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The removal of dissolved zinc and copper from roof runoff:

A downpipe treatment system

A thesis submitted in partial fulfilment of the requirements for the Degree of Master of
Water Resource Management

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February 2018

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Abstract

Anthropogenic activities related to urbanization and industrialization contribute high concentrations of heavy metals from urban stormwater runoff to waterways. In New Zealand, zinc (Zn) and copper (Cu) have been identified as the predominant heavy metals of concern because they have been observed to consistently exceed the Australian and New Zealand Environment and Conservation Council's (ANZECC's) guideline values for the protection of freshwater organisms in urban waterways. These heavy metals originate from a variety of sources, however, galvanized and copper roofs have been observed to contribute the highest per area Zn and Cu loads respectively. More so, >80% of the Zn and Cu released from these roofs are present in the dissolved reactive form making them more bioavailable and thus, potentially more toxic to aquatic organisms.

Current stormwater management strategies have mostly focused on physical removal of particulate and particulate-bound contaminants while the dissolved contaminants are often left untreated. Also, it is difficult to retrofit conventional stormwater treatment devices such as retention ponds and raingardens in established urban areas due to limited space and the presence of underground services such as electricity, water and gas. Given that there are many existing Zn-and-Cu-based roofs in New Zealand whose runoff is discharged directly into the stormwater drainage system and/or waterways, there is a clear need to develop new at-source treatment devices that can remove these dissolved metals from roof-runoff.

Sand have been the main treatment material used in stormwater filter systems, however, its removal efficiency for heavy metals have been observed to be low. As a result, this research explored the use of limestone, zeolite and mussel shells as treatment materials for the removal of dissolved Zn and Cu because of their high neutralization, adsorption and cation exchange capacity. The composition of calcium carbonate (CaCO_3) in the structure of limestone and mussel shells, and the presence of alkali and alkaline earth elements sodium (Na^+), potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}) in the zeolite have neutralizing effects which causes the pH of the stormwater to increase, making it alkaline and consequently reducing the solubility of Zn and Cu. These three materials also possess high ion exchange capacity which allows them to adsorb large quantities of dissolved heavy metals.

To evaluate the effectiveness of a downpipe treatment system containing limestone, zeolite and/or mussel shells in reducing the percentage of dissolved Zn and Cu from roof-runoff, both laboratory and field experiments were conducted. The laboratory experiments were done in two phases. Phase I consisted of batch experiments which assessed the dissolved Zn and Cu removal capacity of the three treatment materials at a grade of $\geq 1.18 \leq 2.36$ mm. Phase II was laboratory column treatment systems that were evaluated to quantify the hydraulic performance and dissolved Zn and Cu reduction capacity of each treatment material at two material depths (0.5 m and 1 m), two flow rates (1 L/min and 3 L/min) and when the materials were disturbed and undisturbed.

For the laboratory column experiments, the untreated concentration of dissolved Zn and Cu from the roof-runoff ranged from 150-254 $\mu\text{g/L}$ and 312-884 $\mu\text{g/L}$ respectively. For the field experiments, Zn and Cu ranged from 406-2262 $\mu\text{g/L}$ and 455-2581 $\mu\text{g/L}$ respectively. The concentration of dissolved Zn and Cu in the untreated roof-runoff was considerably higher than ANZECC's mixed instream guideline values for the protection of 90% of freshwater organisms of 15 $\mu\text{g/L}$ and 1.18 $\mu\text{g/L}$ for total Zn and Cu respectively. Evaluation of the percentage of dissolved Zn and Cu in the untreated roof-runoff from the laboratory column experiment showed that 100% of the Zn was in the dissolved form while dissolved Cu ranged from 78%-91%. These results indicate that Zn and Cu in roof-runoff is present mainly in the dissolved form which is ecotoxic to freshwater organisms.

For the batch experiments, the percentage reduction of dissolved Zn and Cu varied. Limestone gave the highest mean percentage reduction for both Zn and Cu (87% Zn and 91% Cu) followed by mussel shells (78% Zn and 64% Cu) and then zeolite (48 % Zn and 64% Cu). However, for the laboratory column experiments, the amount of dissolved Zn and Cu removed by zeolite, limestone and mussel shells was not significantly different ($p \leq 0.05$). A reduction of 95-99% in dissolved Zn was achieved by all treatment materials at both depths, flow rates and disturbances while all three treatment materials only achieved 90-98% reduction in dissolved Cu at an undisturbed depth of 1 m. In the laboratory column experiments, all three treatment materials reduced dissolved Zn to concentrations well below ANZECC's mixed instream guideline of 15 $\mu\text{g/L}$ total Zn for the protection of 90% of freshwater organism's. Although the reduction in dissolved Cu was not below ANZECC's 90% mixed instream guideline of 1.8 $\mu\text{g/L}$ total Cu, it was reduced to concentrations below 20 $\mu\text{g/L}$ which

was considerably lower than the 312 µg/L – 884 µg/L Cu present in the untreated roof-runoff. Dilution of the treated roof-runoff is expected as it moves downstream which would lead to further reduction in the concentration of dissolved Cu.

The field experiment was conducted to collect data on the performance of the treatment system that would help improve the system design. Therefore, only mussel shells at an undisturbed depth of 1 m was evaluated. For the field experiment, dissolved Zn in runoff from the galvanized roof was reduced by 82-97% while dissolved Cu in runoff from the copper roof was reduced by 86-98%. These field results were comparable to what was obtained in the laboratory column experiments for mussel at an undisturbed depth of 1 m. These results show that the downpipe treatment system is robust and only small alterations to the system design would be required.

From the laboratory column experiments, it was evident that adsorption and ion exchange was the main mechanism by which zeolite reduced the concentration of dissolved Zn and Cu. This is because there was no significant difference between the pH of the untreated roof-runoff and runoff treated by zeolite, however, dissolved Zn and Cu was reduced by >95% for the laboratory column experiments. It was also evident that neutralization contributed to the reduction of dissolved Zn and Cu in runoff treated by limestone and mussel shells in the batch experiments because a greater percentage reduction in dissolved Zn and Cu was observed at higher pH values.

The use of zeolite, limestone and mussel shells were found to be very effective in removing dissolved Zn and Cu from roof-runoff in the laboratory column experiments. Mussel shell was then selected for field trials because it is a low cost and readily available waste product that proved to be just as effective as zeolite and limestone in the laboratory column experiments at removing dissolved Zn and Cu. The downpipe treatment system proved to be very effective under field conditions with >80% reduction in dissolved Zn and Cu achieved across each sampled rainfall event. These results show that factors such as the natural variation of untreated runoff quality that occurs under field conditions seem to have little influence on the Zn and Cu reduction efficiency of mussel shells which is an indication that the downpipe treatment system is effective and robust. Overall, this research contributes scientific understanding of a new stormwater treatment device that has the potential to achieve

considerable reduction in dissolved Zn and Cu from roof-runoff that can be easily maintained and installed in urban areas with limited space.

*This M.Sc. Thesis is dedicated with love and gratitude to **Jonatan D. Charles** who have shown tremendous faith in my competences and skills and have provided selfless support towards my personal development over the years.*

Acknowledgements

Tremendous support, encouragement and guidance was received throughout the duration of this master's degree. Therefore, I would like to extend special thanks to:

Ministry of Foreign Affairs and Trade (MFAT) for allowing me the opportunity to further my education in this amazing country. My journey in New Zealand is one that have improved my competencies and skills and have brought new perspectives to my life. This scholarship has allowed me to experience a different culture and have opened doors to additional opportunities which I am very grateful for.

My Supervisors, Frances Charters and Tom Cochrane, for their willingness to be my supervisors and for making the time to meet with me weekly throughout the duration of thesis component of my degree. This consistent guidance and support that I received from both supervisors have helped to keep me on track and to complete this thesis with minimal drawbacks. The passion that these two have shown towards research work for the improvement of the quality of our environment and the enjoyment they have brought into conducting this research thesis has allowed me to develop a greater appreciation and love for research. For this I will forever be grateful.

Peter McGuigan, Environmental Lab Manager and his assistant Manjula Premaratne who ensured that all materials, laboratory and field setup were available and completed on time. I am particularly thankful for the welcoming environment they provided, their support throughout the experimental phase on my thesis and their willingness to assist me particularly with last minute request.

Sue Bowie and Jayne Borrill (New Zealand Scholarships Administrators), and Suellen Knopick (Waterways Administrator), who have been very supportive in both my academic and personal life and have ensured that I am comfortable. This care, guidance and words of encouragement that I have received from these three lovely ladies even before my arrival has made life for me in New Zealand so much easier.

The staff of the Geomechanics laboratory and the Departments of Geological Sciences and

Mechanical Engineering for allowing me the liberty to use their equipment which made the experimental phase of my thesis much easier.

Charlayne Pankhurst, Lincoln University gym instructor, for her warm and caring nature and going out of her way to ensure that I made it to gym sessions. This support has helped to not only improve my fitness but has also helped improve my focus in my academic work particularly under demanding situations. I am forever grateful.

My mom Ophelia Matthew, my brothers and sister and other family members, friends in New Zealand, the Caribbean and other parts of the world, as well as my fellow postgrads for their support and words of encouragement. The experience and knowledge gained in New Zealand is one that will have a positive impact on my future. Thanks to everyone who have impacted my life both directly and indirectly.

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Abbreviations and Acronyms

| | |
|-------------------|---|
| AlO ₄ | Aluminium oxide |
| ANOVA | Analysis of variance |
| ANZECC | Australian and New Zealand Environment and Conservation Council |
| Ca | Calcium |
| CaCO ₃ | Calcium Carbonate |
| CI | Confidence interval |
| Cu | Copper |
| DO | Dissolved Oxygen |
| EDS | Energy-dispersive X-ray spectroscopy |
| Fe | Iron |
| H | Hydrogen |
| HDPE | High density polyethylene |
| ICP-MS | Inductively coupled plasma mass spectrometry |
| K | Potassium |
| Ksat | Saturated hydraulic conductivity |
| MFAT | Ministry of Foreign Affairs and Trade |
| Mg | Magnesium |
| Na | Sodium |
| Ni | Nickel |
| O | Oxygen |
| P | Phosphorus |
| Pb | Lead |
| PET | Polypropylene terephthalate |
| pH | Acidity or alkalinity of a solution |
| PVC | Polyvinyl chloride |
| r | Correlation coefficient |
| S | Sulphur |
| SD | Standard deviation |
| SDD | Silicone drift detectors |
| Si | Silicon |
| SiO ₄ | Silicate oxide |
| SQIDs | Stormwater quality improvement devices |
| Zn | Zinc |

Chapter 1 Introduction

1.1 Problem Statement

Urbanization, industrialization and their anthropogenic activities have led to high levels of heavy metals in the environment beyond recommended limits that can be detrimental to living organisms (Ancion et al., 2010). Heavy metals are a growing environmental and public health concern because they can be toxic to freshwater organisms at very low concentrations, they are non-degradable and can enter the food chain due to their bioaccumulation tendency (Davis et al., 2001). Zn and Cu have been identified as the major heavy metals of concern in New Zealand's urban stormwater and waterways in which galvanized and copper roofs have been identified as significant sources (Charters et al., 2016b; Wicke et al., 2010).

It has been estimated that roof-runoff contributes half the volume of runoff from impervious surfaces of urban catchments and industrialized countries (Hyun & Lee, 2013) however, roof-runoff continues to be overlooked as a major source of heavy metals found in urban stormwater and waterways (Cheah et al., 2007). Over the years, roads have been considered the major contributor of dissolved Zn in urban stormwater, however, Timperley et al. (2005) highlighted that untreated roof-runoff in many urban regions is discharged directly into the road stormwater network and waterways and as a result, the problem of elevated Zn levels may be attributable to galvanized roofing. Several studies have revealed that roof-runoff should be of great concern because the amount of heavy metals that is transported from urban roofs can cause the maximum acceptable limit for waterways to be exceeded (Cheah et al., 2007). Also, roofs contribute mainly dissolved free Zn^{2+} and Cu^{2+} ions to urban stormwater through dissolution of Zn and Cu caused by the low pH of rainwater (Pennington & Webster-Brown, 2008) which is the form of these metals that are toxic to freshwater organisms (Ayangbenro & Babalola, 2017). Monitoring of Zn and Cu in the waterways of New Zealand's major cities, Wellington by Milne and Keenan (2008) and Alsager (2012), Auckland by Auckland Council (2013) and Auckland Council (2016), and Christchurch by Michele (2009) and Margetts and Marshall (2016) have revealed that over the years, Zn and Cu have consistently exceed ANZECC's mixed instream guideline values for freshwater organisms.

Zn and Cu plays an important role in the biochemical, physiological and metabolic processes of living organisms, however, in stormwater, anthropogenic sources are typically present in

their dissolved and mobile reactive forms (Zn^{2+} and Cu^{2+}), which are highly bioavailable and consequently more toxic to aquatic organisms (Ayangbenro & Babalola, 2017). The solubility and bioavailability of Zn and Cu are influenced by very small changes in pH where metal speciation is shifted to mostly free ions, particularly in acidic conditions (Ayangbenro & Babalola, 2017). Both Zn and Cu can have acute and chronic toxicity effects to freshwater organisms (Reed et al., 1980), however, Cu is of particular concern because it is very toxic at very small concentrations above what is required for growth and reproduction (Hall et al., 1988).

Stormwater treatment devices such as retention ponds, constructed wetlands and treatment systems have been used globally to reduce contaminant loads prior to discharge into receiving environments. Because these treatment systems have primarily been designed to capture sediment and sediment-adsorbed contaminants, a large percentage of untreated dissolved contaminants such as Zn and Cu tend to pass through these conventional designs (Timperley et al., 2005). In addition to this, it is difficult to retrofit conventional stormwater treatment devices in established urban areas due to limited space and the presence of underground services such as electricity, water and gas (Jonasson et al., 2010). As a result, greater attention has been placed on source-control filter systems because they can be retrofitted in areas with limited space and they have the ability to remove significant amounts of both particulate and dissolved metals from stormwater (Hipp et al., 2006).

Sand has been the major treatment material used in stormwater filter systems, however, the removal efficiency for dissolved metals has been shown to be low. Results of a study by Reddy et al. (2014) showed that zeolite removed 97.7-99% Cu and 65-98.7% Zn, calcite removed 98-99.5% Cu and 78-98.9 Zn while sand removed only 5-43% Cu and 43-58% Zn. Because of the low dissolved metal removal efficiency reported for sand in the literature, this research explored the use of three neutralizing materials limestone, zeolite and mussel shells which have been gaining increased attention as treatment materials for stormwater treatment devices. The composition of $CaCO_3$ in the structure of limestone and mussel shells, and the presence of alkali and alkaline earth elements Na^+ , potassium K^+ , Ca^{2+} and magnesium Mg^{2+} in the zeolite has neutralizing effects which causes the pH of the stormwater to increase making it alkaline, and consequently reducing the solubility of Zn and Cu (Pandey et al., 2003;

Hu et al., 2011). In addition to this, these materials possess high ion exchange capacity which allows them to adsorb large quantities of dissolved heavy metals (Westholm et al., 2014).

Despite the recent increase in research on roof-runoff contamination which has identified roofs as significant sources of Zn and Cu found in urban stormwater and knowledge of the adverse effects of Zn and Cu on aquatic organisms, little focus has been placed on the treatment of roof-runoff. As a result, this research was conducted to evaluate limestone, zeolite and mussel shells as potential treatment materials that can be used in a source-control downpipe treatment system for the removal of dissolved Zn and Cu from roof-runoff.

1.2 Research Aim and Objectives

The primary aim of this research was to develop an effective downpipe treatment system containing limestone, zeolite and/or mussel shells for the removal of dissolved Zn and Cu from roof-runoff. To accomplish this overarching aim, the main objectives of this research were to:

1. Evaluate the ability of limestone, zeolite and mussel shells for the removal dissolved Zn and Cu specifically to:
 - a. quantify the hydraulic performance and percentage reduction in dissolve Zn and Cu for each treatment material at varying depths
 - b. quantify percentage reduction in dissolve Zn and Cu for each treatment material at varying flow rates
2. Evaluate the performance of the treatment systems under field conditions.

1.3 Thesis Outline

This thesis is organised in five chapters (including the above introduction) as described below.

Chapter 1: Introduction that outlines the need, scope and objectives of this research.

Chapter 2: Literature Review that provides background information on the issue of dissolved Zn and Cu in urban stormwater and waterways and management strategies that provide context for this research.

Chapter 3: Laboratory Evaluation that describes the methodology used (experimental design, laboratory analysis, statistical analysis) and results obtained on the hydraulic performance and dissolved Zn and Cu reduction efficiency for zeolite, limestone and mussel shells in the batch and laboratory column experiments.

Chapter 4: Field Evaluation that describes the methodology used (downpipe treatment system design, field sampling technique) and observatory results obtained on the performance of a downpipe treatment system and the dissolved Zn and Cu reduction efficiency of mussel shells under field conditions.

Chapter 5: Conclusions drawn from the results obtained for the laboratory and field experiments and **Recommendations** for improvement of the downpipe treatment system and future research areas.

Chapter 2 Literature Review

2.1 Urban Stormwater

The continuous development of society and the surge in urban population have led to a substantial increase of human impact on the environment. While housing developments, office complexes, shopping malls, road networks, industrialization and a range of other amenities have provided conveniences and improvements in the quality of human life, they have created substantial environmental challenges that can no longer be ignored (Erickson et al., 2013). When land is developed for human occupation, the removal of vegetation, compaction of soil by heavy equipment and construction of impervious surfaces such as roads and buildings (Erickson et al., 2013) alters the natural process of stormwater runoff (Pazwash, 2011). Thus, urbanization, industrialization and their anthropogenic activities has led to the challenges of increased urban stormwater volume and velocity as well as a decline in runoff quality (Ancion et al., 2010).

While the most obvious impact of urbanization is the increased rate and volume of surface runoff, stormwater quality is also an important aspect that needs to be considered in the management of urban stormwater (Cahill, 2012). This consideration is essential because in many urban regions, including cities in New Zealand, the drainage and sewer systems are separate, therefore, untreated stormwater is discharged directly into streams, rivers and lakes (Han, 2012; Paddock, 2014) and thus having negative impacts on the water quality which in turn affects the aquatic organisms that live in them. Urban stormwater runoff has been recognized as an important source of water quality problems in urban regions worldwide (Ryding, 1994). Managing urban stormwater runoff to reduce the contaminants it transports to urban waterways includes reducing not only the volume of runoff but also targeting the sources of these contaminants (Cahill, 2012).

The impact of urban runoff is sometimes very difficult for many people to understand because fish kills are the most apparent indicators of water contamination. However, because the quality of receiving waters in urban region are generally poor, the abundance and diversity of aquatic organisms tends to be limited, however, they are usually very resistant to poor water quality (Burton Jr & Pitt, 2001) and as a result thus, fish kills may not occur. Also, in many urban waterways, sensitive native species tend to be displaced or killed long ago, therefore,

an unusual event would be required to cause a fish kill (Hoffman et al., 2002). Ray and White (1976) stated that linking fish kills to heavy metal contamination can be complicated because fish mortality tends to lag behind the first toxic exposure by several days and is often detected several miles downstream from the discharge location. Thus, the concentration of metals that may have caused the fish kill could by then be diluted below detection limits making it impossible to determine the actual cause of the fish kill in many instances. Many factors can cause fish contamination and fish kills however, stormwater runoff has been identified as a primary contributor (Burton Jr & Pitt, 2001).

2.2 Zinc and Copper in Urban Stormwater

Impervious surfaces in urban areas that are directly connected to a stream or drainage system include paved streets, driveways and walkways, parking lots and roofs and thus, the sources of the contaminants found in urban stormwater vary widely (Burton Jr & Pitt, 2001). However, heavy metals are considered one of the most significant environmental contaminants in urban stormwater and waterways (Ayangbenro & Babalola, 2017). The toxicity, bioaccumulation tendency and the non-degradable nature of metal ions (which allows them to persist in the environment) poses a significant threat to aquatic organisms (Ayangbenro & Babalola, 2017; Davis et al., 2001). Additionally, even at very low concentrations, heavy metals can be toxic to freshwater organisms and can also enter the food chain via bioaccumulation in aquatic organisms (Ayangbenro & Babalola, 2017).

In New Zealand, heavy metals in urban waterways, particularly Zn and Cu are of great concern because Zn and Cu have been found to consistently exceed ANZECC's guideline values for the maximum instream concentrations of heavy metals at 80-95% level of protection for freshwater aquatic species (Auckland Council, 2016; Charters et al., 2016b; Margetts & Marshall, 2015; Wicke et al., 2010). 95% level of protection means that 95% of aquatic species are not expected to show adverse effects from Zn and Cu at the maximum concentrations of 15 mg/L and 1.8 mg/L respectively (ANZECC, 2000).

Instream monitoring of urban waterways by councils and independent researchers over the years has consistently identified Zn and Cu concentrations that exceed ANZECC mix instream guideline values in New Zealand's major cities, Wellington by Alsager (2012) and Milne and Keenan (2008), Auckland by Auckland Council (2016) and Macaskill & Martin, 2004, and

Christchurch by Margetts and Marshall (2016) and Michele (2009). Roofs have been identified as key sources of the Zn and Cu found in New Zealand's urban stormwater and waterways as reported by several researchers including Auckland Regional Council (2008); Brown and Peake (2006); Charters et al. (2016a); Milne and Keenan (2008) and Moores et al. (2009). Therefore, new strategies need to be developed and implemented to reduce the concentration of Zn and Cu transported from roof-runoff via stormwater into New Zealand's urban waterways to avoid significant irreversible impacts on water quality and aquatic life (particularly native species).

