order to design a filtration system, testing of various metal adsorbents is necessary as UBC's storm-water is unique and the efficiency of metals adsorption by the adsorbents has not yet been tested.

Most specifically, the short-term tasks of the project are:

1. To examine the behavior of heavy metals in the storm water.
2. To use standard methods to test the efficiency of adsorbents in remove heavy metals.

3. To use the results to examine the technical/economical feasibility of two treatment methods (conventional system and non-conventional) to eliminate heavy metals in UBC's storm-water.

This Document is a proposal providing an overview of this project, outlining design considerations, sources of information, funding and project scheduling. Alternate solutions and existing forms of this design are discussed and critiqued. Projected financial requirements are provided, as are project Gantt and milestone charts.

## **A.2 Scope of Work**

**A.2.1. Task 1 – Identify the properties of heavy metals recorded in the storm-water report to determine design flow and factors that might affect the treatment system.**

- Research typical values and characteristics of metals found in typical stormwater and compare to UBC's stormwater
- Analyse storm defined data: max flow rate, land surveys
- Identify the heavy metals that exceeded water discharge regulations: As, Cd, Cu, Pb, Zn
- Research both chemical and physical properties of the heavy metals

### **A.2.2. Task 2 - Identify the Proper Adsorbents for the System**

- Research methods of heavy metal adsorbents: Soil treatment, Wetland, Plants and Vegetation, adsorbents, Moss, Fungi and Algae
- Identify advantages and disadvantages of the adsorbents chosen.
- Select best adsorbents for testing

### **A.2.3. Task 3 - Test the selected Adsorbents**



- Collect 8-15 samples at the Booming ground outfall during the first 3 hours of a storm.
- Determine concentrations of As, Cd, Cu, Pb, Zn in the collected sample, if above guidelines, use for laboratory testing
- Perform Adsorption capacity tests (repeat testing in different dilutions)
- Perform Column tests (repeat testing in different dilutions)
- Analyse treated storm-water for heavy metal concentration
- Compare the test results and finalise adsorbents to be used in the treatment system

<b>Methods</b>	<b>Advantages</b>	<b>Disadvantages</b>	<b>Pass/ Fail</b>
<b>Algae</b>	Abundant, and relatively inexpensive, Self-replenishing	Live cultures require immobilization in a matrix, low uptake rates and high residence times.	Pass
<b>Bacteria</b>	Very good absorption with some cations	Mediums and immobilization required, for growth and to prevent contamination of water outside. Comparatively slow uptake rates.	Fail
<b>Brewery's waste</b>	Reuse waste products. Cheap to obtain	High concentration of Alcohol Acidic	Pass

<b>Methods</b>	<b>Advantages</b>	<b>Disadvantages</b>	<b>Pass/ Fail</b>
<b>Chitosan</b>	renewable, natural sources, non-toxic, high biodegradability	availability fluctuates seasonally, difficult to extract the pure materials	Pass
<b>Coffee Grounds</b>	Easy and cheap to obtain	Acidic	Pass
<b>Fungi</b>	Abundant, and relatively inexpensive, Self-replenishing	Live cultures require immobilization in a matrix, low uptake rates and high residence times. Need massive land for growth	Fail
<b>Iron Oxide Coated Sand</b>	Very good absorption with some cations	needs to renew material constantly	Pass
<b>Moss</b>	Easy and cheap to obtain	Live cultures require immobilization in a matrix, low uptake rates and high residence times. Need massive land for growth	Fail
<b>Soil treatment</b>	Effective to treat heavy metal	Expansive	Fail
<b>Trees/Plants</b>	Fast absorption rate	Expansive	Fail
<b>Wet land</b>	Large storage	Slow uptake rate, Massive	Fail

<b>Methods</b>	<b>Advantages</b>	<b>Disadvantages</b>	<b>Pass/ Fail</b>
		land required	
<b>Wood and Leaf Compost</b>	contain natural lignin fractions	May contain As	Pass

#### **A.2.4. Task 4 - Design the pilot system by using the selected Adsorbents**

- Design and build a proper pilot system by using the selected adsorbents
- Perform laboratory tests for the treated storm-water
- Quantify the amount of heavy metal removal rate
- Predict flow rates that can be tolerated by the system
- Estimate a maintenance time scale based on typical rainfall values for the Vancouver area.

#### **A.2.5 Task 5- Report**

- Literature review of the alternative technologies available in heavy metal removal
- Literature review of the Bio-filtration Channel's impact on local habitat
- Long-term evaluation of the pilot system
- Design methods for bio-waste product removal
- Tabulate long-term budget for maintaining the system
- Analysis metal removal rate for the bio-filtration channel
- Assessment of the ability of the adsorbents to allow storm-water to meet discharge regulations.

