Characterizing stormwater pollutant yields from urban carparks in a low-intensity rainfall climate

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Abstract

Carparks make up a large portion of impervious urban areas. Stormwater runoff from carparks can, therefore, be a significant source of pollutants to receiving urban waterways, particularly of total suspended solids (TSS), heavy metals (dissolved and particulate) and indicator bacteria (total coliform and *E. coli*). Traffic volume and patterns, vehicle type, and level of vehicle maintenance have been identified as primary factors that contribute to carpark pollutants in urban stormwater runoff. Materials deposited on carpark surfaces from atmospheric deposition can also be an indirect source of pollutants in carparks. The wash-off of these pollutants is dependent on various rainfall characteristics such as rainfall intensity, rainfall depth, antecedent dry days and rainfall duration. However, there is still a lack of quantitative information on how climatic conditions (particularly low-intensity rainfall climate) and carpark land use influence pollutant loads and the corresponding stormwater quality characteristics during first flush and steady-state conditions. There is also limited information on the characterization of pollutants from different carparks based on particle size distribution (PSD). Therefore, the aim of this research is to understand the dynamic nature of pollutant loadings and PSDs from urban carparks under low-intensity rainfall conditions. The long-term goal is to contribute to the development of guidelines for the selection of land use based stormwater treatment systems for individual carparks.

Carpark runoff samples were collected during 21 storm events (rainfall intensity varied from 0.39-6.87 mm/h with an average of 2.3 mm/h) from three urban carparks under different land uses (university, hospital and industrial) in Christchurch, New Zealand. Samples were collected over 14 months using grab and automatic samplers. Samples from first flush (FF) and steady-state (SS) were analyzed for TSS, heavy metals (dissolved and particulate), particle size and *E. coli*.

During first flush, the industrial carpark runoff quality had significantly higher pollutant concentrations. The positive correlations between each heavy metal (Zn, Cu, Pb) at the university and the industrial carparks indicated that in each of these sites heavy metals originated from a similar source. The higher TSS and ratios of different heavy metals at the industrial carpark suggested relatively higher wear and tear from larger commercial vehicles. Rainfall characteristics had a weak positive correlation with pollutant concentrations at all the carparks, but vehicular activities are likely to be the dominant factor in the observed range of contaminant yield values.

During steady-state flow conditions, TSS and heavy metals yield at the industrial carpark were statistically higher than other two carparks studied during period 1 (first 40 mins of rainfall). There was a subsequent reduction in mean pollutant yields from each period except for the university carpark. This shows that the increased rain duration resulted in a decreased supply of pollutants in each period from each carpark. A

linear relationship between total and dissolved metal yields was found at the university and the hospital carpark. The data for all the carparks monitored did not show any seasonal effects on total pollutants yields. Larger rain events (>5 mm) had relatively greater pollutants yields than smaller rain events and average pollutant yields were found to be a relative maximum at 3-6 antecedent dry days.

Particle size during FF and SS showed a similar distribution pattern but had a slightly different median (D50) with an average of 80 and 110 µm respectively. Fine particles (<67 µm) represented 32-40% of the total particles from the carparks.

Indicator bacteria concentrations were statistically higher at the industrial carpark and also exceeded the recommended recreational guidelines established by the NZ Ministry for Environment.

The results of this study indicate that given the range of pollutant types and quantities coming off different carparks, the selection of treatment systems has to be targeted to the individual carpark land use and climatic characteristics. Furthermore, a combination of treatment systems may be needed to achieve optimal removal of pollutants of the types and quantities observed. Various nonstructural management strategies should also be considered to reduce the build-up of pollutants in carparks. These include frequent cleaning and maintaining downpipes and gutters, proper disposal of pet waste and litter, use of vegetation and grass to cover and stabilize exposed soil to prevent sediment wash-off, sweeping and vacuuming of carpark surfaces and so on.

Overall, the knowledge gained through this research contributes to a greater understanding of urban carpark runoff quality and appropriate selection of treatment systems and management of carparks, which will thus result in improvement of the water quality of urban waterways.

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Glossary

ADD	Antecedent Dry Days
AEP	Annual Exceedance Probability
ANOVA	Analysis of variance
ANZECC	Australian and New Zealand guidelines for fresh and marine water quality
BMP	Best Management Practices
CCC	Christchurch City Council
CFU	Colony Forming Units
Cu	Copper
CWA	Clean Water Act
E. coli	*Escherichia coli*
EPA	Environmental Protection Agency
FF	First Flush
HIRDS	High-Intensity Rainfall Design System
ICPMS	Inductively Coupled Plasma Mass Spectrometry
IRD	Initial Rain Depth
IRI	Initial Rain Intensity
MPN	Most Probable Number
NIWA	National Institute of Water and Atmosphere
NPDES	National Pollution Discharge Elimination Systems
NWQMS	National Water Quality Management Strategy
NZTA	New Zealand Transport Agency
PAH	Polycyclic Aromatic Hydrocarbons
Pb	Lead
PSD	Particle Size Distribution
RMA	Resource Management Act
SE	Storm Events
SMPs	Stormwater Management Plans

SQIDS	Stormwater Quality Improvement Devices
SS	Steady-State
TAPE	Technology Assessment Protocol-Ecology
TSS	Total Suspended Solids
WFD	Water Framework Directive
WHO	World Health Organization
Zn	Zinc

Chapter 1

Introduction

1. Introduction

1.1 Problem statement

The degradation of water quality in urban freshwater ecosystems typically occurs when stormwater runoff from impervious surfaces is channeled directly into local waterways (Blakely and Harding 2005; Cochrane et al., 2010; Wicke et al., 2012). Total suspended solids (TSS) and heavy metals, such as Zinc (Zn), Copper (Cu), Cadmium (Cd), Lead (Pb), Nickel (Ni) and Chromium (Cr), have been identified as significant pollutants in stormwater which can be eco-toxic or detrimental to aquatic species in the receiving waterways. The presence of dissolved metals is a key concern as they are readily bioavailable and difficult to remove from runoff with ordinary treatment systems (Pitt et al., 1995). Indicator bacteria such as *Escherichia coli* (*E. coli*) originating from warm-blooded animal droppings on impermeable surfaces (among other sources) are also pollutants found in stormwater which can have an adverse effect on the quality of waterways. Removal of such indicator bacteria from stormwater discharges is of high importance for effective stormwater management (Li, 2014). Hydrocarbons, originating from vehicles, are another group of pollutants found in stormwater which are of particular concern due to their prevalence, toxicity to aquatic organisms and persistence in receiving waterway environments (Brown and Peake, 2006). These non-point source pollutants are the major contributors to the deterioration of urban water bodies resulting in potential public health and environmental hazards (Reddy et al., 2014; Wang et al., 2013).

The nature of urban land use and the type of activity in a catchment have a direct impact on the quantity and quality of stormwater (Goonetilleke et al., 2005). Urban catchments, such as impervious carparks, are a significant source of pollutants. The differences in quantity (build-up) and quality of pollutants from different carparks can be driven by different factors such as traffic volumes, vehicle types, vegetation types, vegetation cover, maintenance activities and population density. The type and the quantity of pollutants carried by stormwater (wash-off) from urban carparks are influenced by rainfall characteristics. Rainfall characteristics such as pH, event duration, antecedent dry days and average rainfall intensity have been found to have a dynamic relationship with suspended solid and heavy metal (dissolved and particulates) yields (Charters et al., 2016).

In Christchurch, New Zealand, the majority of the stormwater from urban carparks is discharged, untreated, directly into urban surface waterways via underground piped networks (CCC, 2003). This has affected the ecological health of freshwater ecosystems due to the deterioration of plant and animal life. However, new land developments now have to obtain a resource consent for the discharge of stormwater, and this requires an improvement in the quality of stormwater discharged into waterways by installing adequate treatment systems. Plans are also being devised to retrofit stormwater treatment systems in older urban areas. The Christchurch City Council (CCC) has developed Stormwater Management Plans (SMPs) which follow an integrated stormwater approach to set water quality objectives for new and old catchments and principles of how stormwater will be planned and managed from 2009 to 2039. The plans mitigate the effects of the future growth of commercial and industrial developments and also take into account retrofitting of existing older developments such as urban carparks wherever practicable.

One of the key strategies of the SMPs is to manage stormwater from commercial, residential or industrial sites/carparks with a particular focus on source control and onsite treatment. Stormwater discharges from carparks (under various land uses) into the CCC stormwater networks are required to meet the Council's water quality guidelines under the new SMPs. To meet the guidelines, residential, commercial or industrial sites/carparks may be required to provide onsite pre-treatment systems designed to capture gross pollutants and prevent or capture chemical spills (Christchurch City Council, 2015) before discharge into CCC networks. Sites that do not discharge to an integrated council facility for treatment are required to fully treat their stormwater onsite. This can be achieved with smaller versions of accepted treatment trains (as outlined in the SMPs) such as the use of pervious pavements and proprietary treatment devices.

For SMPs to be effective, an understanding of the types and levels of pollutants originating from different urban carparks areas are necessary. This information will allow the selection of the most adequate stormwater treatment systems for stormwater management. In other words, it is necessary to quantify and qualify the nature of pollutants loadings and particle size distributions from specific carparks under different land uses (residential-institutional, commercial, and industrial) before the benefits and efficiency of using stormwater treatment systems can be established.

1.2 A need for research

The composition and characteristics of stormwater pollutant loads are likely to vary between large commercial (i.e. hospital), residential-institutional (i.e. university) and industrial carparks, however, there is a lack of information on quantifying how climatic and land use characteristics influence pollutant loads in stormwater runoff. There is a need to better understand the relationship between carpark runoff, climatic conditions and the corresponding stormwater quality characteristics. No studies are available that explain the characteristics of pollutants loading for different carparks under low-intensity rainfall conditions and thus implementing appropriate stormwater treatment systems for each carpark is difficult. Most of the past research on stormwater is focused on road, roof and highways runoff to estimate the discharge of pollutants from those respective surfaces during steady-state (Revitt et al., 2014). In many studies, first flush volumes and the proportion of the pollutant loads in the first flush vs. the total pollutant load are not defined. Accurate characterization of the first flush is crucial as it would influence the selection of stormwater treatment systems, especially in low-intensity rainfall conditions (<5 mm/h) such as those found in cities like Christchurch.

Several studies have been carried out in New Zealand to evaluate the performance of best management practices (Moores et al., 2012), but there is minimal information on the characterization of pollutants from different carparks based on particle size distribution. There is a need to understand the characteristics of the pollutants with respect to particle size distribution and dissolved metals from different carpark for the selection of stormwater treatment systems. Regarding indicator bacteria, the Ministry for Environment has developed some recreational guidelines for *E. coli* in runoff but there does not appear to be any research on quantifying indicator bacteria and its relationship with urban carpark runoff in New Zealand.

Regarding the selection of stormwater treatment systems in New Zealand, there is currently a "one size fits all" approach, where there is minimal information on selecting a particular system at the local level to retrofit individual carparks. There are thus a number of knowledge gaps of relevance for the uptake of targeted treatment technologies in New Zealand and overseas.

1.3 Research aim and objectives

The aim of the research was to understand the dynamic nature of pollutants loadings and particle size distributions from urban carparks to inform the selection of stormwater treatment systems. In order to achieve this aim, the following specific objectives were addressed.

1. The first objective of this research was to quantify potential differences in first flush TSS and heavy metals pollutant concentrations from three different carparks (hospital, university, and industrial), within the same geographical location and under similar low-intensity rainfall conditions. A secondary objective was to assess the influence of antecedent dry days, initial intensity and initial rain depth on the pollutant concentrations during first flush.

2. The second objective of this research was to understand differences in TSS and heavy metal loadings (dissolved and particulate) for various impervious carparks during steady-states as a function of traffic characteristics, drainage area and surrounding topography. A secondary objective was to understand the relationship between pollutant loadings (yield/m^2) and rainfall characteristics (rain depth, rain duration and antecedent dry days (ADD).

3. The third objective was to assess whether there were significant differences in PSD between first flush and steady-state conditions, between the carparks, and within each storm event. A secondary

objective was to assess the relationship between PSD and initial 10 mins rainfall intensity, rain depth, ADD, first 10 mins rain depth and average intensity.