2.3 Sources of Zinc and Copper Found in Urban Stormwater

Vehicles and their associated activities, road surfaces and exposure of buildings to rainfall of low pH are considered the primary sources of heavy metal contaminants found in urban stormwater (Johnson et al., 2003). Continuous research in identifying the sources of contaminants found in urban stormwater and waterways has made it more apparent that road surfaces may not necessarily be the major source of Zn and Cu found in urban stormwater as initially perceived (Timperley et al., 2005). Although roof-runoff have been overlooked as a major source and pathway for contaminants found in urban stormwater, increasing research has identified roofs as an important urban impervious surface which contributes high levels of Zn and Cu in urban stormwater (Cheah et al., 2007). It has been estimated that roof-runoff contributes half the volume of runoff from impervious surfaces of urban catchments and industrialized countries (Hyun & Lee, 2013). It has also been reported that Zn-and-Cu-based roofs have been shown to contribute the highest per area Zn and Cu loads found in urban stormwater respectively (Charters et al., 2016b; Moores et al., 2009). Studies conducted by Cheah et al. (2007) and Charters et al. (2016b) revealed that Cu and Zn concentrations from roof-runoff was significantly higher than that of road-runoff in which Cu roofs and gutter and galvanized roofs were believed to be the primary sources respectively. The high concentration of Zn and Cu found in urban stormwater and waterways can be linked to untreated roof-runoff being discharged directly into urban waterways and the road stormwater network in many urban settlements.

Several studies have indicated that the quality of roof-runoff in urban regions should be of great concern because the collective amount of Zn and Cu that is transported from roofs via stormwater runoff can cause the maximum acceptable limit for waterways to be exceeded

(Cheah et al., 2007; Charters et al., 2016b). Also, galvanized and copper roofs contribute mainly dissolved free Zn^{2+} and Cu^{2+} ions respectively to urban stormwater compared to road runoff where particulate contaminant is of more concern (Cheah et al., 2007). The dissolved reactive form Zn and Cu is the form emanating from roof can be very toxic to freshwater organisms (Ayangbenro & Babalola, 2017).

The water quality from roof-runoff is influenced by the deposition of contaminants from the atmosphere, the type of roofing and gutter material (Polkowska, 2004), the age and inclination of roofing materials as well as intrinsic rainfall quality (Hyun & Lee, 2013). Also, the acidic nature of rainwater tends to react with compounds of roofing materials causing elements such as Zn and Cu to leach (Polkowska, 2004). An investigation of the water quality of the Hayton's Stream Catchment in Christchurch by Moores et al. (2009) showed elevated levels of Zn throughout the catchment in which roof-runoff was identified as the likely source. It was concluded that the specific sources of the contaminants found in the stream should be treated in order to reduce the adverse effects on downstream receiving waters. Results of a study conducted by Davis et al. (2001) in Maryland, U.S.A revealed that heavy metals in roof-runoff from commercial and institutional buildings were significantly higher than residential roofs with the highest Zn concentration of 7600 $\mu\text{g/L}$ emanating from a commercial galvanized roof. It was highlighted that Zn and Cu are common materials used for roofs, thus, their prevalence in commercial and institutional buildings is likely to produce the high levels of Zn and Cu found in roof-runoff from these structures. Therefore, the researchers recommended that a stormwater treatment system that addresses heavy metal contamination directly from roofs should be developed. Investigation into the possible sources of dissolved heavy metals in stormwater in Wellington, New Zealand, found that Zn concentration was higher in galvanized roof-runoff (Alsager, 2012). Research conducted by Charters et al. (2016b) in Christchurch, New Zealand, showed that the highest concentration of Zn and Cu came from galvanized and copper roofs respectively. It was also reported that the concentrations of Zn (75 $\mu\text{g/L}$ to 2,369 $\mu\text{g/L}$) and Cu (423 $\mu\text{g/L}$ to 7,861 $\mu\text{g/L}$) generated by the dissolution of the copper and galvanized roofs were as high as what has been reported internationally. In another study by Charters et al. (2016a), it was observed that galvanized and copper roofs also produced the highest concentration of total Zn (up to 1970 $\mu\text{g/L}$) and Cu (up to 7860 $\mu\text{g/L}$) respectively compared to road surfaces and concrete roofs.

2.4 Impacts of Dissolved Zinc and Copper in Freshwater Ecology

Some heavy metals are essential in the biochemical, physiological and metabolic processes of organisms, however, the biological functions of many of these metals are unknown, and they can be toxic when generated in excess (Ayangbenro & Babalola, 2017). Naturally occurring heavy metals are generally present in the insoluble form with high adsorption capacity which makes them less bioavailable to living organisms. However, anthropogenic sources are typically present in their dissolved and mobile reactive forms, thus becoming highly bioavailable and consequently more toxic to living organisms (Ayangbenro & Babalola, 2017). Very small changes in pH levels can influence the solubility and bioavailability of heavy metals by shifting metal speciation into predominantly free ions, particularly in acidic conditions (Ayangbenro & Babalola, 2017).

In roof-runoff, Zn and Cu occur mainly as free ions, however, they become less soluble as the pH of water increases. The results of studies conducted by Cheah et al. (2007) and Charters et al. (2016b) showed that heavy metals such as iron (Fe), nickel (Ni) and lead (Pb) were present mainly in the particulate form, whereas Zn and Cu were present mainly in the dissolved form. These results are indications that Zn and Cu will have a more significant impact on aquatic organisms. According to the ANZECC mixed instream guidelines, concentrations of Zn and Cu exceeding 1.8 µg/L and 15 µg/L respectively, would be expected to cause adverse impact in >10% of freshwater species (ANZECC, 2000).

2.4.1 Zinc

Zn is an essential trace element for biochemical processes in organisms, however, in natural waterways, dissolved Zn can be toxic to freshwater species. Low pH, low dissolved oxygen (DO) and high temperatures increases the bioavailability of Zn and its level of toxicity to aquatic organisms (Eisler, 2007). Zn toxicity affects freshwater fish by destroying the gill epithelium and causing tissue hypoxia (Reed et al., 1980) and also inhibits the uptake of calcium (Hogstrand, 2011). Eisler (2007) stated that, while most of the Zn that is introduced into waterways via stormwater eventually adsorbs to the sediments, Zn from these sediments can be released and thus increasing its bioavailability under conditions of high DO, inorganic oxides and humic substances as well as low salinity and pH. The results of a survey which assessed the sediments of the Avon River in Christchurch by Gadd and Sykes (2014) showed that Zn concentration at 15 of the 35 sampled sites exceeded ANZECC's sediment quality

guideline values. The results of another survey conducted on the sediment quality of the Heathcote River Catchment by Gadd (2015) also revealed that Zn concentrations exceeded the ANZECC's sediment quality guideline value at 4 of the 6 sites sampled. These high levels of Zn in the sediments is also of concern because they can be converted into the dissolved form under the right conditions. Therefore, new and/or improved strategies need to be developed and implemented to reduce the load of dissolved Zn and Cu entering urban waterways to help reduce the concentration of metals adsorbed to the sediments which can be converted into their dissolved toxic form.

2.4.2 Copper

The heavy metal Cu is also essential for growth and metabolism in organisms, however, in freshwater and aquatic biota, dissolved Cu in the form of cupric ion (Cu^{2+}) is one of the most toxic heavy metals. This is because Cu^{2+} has the potential to bioaccumulate and cause irreversible harm to some aquatic organisms at very small concentrations above what is required for growth and reproduction (Hall et al., 1988). Cu^{2+} is the most bioactive and toxic form of Cu which causes gill damage, interferes with osmoregulation, oxygen transport and energy metabolism which eventually leads to hypoxia in aquatic invertebrates (Eisler, 2007). With Zn and Cu consistently exceeding ANZECC's mixed guideline values in Christchurch and other urban regions in New Zealand, it is critical that these heavy metals are treated to minimize and/reverse the environmental impacts and the possibility of uptake in the food web (e.g. via heavy metal uptake by filter feeders such as those found in the Avon-Heathcote Estuary).

2.5 Management Options for Dissolved Zinc and Copper

In New Zealand, stormwater quality management has focused mainly on sediment and sediment-adsorbed contaminants, however, in recent years, greater attention has been placed on very fine particulate matter and dissolved contaminants. This is because dissolved contaminants including Zn and Cu tend to pass through conventional stormwater quality improvement devices (SQIDs) and are more toxic to aquatic organisms compared to coarser sediments (Timperley et al., 2005). Stormwater filters containing sand, gravel and soil are designs that have been widely used in the treatment of urban stormwater (Sun et al., 2015) with the capability of removing high percentages of coarse particles and particulate-bound contaminants, however, they tend to be less effective in removing dissolved metals (Borne et

al., 2013). Although retention ponds, rain gardens and constructed wetlands are considered effective in removing dissolved metals and are low-cost solutions to stormwater contaminant removal (Westholm et al., 2014), they require large land area (i.e. in terms of land area required per volume of stormwater) and extensive maintenance and/or complete reconstruction if their media becomes saturated with heavy metals (Sun et al., 2015).

In fully developed urban areas, retrofitting conventional stormwater management devices such as retention ponds, swales and rain gardens can be difficult due to limited space and the presence of underground services such as electricity, water and gas (Jonasson et al., 2010). As a result, greater attention is being placed on the use of adsorption, neutralization and precipitation systems for their ability to remove both particulate and dissolved contaminants from urban stormwater in areas with limited space (Hipp et al., 2006). Stormwater treatment devices designed for the reduction of dissolved Zn and Cu from roof-runoff in established urban areas should be able to be installed in areas with limited space and must be effective in capturing and retaining these metals from their dissolved state. Thus, smaller and simpler source-control metal adsorption/precipitation systems need to be developed. An adsorption/precipitation treatment system that can be retrofitted directly onto roof downpipes on industrial and commercial sites may provide a feasible means of reducing dissolved metals at-source for large areas of roofs in establish urban regions.

2.6 Treatment Material Options for Management of Dissolved Zinc and Copper

Granular filters consisting of common media such as sand, gravel and soil have been used extensively in the treatment of stormwater (Paul & Tota-Maharaj, 2015). Sand filters are effective in removing large particles from stormwater, however, their ability to remove dissolved metals have been shown to be inadequate (Borne et al., 2013) which is attributed to their low adsorption capacity neutralising capability (Genç-Fuhrman et al., 2007). Craggs et al. (2010) highlighted that a relatively simple way of enhancing the removal of dissolved heavy metals is by incorporating materials that has a high affinity for dissolved heavy metals. While many metals in stormwater runoff are particulate bound (Clark et al., 2004), research on characterizing urban Zn generation by Charters et al. (2016b) showed that >90% of Zn from roof-runoff in Addington (an urban catchment of Christchurch) was in the dissolved form. In another study of untreated runoff quality from roof and road surfaces by Charters et al. (2016a) it was also observed that Zn and Cu from roof-runoff in a residential/institutional

catchment of Christchurch were predominantly in the ecotoxic dissolved form. Because Zn and Cu in stormwater are predominantly in the dissolved form, Clark et al. (2004) highlighted that adsorption is likely to be the most feasible technique of choice for the removal of these dissolved heavy metals from stormwater.

Neutralising materials such as limestone, zeolite and mussel shells have been gaining increasing attention as potential treatment materials in stormwater treatment devices for the removal of heavy metals due to their neutralizing effect and high adsorption capacity (Westholm et al., 2014). The high neutralising and adsorption capacity of these treatment materials are due to the high negatively charged SiO_4 and AlO_4 tetrahedral framework and the presence of alkali and alkaline earth elements (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) in the zeolite, and the presence of CaCO_3 in the limestone and mussel shells. In addition, these materials are available locally and would require low maintenance if used in a downpipe treatment systems. Mussel shells, which is a waste product of the shellfish industry can be transformed into useful resources which will be beneficial to both solid waste management (Sun et al., 2015) and stormwater management. The three treatment materials can also achieve high percentage removal of dissolved heavy metal regardless of the condition of the site (Westholm et al., 2014). The metals are also able to accumulate in a finite non-toxic accessible volume of treatment material that can be easily disposed of when metal saturation is reached (Westholm et al., 2014). Therefore, these neutralising materials show good potential for providing effective at-source removal of dissolved Zn and Cu in a manner that can be fitted around existing site infrastructure and activities.

2.6.1 Zeolite

Zeolites are naturally occurring alumina-silicates of alkali and alkaline earth elements that consist of a three-dimensional silicate oxide (SiO_4) and aluminium oxide (AlO_4) tetrahedral framework which causes it to have negatively charged surfaces and thus a high ion exchange capacity that makes it suitable for heavy metal adsorption (Ghobarkar et al., 1999). In addition, the exchangeable ions of zeolite are predominantly alkali and alkaline earth elements Na^+ , Ca^{2+} , and K^+ and as a result, divalent Zn and Cu ions are more favourably removed via cation exchange at alkaline pH (Genç-Fuhrman et al., 2007). Because of its high adsorption and cation exchange capacity, the ability of zeolite to remove dissolved metals from wastewater has been investigated by many researchers (Westholm et al., 2014). In a

study conducted by Reddy et al. (2014), results showed that a zeolite galvanize test removed 65-98.7% Zn and 97.7-99% Cu. It was concluded that precipitation, ion exchange and electrostatic adsorption of metal cations to the negatively charged sites on the zeolite particles were the processes responsible for the removal of heavy metals. Studies on the use of zeolite for the removal of heavy metals by Abdel-Salam et al. (2011), Babel and Kurniawan (2003), Erdem et al. (2004), Kim et al. (2010), Pitcher et al. (2004) and Zanin et al. (2017) have all shown that natural zeolite has the potential to remove significant amounts of dissolved heavy metals from metal contaminated water. However, grounded zeolite is expensive and mainly available as a commercial product (cat litter).

2.6.2 Limestone and Mussel Shells

Limestone is a sedimentary rock that is composed of CaCO_3 in the form of calcite and aragonite (Pandey et al., 2003). The primary makeup of mussel shells is also CaCO_3 (aragonite and calcite crystals) as well as chitin, protein and small amounts of phosphate and lipid (Hu et al., 2011). CaCO_3 , which is the main component of limestone and mussel shells, can be used to immobilize the toxic form of heavy metals such as Zn^{2+} and Cu^{2+} (Wise, 2000). When stormwater comes in contact with limestone and mussel shells, Ca^{2+} ions are released causing the pH of the stormwater to increase which immobilizes heavy metals through adsorption and/or precipitation (Komnitsas et al., 2004). At low pH levels, there is competition between hydrogen (H^+) adsorption and Zn^{2+} and Cu^{2+} ions due to the high protonation (addition of a hydrogen ion to a substance) of CaCO_3 surfaces, however, with increasing pH, removal of Zn and Cu increases as a result of decreasing competition between H^+ and other positively charged ions at the surface sites resulting in lower repulsion and greater adsorption of Zn and Cu ions (Aziz et al., 2008). Sdiri et al. (2012) stated that the increase in the pH of wastewater to >8 was due to the CaCO_3 from the limestone in the solution which stimulated the precipitation of metal hydroxide and/or metal carbonate. It was concluded that precipitation and adsorption as metal oxides and metal carbonates were the two main mechanisms by which heavy metals were removed from wastewater when using limestone. Mussel shells and limestone have been shown to be very effective in removing dissolved heavy metals from metal contaminated water. These materials can be crushed and used in stormwater treatment designs such as filter systems. In New Zealand, limestone is quarried while mussel shells is a waste product of shellfish industry in which most of the shells material is dumped.

These materials are readily available and can be obtained at a relatively low cost. Due to the large volume of mussels processed each year and the high cost associated with shells disposal, a commercial use of mussel shells for stormwater treatment would benefit New Zealand's shellfish industry, solid waste company and stormwater management agencies (Craggs et al., 2010; Weber et al., 2015). Research on the use of mussel shells for the treatment of acid mine drainage (AMD) by Auckland Regional Council (2010), Trumm et al., 2015, Uster et al., 2013 and Weber et al., 2015 showed that mussel shells has the potential to remove high percentages of dissolved metals from metal contaminated water. In a laboratory study conducted by Pandey et al. (2003), it was concluded that the increase in pH brought about by the limestone caused the Zn and Cu to become less soluble allowing it to remove >98% of the dissolved Zn and Cu from artificial road runoff. Removal of heavy metals using limestone has been investigated by several researchers to include Aziz et al. (2001), Aziz et al. (2008), Sdiri et al. (2012), Shin et al. (2014) and Ya et al. (2009) have yielded similar results which indicates that limestone is also effective in removing dissolve Zn and Cu from metal contaminated stormwater.

2.7 Factors that Impact the Effectiveness of Treatment Materials

The major factors that affect the amount of heavy metals that treatment systems remove from metal-polluted water are pH, particle size of the treatment material and hydraulic retention time.

pH

The ability of pH to affect the surface charge of solid materials and the speciation of dissolved components makes it one of the most significant parameters that affects the removal of heavy metals by treatment materials (Westholm et al., 2014). Materials without neutralizing ability (e.g. sand) will not be effective in acidic environments such as roof-runoff treatment due to the protonation of their surface groups (Westholm et al., 2014). In a study conducted by Barakat (2008), it was observed that the adsorption capacity of heavy metals was strongly dependent on pH and initial ion concentration in which there was almost complete adsorption for both Zn²⁺ and Cu²⁺ ions at pH >6. Results from a study by Wicke et al. (2014) showed that the pH of rainfall had a significant impact on the concentration of Zn and Cu from roof-runoff. It was observed that the concentration of dissolved Cu at rainfall of pH <4 was 140- 815%

higher than rainfall of pH >6 for brand new copper roofing. Overall, the results showed that dissolved Cu and Zn concentrations exceeded the ANZECC water quality guideline values by factors >1000.

Particle Size of Treatment material and Hydraulic Retention Time

The particle size of a treatment material is also important because it affects the adsorption capacity of the material and the hydraulic retention time. Treatment materials with coarse particles are extremely permeable causing stormwater to pass through very quickly which leads to a short hydraulic retention time and consequently a lower percentage removal of dissolved heavy metal (Clark et al., 2004; Reddy et al., 2014). Reducing the particle size of a material increases its' specific surface area which in turn increases metal adsorption and neutralization. However, fine particle size poses the risk of becoming clogged and causing a decline in flow rate and consequently the volume of stormwater that can be treated (Westholm et al., 2014).

A reduction in the hydraulic conductivity of a treatment system due to clogging can also cause regular and excessive overflows, lengthy water ponding, reduction in treatment volume, as well as aesthetic and public health concerns (Le Coustumer et al., 2012). Thus, identifying the variables and understanding the environment under which a stormwater treatment system will be operating is essential in guiding the design of the system so that it can be effective and sustainable in the long-term. The hydraulic conductivity of the treatment material is also important in evaluating how quickly it will become saturated with heavy metals which can be used to guide how often the treatment material should be replaced (Reddy et al., 2014). Generally, the replacement of a treatment material is dependent on the hydraulic conductivity, the maximum contaminant adsorption capacity of the treatment material, the initial concentration of the contaminant and the adsorption kinetics of the contaminant (Reddy, 2013). In designing a downpipe treatment system for the removal of dissolved Zn and Cu from roof-runoff, it is essential that the grade and volume combination of the treatment material selected provides a balance between hydraulic capacity and heavy metal reduction with the aim of effectively treating a large percentage of roof-runoff (i.e. without needing a flow bypass) particularly during extreme and extended rainfall events.

2.8 Chapter Summary

A review of the literature has shown that Zn and Cu are the major heavy metals of concern in New Zealand's urban stormwater and waterways. Galvanized and copper roofs have been identified as notable contributors of these metals found in urban stormwater, particularly in the dissolved form which is ecotoxic. However, limited research has been conducted on the percentage of dissolved metals that roofs contribute to urban stormwater and the treatment of roof-runoff in New Zealand. This have left gaps in the current knowledge on the gravity of the impacts of roof-runoff in the environment. As a result, treatment of dissolved metals from roof-runoff has not been adequately dealt with and incorporated into the typical stormwater treatment devices currently available in New Zealand. Therefore, this research was conducted to specifically address the following gaps:

- Quantifying the concentration and percentage of dissolved Zn and Cu present in runoff from galvanized and copper roofs.
- Evaluating the potential of an at-source downpipe treatment system containing neutralizing materials zeolite, limestone and/or mussel shells for the removal of dissolved Zn and Cu from roof-runoff.

Chapter 3 Laboratory Evaluation of the Dissolved Metal Removal Capabilities of the Three Treatment Materials

3.1 Introduction

This chapter describes the methodology used to complete the laboratory experiments for this thesis. The laboratory experiments were conducted in two phases. Phase I (Section 3.2.4) comprised of batch experiments that were conducted to assess the dissolved Zn and Cu removal capacity of each treatment material at a selected grade of $\geq 1.18 \leq 2.36$ mm (Figure 3-1). To determine whether retention time influenced the percentage reduction in dissolved metals, an assessment of the percentage reduction of dissolved Zn and Cu by each treatment material at increasing retention time was also conducted. Phase II (Section 3.2.5) comprised of laboratory column treatment systems containing zeolite, limestone and mussel shells that was conducted to evaluate the dissolved Zn and Cu reduction capacity of each treatment material at two flow rates (1 L/min and 3 L/min), two material depths (0.5 m and 1 m) and disturbances (undisturbed and disturbed). The hydraulic conductivity of each treatment system was also evaluated to help calculate the maximum roof area and runoff volume that the treatment systems would be able to drain/treat at varying rainfall intensities.

3.2 Methodology

3.2.1 Preparation of Treatment Materials

The limestone and mussel shells used in this research were purchased from Pearson's LTD Landscape Supplies at \$8 per 30 kg bag each. The zeolite was purchased from The Warehouse as cat litter (Excellence Cat Litter Premium Ultra Hygienic 7L) made of 100% New Zealand zeolite at \$5 per 4 kg bag. Material that were wet upon purchase were left to air dry prior to crushing. From the literature, it was observed that more than 90% of dissolved Zn and Cu was removed from contaminated water using limestone and zeolite at material grades between 2.36 mm - 5 mm, however, this removal percentages were achieved at retention times of >1 hr (Aziz et al., 2001; Aziz et al., 2008; Shin et al., 2014). The water retention time in the downpipe treatment systems was expected to be very short (< 40 seconds), therefore, a smaller material grade between $\geq 1.18 \leq 2.36$ mm (Figure 3-1) was used in this research to help achieve a high percentage reduction in dissolved Zn and Cu.



Figure 3-1. Images showing the three treatment materials crushed to a grade $\geq 1.18 \leq 2.36$ mm.