- Time permitting, the pilot system scaling up consideration

## APPENDIX B: BUDGET AND EXPENDITURES

This is the current budget, as of December 20<sup>th</sup>, there are still a few expenses pending.

Expense Identification	Person with receipt	Purchase Place	Subtotal	GST	PST	Total Amount	Total
<b>1 Sampling Equipment</b>							
sampling equipment	Lin Xu	Home Depot	\$ 54.44	\$ 3.81	\$ 3.79	\$ 62.04	
sampling equipment	Lin Xu	grocery store	\$ 16.30	\$ 1.14		\$ 17.44	
4 flasks, 1 box gloves, stoppers, rack	Royann	CHBE Stores	\$ 116.70	-	-	\$ 116.70	
Chitosan (120.59\$US)		Vanson Halosource				\$ 196.56	
<b>2 Transportation</b>							
Fuel	Lin Xu	Esso	\$ 16.03	\$ 1.12		\$ 17.15	
<b>3 Food</b>							
Working Dinner	Lin Xu	Las Margaritas	\$ 60.78	\$ 4.22		\$ 65.00	
Working Dinner	Anita Ansari	One More Sushi	\$ 80.37	\$ 5.71		\$ 86.08	
Working Dinner	Hank Wong	Daimasu	\$91.00	\$ 5.36		\$ 91.00	
Working Dinner	Peter/Janet					\$ 35.00	
Final Group Dinner	Royann	Banana Leaf Restaurant				\$ 375.00	
<b>4 Testing Services</b>							

Expense Identification	Person with receipt	Purchase Place	Subtotal	GST	PST	Total Amount	Total
11/28/2002	Peter	ALS Environmental Services	\$ 1,274.40	\$ -	\$89.21	\$ 1,363.61	
		ALS Environmental Services				\$ 74.90	
12/6/2002		ALS Environmental Services		\$ -		\$ 419.44	
12/9/2002		ALS Environmental Services		\$ -		\$ 681.38	
<b>Dec. 20th, Overall Total to Date (not final):</b>							<b>\$3,601.30</b>

## **APPENDIX C: EXPERIMENTAL METHODS – SAMPLE PREPARATIONS**

Sample preparation is separated into 4 major sections:

- Bulk runoff sample transfer to individual test flask
- Sorbent weighing
- Sorbent and Sample Mixing
- Sample filtration and centrifugation

### **Bulk Runoff Transfer**

- 1) All required glassware (Erlenmeyer flask, graduated cylinders) was acid washed in low concentration HNO<sub>3</sub> and double rinsed with distilled water
- 2) The bulk sample was shaken for approximately 3 minutes to redistribute all settled particles
- 3) Sample water was then poured to a 1 litre beaker (sample beaker) for metering into a 250 ml graduated cylinder. Precision is plus or minus 0.5 ml.
- 4) From the sample beaker 3, 150 ml samples were measured into 250 ml Erlenmeyer flasks. All three samples are used for 1 sorbent test in triplicate
- 5) A fourth sample is poured from the sample beaker as a sample blank.
- 6) The sample blank pH is tested, this pH is used to represent all 4 samples poured.
- 7) After step 6, the remaining sample in the sample beaker is discarded.
- 8) Steps 2 to 7 are repeated for the remaining sorbents.

### **Sorbent Weighing**

- 1) Sorbents are weighed using an analytical balance with a precision of 0.1 ug.
- 2) Weighing paper is zeroed on the scale, and a specified air-dry sorbent mass is measured onto the paper.

- 3) The sorbent masses are prepared and weighed.
- 4) Each sample is wrapped and set aside for transfer to the runoff sample

In the special case of the brewery waste, which was still very wet, weighing boats were used for measurement, and the mass added to the runoff sample was determined by difference after addition.

### **Sorbent and Sample Mixing**

- 1) Sorbent is added directly to the runoff sample
- 2) Gentle shaking is performed to allow sorbent to mix with runoff
- 3) pH is measured and recorded
- 4) Mixture is covered with parafilm and placed in the shaker
- 5) Steps 1 to 4 are repeated for the remaining samples
- 6) The shaker is set at level 5 and allowed to shake for 24 hours at ambient temperature (19.5°C)

### **Sample Filtration and Centrifugation**

After 24 hours of shaking, the samples were filtered and centrifuged (where necessary)

- 1) Sample is removed from shaker
- 2) Parafilm is removed, and pH is measured
- 3) Mixture is filtered using suction filtration
- 4) Approximately 50 ml of sample is collected in centrifuge tubes
- 5) Steps 1 to 4 are repeated for all samples

It was necessary to filter the brewery waste sample because of high turbidity even after filtering.