4. The fourth objective was to quantify indicator bacteria (total coliform and *E. coli*) in runoff from different carparks. Secondary objectives were to assess the seasonal variations of indicator bacteria, the role of suspended solids, and the influence of rainfall parameters such as initial 10 mins rainfall intensity on indicator bacteria yields.

The following tasks were performed to achieve the project's objectives.

- Three urban carparks were studied in Christchurch (university, hospital and industrial), which had different traffic patterns, but were in a similar climatic region. TSS, heavy metals (dissolved and particulate loadings), and indicator bacteria (*E. coli*) were monitored during first flush and steady-state runoff for several rainfall events.
- The relationship between pollutant yield and rainfall was analyzed.
- Particle size distributions in stormwater runoff from each carpark during first flush and steady-state conditions were analyzed.
- The need for suitable stormwater treatment systems based on the observed differences in pollutant yields was discussed.

1.4 Thesis structure

This thesis includes eight chapters. Chapter 1 is the introduction, aims and objectives of the research study. Chapter 2 provides a critical review of the literature relevant to this study. This chapter includes information relevant to the current research project and addresses the knowledge gaps. Chapter 3 presents the research methodology, sampling sites, data collection, sampling procedure and analysis. Chapter 4 focuses on carpark pollutant yields from first flush stormwater runoff. Chapter 5 describes the influence of low-intensity rainfall and traffic characteristics on pollutant yields from steady-states. Chapter 6 presents the role of particle size distribution in urban carpark runoff for the selection of suitable stormwater treatments systems. Chapter 7 discusses the importance of understanding indicator bacteria in first flush urban stormwater runoff. Chapter 8 presents the research conclusions and recommendations. All the references cited in the thesis are listed in the references section followed by other supplementary documents in Appendices.

Chapter 2

Literature Review

2. Literature Review

The literature review presented herein is divided into seven main sections. In the first and second sections, urban carpark runoff quality and sources of stormwater pollutants from different urban carparks are discussed. This is followed by the third and fourth sections where stormwater pollutants types and loadings, as well as particle size distribution (PSD) in urban carparks, are discussed. The role of land use in stormwater management and associated pollutants are reviewed in the fifth section. In the sixth and seventh sections, an overview of urban stormwater treatment, as well as stormwater policy framework, are discussed.

2.1 Urban carparks runoff quality

Carparks make up a large portion of impervious urban areas. The establishment of carparking spaces continues to grow as the number of vehicles increases together with their associated use for work and leisure activities (Revitt et al., 2014). In New Zealand, there are 4.7 million registered vehicles (3.1 million passenger car/van) and this number continues to grow daily (NZTA, 2014). Carparks have become a key component for both transport and land use planning related to the development of commercial centers, factories, office complexes, residential housing as well as institutional complexes. Carpark surfaces are typically impervious and, like roads, represent a major source of stormwater pollutants such as TSS, heavy metals, anthropogenic organic compounds, nutrients and microbial contaminants (Gobel et al., 2007).

During rainfall events, stormwater runoff originating from carpark surfaces wash-off pollutants and transport them to urban waterways. The decrease in infiltration, increase in peak discharge, increase in runoff volume, decrease in time to peak flow, and increase in runoff velocity are some of the hydrological changes as a result of imperviousness (Wong et al., 2000; Schueler, 1994). These changes can be illustrated in graphical form as shown in (Figure 2.1).

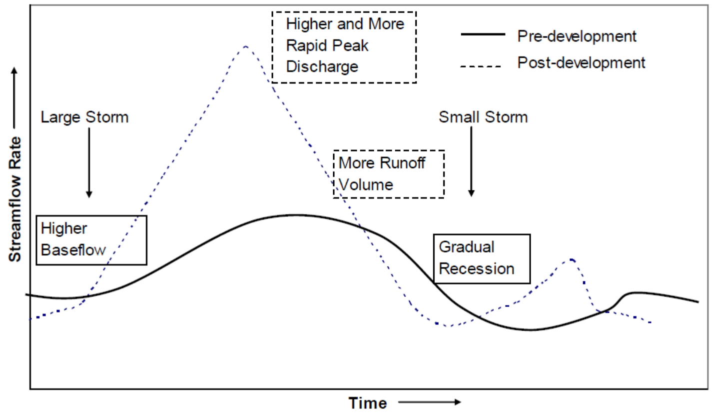


Figure 2-1: Effect of urbanization/imperviousness in stream hydrology (Adapted from Schueler, 1994)

2.1.1 First flush and steady-state runoff

Pollutant concentration in runoff from impervious carparks is usually high during the initial part of the runoff flow, which is commonly known as first flush (FF). The subsequent pollutant concentration during steady runoff is known as steady-state (SS) concentration (Figure 2.2). Consequently, the discharge rate of pollutants in the first flush is greater than in the steady-state (Deletic and Maksumovic, 1998). During the first flush, a substantial quantity of pollutant loads can be discharged into the receiving urban waterways (Lee et al., 2002). Understanding the first flush behaviour is critical since most treatment options are designed to accommodate this initial portion of runoff.

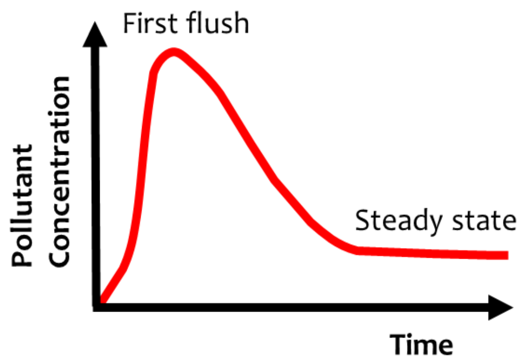


Figure 2-2: A typical runoff hydrograph for urban land use

2.2 Stormwater pollutant sources from carparks

Various studies have identified numerous sources of urban stormwater pollutants (Gnecco et al., 2005; Brown and Peake 2006). The primary sources of pollutants in carpark runoff are as follows.

2.2.1 Vehicular traffic

Traffic is a major source or contributor to many pollutants in urban carparks. Pollutants from traffic can be generated in solid, liquid and gas form. Carpark pollutants are mainly derived from wear and tear of vehicle tires and brake linings, engine emissions, wear of plating, bearings and bushings and other moving parts (Amrhein et al., 1992; Glenn, 2001). Traffic patterns such as speed and vehicle count, maintenance activities as well as road characteristics such as traffic lights and road layout also significantly influence the generation of different pollutants. The concentration and type of pollutants are also influenced by the surrounding land use. For example, industrial and commercial land uses generate more pollutants as compared to residential land use (Migunatanna, 2009). High traffic activities in commercial and industrial land use result in significant heavy metal yields (dissolved and particulates).

2.2.2 Atmospheric deposition

Indirect pollution from atmospheric deposition contributes substantial pollutants in runoff (Murphy et al., 2015). Atmospheric deposition can occur as dry and wet deposition. Dry deposition is the direct settling of particles onto land or surface water via gravitational settling, impaction, or turbulence, depending on the size of the particle (Shrivastav, 2001; Azimi et al., 2003) whereas wet deposition occurs when pollutants are removed from the atmosphere by rainfall events (Gobel et al., 2007).

2.2.3 Corrosions of surface

Roof and other metallic surfaces such as gutters and downpipes are corroded through chemical processes and atmospheric heat and cooling processes. Rainfall washes-off corroded particles and transports them into the receiving waterways. Metallic roofs are the major contributor of metals. For example, Charters et al. (2016) reported that the concentration of copper in urban stormwater runoff from copper roofs was higher than that in road runoff. Some roof surfaces can also discharge stormwater directly into carparks or the carpark drainage network.

2.2.4 Accidental spills and maintenance

Accidental spills of motor oil and hydraulic fluid contain high metal concentrations Madanhire and Mbohwa (1978) and can contribute to high pollutant loads if they are not dealt with before a storm event. Vehicular and industrial activities (while loading and unloading goods) and washing of vehicle parts are also activities which contribute regular or occasional pollutants. Maintenance activities such as sweeping, and power-washing of pavement surfaces also contaminate stormwater runoff.

2.2.5 Birds and waterfowl excreta

The contamination of waterways with warm-blooded animal's excreta (mainly aves and mammals) represents a significant risk to recreational use of urban waterways. A study conducted by Bannerman et al. (1993) in Wisconsin, USA, found that rooftops and urban carparks are considered a dominant source of indicator bacteria. The causes of indicator bacteria in carparks are mainly dogs, rodents, and waterfowl (if a carpark is close to waterways).

2.3 Stormwater pollutant types

Stormwater runoff from urban areas can contain significant amounts of inorganic and organic pollutants such as suspended solids, nutrients, heavy metals, pathogens, and hydrocarbons (Bannerman et al., 1993). The sources and concentration of these pollutants and their contribution to urban stormwater runoff are heavily dependent on the land use and rainfall characteristics (Hatt et al., 2004).

2.3.1 Total suspended solids

Total suspended solids (TSS) are the most prevalent pollutants found in urban stormwater and they also transport many other potentially harmful pollutants (McCarthy et al., 2012). TSS originate from many sources including the erosion of pervious surfaces, dust, litter and other particles deposited on impervious surfaces from human activities and the atmosphere. TSS also have adverse impacts on receiving water bodies, namely, increasing water turbidity, inhibiting plant growth and diversity, affecting river biota, and reducing the number of aquatic species. In addition, many other pollutants such as bacteria and heavy metals are attached to suspended solids (Shammaa et al., 2002).

The nature of the land use influences the concentration of solids in the runoff, for example, Sarukkalige et al. (2012), found that stormwater from industrial areas had the highest amount of the suspended solids whereas residential stormwater had the lowest concentration. The source of the contaminants and rainfall characteristics has an impact on the amount of the solids in the runoff.

TSS can be characterized by two different components. The first is turbidity; the presence of total suspended solids can increase the turbidity of the water. This is caused by suspended matter that interferes with the clarity of the water and can, therefore, be an indirect indicator of potential health risks associated with stormwater runoff (Morgan et al., 2011). The second one is the particle size of the suspended solids. TSS can be characterized in terms of their particle size distribution. This can be useful for stormwater runoff treatment and best management practices selection. Particle size distribution influences the efficiency of stormwater treatment services. There are two reasons for considering particle size distribution in designing stormwater treatment practices. First, size has a major influence on the settling velocity of particles. Second, research has shown the concentration of adsorbed contaminants depends on the particle size (Gulliver et al., 2010).

2.3.2 Heavy metals

The presence of heavy metals in urban runoff is of concern, particularly in their dissolved form when they are considered more toxic due to enhanced bioavailability. Heavy metals are found either as dissolved-dissociated in water or adsorbed onto fine sediments and particulate organic matter (Harrison and Wilson, 1985; Pitt et al., 1995). Most of the heavy metals from road and highway runoff are attached to suspended solids (Bodo, 1989; Dong et al., 1984). Dissolved metals are defined as that materials that passes through a 0.45 µm filter or "the concentrations of elements determined in a sample after the sample is filtered through a 0.45-micron filter" (APHA et al., 2005). Particulate-bound heavy metals are generally removed through various treatment systems such as filtration and sedimentation (Characklis and Wiesner, 1997; Sansalone et al., 1998). Dissolved heavy metals have the potential for acute and long-term toxicity for aquatic life and a greater potential of polluting groundwater (Hatje, 2003; Marsalek et al., 1999; Pitt et al., 1995). The knowledge of partitioning of metal elements and solids is very useful while assessing stormwater treatment systems. This partitioning is influenced primarily by the pavement residence time (i.e. the lag time between rainfall and runoff increments and influences the partitioning of constituents and the loadings dynamics for a best management practices at a particular site), rainfall pH, the nature and quantity of solids present, and the solubility of the metal element (Sansalone and Buchberger, 1997).

Zinc (Zn), copper (Cu) and lead (Pb) are of concern due to their dominance in urban runoff signatures in New Zealand and elsewhere (Zanders, 2005). Zn and Cu were primarily found in dissolved form and lead is found mainly in particulate form according to research conducted on stormwater runoff from urban roadways in Cincinnati, United States (Turer et al., 2001). Roof and road runoff are considered the major direct sources of heavy metals in urban runoff. Roofing materials such as rolled Cu and galvanized metal (a source of Zn) are frequently used worldwide as they are considered to be relatively "maintenance-free", durable and can be adapted to many different design styles (He et al., 2001). Roads are estimated to contribute between 35-75% of heavy metals in urban runoff in New Zealand, although they only comprise approximately 10-20% of an urban catchment (Pandey et al., 2005).