3.2.2 Chemical Characterization of the Treatment Materials

Chemical characterization of the treatment materials was done using an energy-dispersive X-ray spectroscopy (EDS) equipped with silicone drift detectors (SDD). The characterization capabilities of the EDS is dependent on the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum (which is the main principle of spectroscopy) (Goldstein et al., 2017; Russ et al., 2013) (Figure 3-2). The purpose of the SDD is to convert the X-ray energy into voltage signals that is measured by a pulse processor and transferred onto an analyser for data display and analysis (Goldstein et al., 2017; Russ et al., 2013).

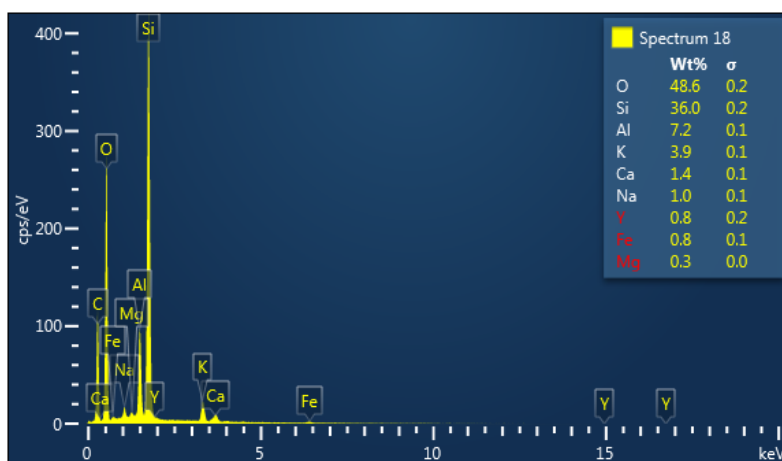


Figure 3-2. Data from an EDS analysis showing the unique peaks for each element.

3.2.3 Site Selection and Roof Runoff Collection

The High Voltage Laboratory (zinc roof) and the E9 Lecture Theatre (copper roof) at the University of Canterbury (Figure 3-3) were used to collect roof-runoff used for both the batch and laboratory column experiments, as well as the field trials. These buildings were chosen

because of ease of access, but more importantly, previous testing had shown that Zn in roof-runoff from the High Voltage Laboratory and Cu in roof-runoff from the E9 Lecture exceeded ANZECC's guidelines for the protection of 90% of freshwater organisms.

Roof-runoff for the laboratory experiments was collected during multiple rainfall events between June 22nd, and September 08th 2017 by placing 250 L water tanks at the end of two downpipes on each building. Roof-runoff for the laboratory column experiment was transported to the Environmental Laboratory by transferring water from the 250 L tanks to 20 L containers (Figure 3-4). Actual roof-runoff was used for all laboratory experiments instead of synthetic stormwater because the results from the laboratory and field experiments were to be compared. The same roof-runoff source was used to ensure consistency among the laboratory experiments and to minimise the introduction of additional variables that could confound the key parameters that were being evaluated in this research.

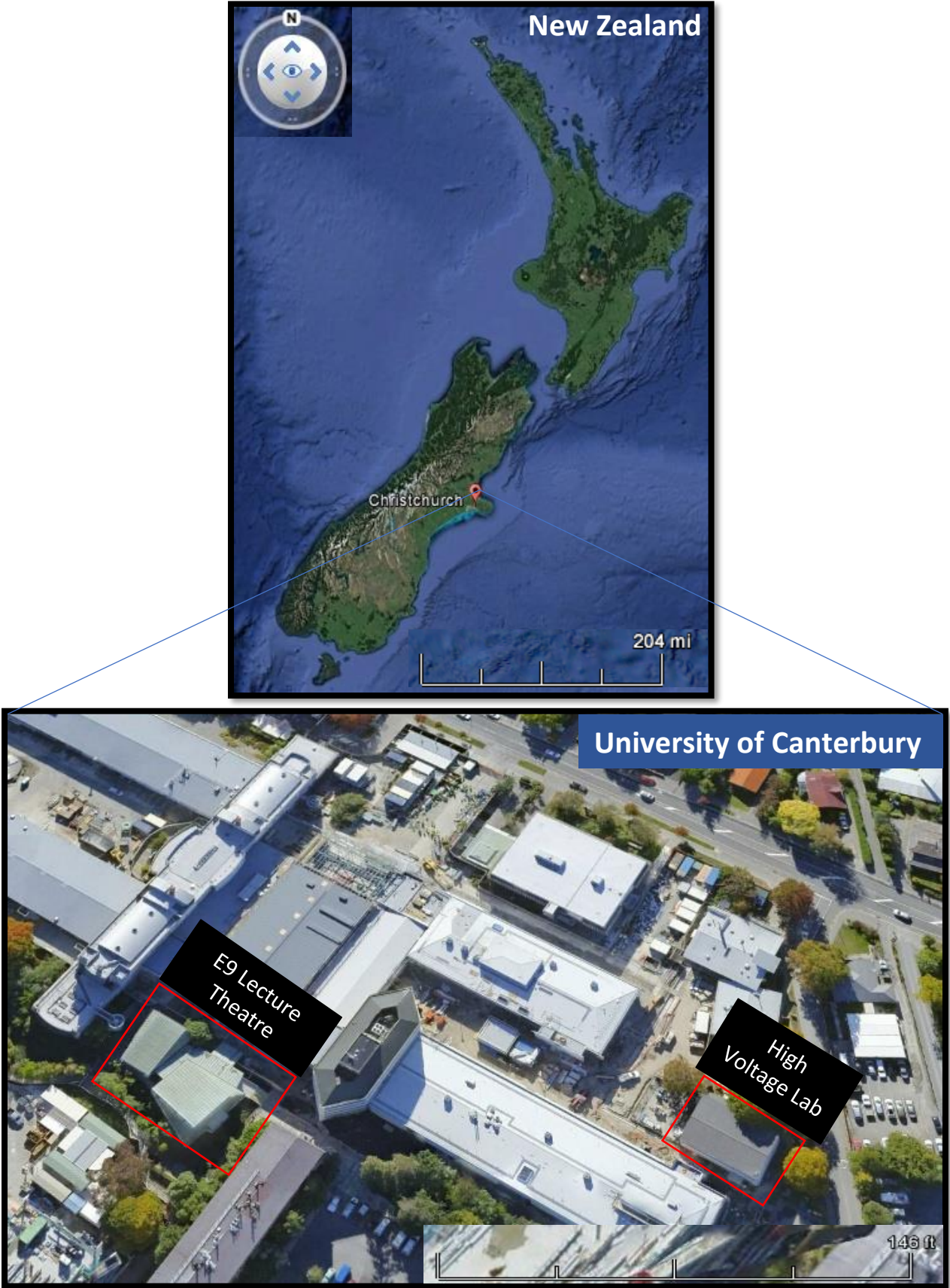


Figure 3-3. Maps showing the location of the E9 Lecture Theatre and the High Voltage Laboratory used to collect roof-runoff and install the treatment systems for field evaluation.



Figure 3-4. Roof-runoff collection and transportation method. Once back at the lab, all runoff was transferred to a 250 L container and mixed to achieve homogeneity.

3.2.4 Phase I – Batch Experimental Procedure

The main purpose of the batch experiments was to evaluate the capability of each treatment material in reducing the percentage of dissolved Zn and Cu from roof-runoff (Objective 1) at the selected grade of $\geq 1.18 \leq 2.36$ mm and to identify whether retention time influenced the percentage reduction of dissolved Zn and Cu. The materials were evaluated using roof-runoff from two rainfall events. The experiments were repeated twice with roof-runoff from the first rainfall event and three times for the second rainfall event. About 5 L of roof-runoff was collected from both the Zn and Cu roofs and stirred constantly in separate 5 L beakers. This was done to prevent the particles in the roof-runoff from settling and to promote homogeneity of the samples being tested.

From the bulk samples, 50 mL of each treatment material was measured, weighed and washed with deionized water to remove the fine particles and were then poured into separate 150 mL beakers. The sequence of the retention time for each repetition of the experiment was done randomly to eliminate bias using randomize.org-listrandomizer. A timer was set to the first water retention time obtained from the randomisation list and 50 mL of roof-runoff was poured into each beaker containing 50 mL of treatment material (1:1 ratio) and stirred

five times using a plastic rod, after which the timer was started. When the timer went off, the treated roof-runoff samples were poured into the empty 50 mL beaker with the designated material and retention time code (Figure 3-5). All the treated runoff samples as well as a 50 mL sample of untreated roof-runoff and deionized water (representative of a blank) was analysed for pH and dissolved Zn and Cu. New treatment materials were assessed for runoff from each roof and rainfall event. For every 10th sample treated a duplicate was done and every 20th sample a triplicate was done while a blank was included for every galvanize. This was done to calibrate the Inductively coupled plasma mass spectrometry (ICP-MS) equipment, and to help trace potential sources of contamination that may have been artificially introduced in the samples as well as helping to estimate sampling and laboratory analysis precision (United States Environmental Protection Agency, 2012).

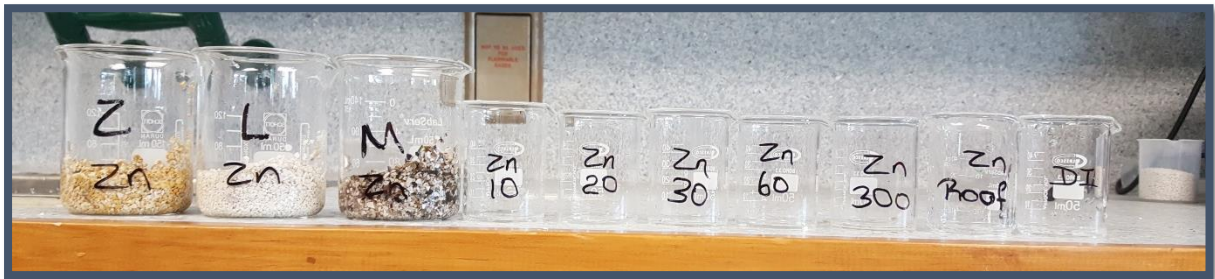


Figure 3-5. Laboratory setup of batch experiments for the evaluation of percentage reduction in dissolved Zn and Cu at material grades of $\geq 1.18 \leq 2.36$ mm at increasing water retention time.

3.2.4.1 Evaluation of Dissolved Zinc and Copper Reduction and pH Change

Using a 15 mL syringe, 10 mL of water was taken from each of the treated samples, as well as the untreated roof-runoff samples and the blanks in the 50-mL beakers. The extracted samples were filtered (using a 0.45 μ m nylon filter) into ICP-MS tubes and two drops of concentrated nitric acid was added as a preservative to ensure pH <2 (Water Environment Federation et al., 2005). All samples were stored in a refrigerator below 4° C until ICP-MS analysis. The pH of all samples was tested after samples for ICP-MS was extracted to avoid contamination by the metal temperature probe of the pH meter.

3.2.5 Phase II – Laboratory Column Treatment Systems

The results for the percentage reduction of dissolved Zn and Cu by each treatment material from the batch experiments was used as a guide to determine whether the grade of $\geq 1.18 \leq 2.36$ mm was suitable for use in the laboratory column treatment systems.

3.2.5.1 Laboratory Column Treatment System Experimental Design

Three clear acrylic pipes (110 mm outside diameter, 100 mm inside diameter) were cut to a length of 1.2 m. A clear pipe was used so that compaction of the materials and movement of the runoff through the treatment materials could be observed. Thirty-three 6 mm holes were drilled in three PVC storm-caps and a 500 μ m mesh was placed inside to prevent the treatment materials from falling through the holes (Figure 3-6). The storm caps were fitted at the base of each pipe and each treatment material was poured into the pipes (Figure 3-7) during which the exterior of the pipe was pounded by hand in a circular-upward motion to increase compaction. Each treatment material at both depths was weighed and poured into the pipes that were set up for the laboratory column experiments (Figure 3-8). The same circular-upward pounding motion was applied. Each treatment material was flushed with tap water to remove the fine particles. A 250 L tank was filled with roof-runoff and a water pump was placed inside the tank to homogenize the water before testing. A peristaltic pump was used to transfer the roof-runoff from the 120 L tanks into each treatment material at flow rates of 1 L/min and 3 L/min. Runoff from the Zn and Cu roofs were assessed separately using fresh treatment materials.



Figure 3-6. Images showing the 6 mm holes drilled and the mesh placed inside the PVC storm-caps which was attached to the base of each column treatment system to prevent the treatment materials from falling through.

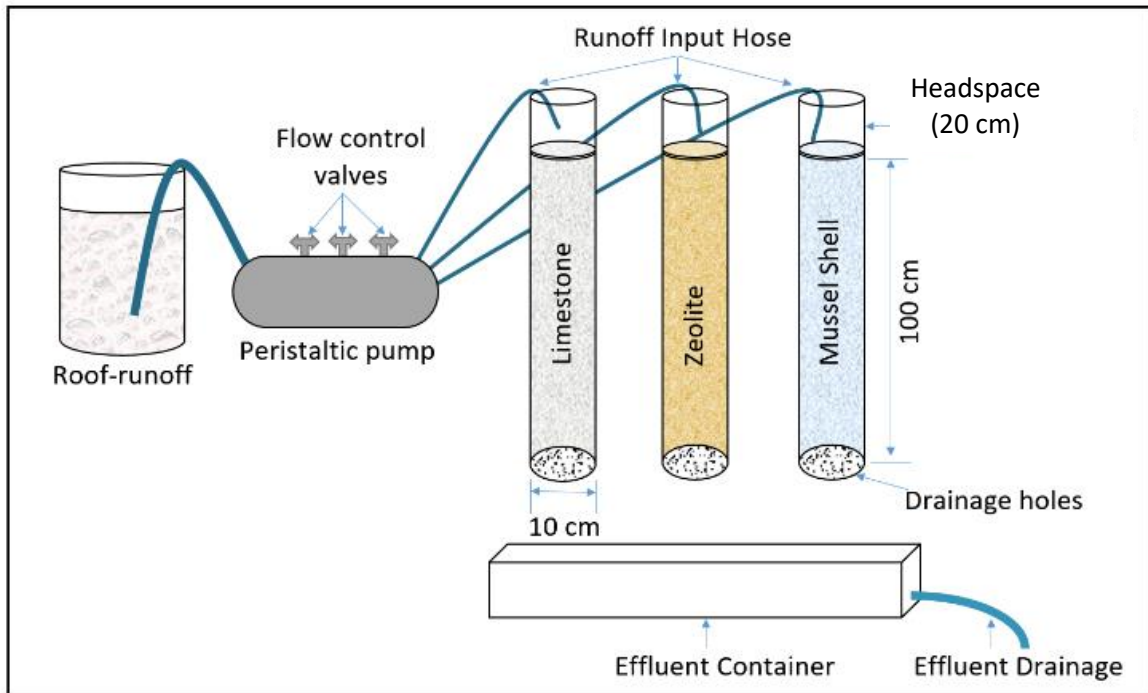


Figure 3-7. The experimental design used to conduct the laboratory column experiments.



Figure 3-8. The set-up of the laboratory column treatment systems with L – limestone, Z – zeolite and M – mussel shells at 1 m and 0.5 m depths.

3.2.5.2 Constant-Head Saturated Hydraulic Conductivity

In designing and assessing the performance of the downpipe treatment systems, the hydraulic conductivity of the treatment materials was a vital design consideration to help determine the maximum roof area and runoff volume at varying rainfall intensity that would be treated before a bypass would be required. After each system was flushed, tap water (via a hose) was allowed to run through each column at a very low rate and slowly increasing the flow until the water was above the treatment materials. The slow increase in water flow from the tap was done to limit the amount of air trapped in the system which could affect the hydraulic conductivity of the materials. The flowrate was adjusted until a constant head of 12 cm above each treatment material was achieved. A 1000 mL measuring cylinder was placed at the base of the treatment system and the time it took to fill was recorded for each treatment material. This was repeated three times for each material and the average time was used in calculating the saturated hydraulic conductivity (K_{sat}) using the derivation of Darcy's Equation:

$$K_{sat} = \frac{Q \times L}{A \times (L + P)} \quad (\text{eqn. 1})$$

Where: K_{sat} = saturated hydraulic conductivity (m/s),

Q = flow through the saturated substrate (m^3/s)

L = depth of the substrate layers (m)

A = cross sectional area of the substrate (m^2)

P = water depth overlying the substrate (m)

The K_{sat} was tested for both undisturbed and disturbed materials at 1 m and 0.5 m depths.

3.2.5.3 Laboratory Treatment System Experimental Procedure

Objective 2 of this research was to quantify the hydraulic performance and dissolved metal reduction of each treatment material at varying depths and flow rates. A material grade of $1.18 \leq 2.36$ was considered satisfactory based on the results obtained from the batch experiments because it was observed that >50% reduction in dissolved Zn and Cu could be achieved by each treatment material. Thus, for the laboratory column experiments, material depths of 1 m (7.8 L of material) and 0.5 m (3.9 L of material) were used as a benchmark to

determine which depth provided a satisfactory combination of hydraulic conductivity and dissolved Zn and Cu reduction. To evaluate the performance of each material at a depth of 0.5 m, half of the material from the 1 m depth experiments was removed. This resulted in materials being disturbed which affected material compaction. Therefore, the performance of the disturbed materials was checked against undisturbed equivalents to determine whether disturbance affected the hydraulic conductivity and percentage metal reduction for treatment materials.

Due to the variation in rainfall intensity, the reduction of dissolved Zn and Cu by each treatment material was also evaluated at a low (1 L/min) and high (3 L/min) flow rate for a duration 15 minutes. The rainfall intensity in Christchurch, New Zealand is typically low in which 95% of the rainfall events with a duration ≥ 6 hour is ≤ 5.1 mm/hr (NIWA, 2017). Thus, at a flow rate of 1 L/min and a rainfall intensity of 5.1 mm/hr, the treatment systems would be able to treat runoff from a roof area of 12 m² before a bypass is required while at a high flow rate of 3 L/min and a roof area of 12 m², the treatment system would be able to treat roof-runoff from a high rainfall intensity of 15 mm/hr before a bypass is required (eqn. 2). A rainfall intensity of 15 mm/hr is representative of a 1.58 years average recurrence interval (ARI) with a duration of 30 minutes for Ilam, Christchurch (NIWA, 2017).

$$\text{Flow rate (m}^3\text{/hr)} = \text{Roof Area (m}^2\text{)} \times \text{Rainfall intensity (m/hr)} \quad (\text{eqn. 2})$$

The process by which the flow rates (1 L/min and 3 L/min) were initially selected was that the performance of the treatment materials was to be assessed at a low and high flow rate for a minimum flow duration of 15 minutes (to identify possible trends with time). Also, a replication of the treatment materials at a depth on 1 m using roof-runoff from the same rainfall event was required to assess the accuracy of the procedure and sampling methods. With a 250 L tank being available to store the roof-runoff in the laboratory; the need to replicate the procedure using roof-runoff from the same rainfall event; and two flow rates of 1 L/min and 3 L/min, the maximum flow duration that could be achieved was 15 minutes. It was only possible to assess two treatment materials at the two flow rates for 15 minutes with the volume of water available from the 250 L tank. Therefore, limestone and mussel shells were assessed using roof-runoff stored in the 250 L tank while the zeolite was assessed using roof-runoff stored in an 80 L tank. Roof-runoff in the 250 L and 80 L tanks were always collected from the same rainfall events for each experiment. The 250 L tank was used to run

the experiment at both flow rates for 15 minutes for all three treatment materials at a depth of 0.5 m since there was no repetition required with roof-runoff from the same rainfall event (Appendix A. The Volume of Roof-Runoff Used in the Laboratory Column Experiments)

Each treatment material was evaluated with runoff from the Zn and Cu roofs from two separate rainfall events at material depths of 1 m and 0.5 m. The performance of each treatment material at a disturbed and undisturbed depth of 1 m and 0.5 m was evaluated using the two flow rates (1 L/min first). Evaluation of materials at 1 m depths was repeated twice for each rainfall event while materials at 0.5 m were evaluated only once for each rainfall event (Appendix B). Separate and fresh treatment materials were assessed for runoff collected from the Zn and Cu roofs.

3.2.5.4 Sampling Method

One of the main purpose of the laboratory column experiment was to assess the percentage reduction in dissolved Zn and Cu that could be achieved using each treatment material when used in a downpipe column. Results from the batch experiments showed that the percentage reduction in dissolved Zn and Cu for each treatment material at increasing retention time was not significantly different ($p \leq 0.05$). Therefore, about 600 mL of treated runoff for each treatment material at both flow rates was collected at 0, 5, 10 and 15 minutes by placing a 1000 mL beaker below each treatment system. To determine the percentage reduction of dissolved Zn and Cu achieved by each treatment material, roof-runoff samples were taken at the end of the hose from the peristaltic pump that fed into the treatment materials at the beginning and end of each experiment for each material. These two roof-runoff samples were taken to observe if there was any disparity in the metal concentration of the untreated roof-runoff. These two samples were taken when the experiment was being conducted at both flow rates and for all three treatment materials. Several researchers including Charters et al. (2016b), Hyun and Lee (2013) and Timperley et al. (2005) have indicated that >80% of the Zn and Cu in roof-runoff is in the dissolved form. As a result, to determine the percentage of Zn and Cu that was in the dissolved form in the untreated roof-runoff used in this research, both total and dissolved Zn and Cu was tested.

3.2.5.5 Evaluation of pH Change, Total and Dissolved Zn and Cu

The pH and dissolved Zn and Cu assessment for the laboratory experiment was done as described in Section 3.2.4.1. For the evaluation of total Zn and Cu, 25 mL of sample from both the untreated and treated roof-runoff taken at 0 and 15 minutes was placed in a centrifuge tube and 5 mL of concentrated nitric acid was added to obtain a pH <2. The tubes were placed in a 120° C digestion block for an hour after which they were left to cool for 15 minutes. 10 mL of each sample was filtered into separate ICP-MS tubes using a disposable syringe and a 0.45 µm, 25 mm nylon syringe filter Federation & Association, 2005. All samples were stored in a refrigerator at a temperature <4° C prior to ICP-MS analysis.