Table 3 Sample Preparation Data

Sample Label	Sample Composition	Volume (ml)	pH pre-sorbent	Sorbent Mass (g)	pH post-sorbent	pH post-shake
W1	stormW+wood	150	6.14	0.0281	6.10	6.5
W2	stormW+wood	152	6.14	0.0281	6.10	6.5
W3	stormW+wood	149	6.14	0.0281	6.12	6.7
SB1	stormW only	148	6.14	0		6.4
P1	stormW+peat	151	6.08	0.0641	6.10	6.1
P2	stormW+peat	150	6.08	0.0639	6.09	6.07
P3	stormW+peat	152	6.08	0.0640	6.11	6.11
SB2	stormW only	149	6.08	0		6.4
C1	stormW+coffee	150	6.09	0.5005	6.12	6.1
C2	stormW+coffee	149	6.09	0.5000	6.14	6.2
C3	stormW+coffee	148	6.09	0.5003	6.16	6.26
SB3	stormW only	150	6.09	0		6.4
Y1	stormW+yeast	150	6.07	20.8498	5.49	5.65
Y2	stormW+yeast	150	6.07	20.2680	5.49	5.65
Y3	stormW+yeast	150	6.07	20.2072	5.50	5.65
WW	distilledW+wood	150	5.10	0.0280	4.94	5.74
PW	distilledW+peat	150	5.07	0.0638	5.07	5.1
CW	distilledW+coffee	150	5.14	0.5000	5.10	5.5
YW	distilledW+yeast	150	5.09	20.5151	5.42	5.54
DW	distilledW	150	5.21	0		4.41

## APPENDIX D: DATA

Table 4: Results of Stormwater Analyses

Metal	Concentration (mg/L)
Arsenic	<0.2
Cadmium	<0.01
Copper	0.13
Lead	<0.05
Zinc	0.12

Source: ICP-AES metals scan from ALS

Table 5: Conductivity for Booming Grounds Creek Stormwater During Sampling Time

Date / Time	Sp Cond mS/cm
11/5/2002 19:30	0.383
11/5/2002 19:45	0.358
11/5/2002 20:00	0.332
11/5/2002 20:15	0.529
11/5/2002 20:30	0.852
11/5/2002 20:45	0.51
11/5/2002 21:00	0.332
11/5/2002 21:15	0.192
11/5/2002 21:30	0.155

Source: Coast River Environmental Services Ltd.

Table 6: Mass of Metal Sorbed per Mass of Sorbent

Mass of sorbent (mg)	Actual Sample Volume (mL)	Sorbent per Volume (g/L)	Metal				
			As	Cd	Cu	Pb	Zn
(mg adsorbed/mg sorbent)							
Blank (2)							
	50		0.0053	0.0002	0.066	0.003	0.082
Blank (1)							
	50		0.004	nd	0.101	0.003	0.071
Sand							
2600	30	87	0.0	nd	3.8E-07	-3.8E-07	1.7E-05
2600	30	87	-3.8E-07	nd	-1.5E-06	-7.7E-07	1.4E-05
7800	30	260	-1.3E-07	nd	-1.5E-05	-7.7E-07	2.7E-06
7800	30	260	0.0	nd	-2.8E-06	-2.6E-07	5.1E-06
23400	30	780	4.3E-08	nd	-8.5E-08	-4.3E-08	2.1E-06
23400	30	780	4.3E-08	nd	-1.5E-05	-3.0E-07	-4.7E-06
Peat							
12.8	40	0.32	-7.8E-05	nd	4.9E-03	7.8E-05	2.2E-03
12.8	40	0.32	-7.8E-05	nd	4.8E-03	7.8E-05	2.2E-03