The sources and origin of these metals are land use dependent. Many heavy metals, especially Pb and Zn have been recognized as traffic-related pollutants (Dong et al., 1984; Sansalone and Bushberger, 1997). Motor vehicle emissions, drips of crankcase oil, wear and tear of a vehicle tire and asphalt road surfaces are all diffuse sources of chemical pollutants including heavy metals in an urban environment (Brown and Peake, 2006). Other specific sources of heavy metals in an urban area include corrosion of buildings (metal roofs) and their fittings, atmospheric deposition, transport, various industrial activities and intentional and accidental spills (Christensen and Guinn, 1979; Davis et al., 2001). High levels of Pb concentrations in runoff can come from painted structures (Davis and Burns, 1999), but also originate from vehicle components, use of leaded fuel, and other sources. Availability of heavy metal from various sources in Maryland, United States were studied and found Cu to originate from vehicle brakes, Zn from tire wear, and Pb, Cu, Cd and Zn attributed to building siding runoff (Davis et al., 2001).

Like TSS loadings, the concentrations of heavy metals also vary widely in stormwater due to various factors such as particle size, pH and water temperature. Metal concentrations generally increase with decreasing particle size (Liebens, 2001; Ujevic et al., 2000) due to the relatively large specific surface area of fine sediments and their higher cation exchange capacity (Dong et al., 1984). In addition, pH strongly influences metal sorption (Bradl, 2004). The solubility of trace metals in surface water is predominately controlled by the water pH (Connell et al., 1984). A lower pH increases the competition between metal and hydrogen ions for binding sites. A decrease in pH may also dissolve metal-carbonate complexes, releasing free metal ions into the water column (Connell et al., 1984). Dissolved metal concentrations in water increase with decreasing pH, with the highest value at about 4 (ie. pH of 4 results in the highest possible concentration of dissolved metals) (Vesely and Majer, 1996). In addition, water temperature also influences the water chemistry. Cold water contains more dissolved oxygen than warm water. Thus, metal concentration in the interstitial water (water occupying the spaces between sediment particles) of the sediment may decrease with decreasing temperature, as more metals are bound to sediment colloids at high rather than low redox potentials (Fo¨rstner and Wittmann, 2012).

2.3.3 Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are toxic and potentially carcinogenic chemicals originating mainly from incomplete combustion, spills of petroleum and traffic emission (Mastral and Callen, 2000). In many urbanized areas, dust deposited on impervious surfaces (mainly roads and roofs) is contaminated by PAHs (Lau and Stenstrom, 2005; Wang et al., 2011; Zhao et al., 2009).

Carpark seal coats are a significant source of PAHs in urban runoff waters. Besides carpark seal coats, motor vehicle emissions, drips of crankcase oil, vehicle tire wear and asphalt road surfaces, are all diffuse sources of hydrocarbons in urban environments. Other diffuse sources of PAHs include domestic fire emissions, the spillage or deliberate dumping of waste oil and the corrosion of roofing materials (Mahler et al., 2005).

PAHs can be transported into local receiving waters by stormwater runoff imposing a considerable risk on aquatic life and human health. PAH concentrations in urban environments have risen over the last two decades due to higher traffic flows and increased consumption of fossil fuel (Van Metre et al., 2000).

2.3.4 Indicator bacteria

Microbial pathogens from non-point source discharges such as stormwater are a significant public health concern (Taylor et al., 2014). Indicator bacteria such as fecal coliform (FC), *Escherichia coli* (*E. coli*) and enterococci, are commonly used as microbiological parameters that indicate fecal pollution in urban runoff (WHO, 2006). Unlike other pollutants in stormwater runoff, predicting and monitoring indicator bacteria are challenging tasks as the growth and removal of microorganisms are dependent upon antecedent rainfall condition, nutrient levels, rainfall intensity, and stormwater quality as shown by an *E. coli* monitoring program conducted at four urban catchments (industrial area, residential area with medium, low and high density) in Melbourne, Australia (McCarthy et al., 2013).

Bacteria may come from many sources, which include runoff from fertilized cropland, animal wastes associated with residential development, ineffective septic or sewer systems and urban storm drains (Jamieson et al., 2003; Moog and Whiting, 2002). Indicator bacteria concentrations in urban stormwater are highly variable, with mean concentrations often ranging by factors of 10 to 100 during a single storm event (Tiefenthaler et al., 2011). For example, in a study by Selvakumar and Borst (2006) in an urban area of New Jersey, USA, the concentration of *E. coli* was found to be higher (12,500 MPN/100 mL) in a high-density residential area and lower (600 MPN/100 mL) in an industrial area. The higher concentration of *E. coli* in the high-density residential area was attributed to sewer cross connection and septic/sewer leakage.

Rainfall conditions also affect the growth and distribution of indicator bacteria. The greatest occurrences of these bacteria normally coincide with or precede the peak flow of the storm hydrograph and generally increase with rainfall intensity (Cho et al., 2010).

Numerous other factors also influence the levels of indicator bacteria in surface water, which include land use, storm characteristics and seasonality (Hathaway and Hunt, 2010; Schoonover and Lockaby, 2006). Although high fecal bacteria concentrations are found in urban stormwater runoff, knowledge of the fate, transport, source and concentrations of these bacteria are still poorly understood, especially in urban catchments.

2.4 Pollutant loading and particle size distribution in urban carparks

Carpark runoff quality, like all diffuse urban runoff quality, is highly variable (Freni et al., 2010) and subject to various factors as highlighted above. Urban pollutants are composed of materials that characteristically reflect a wide range of size fractions and compositions. Both the pollutant load and size distribution of particulates may influence their behaviour and physicochemical mechanisms such as dissolution and settling rates of particles.

Many particle size distribution studies show the predominance of finer particles sizes in runoff from heavily used roads with a tendency to a slightly coarser distribution observed for carparks and residential roads. Three different urban sites (residential roads, light industrial area and a parking lot) were compared in Gold Coast, Queensland and found that the largest amount of sediment collected was from the parking lot (570 carparking spaces) with the particles smaller than 75 µm in size (Herngren et al., 2005). Particle size analysis revealed that the majority of sediments collected at each site were below 76 µm independently of the land use, rainfall intensity and duration. The 0.45-75 µm size class dominated in all samples and up to 85% of the particles were this size. A similarly sized university parking lot (2.43 ha, designed for 500 cars) at the University of California, Davis was studied, and results showed that more than 90% of particles were found smaller than 38 µm (Kayhanian et al., 2012). Similarly, 8-30% (by mass) of particles in stormwater were found to be less than 150 µm in diameter in research carried out at the Fine Arts carparks (2.8 ha) at the University of Canterbury, NZ (Adams et al., 2007). Thus, concentrations of finer particles (less than 75µm) are significant before it entered the sump runoff from carparks in various studies.

The information on particle size range in stormwater is helpful in designing appropriate stormwater treatment systems for carparks. For example, the common approach of targeting of suspended solids for water quality improvement would only be effective if a specific particle size range is removed. The strategy and design of treatment systems to remove suspended solids need to be carefully formulated to suit site characteristics. A "one size fits all" approach may not prove to be adequate for different land uses.

2.5 Role of land use in urban stormwater management

Land use refers to the human modification of the natural environment for a specific purpose within the built environment. In urban catchments, land use can be broadly categorized into residential, commercial and industrial (Sarukkalige et al., 2012). Land use and land cover (vegetation, pavement, and roof surfaces) have a significant influence on stormwater management in an urban environment. The sources and concentrations of stormwater pollutants generated in different land uses are largely dependent upon various anthropogenic activities such as vehicular traffic, pervious cover, and maintenance activities as well as population density (Goonetilleke et al., 2005).

The type and concentration of pollutants vary with land use activities. Industrial land use, for example, was reported to produce more fine particles than residential and commercial land use in the Gold Coast in

Queensland, Australia (Miguntanna et al., 2010). Similarly, a study in Western Australia found the highest amounts of solids coming from an industrial area, whereas commercial land use appeared to produce the lowest amounts of suspended solids (Sarukkalige et al., 2012). This was attributed to anthropogenic activities such as industrial enterprises, traffic characteristics, loading and unloading activities as well as the size of the vehicles involved in the industrial land use. Contrary to these findings, runoff from arterial streets in the commercial land use had the largest loads of solids as compared to industrial and residential areas in Wisconsin, United States (Bannerman et al., 1993). Similarly, runoff from parking lots had the largest loads of solids, dissolved copper, and total copper in industrial land use.

The concentrations of suspended solids were found to be inconsistent with different land use patterns. There may be different factors predicts TSS concentration such as topography, traffic conditions, and rainfall conditions. The two most important components that influence pollutant concentrations in stormwater are a) land use (Bannerman et al., 1993), and b) rainfall characteristics of the catchment (Liu et al., 2015). In the case of land cover, solids from roofs have been noted to have significantly lower loads and be much finer in texture that solids from road surfaces (Egodawatta et al., 2009). This is because roofs do not hold as many pollutants as roads due to their smooth surfaces and the atmospheric deposition is often the primary contributor to pollutant build-up on roofs, apart from the degradation of the roof material itself.

Suspended solids, heavy metals, pathogens, and polycyclic aromatic hydrocarbon (PAHs) concentrations also vary widely between storm events and appear to be most concentrated in the first flush (Hoffman et al., 1984). Research carried out in different land use areas in Rhode Island, United States showed that PAH concentrations were similar in residential and commercial land use but significantly higher in an industrial area and in a highway. No direct relationship of PAH discharges with either rainfall amounts or the length of the dry periods preceding the storms was found. The sources of the PAHs were identified to be the automotive and industrial combustion emissions of PAHs to the atmosphere. However; crankcase oil contributed the highest loadings of PAHs in urban runoff. The dominant particle size range of PAHs was observed between (125-250) µm. Similarly, pollutants build-up and wash-off at the Port of Brisbane, Australia was studied. The PAHs in wash-off were below detection limits (Goonetilleke et al., 2009).

Land use and land cover also influence the prevalence of heavy metals in stormwater runoff. Most of the heavy metals in urban stormwater runoff are attached to suspended solids (Bodo, 1989) however, it is dependent on runoff events and flows and the surface being drained.

As discussed above, land use characteristics play a significant role in pollutant build-up. Their role influences the pollutant species and load generations, pollutant accumulation rate and the spatial and temporal distribution of the pollutants accumulated. These processes are influenced by rainfall intensity, rainfall duration and antecedent dry period. These rainfall parameters primarily influence pollutant transportation from source to sink (Herngren et al., 2010).

2.6 Urban Stormwater treatment

In New Zealand and overseas, urban stormwater has focused mainly on suspended solids and particulate pollutants, however, in recent years, a greater concern has been raised regarding fine particles, dissolved metals and indicator bacteria (disease-causing bacteria). These pollutants are less likely to be efficiently removed through conventional stormwater quality improvement devices (SQIDS) and are more toxic to urban waterways as compared to particulate pollutants (Timperley, 2005). Urban stormwater ponds that are widely used to remove particulate matter treating soluble pollutants (Ivanovsky et al., 2018). Small scale practices, such as bioretention are also more efficient at removing coarser and particulate pollutants (Van Buren et al., 1996). On the other hand, wetland vegetation provides a removal mechanism for fine particles but usually requires a larger area for treatment (Bavor et al., 2001).

It can be difficult to retrofit existing urban carparks with conventional stormwater management systems such as a stormwater pond, swales, rain gardens or bioretention because of larger footprint and the presence of underground services such as electricity, gas pipes and drinking water network (Jonasson et al., 2010). As a result, the most appropriate stormwater treatment system for urban carparks is commercial stormwater treatment systems, which are sometimes capable of removing particulate as well as dissolved pollutants from urban carpark runoff (Vigar, 2009).

In order to enhance the performance of stormwater treatment systems, the selection of the filter media is crucial. There is no standard protocol or data available for the selection of appropriate filter media for different carparks. The performance of filter media for removal of different pollutants (particulate and dissolved) is examined in the following paragraph.