3.2.5.6 Statistical Analysis

One-way analysis of variance (ANOVA) was used to determine whether there were any statistically significant differences in the percentage dissolved Zn and Cu reduction and pH change among the treatment materials. It could not be established that the outliers observed in this research were due to data entry or measurement error, therefore, they were treated as genuinely unusual data points. The outliers were included in the analysis because it was not believed that the result would be materially affected, which was determined by comparing the results of the one-way ANOVA on the original data to the transformed data. The Shapiro-Wilk test and Q-Q plots were used to determine whether the data was normally distributed. For data that was not normal, the one-way ANOVA was still used because it is considered to be fairly robust to deviations from normality, particularly if the sample sizes are equal (Lix et al., 1996), which was the case in this research. One-way ANOVA cannot tell which specific groups are significantly different from each other, therefore, a Turkey's post-hoc test was done as part of the one-way ANOVA procedure. The Pearson's product moment correlation was used to determine the strength and direction of a linear relationship between pH and percentage reduction of dissolved Zn and Cu for roof-runoff treated by limestone and mussel shells.

3.3 Results

3.3.1 Chemical Characterization of Treatment Materials

The results from the EDS analysis for fresh zeolite, limestone and mussel shells showed that the dominant elements for zeolite were oxygen (O) (42-51%) and silicon (Si) (34-41%), for limestone were calcium (Ca) (35-63%) and O (33-58%) and for mussel shells were O (45-59%) and Ca (38-53%) (Figure 3-9).

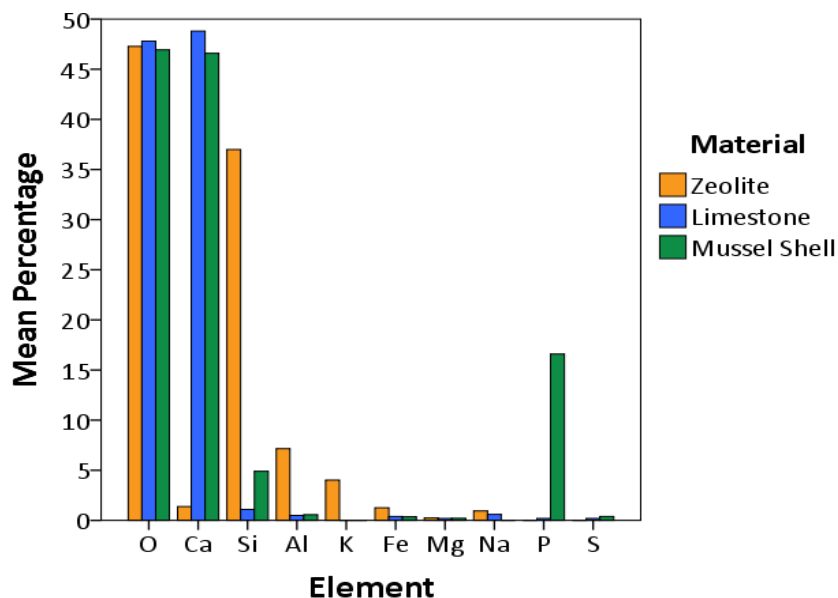


Figure 3-9. Chemical composition of the fresh treatment materials used in this research.

3.3.2 Concentration and Percentage of Dissolved Zinc and Copper in Roof Runoff

Evaluation of the percentage dissolved Zn and Cu in the untreated roof-runoff from both roofs showed that 100% of the Zn was in the dissolved form while dissolved Cu ranged from 78% - 91%. The concentration of both dissolved Zn and Cu was significantly higher than ANZECC’s mixed instream guideline values of 15 µg/L and 1.18 µg/L for total Zn and Cu respectively, for the protection of 90% freshwater organisms (Table 3-1).

Table 3-1. The pH and metal concentration for roof-runoff collected from the high voltage laboratory (galvanized roof) and the E9 lecture theatre (copper roof) for the laboratory column experiment.

| Roof Type | Metal Treated | pH Range | Dissolved Metal Concentration (µg/L) | Dissolved Metal Percentage (%) | 90% ANZECC Guidance Total Metal (µg/L) |
|------------|---------------|-------------|--------------------------------------|--------------------------------|--|
| Galvanized | Zn | 6.17 - 7.83 | 150 - 254 | 100 | 15 |
| Copper | Cu | 6.72 - 7.18 | 312 - 884 | 78 - 91 | 1.8 |

3.3.3 Batch Experiments – Evaluation of Dissolved Zinc and Copper Reduction

Results from the batch experiments showed that the percentage reduction of dissolved Zn and Cu for the batch experiments varied among the three treatment materials and between the roof-runoff type. Comparison of the mean percentage reduction in dissolved Zn and Cu for each treatment material showed that limestone gave the highest mean percentage reduction for both Zn and Cu (87% Zn and 91% Cu) followed by mussel shells (78% Zn and 64% Cu) and then zeolite (48 % Zn and 64% Cu) (Figure 3-10). The concentration of dissolved Zn and Cu in runoff treated by all three treatment materials were still significantly higher than ANZECC’s guideline values for the protection of 90% of freshwater organisms (Table 3-2).

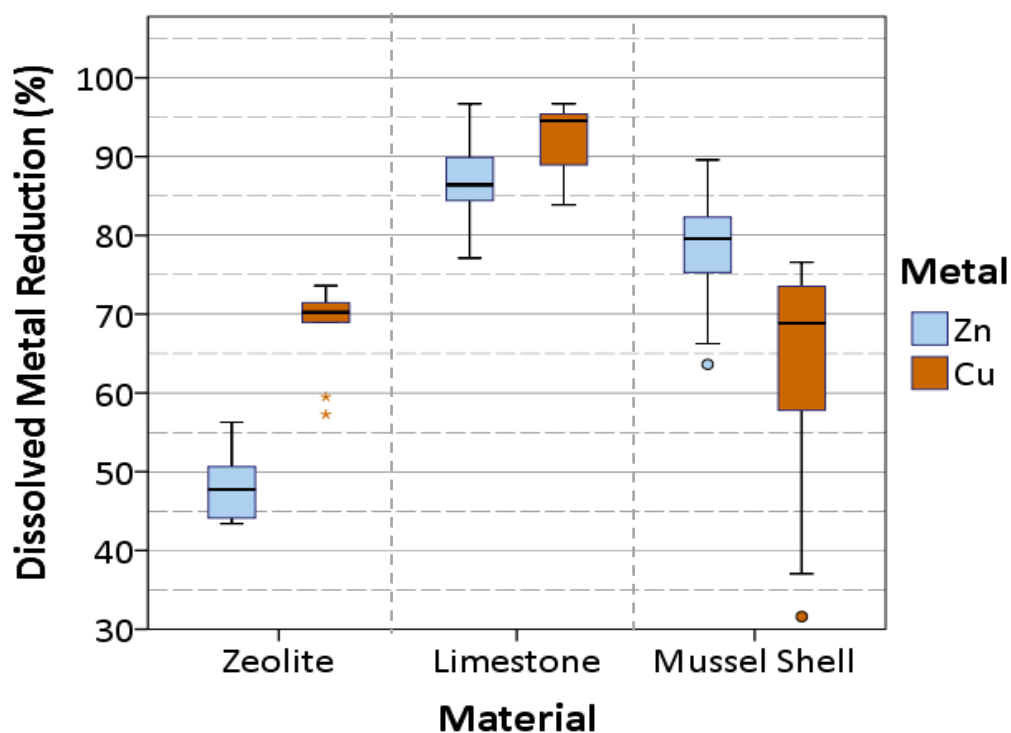


Figure 3-10. Comparison of the percentage reduction in dissolved Zn and Cu in runoff treated by zeolite, limestone and mussel shells.

Table 3-2 Comparison of the pH change and dissolved Zn and Cu concentration in runoff treated by each treatment material.

| Material Type | Metal Treated | pH | | pH Change (%) | | Dissolved Metal Conc. (ug/L) | | Dissolved Metal Removed (%) | | ANZECC 90% Guideline (µg/L) |
|---------------|---------------|------|------|---------------|-------|------------------------------|-------|-----------------------------|-------|-----------------------------|
| | | Mean | ± SD | Mean | ± SD | Mean | ± SD | Mean | ± SD | Freshwater Organisms |
| Zeolite | Zn | 6.95 | 0.14 | -2.22 | 1.93 | 117.46 | 9.43 | 48.23 | 4.16 | Total Zn 15 |
| Limestone | Zn | 9.08 | 0.35 | 29.50 | 11.90 | 21.08 | 10.46 | 87.19 | 4.93 | |
| Mussel Shell | Zn | 8.81 | 0.43 | 25.54 | 11.25 | 37.55 | 19.11 | 78.78 | 6.37 | |
| Zeolite | Cu | 6.95 | 0.12 | 3.45 | 1.81 | 239.71 | 42.28 | 68.51 | 5.55 | Total Cu 1.8 |
| Limestone | Cu | 9.18 | 0.18 | 33.89 | 4.10 | 65.77 | 39.40 | 91.81 | 4.23 | |
| Mussel Shell | Cu | 8.82 | 0.29 | 28.48 | 3.46 | 268.68 | 101 | 64.02 | 12.21 | |

The results from the batch experiments showed that the pH of the roof-runoff treated by zeolite did not differ significantly from the untreated runoff for both the galvanized and copper roofs. However, the pH of runoff from both roofs that were treated by limestone and mussel shells was considerably higher than the pH of the untreated roof-runoff (Figure 3-11). The main mechanism by which zeolite reduces the concentration of dissolved metals from stormwater is via adsorption and ion exchange Pitcher et al., 2004; Sprynskyy et al., 2006 while the main mechanism for limestone and mussel shells occurs by increasing the pH of the untreated runoff Komnitsas et al., 2004. There was a strong positive correlation between pH and percentage metal reduction when both Zn ($r(25) = 0.576 < 0.0005$) and Cu ($r(25) = 0.677 < 0.0005$) was treated with mussel shells. A small positive correlation for limestone was only observed when Cu was treated ($r(25) = 0.224 < 0.05$). The relationship between pH and percentage metal reduction was statistical significant (Table 3-3).

It has been highlighted in the literature that as the pH of metal contaminated water increases the concentration of dissolved metals such as Zn and Cu is expected to decrease (Komnitsas et al., 2004; Sdiri et al., 2012; Wise, 2000). While there were variations in the average percentage reduction in dissolved Zn and Cu at the increasing retention times for all three treatment materials (Figure 3-12) statistical analysis revealed that these differences were not significant ($p > 0.05$).

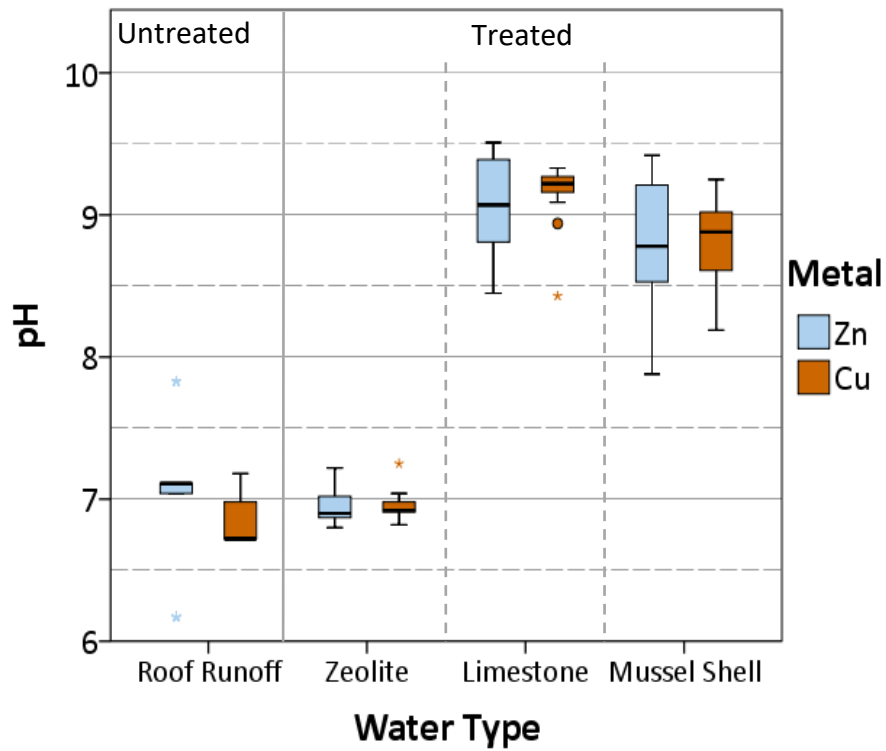


Figure 3-11. A Comparison of the pH of untreated roof-runoff and roof-runoff treated by zeolite, limestone and mussel shells.

Table 3-3. The correlation between pH and percentage metal reduction for roof-runoff treated with mussel shells and limestone.

Correlations

| | Metal Treated | | Metal Reduction (%) |
|--------------------|---------------|---|----------------------|
| pH – Mussel Shells | Zn | Pearson Correlation Sig. (2-tailed) N | .759** .000 25 |
| pH – Mussel Shells | Cu | Pearson Correlation Sig. (2-tailed) N | .823** .000 25 |
| pH – Limestone | Cu | Pearson Correlation Sig. (2-tailed) N | .473* .017 25 |

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

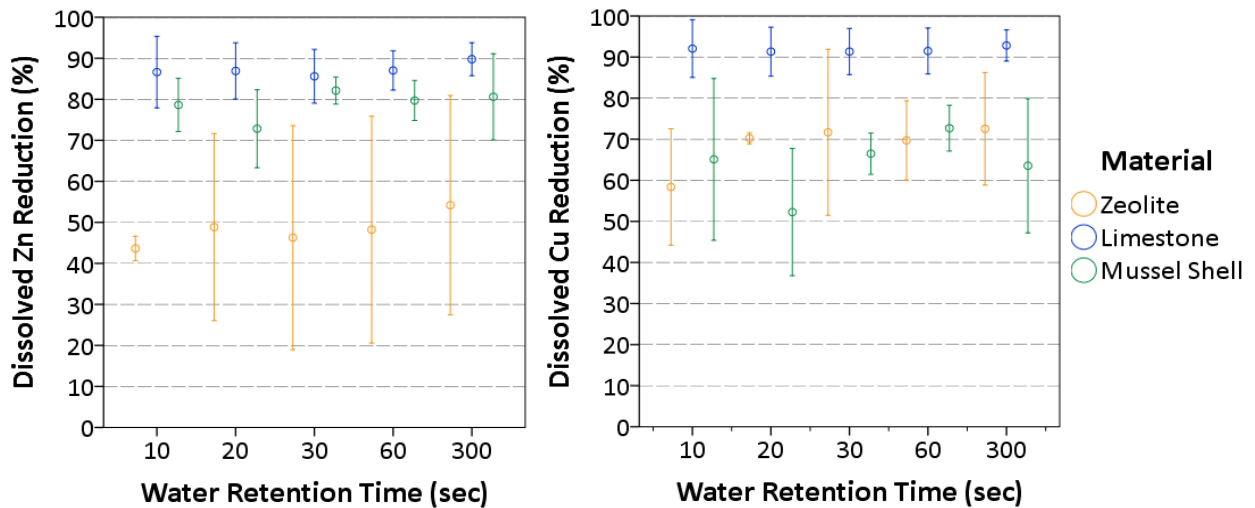


Figure 3-12. Comparison of the percentage reduction in dissolved Zn and Cu in roof-runoff treated by zeolite, limestone and mussel shells at increasing water retention times. The error bars represent the full range of values.

3.3.4 Laboratory Column Experiment – Evaluation of Saturated-Hydraulic Conductivity, pH Change and Dissolved Zinc and Copper Reduction

3.3.4.1 Saturated Hydraulic Conductivity

At a depth of 0.5 m, the hydraulic conductivity for zeolite, limestone and mussel shells ranged from 15.6 m/hr – 46.2 m/hr, 21.6 m/hr – 33.6 m/hr and 12 m/hr – 33.6 m/hr respectively. At a depth of 1 m the hydraulic conductivity for zeolite, limestone and mussel shells ranged from 27 m/hr – 36 m/hr, 27 m/hr – 34.2 m/hr and 24 m/hr – 29.4 m/hr respectively. The results showed that the hydraulic conductivity was the same for all three treatment materials at an undisturbed depth of 1 m but varied greatly when the materials were disturbed. Overall, undisturbed materials at a depth of 0.5 m was observed to have the lowest hydraulic conductivity.

3.3.4.2 Dissolved Zn and Cu Reduction

For the treatment of dissolved Zn, the results showed that 95 – 99% reduction was achieved by all treatment materials at both depths, flow rates and disturbances. On the other hand, it was observed that a significantly higher reduction ($p \leq 0.05$) in dissolved Cu was achieved at a depth of 1 m compared to 0.5 m. However, >90% reduction in dissolved Cu by all treatment materials were only achieved at an undisturbed depth of 1 m. At a depth of 0.5 m, the percentage reduction of dissolved Cu for zeolite, limestone and mussel shells ranged from

30.25% - 99.25%, 18.62% - 97.2% and 35.87% - 97.66% respectively with the lowest values obtained when the materials were undisturbed. Overall, it was observed that the percentage reduction in dissolved Zn was greater and more consistent than Cu for all treatment materials (Figure 3-13).

With mean a percentage reduction of >95% Zn, all treatment materials reduced the dissolved concentration of Zn, which ranged from 150 µg/L - 254 µg/L in the untreated roof-runoff, to concentrations well below ANZECC's mixed instream guideline value of 15 µg/L total Zn for the protection of 90% of freshwater organism's (Figure 3-14). With a mean percentage Cu reduction of >90% at an undisturbed depth of 1 m, none of the treatment materials reduced dissolved Cu to concentrations below ANZECC's 90% mixed guideline of 1.8 µg/L total Cu. However, all the treatment materials reduced the concentration of dissolved Cu, which ranged from 312 µg/L – 884 µg/L in the untreated roof-runoff, to concentrations below 20 µg/L (Figure 3-15).

The results showed that the pH of roof-runoff treated by zeolite was not significantly different ($p > 0.05$) from the pH of the untreated roof-runoff, however, the pH of roof-runoff treated by limestone and mussel shells was significantly higher ($p \leq 0.05$) than the untreated roof-runoff (Figure 3-16). Despite this difference, the results from the Pearson's product-moment correlation showed no evidence of a relationship between the pH and the percentage reduction in dissolved Zn and Cu for roof-runoff treated by limestone and mussel shells in the laboratory column experiment.

At a continuous flow for 15 minutes, the percentage of dissolved Zn and Cu in the treated roof-runoff was evaluated at 0, 5, 10 and 15 minutes to identify whether the performance of the materials changed overtime. The results showed that the percentage dissolved Zn reduction overtime did not change significantly ($p > 0.05$). However, the percentage dissolved Cu reduction for all treatment materials was significantly higher ($p \leq 0.05$) at 0 minutes compared to samples taken at 5, 10 and 15 minutes (which were not significantly different from each other) (Figure 3-17).

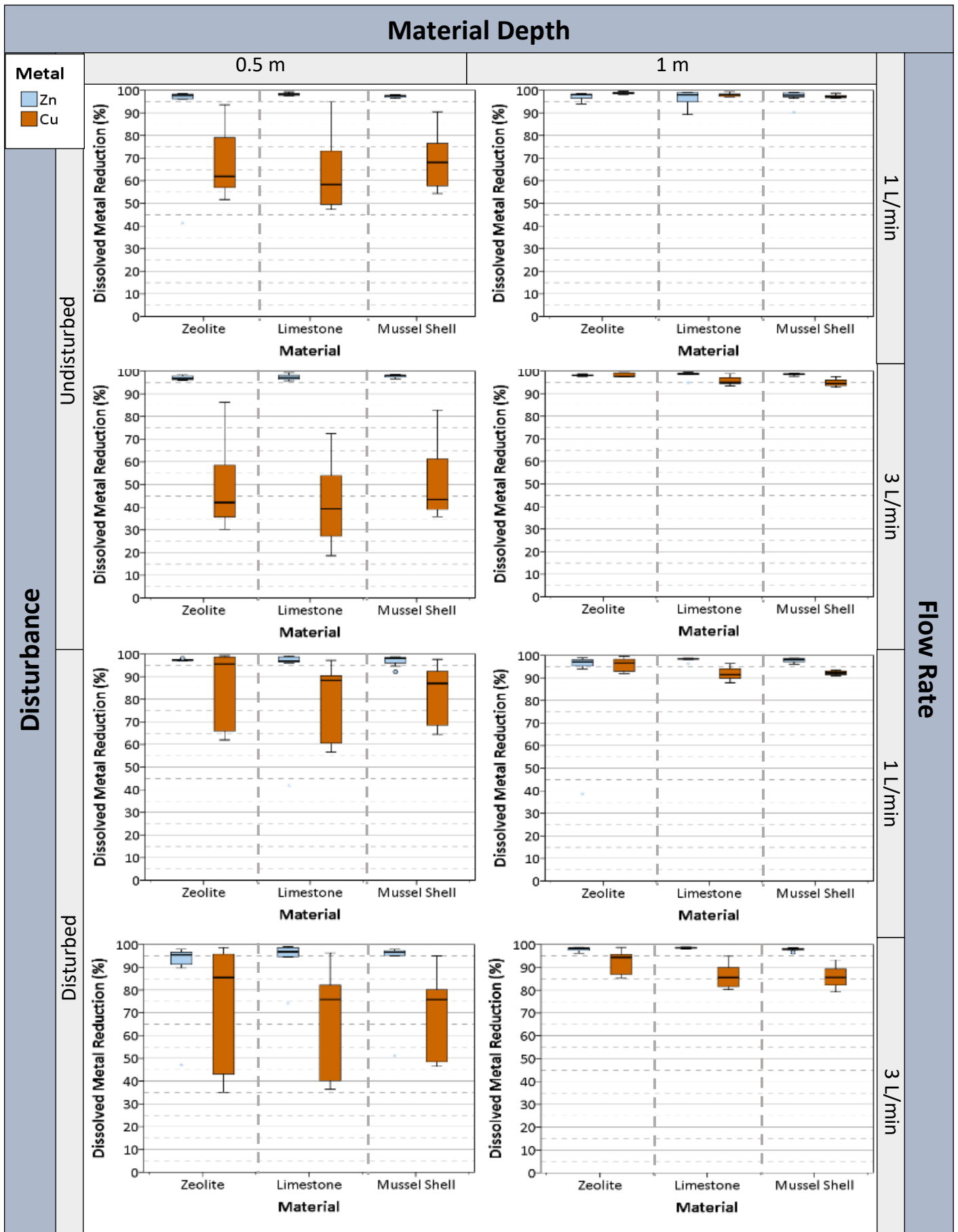


Figure 3-13. Comparison of the percentage reduction in dissolved Zn and Cu in roof-runoff treated by zeolite, limestone and mussel shells at two material depths (0.5 m and 1 m), flow rates (1 L/min and 3 L/min) and when materials were undisturbed and disturbed.