Mass of sorbent	Actual Sample Volume	Sorbent per Volume	Metal				
			As	Cd	Cu	Pb	Zn
*		0.42		nd			1.6E-04
128	40	3.2	-4.7E-05	nd	1.5E-04	-7.8E-06	-7.2E-04
128	40	3.2	-4.7E-05	nd	6.3E-04	nd	4.1E-04
1280	40	32	-5.5E-06	nd	1.3E-05	-7.0E-06	3.2E-05
Coffee							
100	40	2.5	-4.0E-05	nd	5.6E-04	0.0E+00	3.7E-04
100	40	2.5	-3.0E-05	nd	2.7E-04	-5.0E-05	3.6E-04
*	40	3.4		nd			1.5E-05
Yeast							
225	40	5.6	-2.7E-05	nd	-4.4E-06	-4.4E-06	-1.2E-03
675	40	17	-7.4E-06	nd	5.9E-06	0.0E+00	-9.3E-04
2025	40	51	-5.4E-06	nd	-2.1E-04	4.9E-07	-9.1E-04
Compost							
5.6	40	0.14	-1.8E-04	nd	8.9E-03	-1.1E-03	7.3E-03
5.6	40	0.14	0.0E+00	nd	7.5E-03	0.0E+00	7.1E-03
56	40	1.4	-3.6E-05	nd	1.1E-03	-7.1E-05	8.0E-04
56	40	1.4	-1.8E-05	nd	1.2E-03	-1.8E-05	8.8E-04
560	40	14	-2.9E-05	nd	-5.5E-04	-1.5E-04	-4.4E-04
Industrial Chitosan							
1	40	0.025	2.3E-03	nd	7.0E-03	0.0E+00	6.0E-03
10	40	0.25	2.2E-04	nd	5.6E-03	nd	6.0E-03
100	40	2.5	1.0E-05	nd	5.8E-04	nd	6.9E-04
Lactate Chitosan							
1	40	0.025	-1.0E-04	-1.0E-04	-1.0E-02	-1.0E-03	-7.3E-02
10	40	0.25	-5.1E-04	-3.0E-05	-1.6E-02	-1.3E-03	-9.8E-03

\* Third Experiment

Table 7: Data and Observations from Experiment 3

Sample Label	Sample Composition	Volume (ml)	pH sorbent	pre-Sorbent Mass (g)	pH post sorbent	Observations
W1	stormW +wood	150	6.14	0.0281	6.10	
W2	stormW +wood	152	6.14	0.0281	6.10	
W3	stormW +wood	149	6.14	0.0281	6.12	
SB1	stormW only	148	6.14	0		
P1	stormW +peat	151	6.08	0.0641		6.10 slightly darker than P2 and P3 before adding sorbent
P2	stormW +peat	150	6.08	0.0639		6.09 All peat: bits cling to side sometimes ABOVE water
P3	stormW +peat	152	6.08	0.0640		6.11 swirling loosens
SB2	stormW only	149	6.08	0		

Sample Label	Sample Composition	Volume (ml)	pH sorbent	pre-Sorbent Mass (g)	pH post sorbent	Observations
C1	stormW +coffee	150	6.09	0.5005	6.12	slightly darker than C2 and C3 before adding sorbent
C2	stormW +coffee	149	6.09	0.5000	6.14	**NOTE all coffee samples were moist
C3	stormW +coffee	148	6.09	0.5003	6.16	
SB3	stormW only	150	6.09	0		
Y1	stormW +yeast	150	6.07	19.1955	5.49	All yeast: Muddy, looks like cheap chocolate milk
Y2	stormW +yeast	150	6.07	18.6137	5.49	
Y3	stormW +yeast	150	6.07	18.5529	5.50	
WW	distilled W+wood	150	5.10	0.0280	4.94	
PW	distilled W+peat	150	5.07	0.0638	5.07	
CW	distilled W+coffee	150	5.14	0.5000	5.10	
YW	distilled W+yeast	150	5.09	18.8608	5.42	
DW	distilled W	150	5.21	0		

Table 8: Predicted Sorbent Masses to be used for Experiment 3

Sorbent	Original Concentrations tested (mg/ml)	x5 metals (mg/ml)	x150 (mg)	ml	Moisture Content (assumed)	Required Sorbent Sample Mass (g)
Wood	0.037	0.187	28		0	0.028
Peat	0.085	0.427	64		0	0.064
Coffee	0.667	3.333	500		0	0.5
Yeast	1.5	7.500	1125		0.95	22.5

Table 9: Moisture Content of Sorbents for Experiment 3

Sorbent	Moist Sample & Crucible (g)	Crucible Mass (g)	Wet Sample (g)	Dry Sample & Crucible (g)	crucible	Dry Sample (g)	Percent Moisture
Yeast	106.75	70.8965	35.8535	76.7023	70.8965	5.8058	83.81
Coffee	2.8733	1.6487	1.2246	42.0178	41.6004	0.4174	65.92

Peat	3.31575	1.42270	1.89305	40.3411	39.1722	1.1689	38.25
Compost	16.5576	1.41395	15.14365	61.9978	53.3207	8.6771	42.70