2.6.1 Removal of metals

Heavy metals are found either as dissolved phase or adsorbed onto fine sediments and particulate organic matter (Harrison and Wilson, 1985; Pitt et al., 1995). Particulate metals can be removed by filtration whereas dissolved metals are removed by various other processes such as coagulation-flocculation, electrocoagulation, cementation, membrane separation, membrane filtration, solvent extraction, ion-exchange, adsorption and bio-sorption (Meunier et al., 2006, Kurniawan et al., 2006). However, these methods require high capital investment. Natural materials such as sand, soil and gravel have been extensively used in stormwater treatment for the removal of particulate matter and are limited in the removal of dissolved metals and finer particles (Borne et al., 2013) because of their low adsorption capacity.

Various filter media such as limestone, zeolite and mussel shells have been increasingly popular as a potential media filter in urban stormwater treatment for the removal of dissolved heavy metals (Westholm et al., 2014).

Zeolites are a group of naturally occurring alumino-silicates, are highly porous which make them suitable for adsorption and possess a high ion exchange capacity (Westholm et al., 2014). In addition, the exchangeable ions of zeolite are predominantly alkali and alkaline earth elements (Na+, Ca2+, and K+) and as a result, divalent Zn and Cu ions are more favorably removed via cation exchange at alkaline pH (Genç-Fuhrman et al., 2007). This chemical composition makes zeolite very popular for removal of heavy metals from wastewater.

Limestone is a sedimentary rock composed of calcite and aragonite (different crystal forms of calcium carbonate (CaCO3)). The rough surface of the limestone gives solid contact resulting in chemisorption of metal ions (Stipp et al., 1992, Xu et al., 1996,) and also the presence of dissolved calcium carbonate increases the pH of the solution which causes metals to precipitate as metal oxides and probably metal carbonates. Precipitation and adsorption as metal oxides and metal carbonates are two mechanisms by which heavy metals are removed from wastewater (Sturchio et al., 1997, Cheng et al., 1998).

Mussel shell, a waste product from shellfish processing, is another naturally found material which is effective for metal removal from stormwater runoff. The shells of mollusks (e.g., oyster, clam and mussel) and crustaceans (e.g., lobster, crab and shrimp) are composed of a mixture of calcium carbonate, protein and chitin, with relatively small amounts of lipid, phosphate and pigment (Wase and Forster, 1997; Zuo et al., 2001). Dissolved heavy metal removal by shell material has been shown to be dependent upon several variables including pH, temperature, contact time, particle size, metal concentration, metal type and the physio-chemical characteristics of the material (Tudor, 1999; Kim and Park, 2001; Rae and Gibb, 2003).

2.6.2 Removal of Total suspended solids

Various filter media are used to remove TSS from stormwater runoff. Sand and soil are the most common filter media used to remove TSS from stormwater runoff (Farm, 2002). Peat and compost are also commonly used adsorbent used to remove TSS from runoff, but compost is frequently contaminated with metals so many cases, it becomes a source of metals than an adsorbent and peat degrades over time and good grade peat are expensive. In some cases, biochar is also used as a filter media for the removal of TSS from runoff. The removal efficiency of biochar is 86% (Reddy et al., 2014). Research also found that activated carbon, composite, vericulture and zeolite are also effective in removing 85% of TSS from stormwater runoff (Fuerhacker et al., 2011). Some studies also showed the removal of more than 90% (mainly 95-98%) of TSS using porous polypropylene as a filter media (Kim et al., 2007).

2.6.3 Removal of indicator bacteria (e.g *E. coli*)

The removal of *E. coli* depends upon various environmental conditions. Surface attachment (adsorption of bacteria onto the surface of the filter media) is one of the most important methods for removal of *E. coli*. Various by-products such as steel slag, limestone and zeolite are being used to obtain optimal removal efficiencies of *E. coli* from stormwater runoff (Ghaem, 2017). In addition, various BMPs such as wetlands, bioretention area and a proprietary device can remove fecal coliform with an efficiency higher than 50% (Hathaway et al., 2010). Natural materials such as biofilters (*Carex appressa* or *Leptospermum continentale)* have been gaining increasing attention as potential biofilter for removal of bacteria (Chandrasena et al., 2017).

2.6.4 Factor affecting the removal of TSS and heavy metals

The removal of TSS and heavy metals depends on the type and concentration of pollutants as well as the filter media. The removal efficiency is largely influenced by rainfall events, the adsorption capacity of each filter, the typical filter size, loading and concentrations of pollutants present in stormwater runoff as well as other chemical characteristics such as pH (Reddy et al., 2014). However, the ability of pH to affect the surface charge of solids and the dissolved components makes pH, the most influential parameters that affect the removal of metals by media filter. The particle size of the filter material (it affects adsorption capacity) and the hydraulic retention time also equally affects removal. Filter materials such as sand are permeable because of its coarser particle size causing runoff to pass through very quickly which reduces the contact time and consequently the amount of heavy metal removed (Reddy et al., 2014). Reducing the particle size of filter materials will increase hydraulic retention time and as a result, it will also increase the amount of heavy metal removed (Clark et al., 2004). Clogging of the filter media is particularly a concern with using fine particles in filter media. Thus, in-depth testing of various filter media for the removal of a wide range of pollutants is essential.

2.6.5 Importance of mixed media filtration for stormwater runoff treatment

Various studies on measuring the effectiveness of media filter showed that no single filter media is suitable for the removal of all the pollutants of concern in stormwater runoff (Wium-Anderson et al., 2012; Reddy et al., 2014b). Combinations of several filter media are necessary to achieve the removal of multiple pollutants. Different sorption media (sand, compost, zeolite, etc.) were used as an effective for the removal of dissolved metals from runoff (Seelsaen et al., 2006). Calcite was found to be efficient for TSS removal and zeolite was highly effective in removing indicator bacteria such as *E. coli* (Prabhukumar, 2013). In addition, mixed media filtration (calcite, zeolite, sand and iron fillings) was effective for the removal of heavy metals from stormwater runoff (Reddy et al., 2014b). These findings suggested that the combination of filtration systems is desirable in order to remove multiple pollutants to the maximum extent.

2.7 Statutory and policy framework

In the past, stormwater management plans were devised particularly for downstream erosion control and flood prevention (Chen and Adams, 2006). Over time stormwater management evolved to include the protection of urban waterways by mitigating stormwater pollution. These days, stormwater management involves incorporating various approaches such as allocation of funding to stormwater programs, the introduction of long-term asset management strategies, education of a community about ways to improve water quality and most importantly formulation/enforcement of stormwater regulations, policies and strategies.

In the United States, the Environmental Protection Agency (EPA) is responsible for regulating stormwater in accordance with the Clean Water Act (CWA). The aim of CWA is to restore all "waters of the United States" to their "fishable" and "swimmable" conditions. Municipal and industrial discharges are controlled through the issuance of National Pollution Discharge Elimination System (NPDES) permits. In addition to implementing the NPDES permits, many state and local governments have formulated their own stormwater management laws and plans (CWA, 1972).

In Europe, the Water Framework Directive (WFD) was introduced as one of the most important European environmental legislations to restore Europe's waters and rivers. The purpose of the directive was to establish a framework for the protection of European waters in order for Member States to reach "good status" in all water's bodies throughout the EU. With its ambitious and innovative approach to water management, the WFD set goals to achieve good status of water bodies across the EU by 2027 at the latest. (European Commission, 2019).

In Australia and New Zealand, under the National Water Quality Management Strategy (NWQMS), Australian and New Zealand guidelines for fresh and marine water quality and the NWQMS Australian guidelines for water quality monitoring and reporting are key documents of the strategy to address water quality related issues.

In New Zealand, the Resource Management Act 1991 (RMA), was introduced to promote "the sustainable management of natural and physical resources such as land, air and water". RMA is New Zealand's principle legislation for environmental management. The RMA direct all other environment-related policies, standards, plans and decision making.

Some of the plans and guidelines formulated to improve urban stormwater quality are presented in (Table 2.1). These plans and guidelines are used as a source of information to achieve overall stormwater management goals.

Table 2.1: Published guidelines and plans related to stormwater management in New Zealand

Title	Publisher
Waterways, Wetlands and Drainage Guide	Christchurch City Council (CCC)
Christchurch stormwater tree pit design criteria: detailed report	Christchurch City Council
Christchurch rain garden design criteria	Christchurch City Council
StormFilter design rainfall intensity criterion report	Christchurch City Council
New Zealand building code clause E1 surface water	Department of building and housing
Auckland design manual	Auckland City Council
Technical Publication 108 - Guidelines for stormwater runoff modelling in the Auckland region	Auckland City Council
Stormwater treatment for state highway infrastructure	New Zealand Transport Agency
Onsite stormwater management guidelines	New Zealand Water Research Foundation/Ministry for Environment (MfE)
MfE National policy statement for freshwater management 2014	Ministry for Environment
MfE Urban design toolkit	Ministry for Environment
Wellington water sensitive urban design guide	Wellington City Council

The onsite stormwater management guidelines provide a useful summary of information about onsite stormwater treatment in the New Zealand context. With the growing interest in sustainable urban design and improvements in water quality, "the Onsite Stormwater Management Guideline" (NZWERF, 2004) will allow local government, private sector designers and homeowners to design stormwater systems to reduce stormwater pollution and flooding. The guideline is suitable for use on residential, commercial and industrial sites in urban, suburban and rural areas. The overview of potential stormwater management tools for the selection of onsite treatment systems is shown in (Figure 2.3). To implement the guidelines, the main legislation relevant to stormwater runoff discharges from sites is the RMA, the Local Government Act 2002 and the building Act 1991.

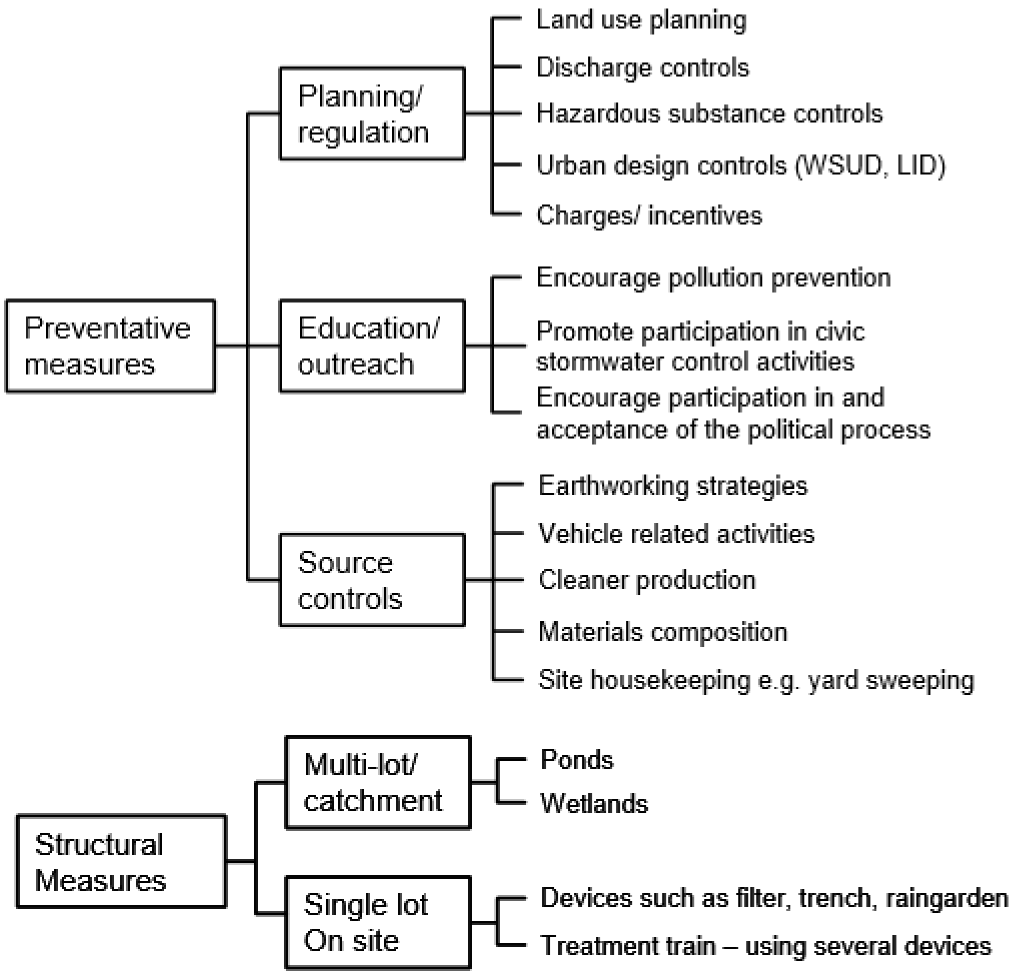


Figure 2-3: Potential stormwater management tools (Figure adapted from on-site stormwater management Guidelines, October 2004).