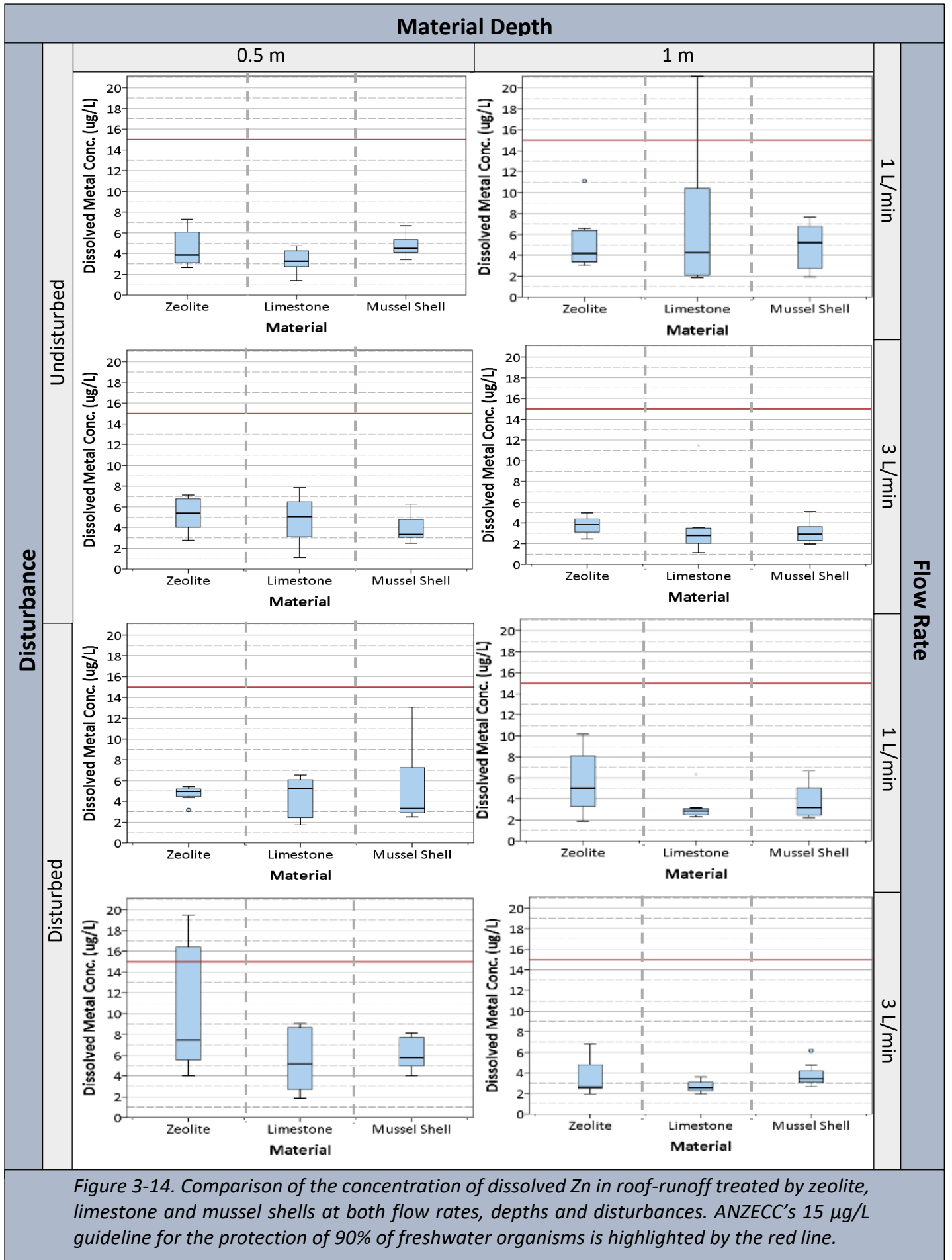


Figure 3-14. Comparison of the concentration of dissolved Zn in roof-runoff treated by zeolite, limestone and mussel shells at both flow rates, depths and disturbances. ANZECC's 15 $\mu\text{g/L}$ guideline for the protection of 90% of freshwater organisms is highlighted by the red line.

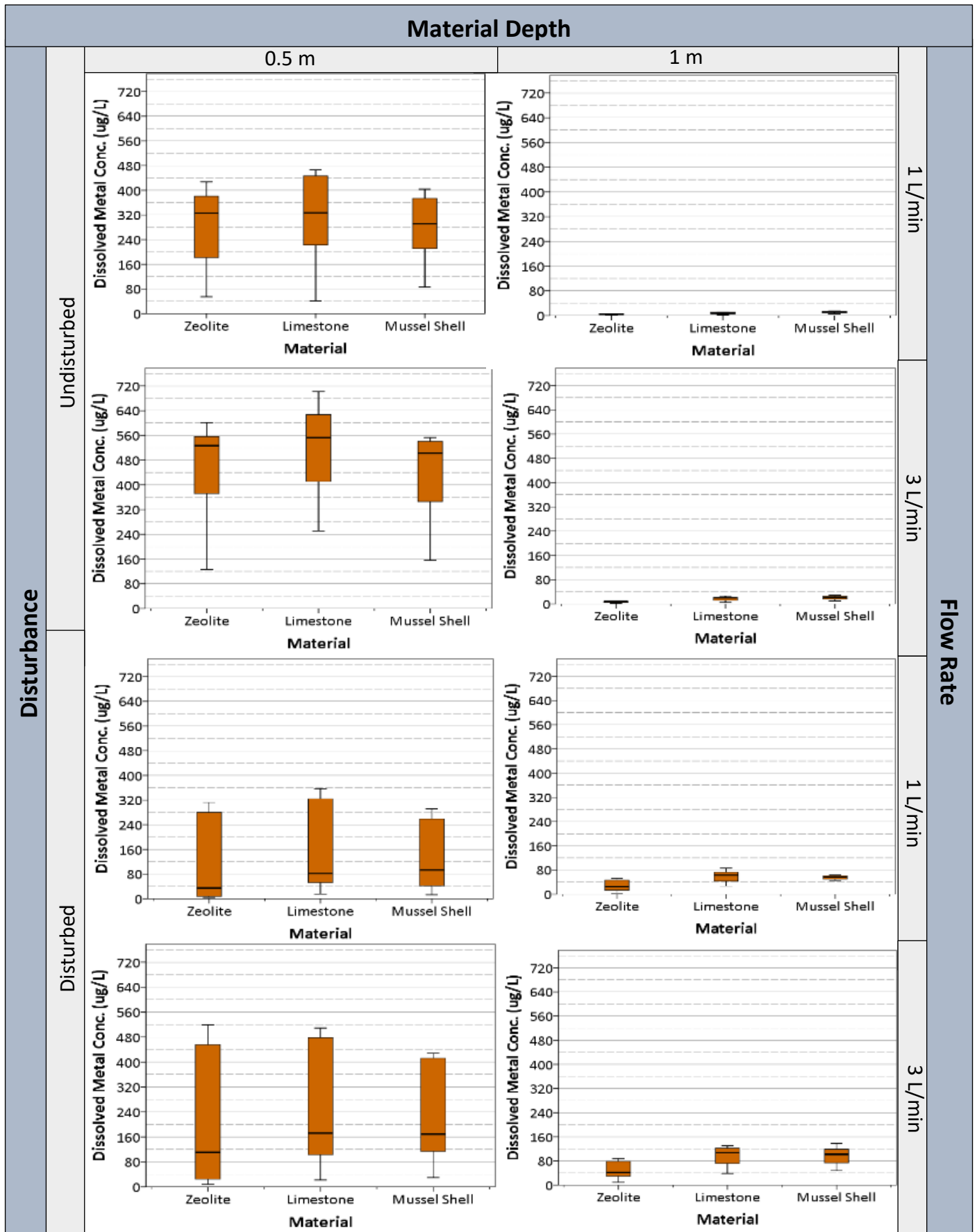


Figure 3-15. Comparison of the concentration of dissolved Cu in roof-runoff treated by zeolite, limestone and mussel shells at both flow rates, depths and disturbances.

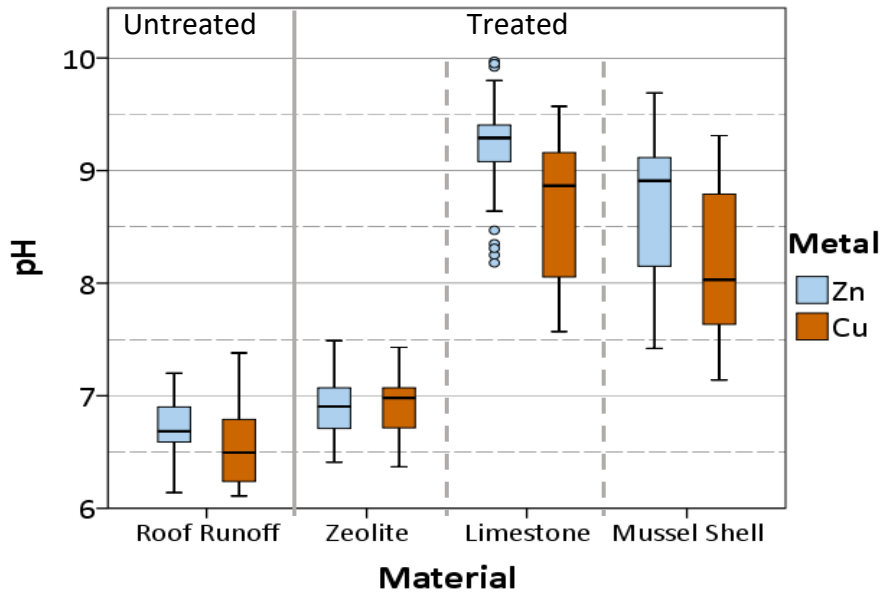


Figure 3-16. Comparison between the pH of untreated roof-runoff from the Zn and Cu roofs and the runoff treated by zeolite, limestone and mussel shells.

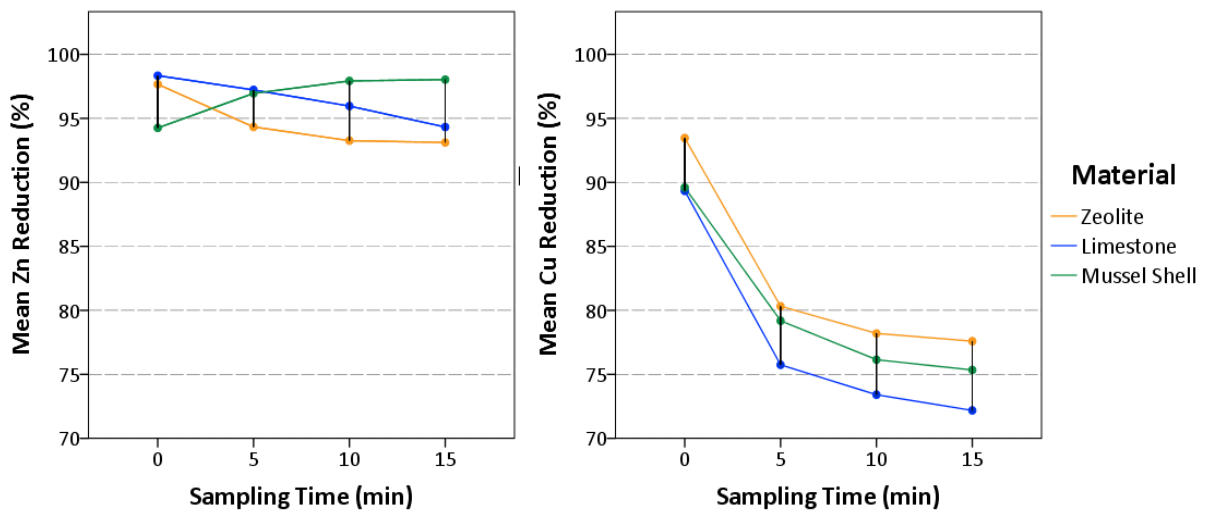


Figure 3-17. Comparison of the mean percentage reduction in dissolved Zn and Cu for roof-runoff treated by zeolite, limestone and mussel shells at five minutes interval during continuous flow of 15 minutes.

3.4 Discussion

3.4.1 Chemical Characterization of Treatment materials

The results from the EDS analyses of the fresh treatment materials used in this research showed that the dominant elements for zeolite were O and Si. This is an indication that silicate oxide is the element that plays a more substantial role in the removal of dissolved Zn and Cu

from roof-runoff when zeolite is used as reported by Ghobarkar et al. (1999). For limestone and mussel, O and Ca were the dominant elements. These results confirmed that CaCO_3 is the main component that immobilizes dissolved metals when limestone and mussel shells is used as stated by Wise (2000).

3.4.2 Dissolved Zinc and Copper Reduction Mechanisms

The percentage reduction in dissolved Zn and Cu for all three treatment materials was much lower in the batch experiments compared to the laboratory column experiments. This difference may be attributed to the much larger volume of material (7.8 L compared to 50 mL) used in the laboratory column experiments, in which the surface area was considerable higher. As a result, increased adsorption sites and calcium ions may have led to increased adsorption and cation exchange (Westholm et al., 2014). Also, the downward flow of the roof-runoff through the materials in the laboratory column experiments may have also lead to increased adsorption and cation exchange compared to the batch experiments where the roof-runoff was stagnant in which dissolved ions in the runoff ponding above the materials had no direct contact for adsorption unless they diffused towards the materials. For the treatment of Cu in the laboratory column experiment, it was evident that all three treatment materials were more effective in reducing the concentration of dissolved Cu at undisturbed depths of 1 m.

For both the batch and laboratory column experiments, it was evident that adsorption and ion exchange was the main mechanism by which zeolite reduced the concentration of dissolved Zn and Cu. This is because there was no significant difference between the pH of the untreated roof-runoff and runoff treated by zeolite, however dissolved Zn and Cu in the laboratory column experiments was reduced by >95%. It was also evident that increasing pH contributed to the reduction of dissolved Zn and Cu in runoff treated by limestone and mussel shells in the batch experiments where greater reduction in dissolved Zn and Cu was achieved at higher pH values. A stronger correlation between pH and percentage dissolved Zn and Cu reduction was observed for runoff treated by mussel shells because the SD of the pH for runoff treated by mussel shells was wider compared to the SD of the pH obtained for runoff treated by limestone. This wider SD in the pH of runoff treated by mussel shells allowed for a trend to be identified between pH and percentage metal reduction (Figure 3-18).

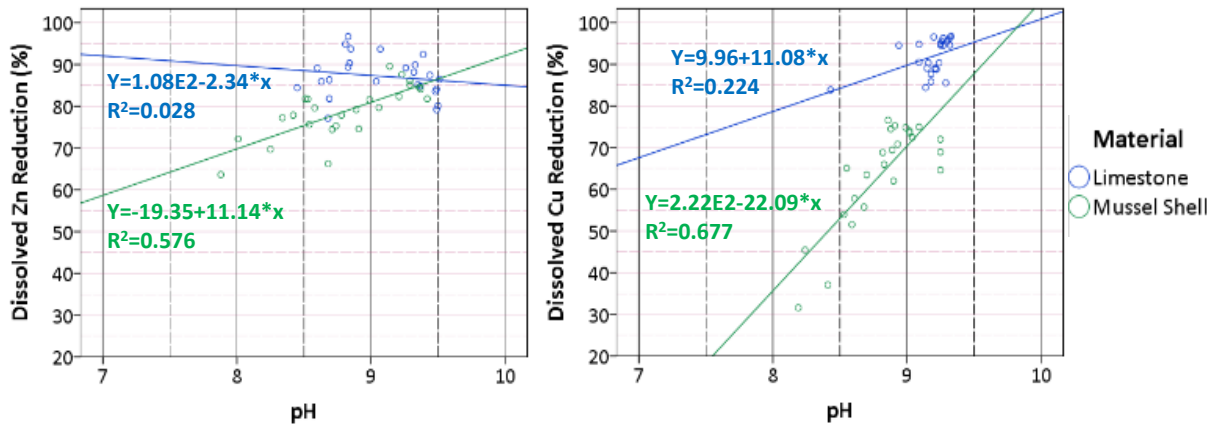


Figure 3-18. Correlation between pH and percentage reduction of dissolved Zn and Cu in roof-runoff treated by limestone and mussel shells.

One of the factors that affect the reduction in the concentration of dissolved metals by treatment materials is the initial concentration of these metals in the untreated water (Abdel-Salam et al., 2011; Barakat, 2008). Dissolved Cu concentrations were considerably higher than Zn concentrations found in untreated roof-runoff thus, this may have been one of the reasons why a higher reduction in the concentration of Zn was obtained. To verify whether the initial concentration of dissolved metals influenced the reduction in the concentration of dissolved Zn and Cu, an assessment could be done using synthetic roof-runoff with increasing concentrations of Zn and Cu.

The adsorption characteristics of the treatment materials also influences the percentage reduction of various ions (Shin et al., 2014). Assessment of the adsorption characteristics of multi-metal ions by Shin et al. (2014) and Babel and Kurniawan (2003) showed that zeolite and limestone had a greater affinity for Cu which is consistent with the results obtained in the batch experiments but not the laboratory column experiments. More variables were evaluated in the laboratory column experiments, and as a result, confounding factors may have contributed to the zeolite and limestone achieving greater reduction of dissolved Zn than Cu. For both the batch and laboratory column experiments, a greater reduction in dissolved Zn was achieved with mussel shells. Information on the adsorption characteristics of mussel shells could not be obtained from the literature, therefore, it could not be determined whether mussel shells had a greater affinity for Zn. However, results from a research on the potential of mussel shells as a bio-sorbent for stormwater treatment by

Craggs et al. (2010) showed that mussel shells was more effective in removing Zn than Cu, but it did have the potential to significantly reduce the aqueous concentration of both metals in stormwater.

Although the SD of the pH for roof-runoff treated by limestone and mussel shells was wider for the laboratory column experiments than the batch experiments, results from the Pearson's product-moment correlation showed no evidence of a relationship between pH and percentage dissolved metal reduction. This can be attributed to adsorption and cation exchange playing a greater role in the reduction of dissolved Zn and Cu due to the increased number of adsorption sites and Ca cations competing with the Zn and Cu ions for complexing sites because of the significant volume increase of these materials. Additionally, limestone and mussel shells do not only reduce dissolved metals by increasing pH, but are also able to cause increased Zn and Cu carbonate complexes and thus a reduction in free Zn and Cu ions (Hyne et al., 2005). Collectively, the involvement of these additional Zn and Cu reduction mechanisms may have had a masking effect on the correlation between pH and the percentage reduction of dissolved Zn and Cu in runoff treated by limestone and mussel shells in the laboratory column experiments.

For the laboratory column experiments, the percentage reduction of dissolved Zn by all three treatment materials were not significantly different at sampling times of 0, 5, 10 and 15 minutes. However, the percentage reduction of Cu was significantly higher ($p \leq 0.05$) in samples taken at 0 minutes. This might be attributed to adsorption of Cu to the suspended solids in samples taken at 0 minutes thus causing the concentration of dissolved Cu to be lower at 0 min compared to samples taken at 5, 10 and 15 minutes. Although the results showed that the dissolved concentration of Cu increased with time, the total Cu concentration in samples taken at zero minutes may not have been significantly different from the total Cu in the other samples. To determine whether adsorption to the fine particles was a contributing factor to the lower concentration of dissolved Cu observed in samples taken at 0 minutes, both total and dissolved concentration of Cu at each sampling time should be assessed and compared. Although no significant differences were observed for Zn, this assessment should still be carried out to help identify the reason(s) for the differences between the two metals.

3.4.3 Zinc and Copper Guidelines for Freshwater Organisms

With >95% reduction in dissolved Zn, the concentration of dissolved Zn in runoff treated by all three materials in the laboratory column experiments were well below ANZECC's mixed instream guideline values. Thus, all the treatment materials proved to be extremely effective in reducing the concentration of dissolved Zn from roof runoff. While none of the materials reduced the concentration of dissolved Cu below ANZECC's 90% guidance, with a percentage Cu reduction of >90% at an undisturbed depth of 1 m, all the treatment materials reduced the concentration of dissolved Cu to < 20 µg/L (from 312 – 884 µg/L) which was a significant reduction. Also, dilution of the treated roof-runoff is expected as it moves downstream which would lead to further reduction in dissolved Cu concentration. As a result, the concentration of Cu may be further reduced to concentrations below ANZECC's mixed instream guideline value for Cu. Thus, the treatment of dissolved Cu by all three treatment materials was very effective at an undisturbed material depth of 1 m.

3.4.4 Saturated-Hydraulic Conductivity

The hydraulic conductivity of the treatment system is influenced not only by the particle size of the materials, but also the degree of compaction, the amount and size of the drainage holes at the base and the size of the plastic mesh used at the base. As a result, obtaining a consistent hydraulic conductivity can be difficult particularly at a 0.5 m depth where greater variation in compaction was observed. Despite this, decreased hydraulic conductivity was only observed in materials with a flow rate capacity below 3 L/min which may be entirely due to compaction because the amount of debris from the roof-runoff which accumulated on the surface of the materials was very low/insignificant. Under field conditions, the initial hydraulic conductivity is expected to be high, however, it is also expected to diminish overtime and eventually clog due to the accumulation of debris emanating from the roof. Therefore, to help reduce the rate and frequency of clogging, a mechanism for the removal of debris emanating from the roof needs to be factored into the system design such as a leaf guard or plastic mesh. This device should be easy to remove to allow for regular cleaning. If the material in the system must be disturbed, it should be dried before repacking particularly for the treatment of dissolved Cu where it was observed that a higher percentage reduction was achieved when the materials were undisturbed. Drying the materials will help obtain a more evenly

compacted material, a reduction in the number of macro-pores and a preferential flow paths which will affect the hydraulic conductivity and percentage reduction in dissolved metals.