Table 10: Observations and pH after Shaker but before Filtration – Experiment 3

Sample Label	Sample Composition	pH	Observations
W1	stormW+wood	6.5	Small amount of dark brown particles floated to the top. Very light yellow/brown supernatant, small particles of solids settled on bottom.
W2	stormW+wood	6.5	
W3	stormW+wood	6.7	
SB1	stormW only	6.4	slightly turbid, small particles settled.
P1	stormW+peat	6.1	Slightly turbid, solids settled
P2	stormW+peat	6.07	
P3	stormW+peat	6.11	
SB2	stormW only	6.4	same as SB1
C1	stormW+coffee	6.1	Medium turbidity, solids settled
C2	stormW+coffee	6.2	
C3	stormW+coffee	6.26	
SB3	stormW only	6.4	same as SB1
Y1	stormW+yeast	5.65	Very turbid, light brown supernatant with solids settled forming a layer at the bottom. High turbidity was not decreased through filtration, centrifugation was carried out.
Y2	stormW+yeast	5.65	
Y3	stormW+yeast	5.65	
WW	distilledW+wood	5.74	Clear supernatant with small particles settled.
PW	distilledW+peat	5.1	Clear supernatant with small brown particles settled.
CW	distilledW+coffee	5.5	Light tea color with black solids (coffee grounds) settled out.
YW	distilledW+yeast	5.54	Same as Y1,2 and 3
DW	distilledW	4.41	Clear solution, no solids.
Temperature: 19.5 deg C			

Table 11: Analyses Data from Experiment 3

	Replicate	Physical Tests	Total Metals							
		Hardness CaCO3	Calcium T-Ca	Magnesium T-Mg	Copper T-Cu	Avg Cu/ Stdev	Lead T-Pb	Avg Pb/ Stdev	Zinc T-Zn	Avg Zn/ Stdev
Compost	1	-	-	-	0.076	0.058	0.004	0.003	0.063	0.059
	2	-	-	-	0.058	0.018	0.002	0.001	0.066	0.0096437
	3	-	-	-	0.04		0.003		0.048	
Peat	1	-	-	-	0.029	0.034	0.004	0.00375	0.038	0.0365
	2	-	-	-	0.034	0.0033	0.003	0.0005	0.04	0.0034157
	3	-	-	-	0.034		0.004		0.036	

	4	-	-	-	0.037		0.004		0.032	
Coffee	1	-	-	-	0.061	0.0528	0.006	0.0044	0.048	0.0342
	2	-	-	-	0.059	0.0071903	0.004	0.0008944	0.027	0.0086429
	3	-	-	-	0.052		0.004		0.037	
	4	-	-	-	0.048		0.004		0.028	
	5	-	-	-	0.044		0.004		0.031	
Yeast	1	-	-	-	0.31	0.3133333	<0.002	0.003	1.24	1.21
	2	-	-	-	0.3	0.0152753	<0.002		1.2	0.0264575
	3	-	-	-	0.33		0.003		1.19	
Storm water blanks	1	45.5	15.5	1.7	0.033	0.039	0.002	0.0027	0.064	0.067
	2	45.7	15.5	1.7	0.041	0.005	0.003	0.0006	0.071	0.004
Sorbent+ water	3	44.1	15	1.6	0.042		0.003		0.067	
Compost	1	-	-	-	0.008		<0.001		<0.005	
Peat	1	-	-	-	<0.005		<0.001		<0.005	
Coffee	1	-	-	-	0.019		<0.001		<0.005	
Yeast	1	-	-	-	0.3		<0.002		0.68	
Distilled Water	1	-	-	-	0.008		<0.001		<0.005	

Table 12: Average Metal Sorbed in Distilled Water for Each Sorbent

Sorbent	Sorbent Conc. (g/ml)	Cu (mg/L)	Pb (mg/L)	Zn (mg/L)	Cu sorbed (mg/L)	Pb sorbed (mg/L)	Zn sorbed (mg/L)	mg Cu/mg sorbent	mg Pb/mg sorbent	mg Zn/mg sorbent
Compost	1.9E-04	5.8E-02	3.0E-03	5.9E-02	-1.9E-02	-3.3E-04	8.3E-03	-1.0E-04	-1.8E-06	4.5E-05
Peat	4.2E-04	3.4E-02	3.8E-03	3.7E-02	5.2E-03	-1.1E-03	3.1E-02	1.2E-05	-2.6E-06	1.6E-04
Coffee	2.2E-03	5.3E-02	4.4E-03	3.4E-02	-1.4E-02	-1.7E-03	3.3E-02	-6.5E-06	-7.9E-07	1.5E-05
Yeast	1.4E-01	3.1E-01	3.0E-03	1.2E+00	-2.7E-01	-3.3E-04	-1.1E+00	-2.0E-06	-2.4E-09	-8.4E-06
Stormwater	0	0.038667	0.002667	0.067333						