Many plans and policies have been being formulated to maintain overall "sustainable goals", there are still a number of gaps identified which hinder putting plans into practice. The following are some of the gaps identified while reviewing published stormwater management policies documents.

1) Lack of clear information on what local guidelines are suitable for use. In many cases, there are national and international guidelines, but many documents (which were reviewed and listed above in the (Table 2.1) lack clear guidance on how to adapt these guidelines for local application.
2) There is minimal information on pollutant generation, likely pollutants, typical concentrations and annual loadings at a local level.
3) Internationally, stormwater treatment technologies are reviewed and certified by the Technology Assessment Protocol - Ecology (TAPE). The TAPE program is the Washington State Department of Ecology's process for evaluating and approving emerging stormwater treatment best management practices) (WDOE, 2008), but there is a lack of locally accepted methods of measuring the effectiveness of runoff quality treatment systems in NZ.
4) Minimum mention of onsite characterization and how a particular site/land use will respond to a local rainfall event and the possible environmental effects.

In-depth understanding and research are needed to address these gaps before implementing the available plans, policies and guidelines.

2.8 Summary

The influence of land use on urban waterways includes water quantity and water quality. The presence of impervious surfaces such as urban carparks increases runoff volume and decreases time to peak. On the other hand, untreated wash-off pollutants are transported to urban waterways causing long term environmental impacts. The sources of pollutants are land use dependent and influenced by various other factors such as rainfall and local topography. However, it is not clear how rainfall and land use affect overall urban waterway runoff quality. There is a lack of knowledge on pollutant yields from different land uses which makes the appropriate selection of a treatment system for a particular site difficult. Hence establishing the effectiveness of treatment systems is extremely misleading and difficult. Numerous plans and policies are available to guide and improve the quality of stormwater management, but there are many voids regarding implementation. For example, there is a lack of technical knowledge on pollution generation, discharge of pollutants and yields from different land uses.

Chapter 3

Materials and Methods

3. Materials and Methods

This chapter describes the methodology for monitoring pollutant loadings from urban carparks in Christchurch and analyzing the influence of rainfall characteristics on urban stormwater quality.

3.1 Study Areas

Christchurch is built on a low lying coastal plain and is skirted by the ancient volcanic rocks of the Bank Peninsula. Christchurch has the second largest population (i.e. 372,600, 8% of the NZ population) of all New Zealand territorial authorities after Auckland City (CCC, 2010). The city has a total zoned land area of 1, 49,345 hectares and 13% of Christchurch (19,075 hectares) is urban land use, where 9.3% of the land is categorized as residential, 1.3% is industrial and commercial and the remaining 1,28,788 hectares is non-urban with open space, rural conversation, and rural industrial and residential. Christchurch has unique rainfall patterns which are largely affected by the winds travelling across from the western Tasman Sea and has a much drier climate and less rainy weather than other areas in the South Island. The average annual rain days (1 mm or more) in the city is 84 and average annual rainfall is 627 mm. The city is characterized by more than 360 km of open waterways and over 50 wetlands. The south branch of the Waimakariri River and the Styx River/Purakaunui flow north into the Waimakariri river, while the Avon/Otakaroro and Heathcote/Opawaho rivers flow east into the Avon-Heathcote Estuary (Te Ihutai) (waterways, wetlands and drainage guide, 2003). These rivers run through urban areas and receive a substantial amount of pollutants from various sources.

3.2 Characteristics of land use area and sampling locations

The research study was carried out at urban carparks representing different land uses. The land uses were selected based on the following criteria.

1) To comprehend a diversity of various land use characteristics such as residential, commercial and industrial
2) To understand the influence of various land use activities such as vehicular traffic, traffic patterns, traffic volume and maintenance activities
3) Accessibility to the sampling sites, the safety of people and sampling equipment (grab and autosamplers, batteries, etc.) and maintenance of the sampling equipment were considered as well.

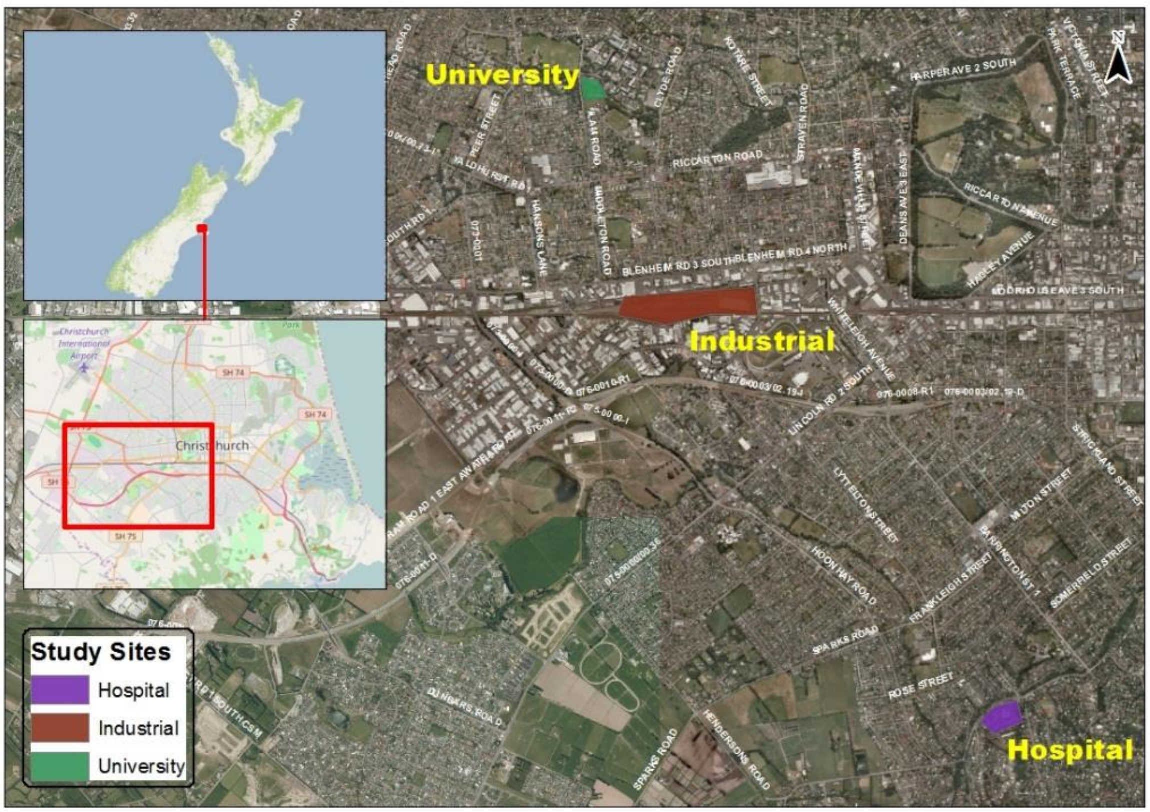


Figure 3-1: The three sampling sites: 1) university, 2) hospital and 3) industrial

Three urban carparks (Figure 3.1) (a university, a hospital and an industrial) were chosen for the study. The carparks experience similar rainfall characteristics which ensured that rainfall factors would not separately influence the stormwater runoff quality. The carpark at the university (Figure 3.1) was within a residential area.

The university sampling site (Figure 3.1) was located at the south-west corner of the main campus. This represents a mixed catchment constituting of roofs, parking lots, trees and lawns. The site was characterized by low to medium traffic predominated by light vehicles. The carpark in an industrial area comprised of light industry such as rail and road freight infrastructure and a large steel framed distribution warehouse with a two-storey concrete framed administration office. The majority of the stormwater was contributed from the carpark transit road and carparks. The site has a daily average traffic of >1000 vehicles/day, many of them were 16-wheeler commercial trucks (Table 3.1). The third sampling site was in the premises of a public hospital. The hospital was located at the foot of the Port Hills at the western edge of the suburb of Cashmere and in a commercial setting. Most of the carparks were asphalt with little previous cover.

Geographically, the carparks were within a radius of 6 km, but the hospital carpark was located at the foothills of the Banks Peninsula whereas the other two carparks were in the flat part of the city. Average daily traffic differs among the carparks, ranging from 600 to over 1000 vehicles a day. Carpark surfaces were asphalt and their drainage area ranged between 1752 and 5036 square meters (Table 3.1).

Table 3.1: Land use characteristics and estimated daily traffic from urban carparks

Carpark	**[1] Estimated daily traffic**	**Characteristics of vehicles and land use category**	**[2]Drainage area (m^2)**
University	900 vehicles/day	Residential/institutional: private car, occasionally (truck for loading/unloading)	5036
Hospital	600 vehicles/day	Commercial/institutional: private car-occasionally bus and truck	1752
Industrial	>1000 vehicles/day	Industrial: truck (mainly 16-wheeler), van and private car	3042

[1] total parking lots were surveyed during the site visit. Total vehicle count was estimated based on field observation at the hospital carpark and with a data logger at the university and industrial carparks
[2]carpark areas were estimated using ArcGIS 10.3

3.3 Sampling layout and sample collection

At the university carpark, stormwater runoff from the carpark was carried to underground stormwater pipes networks before it discharged into nearby open waterways. The stormwater system with manholes and sumps (Figure 3.2) was designed to collect runoff from the carpark before discharge to open waterways.

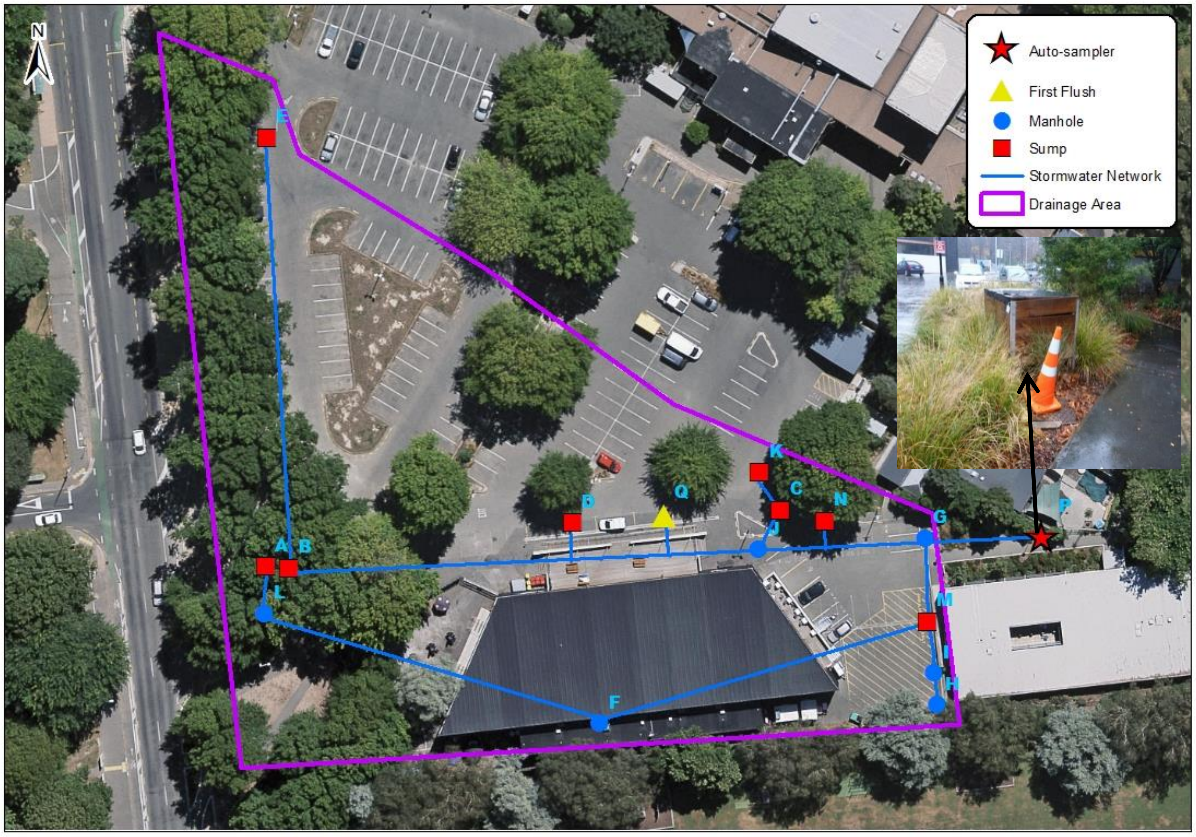


Figure 3-2: Drainage area and sampling locations at the university carpark

Various manholes (L, F, J, I, H, G) are provided at each change of direction and gradient at each branching line of stormwater pipes. Finally, stormwater runoff is collected at the main connecting manhole (P) before it discharges into a waterway. This is the same manhole where an autosampler was placed to collect carpark runoff samples. There are various sumps at locations E, A, B, D, Q, K, C, N, M (Figure 3.2) to ensure the total design flow can enter the stormwater system without surcharging. Discharges from these sumps are directly connected into the sampling manhole (Figure 3.2). During the sampling, first flush surface runoff samples were collected from sump Q before they entered into the drainage network. This sump was selected due to its easy access and location. The sumps and manholes provide ample opportunity for the settling of coarse sediments during the course of discharge. The total drainage area of the catchment was 5036 m^2 (0.5 hectares).