At undisturbed depths of 1 m, all three treatment materials had the same hydraulic conductivity which was expected due to the same particle size and volume of materials used. However, at undisturbed depths of 0.5 m, the hydraulic conductivity varied among the three materials which can be linked to increased compaction of varying degrees being achieved among the treatment materials due to a lower volume of material being used. This increased compaction is reflected by the mass of the materials at both depths (Appendix C) Appendix C. Physical Properties of Each Treatment Material Used in the Laboratory Column Experiments. The hydraulic conductivity of all three treatment materials increased at disturbed depths of both 0.5 m and 1 m which can be attributed to the materials being repacked when wet and consequently causing a reduction in material compaction, the creation of larger macrospores and possible preferential flow pathways.

3.5 Chapter Summary

Zeolite, limestone and mussel shells have proven to be very effective in reducing the percentage of both dissolved Zn and Cu from roof-runoff. Batch and laboratory column experiments were conducted and parameters such as pH and percent reduction in dissolved Zn and Cu were evaluated. For the laboratory column experiments, >95% reduction of dissolved Zn and Cu was achieved at both material depths, flow rates and disturbances for runoff treated by zeolite while <70% reduction in dissolved Zn and Cu was achieved in the batch experiments for zeolite. The difference in performance of zeolite for the batch and column experiments may be attributed to the higher volume of material used in the laboratory column experiments in which there was considerable higher surface area for adsorption and cation exchange to take place. The pH of runoff treated by zeolite was not different from the pH of untreated roof-runoff for both the batch and laboratory column experiments. Thus, this was an indication that adsorption and cation exchange are the main mechanisms by which zeolite reduces the concentration of dissolved metals from untreated roof-runoff.

For roof-runoff treated by limestone and mussel shells, >95% reduction in dissolved Zn was also achieved at both material depths, flow rates and disturbances, however, >95% reduction

in dissolved Cu was only achieved at an undisturbed depth of 1 m and a flow rate of 1 L/min in the laboratory column experiments. Dissolved Cu reduction between 90%-95% was only achieved at an undisturbed depth of 1m for all materials. The pH of runoff treated by limestone and mussel shells was considerably higher than the pH of the untreated roof-runoff. A strong correlation between pH and percentage reduction in dissolved Zn and Cu was observed in the batch experiments for runoff treated by mussel shells while a small correlation was only observed when Cu was treated by limestone. The relationship between pH and metal reduction was more pronounced for mussel shells because the SD of the pH for roof-runoff treated by mussel shells was wider than the SD of the pH for roof-runoff treated by limestone. The wider SD in pH obtained for runoff treated by mussel shells allowed for a trend between pH and percentage metal reduction to be identified. Although the pH of runoff treated by limestone and mussel shells had a wider SD than in the batch experiments, a correlation between pH and percentage dissolved Zn and Cu reduction was not evident in the laboratory scale column experiments. This difference can be attributed to metal removal mechanisms such as adsorption and cation exchange playing a greater role in the reduction of dissolved Zn and Cu due to the increased number of adsorption sites thus having a masking effect of the correlation between pH and percentage metal reduction.

For the laboratory column experiments, statistical analysis revealed that the percentage reduction in dissolved Zn and Cu was not significantly different ($p \leq 0.05$) among the three treatment materials. Material depth, flow rate and disturbance did not appear have a strong influence on the percentage reduction of dissolved Zn, however, all these variables seemed to have influenced the percentage reduction of dissolved Cu in which >90% Cu reduction was only achieved at undisturbed depths of 1 m. A more consistent hydraulic conductivity was also achieved at undisturbed depths of 1 m. Therefore, all treatment materials at undisturbed depths of 1 m would be more suitable and effective for treating dissolved Zn and Cu from roof-runoff.

The laboratory column experiments were not completely reflective of field conditions, for example, a constant flow of roof-runoff for only 15 minutes at 1 L/min and 3 L/min was not characteristic of rainfall duration and intensity which fluctuates under field conditions. However, evaluation of the treatment system under controlled laboratory conditions was

essential because it allowed for a better understanding of the hydraulics and dissolved metal removal efficiency of the treatment systems which guided its applicability in the field.

Chapter 4 Field Evaluation of the Downpipe Treatment System

4.1 Introduction

This chapter describes the methodology used to complete the field evaluation of the downpipe treatment system (Objective 2) and the results obtained. Only one treatment material (mussel shells) was selected for this initial field evaluation and a single treatment system was installed (in a downpipe of a galvanized and a copper roof). The downpipe treatment systems were evaluated for 2 months during which the Zn and Cu removal capacity of the mussel shells was evaluated under varying rainfall intensities and duration which were then compared to results from the laboratory column experiments. The functionality of the treatment systems was visually assessed for clogging and other operational issues. At the end of the 2 months field trial, EDS analysis was done to identify whether Zn and Cu ions were visible on the surface of the mussel shells.

4.2 Methodology

4.2.1 Site Selection

The buildings used to conduct the field experiments were the E9 Lecture Theatre and the High Voltage Laboratory, which were the same buildings where roof-runoff was collected to conduct the laboratory experiments (Figure 3-5). Runoff from the same buildings were used for the laboratory and field experiments to ensure consistency and to minimise the introduction of additional variables that could confound the key parameters that were being evaluated in this research, thus enabling comparison of the results from the laboratory and field experiments.

4.2.2 Treatment Material Selection

The field experiment was conducted to collect data on the performance of the treatment system that would help improve the design. Therefore, only one treatment material (mussel shells) at an undisturbed depth of 1 m was selected for field evaluation. The criteria used to select a treatment material for field evaluation was based on the materials ability to achieve a high percentage reduction in both dissolved Zn and Cu in the laboratory experiments, its

associated cost and availability and whether the current use of the material was for commercial purposes or as a waste product (waste product being preferential in this research as it can be recycled into a beneficial management system for the removal of dissolved metals).

Treatment material at an undisturbed depth of 1 m was selected because the results from the laboratory column experiments showed that at this depth a higher percent reduction in both dissolved Zn and Cu and a more consistent hydraulic conductivity was achieved for all three treatment materials. The results from the batch experiments showed that a higher percentage of dissolved Zn and Cu was removed by limestone followed by mussel shells and then zeolite. However, there was no significant difference in dissolved Zn and Cu reduction among the three treatment materials at a 1 m depth. Therefore, based on the results obtained in the laboratory column experiments, all three materials were suitable for further evaluation under field conditions. The weight of the material was an important aspect that needed to be considered since the treatment system had to be attached to the downpipe of the roof. The results showed that zeolite was the least dense followed by mussel shells and then limestone (Appendix C). On a mass basis zeolite and mussel shells would have therefore been the most suitable materials. However, cost was a critical economical component that had to be considered. Zeolite is mainly available as a commercial product, and therefore is very expensive while mussel shells is a waste product of the shellfish industry that is readily available at minimal cost. Clean mussel shells (with no flesh) is readily available at gardening supply outlets at relatively cheap prices (<\$10 NZD/30kg bag). Based on the overall comparison of the three treatment materials, mussel shell was selected for further evaluation under field conditions because it was cheap and readily available in large quantities. Also, unlike zeolite and limestone that are available as commercial products, mussel shells is a waste product that proved to be very effective in removing of dissolved Zn and Cu in both the batch and laboratory column experiments. The mussel shells used to conduct the laboratory column experiments was not expected to be saturated with Zn and Cu, therefore, it was air dried and re-used in the field experiments.

4.2.3 Downpipe Treatment System Design and Installation

The downpipe treatment system evaluated in the field trial was a similar design to the laboratory column treatment system as described in Section 3.2.5.1, however, stormwater PVC pipes (instead of clear acrylic pipes) were used. Two PVC pipes (110 mm outside diameter, 100 mm inside diameter) were cut to a length of 1.2 m. Thirty-three 6 mm holes were drilled in three PVC storm-caps and a 500 μm mesh was placed inside to prevent the treatment materials from falling through the holes (Figure 3-6). The storm caps were fitted at the base of each pipe and the 1 m depth of mussel shells used in laboratory column experiments for the treatment of dissolved Zn and Cu were poured into separate pipes. While pouring the mussel shells into the pipes, the exterior of each pipe was pounded by hand in a circular-upward motion to increase compaction. Each treatment system containing Zn-treated and Cu-treated mussel shells was attached vertically to the existing downpipe of their corresponding building (i.e. Zn-treated mussel shells attached to galvanized roof). A bypass was included in the design to avoid water from backing up to the roof when rainfall rate exceeded the hydraulic capacity of the treatment material.

To determine the percent reduction in dissolved Zn and Cu achieved by the mussel shells, both untreated and treated roof-runoff samples were required. To collect untreated roof-runoff samples, a 10 mm hole was drilled through the downpipe above the treatment material. A small funnel was glued on the inside the pipe above the hole and an attached tube was pushed through the hole. A 1 L ThermoFisher Scientific™ Nalgene™ high-density polyethylene (HDPE) bottle was attached below the tube to collect untreated runoff samples and one was secured at the base of the downpipe to collect treated runoff samples. The 1 L HDPE bottles were used to collect untreated and treated first flush roof-runoff samples because it was not always possible to be present at the beginning of a rainfall event particularly at nights (Figure 4-1). Clean 1 L polypropylene terephthalate (PET) bottles were used to collect untreated and treated roof-runoff samples during steady state rainfall.

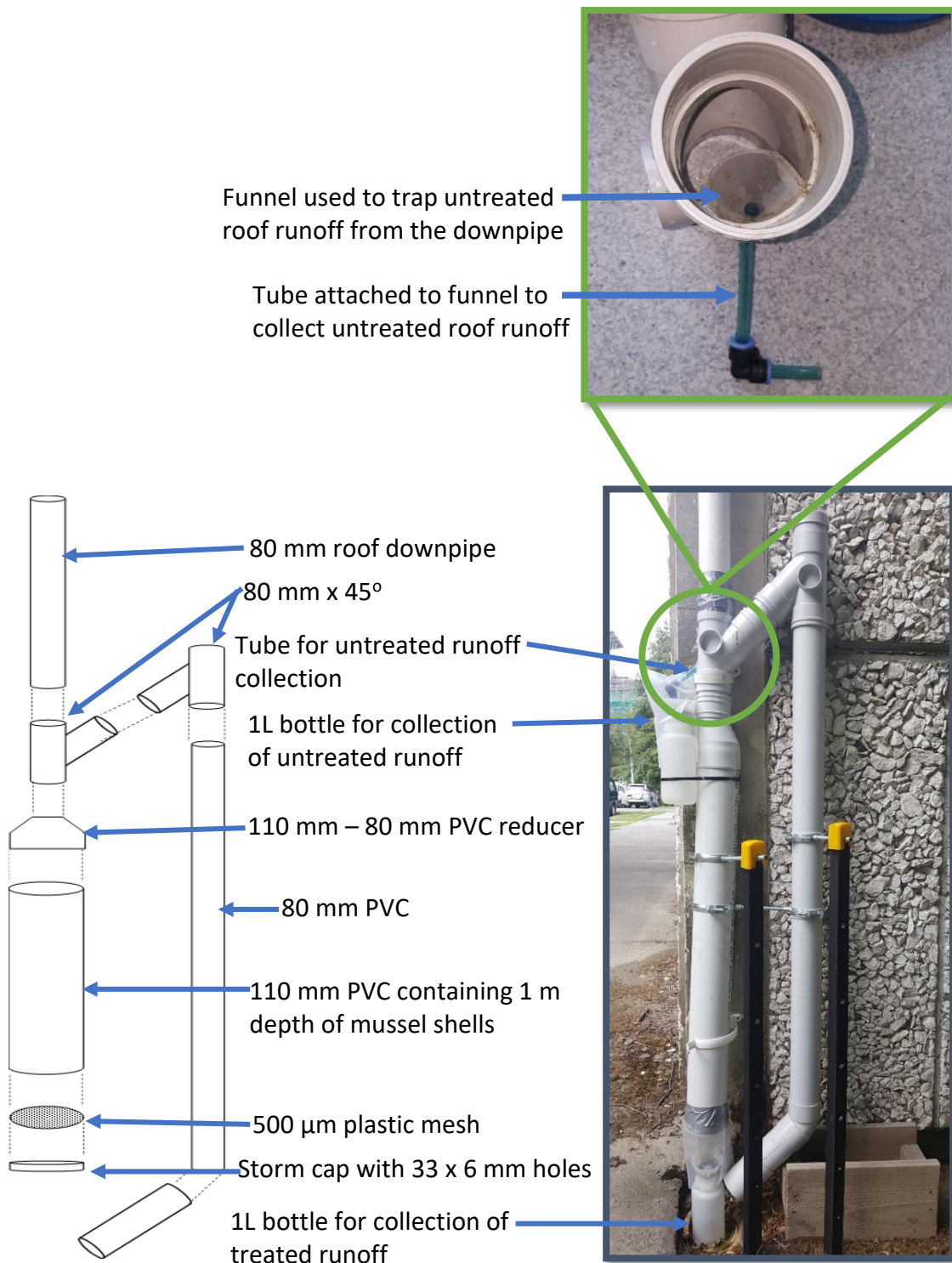


Figure 4-1. Downpipe treatment system assembling parts and prototype containing mussel shells installed for field evaluation with an inserted funnel and tube for the collection of untreated roof-runoff.

4.2.4 Sampling Method

The weather station at the University of Canterbury Environmental Laboratory was used to collect rainfall data for the sampled events. First-flush samples were collected for rainfall events that occurred during the day and night while steady state samples were collected only for events that occurred during the day. At each sampling time, both untreated and treated roof-runoff were collected to assess the percentage reduction in dissolved Zn and Cu at the given time. Time series sampling at multiple times during a single rainfall event was attempted, however, this was only able to be achieved for two events, which was insufficient to be able to draw any conclusions about intra-event trends (refer to Appendix E). The duration of rainfall events and the time samples were collected were guided by weather forecasts. For the purpose of this research, an individual rainfall event was considered to be rainfall that began at least 6 hours after a dry period.

4.2.5 Evaluation of pH Change and Dissolved Zinc and Copper

The pH and dissolved Zn and Cu assessment for the field experiment was done using the same methods for the laboratory experiments as described in Section 3.2.4.1.

4.2.6 Adsorption of Zinc and Copper to the Treatment Material - Mussel Shells

The chemical characterization of the mussel shells used in the field experiment was assessed to determine whether Zn and Cu from the roof-runoff that were being adsorbed to the mussel shells were identifiable after being used in the laboratory column experiment and being out in the field for 2 months. This chemical characterization was done as described in Section 3.2.2. This characterization was important to determine if the metals were being held in the system. This information could also be used as a guide to help tabulate the time it would take for a treatment system containing mussel shells to become saturated with heavy metals and when replacement of the material would be required.

The treatment system from each building was uninstalled and the mussel shells was poured out. A cross section sample of mussel shells was taken from the top, middle and bottom layers (Figure 4-2). These samples were taken to identify whether Zn and Cu that adsorbed to the mussel shells would be visible and whether there was a difference in the concentration of Zn

and Cu adsorbed to the mussel shells from the top to the bottom layer of the treatment system.

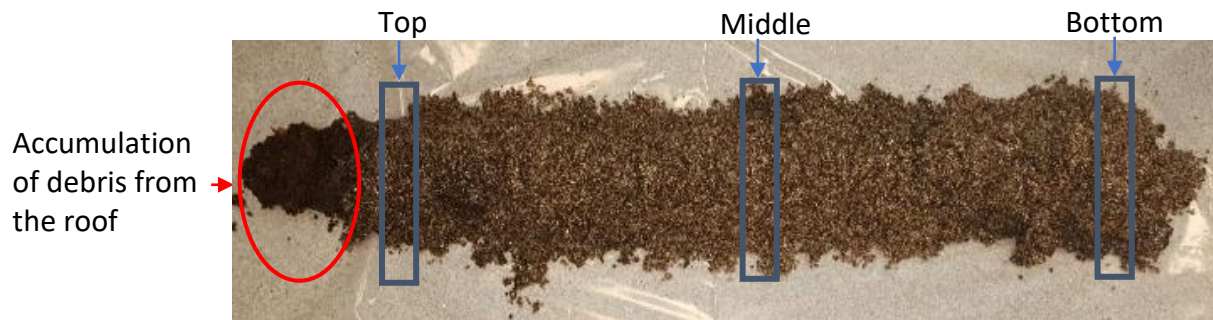


Figure 4-2. Location that mussel shells samples were taken for chemical characterization to determine whether Zn and Cu was present on the surface of the shells.

4.3 Results

4.3.1 Characterization of Sampled Rainfall Events

Rainfall intensity and frequency between October 26th, 2017 to January 06th 2018 was particularly low and sparse in which the rainfall intensity for all the sampled events was below 3 mm/hr. Of the 7 rainfall events assessed for the field experiment, only 2 continuous rainfall events occurred during the day (Table 4-1).

Table 4-1. Sampled events rainfall data collected between October 26th, 2017 and January 06th 2018 during which the field experiment was being conducted.

| Date | Rainfall Time | Rainfall Duration (hrs.) | Total Rainfall Depth (mm) | Rainfall Intensity (mm/hr.) | No. of First Flush Samples | No. of Steady State Samples |
|----------------------|---------------|--------------------------|---------------------------|-----------------------------|----------------------------|-----------------------------|
| Oct 27 th | Night | 6 | 2 | 0.33 | 1 | 0 |
| Nov 08 th | Day | 1 | 1.2 | 1.2 | 1 | 1 |
| Dec 09 th | Day | 4.5 | 1.2 | 0.27 | 1 | 0 |
| Dec 12 th | Day | 0.5 | 0.4 | 0.8 | 1 | 0 |
| Dec 13 th | Day | 2 | 4.8 | 2.4 | 1 | 3 |
| Dec 26 th | Night | 1 | 0.4 | 0.4 | 1 | 0 |
| Jan 05 th | Night/Day | 20 | 47.8 | 2.39 | 1 | 6 |

4.3.2 Concentration and Percentage Reduction of Dissolved Zinc and Copper

Evaluation of the concentration of dissolved Zn and Cu in the untreated runoff from both roofs showed that dissolved Zn from the galvanized roof ranged from 406 – 2,262 µg/L while dissolved Cu from the copper roof ranged from 455 – 2,581 µg/L. The concentration of both

dissolved Zn and Cu was significantly higher than ANZECC’s mixed instream guideline values of 15 µg/L and 1.18 µg/L for total Zn and Cu respectively for the protection of 90% freshwater organisms (Table 4-2). The concentration of dissolved Zn (406 – 2,262 µg/L) and Cu (455 – 2,581 µg/L) in the roof-runoff evaluated during the field trial reached levels that were considerably higher than the dissolved Zn (150 – 254 µg/L) and Cu (312 – 884 µg/L) concentrations obtained for the roof-runoff used in the laboratory experiments. For roof-runoff treated with 1 m depth of undisturbed mussel shells, it was observed that the concentration of dissolved Zn (1.95 – 7.63 µg/L) and Cu (3.64 – 4.06 µg/L) in the laboratory experiments were reduced to lower concentrations compared to the dissolved Zn (41 – 287 µg/L) and Cu (11 – 182 µg/L) in the field experiments. The concentration of both dissolved Zn and Cu obtained in the treated runoff for the field experiments was also higher than ANZECC’s mixed instream guideline values of 15 µg/L and 1.18 µg/L for total Zn and Cu respectively, for the protection of 90% freshwater organisms (Table 4-2).

Table 4-2. Comparison of the pH and metal concentration of the untreated and treated roof-runoff from the high voltage laboratory (galvanized roof) and the E9 lecture theatre (copper roof) when the field experiment was conducted.

| Metal | Roof Runoff | pH | Metal Conc. (µg/L) | Metal Reduction (%) | 90% ANZECC Guidance (µg/L) |
|--------------|--------------------|-------------|---------------------------|----------------------------|-----------------------------------|
| Zn | Untreated | 5.92 – 7.45 | 406 – 2262 | 81 – 97 | 15 |
| | Treated | 6.68 – 7.98 | 41 – 287 | | |
| Cu | Untreated | 6.33 – 7.94 | 455 – 2581 | 85 – 98 | 1.8 |
| | Treated | 7.23 – 8.91 | 11 – 182 | | |

The results showed that dissolved Zn in runoff from the galvanized roof was reduced by 82 – 97% while dissolved Cu in runoff from the copper roof was reduced by 86 – 98% (Figure 4-3). The results obtained in the field experiments were comparable to the percentage Zn (90 – 99%) and Cu (92 – 99%) reduction obtained when 1 m depth of undisturbed mussel shells was used in the laboratory column experiments. However, the concentration of dissolved Zn and Cu in roof-runoff treated by mussel shells in the laboratory column experiment was much lower than what was obtained in the field experiments.

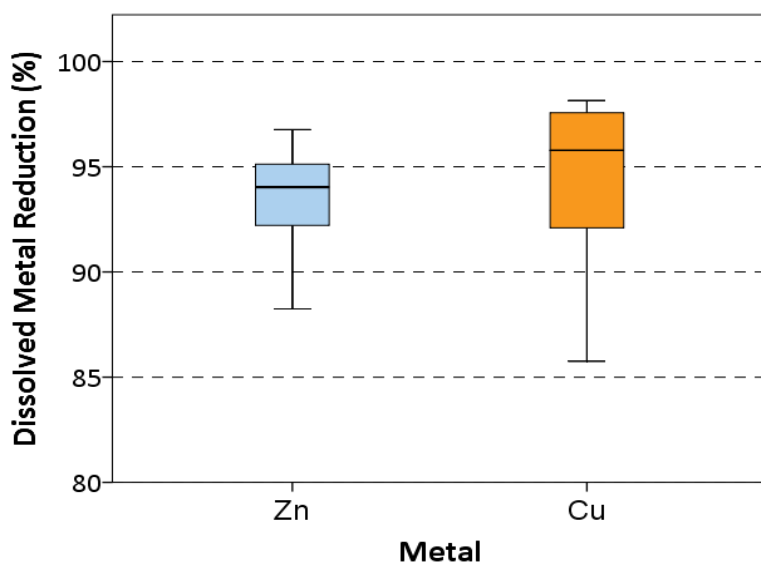


Figure 4-3. The percentage reduction of dissolved Zn from the galvanized roof and Cu from the copper treated by mussel shells.