Table 13: Rough Cost Estimate to Remove Zinc Using Chitosan for a 2-year Storm

Sorbent per Volume (g/L)	mg Zn absorbed/mg sorbent	Zn removal (mg/L)	mg sorbent	Cost (\$)
0.025	0.006	0.006	4320000	138
0.250	0.006	0.06	4320000	138
2.500	0.00069	0.069	37565217	1202

## **APPENDIX E: LAWS**

The three federal legislative documents that are most related to discharging stormwater are the Environment Management Act, the Waste Management Act, and the Fisheries Act.

To expand on these acts, there have been guidelines published which describe acceptable levels of pollutants in different aquatic environments including fresh water, marine or recreational use. The Provincial Government has published BC Approved Water Quality Guidelines (BC WQ) that state specific concentration discharge limits for certain common pollutants, these include guidelines for copper, lead and zinc. For other metals not covered by BC WQ guidelines, there is a working document called BC Working Water Quality Criteria (BC WWQ). BC WWQ criteria does not differentiate between different aquatic environments, and the levels are seen as a general benchmark. To determine the acceptable limits for metals which fall outside of the BC WQ, the Canadian Council of Ministers of the Environment (CCME) have prepared Water Quality Guidelines (CCME WQ), which both differentiate between aquatic habitats, and include a larger array of pollutants than the BC WQ criteria.

In preliminary testing of UBC's storm-water runoff, several heavy metals (Cadmium, Copper, Lead, Zinc and Arsenic) were found to be above both the BC Water Quality guidelines and the BC Working Water Quality Guidelines for the protection of fresh water aquatic life.

Whether or not discharging stormwater containing metals above that specified in the guidelines is in contravention of a law, has not been determined.

From a review of the three legislative acts mentioned above, the seemingly strongest worded section is from the fisheries act, which states on line 35. (1) “No person shall carry on any work or undertaking that results in the harmful alteration, disruption or destruction of fish habitat”; additionally, the Act states on line 36. (3) “Subject to subsection (4), no person shall deposit or permit the deposit of a deleterious substance of any type in water frequented by fish or in any place under any conditions” It should be noted that in this law, fish is described as any aquatic organism.

It follows from the above paragraph, that if the stormwater is harming aquatic life, then it’s discharge would be in contravention of the fisheries act.

Table 14 Guidelines for Selected Metals Concentrations

	Freshwater Aquatic Life			Recreational Use		Marine Environments		
	BC AWQ	BC WWQ	CCME WQ	BC AWQ	BC WWQ	BC AWQ	BC WWQ	CCME WQ
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Arsenic		5	5		10		12	12.5
Cadmium		$10^{(0.86\log\{\text{hardness}\}-3.2)}$	0.017				0.1	0.12
Copper	$0.094*(\text{hardness})+2$		2	1000		3		
Lead	$e^{(1.273\ln(\text{hardness})-1.460)}$		1	50		140		
Zinc	$33+0.75*(\text{hardness}-90)$		30	5000		10		
Note: Used maximum concentrations for BC AWQ Guidelines, 30-day average values were often much lower.								
Note 2: BC AWQ = BC Approved Water Quality Guidelines, BC WWQ = BC Working Water Quality Guidelines								
CCME WQ = Canadian Council of Ministers of the Environment Water Quality Criteria								



## APPENDIX F: COST ANALYSES OF TRADITIONAL TREATMENTS

The cost of implementing a new minimum storm-water control requirements for new developments and redevelopments is very high. Such treatment system include provisions for controlling erosion and sediment transport during construction, as well as permanent facilities for treating and controlling peak runoff flows from developed sites. A basic cost analysis has been compared in between several residential and commercial treatment systems similar to the one is needed for UBC. Similar to the west coast soil and weather conditions, several compared sites include: a 10-acre single-family residential development (site 1), a 1-acre commercial development (site 2), and a 10-acre commercial development (site 3). These examples are based on the assumption that new development has no existing development on the sites, that greater than 2,000 square feet of impervious surface is added, and that greater than 7,000 square feet of land area is cleared.

Several different treatment designs are used for the storm-water treatment. Both Capital cost and Annual maintenance are compared for the three sites. Such comparison indicates that it is very expensive to build and to maintain a web-land storm-water treatment system that is capable for treating storm-water quality similar to the ones at UBC. The total capital cost only does not include the cost land. Since land in UBC area is extremely expensive, large land usage will increase the cost dramatically.