At the industrial carpark, runoff generated from the carpark and transit road to carparks (Figure 3.3) discharged directly into a single sump where the first flush was sampled and the autosampler was located. Unlike the university, the sampled storm runoff from the carpark surface was the direct surface discharge into the sampling sump X. The total drainage area at the industrial carpark was3042 m^2 (0.3 hectares).

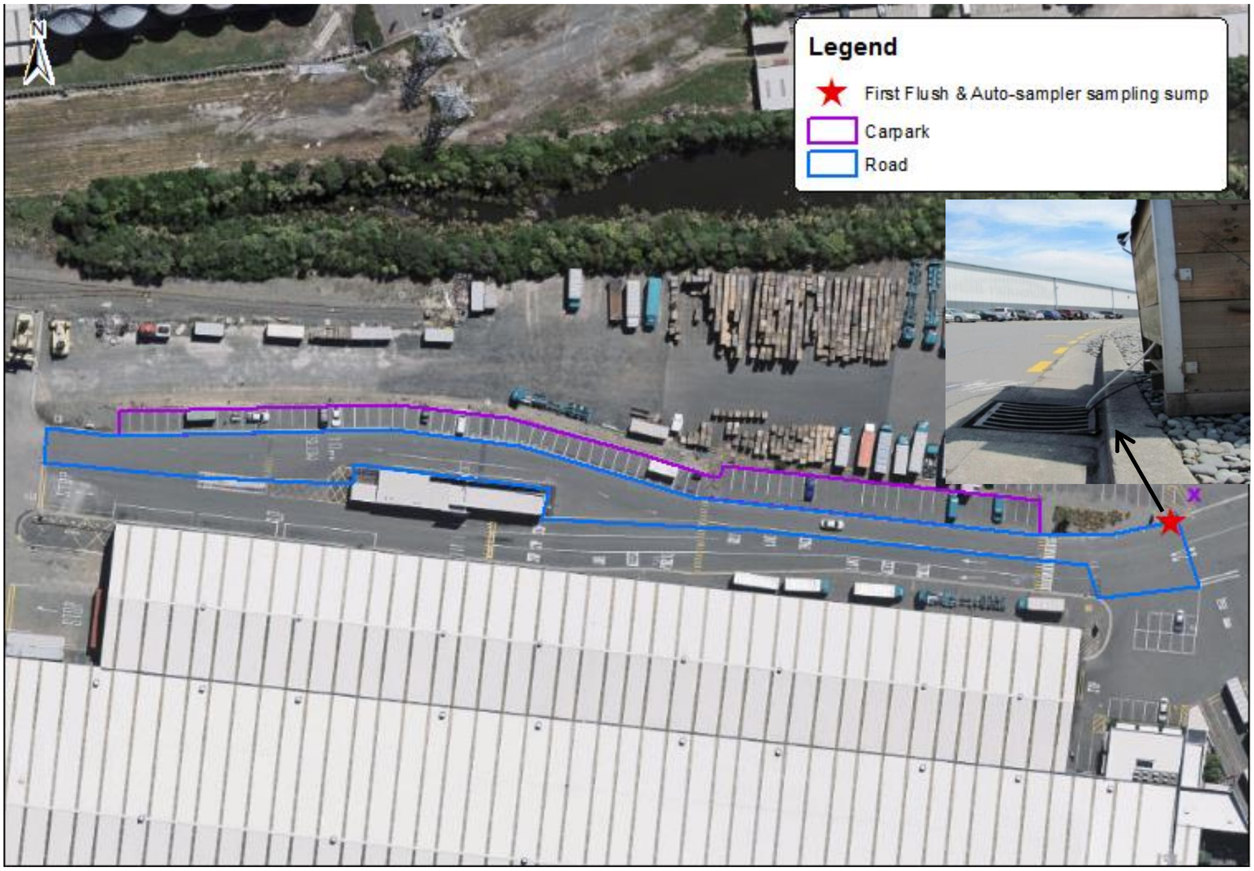


Figure 3-3: Drainage area and sampling locations at the industrial carpark

Figure 3-4: Drainage area and sampling locations at the hospital carpark

At the hospital carpark, runoff generated from the carpark (Figure 3.4) discharged directly into a single sump where first flush and autosamplers were located (Figure 3.4). Runoff from the carpark surface was discharged directly into the sampling sump X. The total drainage area at the hospital carpark was 1752 m^2 (0.2 hectares).

No scheduled maintenance activities (i.e. sweeping and cleaning) were reported during the sampling period.

3.4 Sampling equipment

A combination of Nalgene™ stormwater first flush samplers (1 L HDPE bottles) and three automatic samplers (ISCO 6712 compact portable, Teledyne Isco, USA) were used to collect the samples from the three different carparks (university, hospital and industrial).

3.4.1 First flush samplers

The first flush sampling bottles were used to collect a one-liter grab sample of first flush stormwater runoff. In this study, first flush is defined as initial 1L of runoff captures (i.e. that initial portion of runoff until 1L bottle is filled). First flush samples collected represent initial carpark runoff quality. During a sampling, samplers were positioned at a convenient place prior to a rain event and left in place until after the storm (Figure 3.5). The sampling mechanism closed after sample collection to prevent mixing and dilution with later runoff and losses due to evaporation. After the rain started, water flowed through the sampler's collection funnel, and directly into a sampler. When a sampler was full a floating ball valve seal it off the sample collection port. Once the sample was retrieved, the collection funnel was removed and closed to prevent leaking.

Figure 3-5: (a) first flush sampler, (b) an example of deployed first flush sampler (c) sampling sump

3.4.2 Autosamplers

Three automatic samplers (ISCO 6712 compact portable, Teledyne Isco, USA) were used to collect the samples from three different carparks (a university, a hospital and an industrial). These autosamplers were the primary means of collecting samples and considered most reliable in stormwater sampling by various researchers (Table 3.2). Samplers used 24 bottles each with 500 ml capacity. Samples were collected from 21 storm events during steady-state conditions. At the university and hospital carparks, autosamplers were triggered with the help of water level actuators which were placed at 4 cm and 2 cm above the outlet pipe in the sump. The autosampler placed at the industrial site was triggered with an area velocity meter set up as greater than 2 mm. Samples were time paced (at 5 mins interval) after the samplers were enabled.

Steady-state conditions were classified as period 1, period 2 and period 3. For each period, 1-8 sampling bottles (each with 500ml) were combined to make a composite sample. Similarly, 9-16 sampling bottles were categorized as period 2 and 17-24 sampling bottles were categorized as period 3.

Autosamplers are widely used methods to collect stormwater runoff samples and they record various information such as the time of sampling, the number of the next bottle, whether the sample is enabled or disabled etc.

Table 3.2: Examples of autosamplers used to monitor stormwater runoff from different land use

Authors	Sampling Methods	Location	Pollutants monitored
McCarthy et al., 2013	autosampler	Melbourne, Australia	*Escherichia coli*
Roseen et al., 2006	autosampler	Washington, US	TSS, TPD-D, dissolved inorganic nitrogen, Zinc
O'Sullivan et al., 2012	autosampler	Christchurch, NZ	TSS, heavy metals
Goonetilleke et al., 2005	autosampler	Queensland, Australia	pH, SS, TN, TP, TOC
Moores, 2009	autosampler	Auckland, NZ	Copper, Zinc

3.5 Carpark stormwater runoff quality analytical methods

All the analytical methods used for analyzing each pollutant/parameter were performed in accordance with the Standard Methods for Examination of water and wastewater jointly produced by the American Public Health Association (APHA et al., 2005).

3.5.1 Total suspended solids

Samples were vacuum filtered through pre-weighed 1.2 µm glass fibre filter papers. Where possible, coarse leaf material was excluded (following the method of Stone and Marsalek, 1996). The filter papers were placed in an oven (at 105 °C) and dried for 1 hour, and then the combined TSS and filter paper were weighed. The resultant difference in weight (i.e. the TSS) was converted to concentration (mg/L) by accounting for the volume of sample used, as follows:

$$TSS = \frac{Mass_{(solids+filte)} - Mass_{(filter)} - Mass\ (loss) * 1000000}{Volume\ of\ sample} \quad \text{(mg/L)}$$

At least two blanks were done in each batch, using deionized water, to identify the weight of glass fibre washed out of the filter paper during each filtration. An average of the blanks' results was then added onto each sample's weight to account for this loss of glass fibres.

3.5.2 Turbidity

The turbidity meter (Hach Model 2100P) was calibrated with freshly prepared formazin standards (0, 20, 100 and 800 NTU). Calibrations were checked prior to sampling with a 0-10 NTU range, 0-100 NTU range, and 0-1000 NTU range Gelex secondary turbidity standards. TSS and turbidity were measured within 48 hours in accordance with SM2540-D (APHA 2005).

3.5.3 Specific conductivity

Specific conductivity was measured using the YSI 30 conductivity meter. The meter was maintained and calibrated following the manufacturer's guidelines. Calibration of the instrument occurred prior to sampling using a standard of 0.01 M KCl (1412 μS/cm at 25 °C).

3.5.4 pH

pH was analyzed using an EDT RE 357Tx Microprocessor. The pH meter was calibrated prior to analyses with fresh 4.0, 7.0 and 10.0 S.U. buffers in accordance with the manufacturer's guidelines.

3.5.5 Heavy metals

Total recoverable metal (Zn, Cu and Pb) samples were preserved with concentrated HNO_3 (70% Fisher, trace analysis grade) to a pH < 2.0 (APHA 2005). The total recoverable metal digestions were prepared by mixing 25 ml of homogenized sample with 5 ml of HNO_3 into a 50 ml polypropylene centrifuge; the mixture was boiled for one hour in a heating block and allowed to cool. The cooled samples were filtered through an encapsulated 0.45 μm polyvinylidene difluoride (PVDF) filter (47 mm, Labserv) before ICP-MS analysis (Wicke et al., 2012). A method blank using deionized water was also done for each sample set. Dissolved metal samples were filtered through a 0.45 μm PVDF filter before being preserved with HNO_3 to a pH < 2.0. All heavy metals were analyzed by ICP-MS (Agilent) according to SM3125-B (APHA 2005). Duplicates and blanks were included in each analysis batch. Due to the addition of 5 ml nitric acid during the digestion process, which diluted the sample by 12.5% (i.e. 5 ml into 25 ml), the ICP-MS result for each total metal was multiplied by 1.2 to account for the dilution.