Results from the Pearson’s product-moment correlation showed a strong positive correlation between the pH and the percentage reduction in dissolved Cu in the treated runoff from the copper roof, however, no correlation was observed for Zn in treated runoff from the galvanized roof (Table 4-3). The results also showed no evidence of a correlation between rainfall duration and percentage metal reduction or rainfall depth/intensity and percentage metal reduction. Comparison of the pH results obtained in the field and laboratory column experiments for roof-runoff treated by 1 m depth of undisturbed mussel shells showed that the pH of Zn (7.42 – 9.12) and Cu (7.14 – 9.31) treated runoff in the laboratory experiments reached levels that were generally higher than the pH of Zn (6.68 – 7.98) and Cu (7.23 – 8.91) treated runoff in the field experiments.

Table 4-3. The correlation between pH and percentage reduction in dissolved Zn from the galvanized roof and Cu from the copper roof for roof-runoff treated with mussel.

Correlations

| | Metal Treated | | Metal Reduction (%) |
|--------------------|---------------|---------------------|---------------------|
| pH – Mussel Shells | Zn | Pearson Correlation | .483 |
| | | Sig. (2-tailed) | .132 |
| | | N | 11 |
| pH – Mussel Shells | Cu | Pearson Correlation | .656* |
| | | Sig. (2-tailed) | .021 |
| | | N | 12 |

*. Correlation is significant at the 0.05 level (2-tailed).

4.3.3 Adsorption of Zinc and Copper to the Treatment Material - Mussel Shells

Chemical characterization of the used mussel shells from the field experiment showed traces of Zn and Cu. However, Zn was only present in the top layer of the treatment system while Cu was present in all three layers (top, middle and bottom). It was observed that the percentage of Cu adsorbed to the mussel shells decreased with depth. It was also observed that the percentage of Cu adsorbed to the mussel shell was higher than Zn (Figure 4-4).

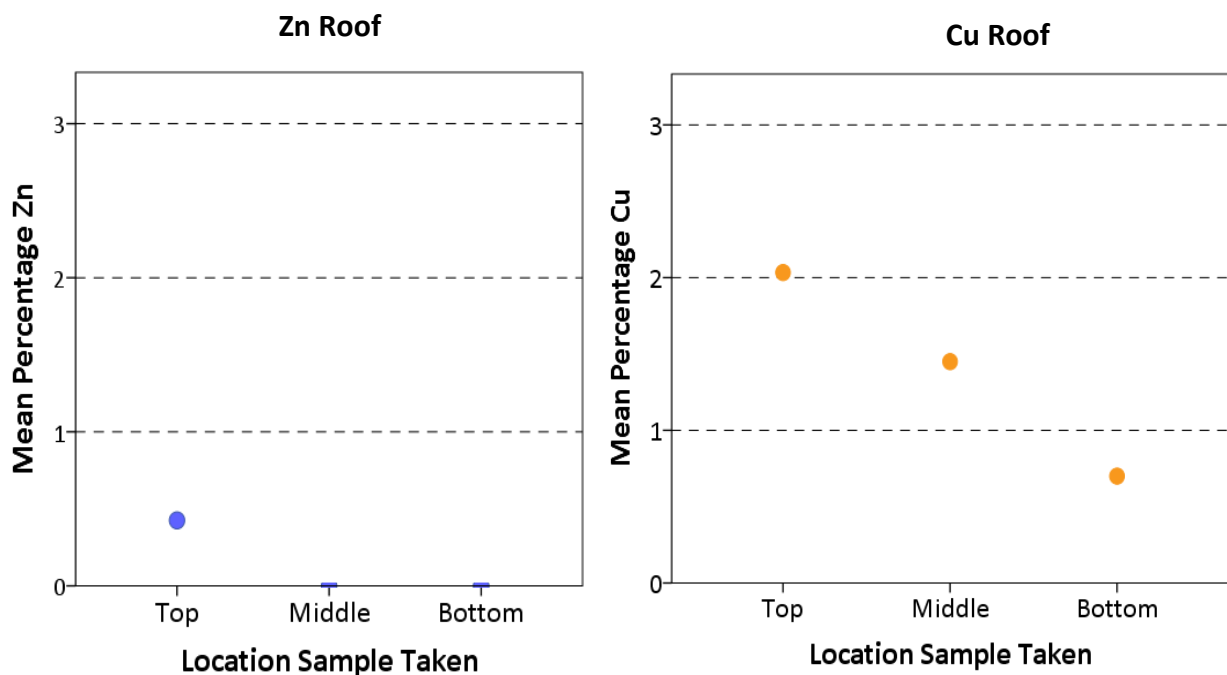


Figure 4-4. Graphs showing the average percentage of Zn and Cu adsorbed to mussel shells samples taken at the top, middle and bottom of the treatment systems that were installed on the Zn and Cu roofs.

Further assessment of the chemical composition of the used mussel shells revealed that the percentage of Zn and Cu was higher on the outer layer of the shells while the percentage of Ca was higher on the inside layer (Appendix D). A visual assessment of the mussel shells was done, and it was observed that the inside layer was smooth and glossy while the outside layer was rough and coated with an organic material (Figure 4-5).

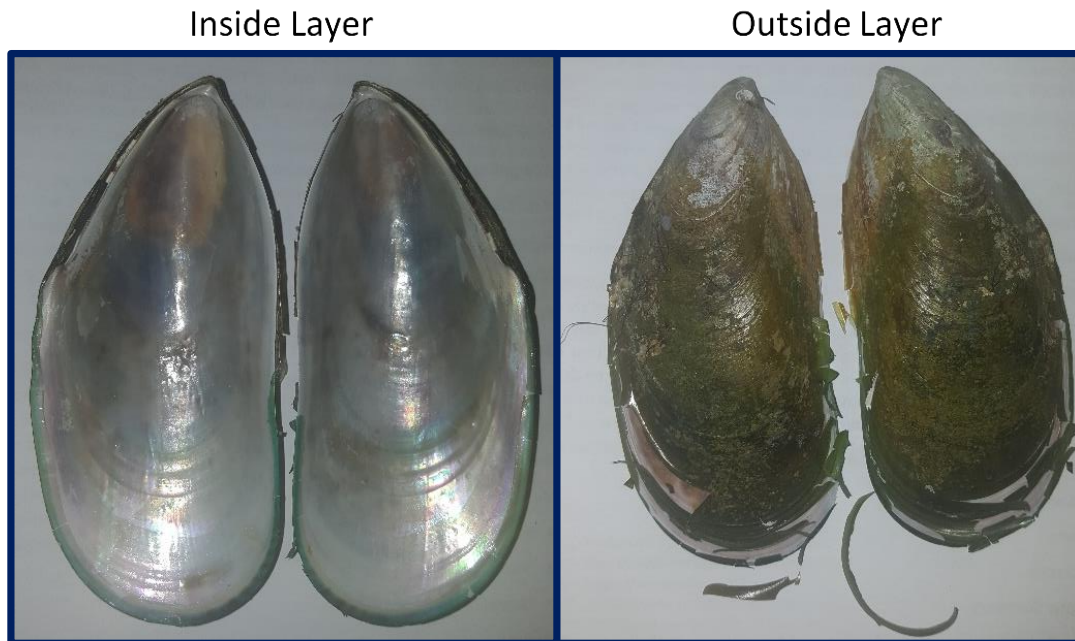


Figure 4-5. Images showing the difference in the texture of the inside and outside layers of the mussel shells and the presence of an organic coating on the outside layer of the shells.

4.3.4 Field Observation

Overtime the system became clogged from leaf and other debris emanating from the roof (Figure 4-2). During the time the treatment system became clogged, the bypass was observed to function as intended, however, the design of the bypass made the system bulky which caused it to be unaesthetically pleasing and costlier.

4.4 Discussion

4.4.1 Concentration of Dissolved Zinc and Copper in Roof Runoff

The concentration of dissolved Zn and Cu from the untreated roof-runoff for the field experiments varied considerably. This variation can be attributed to various reasons which includes the length of dry days prior to a rainfall event as well as variation in rainfall intensity and duration. Roof-runoff from a rainfall event preceding a dry period of several days is expected to contain higher concentrations of dissolved Zn and Cu (Hyun & Lee, 2013) compared to a rainfall event that precedes a dry period of just a few hours. This is because, during the long dry period, weathering of the roofing material occurs, and thus dissolution rates of Zn and Cu is higher (Polkowska, 2004). It is also expected that runoff from low intensity rainfall events contain higher concentration of dissolved Zn and Cu than high

intensity rainfall events. This is because the higher the rainfall intensity the greater the roof-runoff volume which leads to higher dilution and consequently a lower concentration of dissolved Zn and Cu. Also, with low rainfall intensities, the rainwater have a longer contact time with the roofing material allowing for higher dissolution of Zn and Cu (Hyun & Lee, 2013) especially when the rainwater is acidic (Polkowska, 2004).

It was also observed that the concentration of dissolved Zn and Cu from untreated roof-runoff for the field experiments reached levels (2000+ µg/L) that were considerably higher than what was obtained for runoff used in the laboratory column experiment. This may have been because roof-runoff used in the laboratory column experiment was collected in bulk during winter when rainfall occurred more frequently and at higher intensities. Collectively, these factors would have led to greater dilution of the dissolved Zn and Cu in the untreated roof-runoff. Also, concentrations of dissolved Zn and Cu in roof-runoff collected during winter may have been lower because rainfall is typically more frequent with higher intensities and longer durations. As a result, there would have been shorter dry periods between rainfall events and consequently lower ultraviolet (UV) radiation and weathering of the roofing material and thus lower levels of metal dissolution from the roofing material.

4.4.2 Dissolved Zn and Cu Reduction

The percentage reduction in dissolved Zn and Cu was similar which indicated that the type of metal treated did not influence the percentage metal reduction when mussel shells was used under field conditions. The percentage reduction in dissolved Zn (82 – 97%) and Cu (86 – 98%) achieved in the field experiment was comparable to the percentage reduction in dissolved Zn (95 – 99%) and Cu (90 – 98%) obtained in the laboratory column experiment when 1 m depth of undisturbed mussel shells was used. These results indicate that the additional variables present under field conditions such as variation in rainfall intensity, rainfall duration, initial metal concentration and debris from the roofs did not have a significant impact on the dissolved Zn and Cu reduction capacity of the system on a percentage basis. Despite the high percentage reduction of dissolved Zn and Cu obtained in the field experiment (>80%), assessment of the reduction in dissolved Zn and Cu on a concentration basis showed that much higher concentrations of dissolved Zn and Cu were present in the treated runoff in field experiments which were much higher than ANZECC's mixed instream guideline values. The

initial concentration of metals can affect the concentration of metals that is removed by treatment materials (Abdel-Salam et al., 2011; Barakat, 2008). Therefore, the considerably higher concentration of dissolved Zn and Cu observed in the untreated runoff for the field experiments may have been the main contributing factor for the differences observed in the runoff treated by mussel shells in the laboratory column and field experiments. To determine whether initial metal concentration was the contributing factor to the higher concentrations of dissolved Zn and Cu obtained in treated runoff for the field experiments, laboratory experiments using synthetic roof-runoff dosed with increasing concentrations of Zn and Cu can be evaluated. If concentrations of dissolved Zn and Cu in the untreated runoff are extremely high ($>2000 \mu\text{g/L}$), it may lead to concentrations of dissolved Zn and Cu in the treated runoff that are considerably higher than ANZECC's guideline values even if a very high percent reduction is achieved. In the laboratory column experiment it was observed that a higher reduction in dissolved Zn and Cu was obtained at a 1 m depth compared to the 0.5 m depth. Thus, the use of a longer depth of treatment material ($> 1 \text{ m}$ which will increase the surface area and contact time of roof-runoff with the treatment material), could be explored to help achieve further reduction in the concentration of dissolved Zn and Cu in such cases. Despite this, the results obtained from the field experiments were very positive because the dissolved Zn and Cu concentrations from the roof-runoff were reduced by $>80\%$ with further dilution expected to occur as the treated runoff moves downstream. This high percentage reduction in dissolved Zn and Cu obtained for the field evaluation is also an indication that the system is robust and only small alterations to the system design would be required.

A strong correlation was observed between the pH of the treated runoff and the percentage reduction in dissolved Cu from the copper roof while no correlation was observed for Zn (Figure 4-6). The strong correlation between pH and percentage metal reduction was attributed to the wider SD obtained in the pH for treated runoff from the copper roof allowing for a trend to be observed compared to the smaller SD in pH obtained for treated runoff from the galvanized Zn roof. For the laboratory scale experiments, the stronger correlation observed between pH and percentage reduction in dissolved Zn and Cu for runoff treated by mussel shells compared limestone was also attributed to the wider SD in pH obtained for runoff treated by mussel shells (Section 3.4.2).

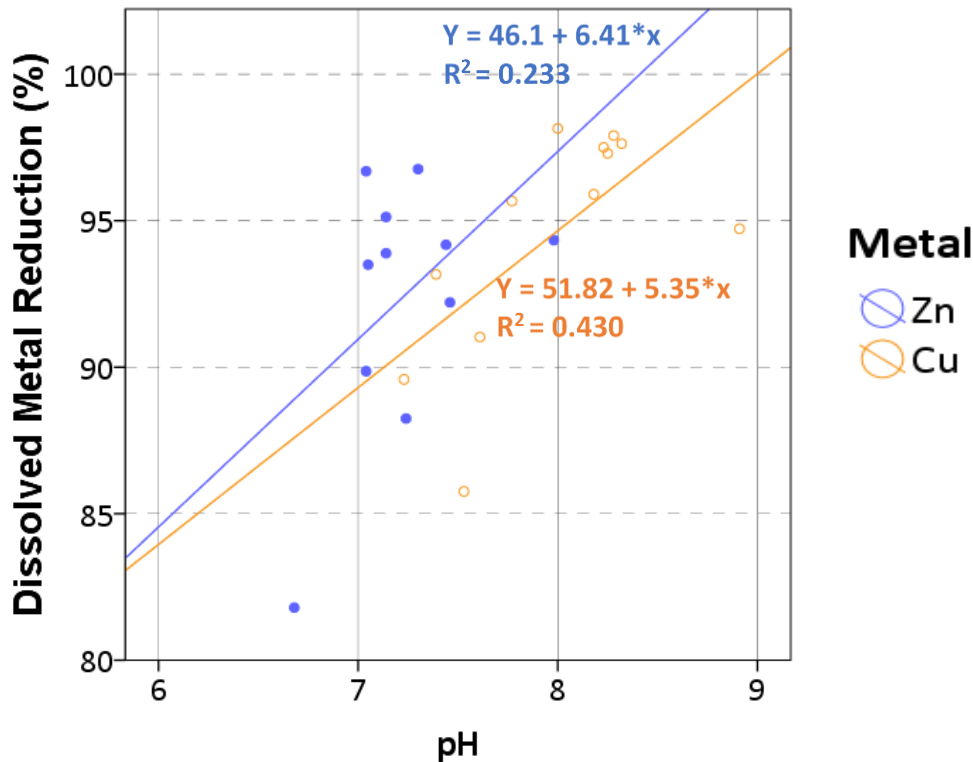


Figure 4-6. Correlation between pH and percentage reduction of dissolved Zn and Cu in roof-runoff treated by mussel shells.

The results showed no evidence of a correlation between rainfall duration and percentage metal reduction nor rainfall depth/intensity and percentage dissolved Zn and Cu reduction. The field experiment was conducted during a particularly dry summer period where rainfall frequency, duration and intensity was very low and as a result only 7 rainfall events were evaluated in a 2 months period in which only 2 daytime events lasted more than 4 hours. Consequently, there was not sufficient data for trends between rainfall characteristics and percentage dissolved metal reduction to be observed. As a result, it is recommended that the field experiment be conducted for a least a year (due to seasonal differences in weather) so that more robust data on rainfall characteristics and percentage dissolved metal reduction can be obtained for comparisons to be made.

4.4.3 Percentage Zinc and Copper Adsorbed to the Mussel Shells

Traces of Zn and Cu were observed when chemical characterization of the mussel shells used in the in the field experiment was done. These results suggest that the Zn and Cu were being adsorbed to the shells which is an indication that that further treatment of the roof-runoff

may not be required since the heavy metals were being held in the system rather than being transformed and transported further downstream in the treated runoff.

It was observed that Zn was present only in the top layer of the treatment system while Cu was present in all three layers sampled. The presence of Zn in only the top layer may have occurred because the treatment system installed on the galvanized roof eventually clogged causing roof-runoff to make contact with only the top layer of the system. Consequently, only mussel shells in the top layer of the system would have been able to adsorb the Zn from the untreated roof-runoff. The percentage of Cu adsorbed to the mussel was observed to decrease with depth which was an indication that the top layer of the system would be expected to become saturated first. The results also showed that the percentage of Cu adsorbed to the mussel shells was higher than Zn which may have been because the total load of Cu treated by the system on the Cu roof was higher than the total Zn load treated by the system installed on the galvanized roof. Also, this could have occurred because adsorption of Cu ions tend to occur more easily than Zn ions (Arias et al., 2005; Chen & Wang, 2000; Małeckı et al., 2015).

Further assessment of the results showed that the percentage of Zn and Cu adsorbed to the mussel shells was higher on the outer layer while Ca was higher on the inside layer. These differences can be attributed to the variation in the texture of the inside and outside layer of the shells. Because there is no organic layer on the inside layer of the shells, only shell material would have been assessed by the EDS thus giving a higher Ca value while proportions of the outer layer would have been covered by the organic layer and consequently giving a lower Ca value. The percentage of Zn and Cu may have been higher on the outside layer because of its roughness which consequently gives rise to a higher percentage of adsorption sites compared to the smooth, glossy inside layer. These results show that crushing of the mussel shells will help remove some of the organic layer so that more of the shells material can become exposed for adsorption of Zn and Cu. Also, crushing does not only increase the total surface area but also the adsorption sites which will in turn increase the percentage of dissolved metals removed from the untreated roof-runoff.

4.5 Chapter Summary

The field experiment was conducted to collect data on the performance of the downpipe treatment system to help improve the system design. As a result, only mussel shell was evaluated because it was just as effective as zeolite and limestone in removing dissolved Zn and Cu from roof-runoff in the laboratory column experiment. More so, it was a cheap and readily available waste material that can be recycled into a beneficial management system for the removal of dissolved Zn and Cu from roof-runoff. During the 2 months field evaluation, the dissolved Zn and Cu removal capacity of the mussel shells was assessed under varying rainfall intensity and duration and compared to results from the laboratory column experiments. The functionality of the treatment systems was visually assessed for clogging and other operational issues. At the end of the 2 months field trial, an ESD analysis was done to identify whether Zn and Cu were visible on the surface of the mussel shells.

The mussel shells also proved to be very effective under field conditions in which the percentage reduction in dissolved Zn (82 – 97%) and Cu (86 – 98%) achieved was comparable to the percentage of percentage reduction in dissolved Zn (95 – 99%) and Cu (90 – 98%) obtained in the laboratory column experiment. Although a considerably lower reduction in dissolved Zn and Cu on a concentration basis was obtained in the laboratory column experiments for mussel shells, results from the field experiments were still very positive because >80% reduction in dissolved Zn and Cu was obtain. The high percentage reduction of dissolved Zn and Cu achieved in the field experiments indicated that the mussel shells is very effective in removing dissolved Zn and that the system is robust and therefore only small alterations to the system design would be required.

For the field experiments, a strong positive correlation between pH and percentage dissolved Cu reduction was observed while there was no evidence of a correlation for dissolved Zn. This relationship between pH and percentage dissolved Cu reduction was attributed to the wider SD in the pH values obtained for Cu treated runoff thus allowing for a trend to be identified. There was no evidence of a correlation between rainfall duration and percentage dissolved Zn and Cu reduction nor rainfall depth/intensity and percentage dissolved Zn and Cu reduction. This was because the field experiment was conducted during a summer period where rainfall frequency, intensity and duration was particularly low and consequently the

rainfall data was not sufficient for a trend to be observed. As a result, field evaluation should be conducted for at least a year so that a more robust data set can be obtained.

Chemical characterization of the mussel shells used in the field experiments showed traces of Zn and Cu which was an indication that these metals were being held in the system. The retention of the Zn and Cu in the system, coupled with further dilution as the treated runoff moves downstream are indications that additional treatment of the roof-runoff may not be required. Further assessment of the chemical composition of the mussel shells used in the field experiment revealed that the percentage of Zn and Cu adsorbed to the mussel shells was higher on the outer layer while Ca was higher on the inside layer. These differences can be attributed to the variation in the texture of the inside and outside layer of the shells in which the outside layer was observed to be rough and coated with an organic material while the inside layer was smooth and glossy. The percentage of Zn and Cu may have been higher on the outside layer because of its roughness which consequently gives rise to a higher percentage of adsorption sites compared to the smooth, glossy inside layer. The percentage Ca may have been higher on the inside layer because it was not obstructed by the organic layer allowing for only the shells material to be assessed by the EDS. These results suggest that crushing of the mussel shells could help remove some of the organic layer and increase the surface area (i.e. the number adsorption sites) which will in turn increase the percentage of dissolved metals removed from the untreated roof-runoff.