Table 15: Cost Summary of Traditional Storm-water management

Methods	Total Capital Cost (US\$)	Total Annual Maintenance Cost (US\$)
10-acre residential development with infiltration	\$488,000	\$15,600
10-acre residential development without infiltration and with wet season shutdown	\$323,000	\$9,100

Methods	Total Capital Cost (US\$)	Total Annual Maintenance Cost (US\$)
10-acre residential development without infiltration.	\$230,000	\$14,500
1-acre commercial development with infiltration.	\$280,000	\$6,900
1-acre commercial development without infiltration.	\$570,000	\$8,600
10-acre commercial development with infiltration.	\$320,000	\$54,200
10-acre commercial development without infiltration.	\$860,000	\$62,900
10-acre commercial development without infiltration and with open air sand filter.	\$490,000	\$6,200

Reference:

Herrera Environmental Consultants (2001). Cost Analysis: Washington Department of Ecology Year 2001 Minimum Requirements for Stormwater Management in Washington State. Washington State Department of Transport, Washington.

## Appendix G: Metals

Heavy metals are elements having atomic weights between 63.546 and 200.590 (Kennish, 1992), and a specific gravity greater than 4.0 (Connell et al., 1984). Living organisms require trace amounts of some heavy metals, including cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc. Excessive levels of essential metals, however, can be detrimental to the organism. Non-essential heavy metals of particular concern to surface water systems are cadmium, chromium, mercury, lead, arsenic, and antimony (Kennish, 1992).

All heavy metals exist in surface waters in colloidal, particulate, and dissolved phases, although dissolved concentrations are generally low (Kennish, 1992). The colloidal and particulate metal may be found in 1) hydroxides, oxides, silicates, or sulfides; or 2) adsorbed to clay, silica, or organic matter. The soluble forms are generally ions or unionized organometallic chelates or complexes. The solubility of trace metals in surface waters is predominately controlled by the water pH, the type and concentration of ligands on which the metal could adsorb, and the oxidation state of the mineral components and the redox environment of the system (Connell et al., 1984).

### **Arsenic**

Arsenic is an ever-present element that ranks 20<sup>th</sup> in abundance in the earth's crust, and 12<sup>th</sup> 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 is 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, dessicants, 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 several effects in humans; it causes respiratory, pulmonary, cardiovascular, gastrointestinal, hematological, hepatic, renal, dermal, neurological, developmental, reproductive, immunologic, genotoxic, mutagenetic, 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 a given water system, since it accumulates to toxic levels within organisms over time.

Traditional methods of reducing arsenic levels in water are precipitation/coagulation and ion-exchange (Dambies, 2001). For precipitation/coagulation, the chemistry of the type of arsenic in the water is studied and reduced by oxidizing it into a solid state. Ion exchange is a more applicable water treatment method, since it does not involve the studies have been carried out with commercial resin Amberlite IRA 900. The results indicated that the best pH is around 6 and the maximum uptake capacity is about 75 mg/g of resin dry weight. However, can be quite expensive when treating a large body of water, so other treatment methods for arsenic reduction are still in the making.

## **Cadmium**

Cadmium can exist in water as the hydrated ion, as inorganic complexes such as carbonates, hydroxides, chlorides or sulphates, or as organic complexes with humic acids.

At sufficiently high levels is very toxic to both humans and aquatic and other organisms. The most serious consequence of chronic cadmium poisoning is cancer (lung and prostate). The first observed chronic effect is generally kidney damage. Cadmium also is believed to cause pulmonary emphysema and bone disease (osteomalacia and osteoporosis). Fish are typically more sensitive to cadmium in aquatic habitat than are humans to drinking water. Cadmium causes hyperplasia, breakdown of the secondary lamellae of the gills (Ministry of Technology, 1970), extensive gill degeneration (Bilinski and Jonas, 1973), pathological changes in kidney and intestinal tract. 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 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 may be present in 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 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 and 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, ready availability, and high recyclability. Additionally, copper, which is an essential nutrient to humans and other life forms, 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/available form. From the information available, it appears that the brake pad-derived copper is in nontoxic/non-available forms. That situation does not apply to all sources of copper in all water bodies. Copper is extremely toxic to aquatic organisms and it kills in the parts per billion range.

Sources of copper in stormwater runoff include petroleum products, wood product, mining sources, antifreeze, brake linings, asphalt, concrete and engine wears. Another source of copper in urban stormwaters is from copper algicide. (Kelevin, 1998). Possible sources of copper from UBC stormwater may include wood compost leakage, brake linings from parking lot, antifreeze from cars, concrete and engine wears. Copper comes from car exhaust and wear, paints, and downspouts, as well as from fossil fuel combustion.