3.5.6 *E. coli*

Total coliform and *Escherichia coli* (*E. coli*) in the samples were measured using the Colilert 18 system. The Colilert is a commercially available enzyme substrate liquid broth medium that allows the simultaneous detection of total coliforms and *Escherichia coli.* A specially designed disposable incubation tray called the Quanti-Tray (Figure 3.6) was used to estimate the most probable number (MPN). The quanti tray was incubated for 18 to 24 h at 34 ^{0}C. The total coliform-positive reactions were counted when it turned the medium yellow and an *E. coli* positive reaction turned the medium to fluoresce under a long wave ultraviolet light. A 1:100 dilution was chosen with the Colilert technique for these carpark runoff samples. This dilution was selected to enumerate *E. coli* concentrations found in stormwater runoff (McCarthy et al., 2007). *E. coli* concentrations were used without adjustment (i.e. >2,400 was used as 2,400).

The initial 14 samples from four storm events were transported to ESR (Institute of Research and Environmental Studies), one of the crown research institutes in NZ, immediately after sample collection for analysis. The rest of the samples were analyzed in the University of Canterbury, Environmental Engineering lab using the same methods.

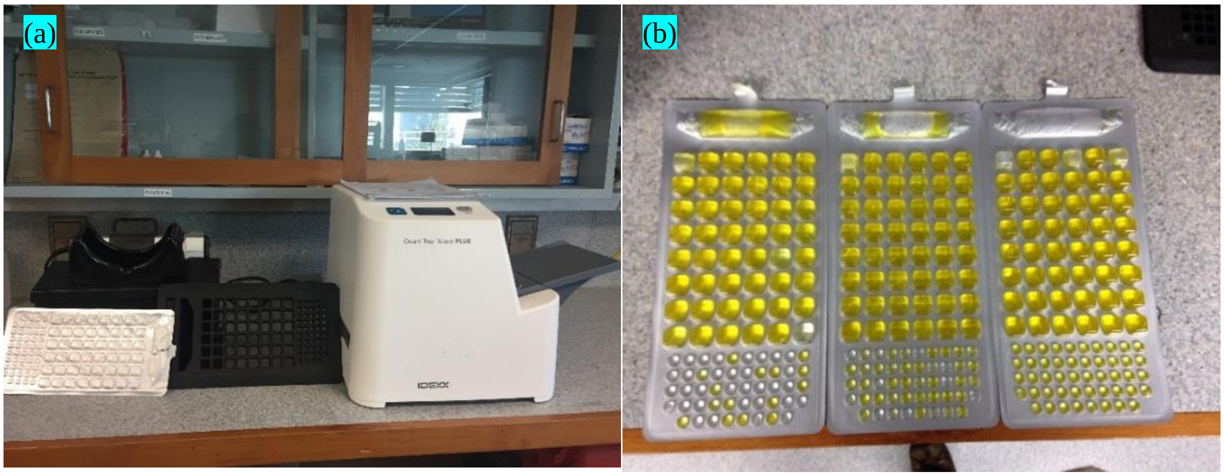


Figure 3-6: (a) IDEXX Quanti-Tray/2000 and Quanti tray sealer and (b) incubated Quanti tray

Samples were also collected for Polycyclic Aromatic Hydrocarbons analysis and collected samples were sent out to a commercial lab. PAHs concentrations were found to be consistently low (i.e <0.0001 g m-3) for most storm events. To further confirm low PAH values, sediment samples were collected from respective sumps and results were very low and insignificant for discussion and comparison purposes. Hence, PAHs were not analyzed further during the sampling period.

3.5.7 Particle Size Distribution (PSD) analysis

A Horiba LA-950 laser diffraction analyzer was used to measure the PSD on a volume basis (range of 0.1-3000 μm). The central idea in laser diffraction is that a particle will scatter light at an angle determined by that particle's size. Larger particles will scatter at small angles and smaller particles scatter at wide angles. A collection of particles will produce a pattern of scattered light defined by intensity and angle that can be transformed into a particle size distribution result.

The laser diffraction analyzer method used in this analysis has a wide range of particle coverage (0.1-3,000 μm), provides easy duplication of data and used a smaller sample volume for the analysis. The refractive index value of 1.56 (i.e. 1.17 * RI water) + 0.0001i was used to analyze stormwater runoff samples (following Charters et al., 2015 and Andrew et al., 2010).

3.6 Quality control and quality assurance

A quality assurance/quality control (QA/QC) plan has been implemented to minimize any errors in the data acquisition. All samples were collected, preserved and analyzed following the (APHA et al., 2005) guidelines. At least 10% of the samples were duplicated. Sampling instruments were calibrated and maintained according to the manufacturer's manual. All samples were analyzed within the holding time and preserved in accordance with the (APHA, 2005).

3.7 Acid wash procedure

All sampling equipment was acid washed with 10% HCl for a minimum of 3-7 days and rinsed with deionized water and dried prior to use for a subsequent event.

3.8 Sampling preservation and storage

Samples were preserved and stored in accordance to APHA guidelines (Table 3.3). 90% of samples were analyzed within the same day of collection. Though heavy metal samples were held for 6 months, all the samples for heavy metals were prepared on the day of collection. Samples for *E. coli* were prepared as soon as possible on the same day.

Table 3.3: Summary of sample preservation and storage requirements

Analytical Parameter	Container	Minimum Sample Size (ml)	Preservation	Maximum Storage	
				Recommended	Regulatory
Alkalinity	P, G	200	Refrigerate	24 hrs	14 days
Color	P, G	500	Refrigerate	48 hrs	48 hrs
Metal	P(A), G(A)= rinsed with 1+1HNO3	1000	for dissolved metal filter immediately add HNO_3 to pH <2	6 months	6 months
PH	P, G	50	Analyze immediately	0.25 hr	0.25 hr
Turbidity	P, G	100	Analyze same day, store in dark up to 24hr, refrigerate	24 hrs	48 hrs
Total Particle Size	P, G	100	Refrigerate and restored to room temperature before analysis	1-2 hrs	24 hrs
Pathogens	P, G	100	Refrigerate	6 hrs	
Hydrocarbons	P, G	100	Refrigerate	10 days	

P = plastic (polyethylene or eqv)
G = Glass
G (A) or P (A) = rinsed with 1+1HNO_3
G (B) = glass, borosilicate
Refrigerate = Storage at 4 ^{0}C±2 ^{0}C in the dark
Analyze within 15 min of sample collection = Analyze Immediately
Source: APHA 2005 pg 1-33, Ref Table 1060

3.9 Health and Safety

A health and safety plan was developed and approved by the Department of Civil and Natural Resources Engineering prior to starting sample collection. The plan was developed to identify and mitigate possible risk while working at different sites. In addition to the departmental safety protocols, special safety induction was also provided by respective site managers to comply with their health and safety protocols. The plan was utilized during each site visit.

3.10 Sampling and subsampling procedure

All sampling equipment (autosampler and first flush samplers) was set up prior to the rain event. First flush bottles were placed at the same sump for all the rainfall events. After a rain event, stormwater was collected as soon as possible. In some situations, i.e. when the storm event lasted all day and night, samples were collected in the morning for health and safety reasons. All sample bottles were labelled and stored around 4 ^{0}C and transported to the University of Canterbury, Natural Resources Engineering lab for analyses.

Samples from first flush were analyzed separately for each parameter. Each autosampler consisted of 24 sampling bottles (500 ml each) with samples collected every 5 minutes. Sampler enable and disable times were recorded electronically in the sampler. Turbidity was measured using the turbidity meter (Hach Model 2100P) for all the sampling bottles from all the carparks to observe the concentrations of suspended particles in each bottle. Higher values of turbidity were found in the first 8 bottles in each site and turbidity decreased over time in each sampling bottles. Three sets of composite samples were produced from 8 sampling bottles each. Samples were categorized as period 1 (first 40 mins, samples from first 8 sampling bottles), period 2 (41-80 mins after rain event which collect the samples from 9-16 sampling bottles and remaining was categorized as period 3 (81 to 120 mins, from 17-24 sampling bottles).

3.11 Sampling rainfall characteristics

Weather data from a Campbell weather station (Table 3.4), situated at the University of Canterbury's Department of Civil and Natural Resources Engineering building were used for the analysis. The weather station data were compared against meteorological records from the National Institute of Water and Atmosphere's (NIWA) weather station to verify its accuracy. Data between stations were similar and therefore the University's weather data, which was the closest to the carparks, were used for this research. Event average rainfall intensity, antecedent dry days (ADD), rain duration and total rain depth were monitored for all 21 storm events. The average (minimum-maximum) values were found to be: initial 10 mins rainfall intensity 3.5 (1.2-10.8) mm/h, ADD 6 (0.25-20.18) days, rain duration 3 (0.9-11.8) hours and total rain depth 5.4 (1-12.6) mm and average rainfall intensity 2.3 (0.39-6.87) mm/h.

Table 3.4: Rainfall events characteristics

Storm event	Date	10 mins rain depth (mm)	10 mins initial rain intensity (mm/h)	average intensity (mm/h)	rain depth (mm)	rain duration (h)	antecedent dry days (day)
SE1	10/09/2015	1.8	10.8	10.8	1.8	0.16	4.49
SE2	22/09/2015	0.4	2.4	0.91	2.2	2.42	2.02
SE3	27/01/2016	0.2	2.4	2.96	10.6	3.6	0.25
SE4	17/02/2016	0.4	4	2.81	7.6	2.7	20.18
SE5	15/03/2016	0.6	3.6	1.24	3.2	2.58	6.61
SE6	24/03/2016	0.2	1.2	2.05	10.6	5.17	7.5
SE7	08/04/2016	0.2	1.2	2.4	2	0.9	3.75
SE8	20/05/2016	0.6	3.6	3.3	7.8	2.3	3.76
SE9	22/05/2016	0.4	2.5	1.1	4	3.5	1.15
SE10	28/05/2016	0.4	2.5	3.23	7.8	2.4	1.3
SE11	22/06/2016	0.4	2.5	0.65	0.6	0.92	9.4
SE12	23/06/2016	0.2	1.25	0.91	1.7	1.9	1.26
SE13	08/07/2016	0.2	1.25	0.81	4.2	5.2	7.3
SE14	13/07/2016	1	6.25	6.87	12.6	1.8	5.6
SE15	03/08/2016	0.2	1.25	1.09	1	0.9	3.4
SE16	12/08/2016	0.2	1.25	0.39	4.6	11.8	4.2
SE17	26/08/2016	0.8	5	1.97	4.6	2.3	12.9
SE18	06/09/2016	0.2	1.25	1.1	1	0.9	9.7
SE19	27/09/2016	1	6.25	6.25	5	1.1	18
SE20	06/10/2016	1.2	7.5	4.6	5	1.1	1.24
SE21	14/10/2016	0.8	5	1.6	3.2	2	2.12
Average		**0.54**	**3.5**	**2.3**	**5.4**	**3**	**6**
(Min-Max)		**(0.2 - 1.8)**	**(1.2 - 10.8)**	**(0.39 - 6.87)**	**(1 - 12.6)**	**(0.9 - 11.8)**	**(0.25 - 20.18)**

3.12 Comparison with the past weather condition

Rainfall patterns during the year of sampling were compared to the average monthly rainfall from the previous five years. 2015 and 2016 were the driest years as compared to previous years (Table 3.5).

Table 3.5: Monthly rainfall amount (mm) during the sampling period compared to the average monthly rainfall pattern of Christchurch in the last five years

Month	2011	2012	2013	2014	2015	2016
Jan	56.2	39	34	17.2	7.6	99.8
Feb	36.6	24	20.4	42.4	8.4	17.6
March	49	63	22	199.6	35.2	55.4
April	67.2	34.4	62.2	224.2	66	8.6
May	42.6	9.8	127.2	35.4	15.8	104
June	58.6	88.2	220.4	68	100.8	31
July	39.6	67.6	49.4	43.4	31.2	25.5
August	81.6	138.4	44.4	17.8	52.4	38.5
September	23.6	32.4	31.8	22.6	64.4	37.5
October	98.8	64.6	54.4	18.8	9	73
November	58.8	50.4	29.2	67.6	11.2	37.5
December	67.8	88.2	65.2	18.2	50.4	42.5
Total rainfall (mm)	**680**	**700**	**760**	**775**	**452**	**570**

Note: 2015-2016 was the sampling year

3.13 Comparison of rainfall events to extreme weather conditions

Rainfall characteristics such as average rainfall intensity, depth and duration were reviewed against the Average Return Intervals (ARI) and Annual Exceedance Probability (AEP) values developed for the catchment by NIWA's High-Intensity Rainfall Design System Version 3 (HIRDS.V3) (NIWA, 2011) (Figure 3.7). The Annual Exceedance Probability (AEP) is the probability of a given rainfall being exceeded in any one year. All the sample events are considered as normal rainfall for Christchurch.