Chapter 5 Conclusions and Recommendations

5.1 Conclusions

5.1.1 Dissolved Zn and Cu in Roof Runoff

For the laboratory column experiments, the concentration of dissolved Zn and Cu from the roof-runoff ranged from 150-254 µg/L and 312-884 µg/L respectively while for the field experiment Zn and Cu ranged from 406-2262 µg/L and 455-2581 µg/L respectively. Evaluation of the percentage dissolved Zn and Cu in the untreated roof-runoff from the laboratory samples showed that 100% of the Zn was in the dissolved form while dissolved Cu ranged from 78%-91%. These results have provided additional evidence that roofs are major contributors of Zn and Cu found in urban stormwater and waterways and that these metals occur mainly in the dissolved form as previously reported by Charters et al. (2016b) and Cheah et al. (2007), which is the form that is most toxic to freshwater organisms. The concentrations of Zn and Cu obtained in the untreated runoff assessed in both the laboratory and field experiments were considerably higher than ANZECC's mixed instream guideline values of 15 µg/L and 1.18 µg/L for total Zn and Cu respectively, for the protection of 90% freshwater organisms. It was observed that roof-runoff from the buildings used in this research, which contained extremely high concentrations of dissolved Zn and Cu was being discharged directly into the Okeover Stream. This is additional proof that an at source treatment system is required for the reduction of dissolved Zn and Cu from roof-runoff as suggested by Davis et al. (2001) and Moores et al. (2009) to help improve the quality of urban fresh waterways.

5.1.2 Dissolved Zinc and Copper Reduction

For the laboratory column experiments, zeolite, limestone and mussel shells were able to remove >90% of dissolved Zn and Cu from roof-runoff thus proving their effectiveness. The similarity in the percentage reduction in dissolved Zn and Cu obtained for the three treatment materials in the laboratory column experiment suggest that any of the three treatment materials could be utilized in the downpipe treatment system for the field evaluation. Therefore, in selecting a treatment material for the field evaluation, the main factors considered were cost, availability, and present use (commercial or waste product) in which a

waste product was preferable. Of the three treatment materials, limestone and mussel shells were the cheapest and most readily available in large quantities as grounded zeolite was sold mainly as a commercial product (cat litter) causing it to be very expensive. In New Zealand, mussel shell is a waste product that is expensive for the shellfish industry to dispose of and as a result, it is readily available at a low cost. Taking these factors into consideration, mussel shells was considered the most plausible treatment material to be used in the downpipe treatment system for field evaluation because is a waste product that proved to be just as effective as zeolite and limestone in removing dissolved Zn and Cu from roof-runoff.

For both the batch and laboratory column experiments, it was evident that adsorption and ion exchange was the main mechanism by which zeolite reduced the concentration of dissolved Zn and Cu. This was because there was no significant difference between the pH of the untreated roof-runoff and runoff treated by zeolite, however in the laboratory column experiment dissolved Zn and Cu was reduced by >95%. For both the laboratory column and field experiments a strong positive correlation between pH and percentage metal reduction was observed for roof-runoff treated by mussel shells while no correlation was observed for limestone. The wider SD in the pH obtained when mussel shells was used allowed for a trend to be observed. These results suggest that neutralization by mussel shells was a contributor in the reduction of dissolved Zn and Cu. However, because of the small media size (i.e. large surface area) and large volume of material used, adsorption and cation exchange also played a significant role in the reduction of dissolved Zn and Cu which may have masked the contribution of neutralization when limestone was used.

The percentage reduction in dissolved Zn (82 – 97%) and Cu (86 – 98) achieved in the field experiment was comparable to the percentage reduction in dissolved Zn (95 – 99%) and Cu (90 – 98%) obtained in the laboratory column experiment when 1 m depth of undisturbed mussel shells was used. These results showed that the additional variables present under field conditions such as variation in rainfall intensity, rainfall duration, metal concentration and debris from the roofs did not have a significant impact on the performance of the system. These results suggest that the treatment system is robust and only small alterations to the system design would be required.

5.1.3 Chemical Characterization of Treatment Materials

Chemical characterization of the mussel shells used in the field experiment showed traces of Zn and Cu. This suggest that Zn and Cu were being held in the system and thus, additional treatment of the roof-runoff may not be required. While the downpipe treatment system containing mussel shells prevents the release of dissolved Zn and Cu into urban stormwater and waterways, proper disposal of the treatment materials is essential as they too can have potential negative impacts on the environment.

Further assessment of the results showed that the percentage of Zn and Cu adsorbed to the mussel shells was higher on the outer layer while Ca was higher on the inside layer. These differences were attributed to the variation in the texture of the inside shell layer which was smooth and glossy and outside shell layer which was rough and coated with a layer of organic material. These results suggest that crushing of the mussel shells increases the surface adsorption sites and the release of Ca for neutralization. Collectively, crushing helps increase the adsorption and neutralization capacity of the mussel shells which in turn increases the percentage reduction in dissolved Zn and Cu as well as the life span of the treatment material.

5.1.3 Downpipe Treatment System Design

Clogging of the downpipe treatment system by leaves and other debris from the roofs was the main problem encountered with the prototype. This suggest that installation of a leaf guard and regular cleaning of the guttering would be required for the treatment system to function efficiently.

5.2 Recommendations

5.2.1 Recommendations for the Physical Design of the Downpipe Treatment System

The main problem encountered during the field experiment was clogging. This was due to the accumulation of leaves and other debris from the roofs. As a result, a leaf guard or plastic mesh should be incorporated into the design. The bypass added to the system design was essential to prevent excess weight and water from backing up to the roof. Although the bypass functioned as intended, it made the system more expensive, bulky and less aesthetically pleasing. Therefore, alternatives such as flexible hoses or a system where the bypass water is allowed flow freely down the outside of the downpipe should be explored.

5.2.2 Recommendations for Future Research

Further research into the treatment of dissolved Zn and Cu from roof-runoff using zeolite, limestone and mussel shells is recommended to complement and further validate the results of this research. Key areas for additional investigation include:

- Quantifying the percentage of dissolved metals that each material can remove at larger media particle sizes. This is an important aspect because only one material grade was evaluated in this research which was very fine ($\geq 1.18 \leq 2.36$ mm). The larger the media particle size (i.e. the higher the hydraulic conductivity), the greater the volume of roof-runoff and/or roof area that could be treated which would help reduce the number of downpipe treatment systems required per building.
- Evaluating the performance of each treatment material at very high Zn and Cu concentrations ($>1000 \mu\text{g/L}$) under controlled laboratory conditions. The dissolved Zn and Cu concentrations from untreated roof-runoff for the field experiment was considerably higher than what was used for the laboratory experiments. Concentrations of Zn and Cu $> 1,000 \mu\text{g/L}$ from severely weathered galvanized and copper roofs respectively have also been recorded by Charters et al. (2016b) in Christchurch, New Zealand.
- Quantifying the lifespan of the treatment materials is also an important aspect that needs to be evaluated to help determine when the treatment materials require replacement. This can be assessed under laboratory conditions by subjecting each treatment material to high loading rates of dissolved Zn and Cu until saturation is achieved. Accelerated dosing can also be evaluated in the field, however, it will take a longer time to obtain results.
- Assessing the total load that the system treats under field conditions is also an important aspect that should be investigated because this information can be used to help identify changes in the performance of the treatment system overtime (Appendix E) and to also help determine the lifespan of the treatment material. The total load of Zn and Cu treated by the system can be done by collecting both first flush and steady state untreated roof-runoff samples at equal intervals for the duration of each rainfall event and applying mathematical calculations.

- Evaluation of all three treatment materials under field conditions with duplicates/triplicates for at least a year to obtain more robust data that will further validate the results obtained in this research and assist in selecting the most suitable treatment material(s). Evaluation of the three treatment materials is important because only one treatment system containing mussel shells was installed on each building. Further to this, assessment was done for only two months during the summer period when rainfall frequency, intensity and duration was particularly low. As a result, the data obtained was limited, therefore, it was not possible to identify trends between rainfall characteristics and treatment system performance. Relationships between rainfall characteristics and media performance could not be identified with the small dataset obtained in the field experiment for this research. Thus, within a year of field evaluation, a greater range of event characteristics is expected to be captured which will allow for the identification of possible relationships between rainfall characteristics and media performance. This year long evaluation will also provide real-world performance as proof for investors and potential users of the downpipe treatment system.
- Further research into the drivers of metal removal (surface adsorption, neutralization, molecular/chemical binding and precipitation) for limestone and mussel shells is also relevant. The literature has highlighted that increase in pH is the main mechanism by which limestone and mussel shells removes dissolved metal (Komnitsas et al., 2004). However, it was difficult to identify consistent relationships between pH and metal reduction for mussel shells and limestone in this research because of the possible masking effect of other mechanisms such as adsorption and cation exchange and the small SD obtained for the pH values of treated runoff.
- Evaluation of the potential risk associated with the disposal of materials laced with high concentrations of Zn and Cu is an essential aspect that should be considered because the metals were observed to be held in the downpipe treatment system. However, disposal of saturated materials is not expected to have detrimental effects on the environment because:
 - The Zn and Cu will be adsorbed to the material and would no longer be in their dissolved toxic form.

- The saturated material would be contained in the landfill therefore, leaching is expected to be minimal.
- The disposal of scrap metal is expected to have a greater impact on the environment since it contains considerably higher concentrations of Zn and Cu than what will be adsorbed from roof-runoff by the treatment materials.
- Investigate potential materials that can reduce the pH of runoff treated by limestone and mussel shells to a neutral pH range. The pH results for roof-runoff treated with limestone and mussel shells showed high alkalinity which can also have potential detrimental effects on freshwater organisms in the long run.
- An automated system to collect untreated and treated samples under field conditions should be explored so that a greater number of rainfall events (including rainfall that occurs at night) can be assessed. Manual collection of samples is time consuming and will be very difficult if samples are to be collected for a full year.
- Further research into both the capital costs and the operation and maintenance costs of the system should be done for investment purposes.

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Appendix A. The Volume of Roof-Runoff Used in the Laboratory Column Experiments

The volume of water required to complete experiments at flow rates of 1 L/min and 3 L/min for a duration of 15 minutes at material depths of 1 and 0.5 m using roof-runoff from one rainfall event.

| Treatment material | Material Depth (m) | Reps per rainfall event | Flow Rate (L/min) | Flow Duration (min) | Volume Runoff Required (L) |
|--------------------|------------------------|-------------------------|-------------------|---------------------|----------------------------|
| Limestone | 1 | 2 | 1 and 3 | 15 | 60 |
| Mussel Shells | 1 | 2 | 1 and 3 | 15 | 60 |
| Total | 250 L tank used | | | | 240 |
| Zeolite | 1 | 2 | 1 and 3 | 15 | 60 |
| Total | 80 L tank used | | | | 120 |
| Zeolite | 0.5 | 1 | 1 and 3 | 15 | 60 |
| Limestone | 0.5 | 1 | 1 and 3 | 15 | 60 |
| Mussel Shells | 0.5 | 1 | 1 and 3 | 15 | 60 |
| Total | 250 L tank used | | | | 180 |

Appendix B. Experimental Design Used to Conduct the Laboratory Column Experiments

| Treatment material | Rainfall Event | Repetition | Material Depth (m) | Disturbance | Flow Rate (L/min) |
|--------------------|----------------|------------|--------------------|-------------|-------------------|
| Zeolite | 1 | 1 | 1 | No | 1 |
| Limestone | 1 | 1 | 1 | No | 1 |
| Mussel Shells | 1 | 1 | 1 | No | 1 |
| Zeolite | 1 | 1 | 1 | No | 3 |
| Limestone | 1 | 1 | 1 | No | 3 |
| Mussel Shells | 1 | 1 | 1 | No | 3 |
| Zeolite | 1 | 2 | 1 | No | 1 |
| Limestone | 1 | 2 | 1 | No | 1 |
| Mussel Shells | 1 | 2 | 1 | No | 1 |
| Zeolite | 1 | 2 | 1 | No | 3 |
| Limestone | 1 | 2 | 1 | No | 3 |
| Mussel Shells | 1 | 2 | 1 | No | 3 |
| Zeolite | 1 | 1 | 0.5 | Yes | 1 |
| Limestone | 1 | 1 | 0.5 | Yes | 1 |
| Mussel Shells | 1 | 1 | 0.5 | Yes | 1 |
| Zeolite | 1 | 1 | 0.5 | Yes | 3 |
| Limestone | 1 | 1 | 0.5 | Yes | 3 |
| Mussel Shells | 1 | 1 | 0.5 | Yes | 3 |
| Zeolite | 2 | 1 | 1 | Yes | 1 |
| Limestone | 2 | 1 | 1 | Yes | 1 |
| Mussel Shells | 2 | 1 | 1 | Yes | 1 |
| Zeolite | 2 | 1 | 1 | Yes | 3 |
| Limestone | 2 | 1 | 1 | Yes | 3 |
| Mussel Shells | 2 | 1 | 1 | Yes | 3 |
| Zeolite | 2 | 2 | 1 | Yes | 1 |
| Limestone | 2 | 2 | 1 | Yes | 1 |
| Mussel Shells | 2 | 2 | 1 | Yes | 1 |
| Zeolite | 2 | 2 | 1 | Yes | 3 |
| Limestone | 2 | 2 | 1 | Yes | 3 |
| Mussel Shells | 2 | 2 | 1 | Yes | 3 |
| Zeolite | 2 | 1 | 0.5 | Yes | 1 |
| Limestone | 2 | 1 | 0.5 | Yes | 1 |
| Mussel Shells | 2 | 1 | 0.5 | Yes | 1 |
| Zeolite | 2 | 1 | 0.5 | Yes | 3 |
| Limestone | 2 | 1 | 0.5 | Yes | 3 |
| Mussel Shells | 2 | 1 | 0.5 | Yes | 3 |
| Zeolite | 3 | 1 | 0.5 | No | 1 |
| Limestone | 3 | 1 | 0.5 | No | 1 |
| Mussel Shells | 3 | 1 | 0.5 | No | 1 |
| Zeolite | 3 | 1 | 0.5 | No | 3 |
| Limestone | 3 | 1 | 0.5 | No | 3 |
| Mussel Shells | 3 | 1 | 0.5 | No | 3 |
| Zeolite | 4 | 1 | 0.5 | No | 1 |
| Limestone | 4 | 1 | 0.5 | No | 1 |
| Mussel Shells | 4 | 1 | 0.5 | No | 1 |
| Zeolite | 4 | 1 | 0.5 | No | 3 |
| Limestone | 4 | 1 | 0.5 | No | 3 |
| Mussel Shells | 4 | 1 | 0.5 | No | 3 |

Appendix C. Physical Properties of Each Treatment Material Used in the Laboratory Column Experiments

A summary of the saturated hydraulic conductivity obtained for zeolite, limestone and mussel shells used to treat both Zn and Cu at material depths of 1m and 0.5 m for both undisturbed and disturbed materials.

| Material | Metal Treated | Disturbance | Material Depth (m) | Flow Rate (L/min) | Ksat (m/hr) | Material Mass (Kg) | Density (Kg/m ³) |
|---------------|---------------|-------------|--------------------|-------------------|-------------|--------------------|------------------------------|
| Zeolite | Zn | Undisturbed | 1 | 4.00 | 27.0 | 4.6 | 590 |
| Zeolite | Cu | Undisturbed | 1 | 5.00 | 34.2 | 4.5 | 577 |
| Zeolite | Zn | Disturbed | 1 | 4.29 | 29.4 | 4.6 | 590 |
| Zeolite | Cu | Disturbed | 1 | 5.29 | 36.0 | 4.5 | 577 |
| Zeolite | Zn | Undisturbed | 0.5 | 4.29 | 15.6 | 2.4 | 615 |
| Zeolite | Cu | Undisturbed | 0.5 | 2.73 | 16.8 | 2.3 | 590 |
| Zeolite | Zn | Disturbed | 0.5 | 2.50 | 26.4 | Not weighed* | |
| Zeolite | Cu | Disturbed | 0.5 | 7.50 | 46.2 | Not weighed* | |
| Limestone | Zn | Undisturbed | 1 | 4.00 | 27.0 | 11.2 | 1436 |
| Limestone | Cu | Undisturbed | 1 | 5.00 | 34.2 | 10.3 | 1321 |
| Limestone | Zn | Disturbed | 1 | 4.00 | 27.0 | 11.2 | 1436 |
| Limestone | Cu | Disturbed | 1 | 5.00 | 34.2 | 10.3 | 1321 |
| Limestone | Zn | Undisturbed | 0.5 | 5.00 | 26.4 | 5.7 | 1462 |
| Limestone | Cu | Undisturbed | 0.5 | 3.53 | 21.6 | 5.8 | 1487 |
| Limestone | Zn | Disturbed | 0.5 | 4.29 | 30.6 | Not weighed* | |
| Limestone | Cu | Disturbed | 0.5 | 5.45 | 33.6 | Not weighed* | |
| Mussel Shells | Zn | Undisturbed | 1 | 3.53 | 27.0 | 8.7 | 1115 |
| Mussel Shells | Cu | Undisturbed | 1 | 5.00 | 34.2 | 7.3 | 936 |
| Mussel Shells | Zn | Disturbed | 1 | 3.53 | 24.0 | 8.7 | 1115 |
| Mussel Shells | Cu | Disturbed | 1 | 4.29 | 29.4 | 7.3 | 936 |
| Mussel Shells | Zn | Undisturbed | 0.5 | 3.33 | 12.6 | 4.2 | 1077 |
| Mussel Shells | Cu | Undisturbed | 0.5 | 3.00 | 18.6 | 4.7 | 1205 |
| Mussel Shells | Zn | Disturbed | 0.5 | 2.00 | 20.4 | Not weighed* | |
| Mussel Shells | Cu | Disturbed | 0.5 | 5.45 | 33.6 | Not weighed* | |

*Not possible to weigh because these were wet materials poured out from the 1 m depth for evaluating disturbed materials at a 0.5 m depth. There was not sufficient time to dry the materials between repetitions.

Appendix D. Chemical Composition of Mussel Shells Used in the Field Experiments

The chemical composition of used mussel shells taken from the top, middle and bottom of the treatment systems on the zinc and copper roofs highlighting the higher percentage of Ca and lower percentage of Zn and Cu obtained on the inside layer of the shells.

| Metal | Sample | Shell Side | Element (%) | | | | | | | | | | | |
|-------|--------|------------|-------------|-----|-----|-----|------|-----|-----|-----|-----|-----|-----|-----|
| | | | O | Si | Al | K | Ca | Fe | Na | Mg | S | P | Zn | Cu |
| Zn | Top | Outside | 58.3 | 3.4 | 1.6 | - | 33 | 1 | 0.6 | 0.3 | 0.9 | 0.3 | 0.5 | - |
| Zn | Top | Outside | 54.5 | 2.5 | 1.3 | - | 38.8 | 0.8 | 0.6 | 0.3 | 0.5 | 0.3 | 0.4 | - |
| Zn | Top | Inside | 49 | 1 | 0.5 | - | 48 | 0.2 | 0.7 | - | 0.2 | 0.2 | 0.2 | - |
| Zn | Top | Outside | 54.9 | 6.3 | 2.2 | 0.5 | 32.1 | 1.1 | 0.7 | 0.5 | 0.5 | 0.4 | 0.6 | - |
| Zn | Middle | Inside | 53.4 | 0.4 | 0.2 | - | 45.2 | - | 0.7 | - | 0.1 | - | - | - |
| Zn | Middle | Outside | 58 | 2 | 1 | - | 36.8 | 0.4 | 0.6 | 0.2 | 0.4 | 0.7 | - | - |
| Zn | Middle | Outside | 59.1 | 2.3 | 1.3 | - | 34.8 | 0.7 | 0.6 | 0.2 | 0.7 | 0.2 | - | - |
| Zn | Bottom | Inside | 46.9 | 0.8 | 0.3 | - | 50.9 | 0.2 | 0.7 | - | 0.1 | 0.1 | - | - |
| Zn | Bottom | Outside | 56.8 | 2.7 | 1.4 | 0.3 | 36.4 | 0.8 | 0.7 | 0.2 | 0.5 | 0.2 | - | - |
| Zn | Bottom | Outside | 57.1 | 3.3 | 1.6 | 0.4 | 35 | 0.8 | 0.7 | 0.3 | 0.5 | 0.2 | - | - |
| Cu | Top | Inside | 48.9 | 0.9 | 0.4 | - | 48.9 | 0.2 | 0.6 | - | 0.2 | - | - | 0.6 |
| Cu | Top | Outside | 50.7 | 3 | 1.3 | - | 38.3 | 0.6 | 0.5 | 0.2 | 0.2 | 0.2 | - | 4.8 |
| Cu | Top | Inside | 51.5 | 2.4 | 1 | - | 42.7 | 0.6 | 0.4 | 0.3 | 0.2 | 0.2 | - | 0.7 |
| Cu | Middle | Outside | 58.4 | 5.6 | 3.4 | 0.5 | 28.2 | 1.6 | 0 | - | 0.6 | 0.2 | - | 1.2 |
| Cu | Middle | Inside | 52.8 | 0.6 | 0.4 | - | 45.1 | 0.2 | 0.6 | - | 0.2 | - | - | - |
| Cu | Middle | Outside | 58.4 | 6.3 | 2.9 | 0.5 | 27 | 1.3 | 0.9 | - | 0.8 | 0.2 | - | 1.7 |
| Cu | Bottom | Outside | 59.8 | 3.1 | 1.9 | - | 31.5 | 0.8 | 0.7 | 0.3 | 0.9 | 0.2 | - | 0.8 |
| Cu | Bottom | Inside | 57.2 | 0.1 | 0.1 | - | 41.8 | | 0.7 | - | 0.1 | - | - | - |
| Cu | Bottom | Outside | 56.5 | 3.1 | 1.9 | - | 35.2 | 0.9 | 0.7 | 0.3 | 0.6 | 0.2 | - | 0.6 |

Appendix E. The Concentration of Dissolved Zinc and Copper in the Untreated Roof-Runoff at Each Sampling Time for the Field Experiments

The graphs below show the concentration of dissolved Zn and Cu that was present in the untreated roof-runoff collected at each sampling time. From the results obtained, it was observed that the concentration of dissolved Zn and Cu was considerably higher in the first flush. The number and duration of rainfall events was very low, therefore, the number of steady state samples obtained was not sufficient to identify changes in the performance of the system for the duration of a rainfall event. Data on the concentration of dissolved Zn and Cu at intervals for the duration of a rainfall event is essential because it helps identify the changes in the performance of the system overtime. This data can also be used to calculate the total load of Zn and Cu that has been treated by the system which can then be used to estimate the lifespan of the treatment material.