The copper concentration in the runoff sample collected for the November 5th, the concentration of copper tested 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.

Only a small part of the total copper and, for some sources, dissolved copper is in a toxic/available form. From the information available, it appears that the brake pad-derived copper is in nontoxic/non-available forms. That situation does not apply to all sources of copper in all water bodies. Copper is extremely toxic to aquatic organisms and it kills in the parts per billion range. For juvenile fish, at the temperature of 22C, sub-lethal dose of copper at 0.2ppm to 1.2ppm for four weeks will result accumulation within the fish. This will result fetal problems.

Copper is a pertinacious precipitant; it causes fish to produce more mucus. This may aid the in the suffocation or sloughing off of parasites, but also interferes with respiration through their skin and gills. Species of "native" fishes; trout, sunfishes, catfish are very sensitive, dying near concentrations near 0.10 ppm. Most desirable aquatic plants are unaffected at these doses.

- Iron-Infused Media

SMI's newest addition to media filtration is the iron-infused media. This open-cell structured media is infused with small bits of iron to remove dissolved phosphate. This media has also been shown to reduce soluble copper and zinc, making it extremely valuable for sensitive watersheds with nutrient loading problems.

- 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's 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 effectiveness of copper decreases as water hardness increases. A significant reduction occurs when the bicarbonate alkalinity exceeds 150 ppm as calcium carbonate. Conversely, toxicity to fish decreases as alkalinity increases.

Copper is almost ineffective at temperatures below 60 degrees F. and likewise more algicidal when algae are at their most active metabolically. Sunny days between 10:00 and 2:00 are optimal treatment times. Overcast or murky waters are contraindicated; wait till it's warm and sunny to apply copper.

## **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 can 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. Because of 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 170000 ug/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 then adsorb either onto or into the sorbent. Activated carbon is widely used sorbent used for removing contaminants from liquid and gas streams. A large amount of research has been devoted to finding 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, chalcopyrite, and barite (Rashed M.N. 2001)
- Crab shell (An H.K. 2001)

The percent removal of Lead from solution depends on several factors such as: pH, 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).

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).

Chemical precipitation works by complexing the Lead ion with another chemical and thereby reducing its solubility. There are 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 manufactured reagents and tend to be expensive. There addition and removal, and regeneration or disposal are maintenance problems. Also, some complexes begin breaking down in a relatively short amount of time (20 hours) (Matlock M.M. et al. 2002).

Lead dissolves readily in water in its various ionic forms. In general as temperature increases, the solubility of Lead increases (CRC Handbook). Based on water quality guidelines, the allowable concentration of Lead in water increases as hardness increases. For the purposes of adsorption, a high pH is less favorable for Lead removal.

### **Zinc**

Zinc is typically 5 to 45  $\mu\text{g/L}$  in river water. Streams affected by mine drainage commonly contain 100  $\mu\text{g/L}$  or more

Above 5mg/L (upper limit by Water Quality Criteria, 1972), people 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 has much lower tolerance for the level of zinc concentration.

Too much zinc can lead to respiratory incapacitation, as indicated by increased respiratory activity (i.e. breathing rate, volume and frequency of ventilation, coughing,

decrease in oxygen uptake efficiency). Zinc damage enhances lactic acid production/accumulation as temperature and exposure time are increased

Zinc can 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 causes oxygen tension in the arterial blood of fish

Chronically 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, e.g. water hardness, oxygen and CO<sub>2</sub> conc., pH, salinity, and temperature. Influences of age, stage in life cycle, behavior, metabolism, acclimation, and selective mortality must be considered/controlled while studying zinc as well.

Zinc has only 1 significant oxidation state (Zn<sup>2+</sup>), more soluble in most types of natural water than the other 2 metals; it is widely used in metallurgy, especially as a

constituent of alloys, e.g. brass and bronze; it's 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 1 of the 3 major trace metals in stormwater runoff along with lead and copper → account for 90-98% total metals observed. Of this amount, zinc accounted for approx. 35% (lead 54% and copper 9%).

Peak concentrations of zinc generally observed shortly after runoff begin, usually within first 30 min. Solids tend to settle out at latter stages of a storm as flow tapers off.

Zinc availability for solution in water has increased due to industrial civilization (higher concentration near industrial and commercial land-use than residential.)

Over the pH range from 8 to 11, with water containing 610mg/L  $\text{HCO}_3^-$ , there should be less than 100 $\mu\text{g/L}$  of zinc. Presence of zinc silicate willemite and adsorption to other mineral inhibit zinc concentration at the same pH range.

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