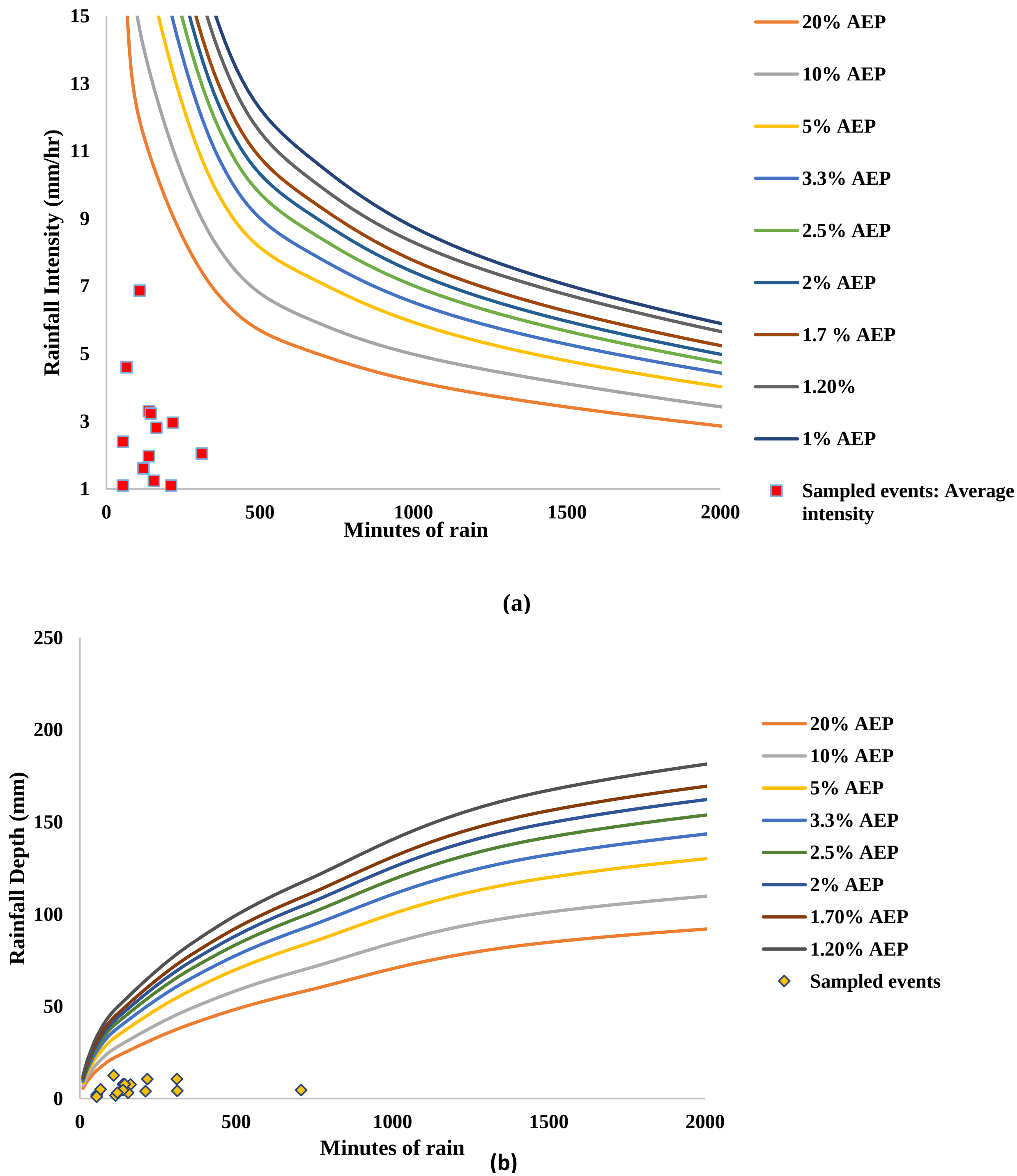


Figure 3-7: Comparison of sampled rain events to high-intensity rainfall design system (HIRDS) a) Average Rainfall intensity (mm/h) and b) Rainfall depth (mm) with minutes of rain

Chapter 4

Carpark pollutant yields from first flush stormwater runoff

4. Carpark pollutant yields from first flush stormwater runoff

4.1 Introduction

Urban carparks represent a major source of stormwater pollutants such as Total Suspended Solids (TSS), heavy metals (Zn, Cu and Pb), anthropogenic organic compounds, nutrients and pathogens (Gobel et al., 2007). Runoff from carparks is therefore considered to be a significant source of pollutants to local receiving waterways affecting aquatic life and ultimately the food chain (Tiefenthaler et al., 2001; Cochrane et al., 2010, Brown and Peake, 2006; Reddy et al., 2014; Wang et al., 2013). The quality of carpark runoff can be improved through the installation of stormwater treatment systems. However, it is critical to quantify and understand the nature of untreated carpark runoff in order to optimize the selection of stormwater treatment systems and to estimate their potential efficiency.

Vehicles are the primary source of pollutants in carparks and the majority of suspended solids picked up by stormwater runoff originate from vehicles (Tiefenthaler, 2001; Shaheen, 1975). Traffic patterns such as speed and vehicular movement, vehicle count and type (car, van or truck), maintenance activities (washing/ cleaning of vehicles) and institutional regulations (such as posted speed sign, parking hour, etc.) influence the accumulation of TSS and heavy metals on impervious surfaces (Davies et al., 2001;Sartor and Boyd 1972). Heavy metals from vehicles originate from brake pad wear products (Cu), tire (Zn), combustion exhaust, galvanized parts and railings, fuel and oil, wear of plating, bearings and bushings and other moving parts (Cu), wire corrosion, brake lining (Pb, Cu and Zn), and radiator fluid (Cu) (Amrhein and Strong 1990; Amrhein et al., 1992, Glenn, 2001, Councell et al., 2004). The accumulation of these pollutants is influenced by atmospheric deposition, topography and the size of the drainage area (Lau et al., 2009). In addition, atmospheric deposition, wind transport and various intentional and accidental spills have also been identified as major sources of pollutants (Christensen and Guinn, 1979; Davis et al., 2001).

Pollutant loads are usually higher during the initial period of storm (commonly known as first flush) as compared to later periods (Lee et al., 2002). First flush events are usually associated with small impervious areas such as highways and carparks and have been identified as one of the primary causes of deterioration of the quality of urban waterways (Barco et al., 2008). Quantifying first flush loads is critical since most treatment options are designed to treat this initial portion of runoff events (Deng et al., 2005). Build-up and wash-off mechanisms influence first flush stormwater quality in urban carparks. Pollutants will accumulate on carparks over time from vehicular traffic, from atmospheric deposition, from pavement wear and will subsequently wash-off during storm events.

Most stormwater quality studies have only considered larger catchment areas (i.e. over 100 ha), long durations and moderate to high-intensity rainfall (>5 mm/h) for the analysis of first flush pollutant concentrations (Bach et al., 2010, Sansalone et al., 1998). Stormwater quality behavior from smaller carparks (almost 100% imperviousness) with a low-intensity rainfall climate is not well understood. Furthermore, most studies have focused on urban roads and highway runoff with a wider range of geographic coverage and rainfall conditions (Lee et al., 2002, Wang et al., 2013). The contribution of low-intensity rainfall on runoff quality from different carparks within the same geographic area and under similar rainfall characteristics is not well understood. Therefore, there is a dearth of information regarding how carpark characteristics (especially traffic pattern, vehicle type, surrounding topography, drainage area) influence runoff pollutant concentrations and metal partitioning under low-intensity rainfall (86% of storms were less than 5 mm/h; during the sampling year) climate.

The main objective of this research was thus to quantify potential differences in first flush TSS and heavy metals pollutant concentrations from three different carparks (hospital, university, and industrial), within the same geographical location and under similar low-intensity rainfall conditions. A secondary objective was to assess the influence of antecedent dry days, initial 10 mins rainfall intensity and initial rain depth on the pollutant concentrations during first flush storm events. Findings from this research will help inform the selection of the most appropriate stormwater treatment systems for individual carparks.

4.2 Methods

4.2.1 Sampling sites

Three sampling sites (a hospital, a university and an industrial) were selected to assess the influence of vehicular traffic on the quality of urban carpark runoff in Christchurch, New Zealand. The sites were representative of major carpark types in the city. Geographically, the carparks were within a radius of 6 km, but the hospital carpark was located at the foothills of the Banks Peninsula whereas the other two carparks were located in the flat part of the city. Average daily traffic differs among the carparks, ranging from 600 to over 1000 vehicles a day. Carpark surfaces were mainly asphalt and their drainage area ranged between 1752 and 5036 square meters (Refer to chapter 3, section 3.2 (Table 3.1) for detail).

4.2.2 Sample collection and analysis procedure

Twenty storm events were sampled from September 2015 to October 2016. For events 1 and 2, first flush stormwater samples from the industrial site were not sampled and for event 11, the hospital carpark was not sampled due to logistics. At the hospital, 11 storm events were sampled from September 2015 to June 2016 when the carpark was operational (active carpark) and 9 storm events were sampled from July 2016 to October 2016 after when the carpark was non-operational (passive carpark).

Nalgene™ stormwater first flush samplers (1 L HDPE bottles), which meet the USA EPA grab sampling requirements, were used for sampling runoff into sumps within each of the three urban carparks. The samplers were suspended from the sump grate with a cable tie in the corner of the sump where the initial runoff would flow into the sampler (Refer to chapter 3 for detail).

All first flush samples were stored at 4 ^{0}C and transported to the University of Canterbury Environmental laboratory for chemical analysis. First flush stormwater samples were analyzed within 24 hours of the sampling. TSS were measured within 24 hours of sampling in accordance to SM2540-D (APHA 2005). TSS analysis was done via vacuum filtration (Refer to chapter 3, section 3.5.1). Samples for heavy metals (Zn, Cu and Pb) were analyzed following APHA guidelines (APHA, 2005) (Refer to Chapter 3, section 3.5.5, 3.6, 3.7 and 3.8 for detail description). Quality assurance protocols including blanks, duplicates (at least 10% of samples), standards, and instrument calibration were conducted on all occasions. Also, all first flush samplers were soaked in 10% HCl for 3 days, rinsed with deionized water and air dried before use to avoid any potential contamination. Following each sampling event, the first flush samplers were replaced with fresh acid-washed first flush samplers.

Weather data from a Campbell weather station, situated at the University of Canterbury's Department of Civil and Natural Resources Engineering building were used for the analysis. The weather station data was compared against meteorological records from the National Institute of Water and Atmosphere's (NIWA) weather station to verify its accuracy. Data between stations were found to be similar and therefore University's weather data, which was the closest to the carparks, were used for this research. Event average rainfall intensity, antecedent dry days (ADD), rain duration and total rain depth were monitored for all 20 storm events. The average (minimum-maximum) values were found to be: initial 10 mins rainfall intensity 3.5 (1.2-10.8) mm/h, ADD 6 (0.25-20.18) days, rain duration 3 (0.9-11.8) hours and total rain depth 5.4 (1-12.6) mm.

4.3 Data Analysis

Statistical analyses were conducted using IBM® SPSS® Statistics (version 23) software.

Scatter and box plots were used for initial graphical inspection of distribution patterns of runoff data. The distribution patterns of first flush runoff data were further confirmed with the Shapiro-Wilk test. Carpark pollutant concentrations were from independent observations (independent storm events), and thus non-parametric tests were selected. The Kruskal-Wallis test was performed to ascertain whether statistically significant differences existed in TSS and total metal concentrations between three carparks. Since the data were not normally distributed and had an unequal sample size (i.e. 20 storm events from university, 18 from the industrial carpark, and 8 from active hospital carpark), mean ranks were compared instead of median values (Charters et al., 2016). The Kruskal-Wallis method ranks each data point for the dependent variable (i.e the water quality parameter) irrespective of which carpark surface it is associated with (Kruskal and Wallis, 1952; Charters et al., 2016). To further identify which particular carparks differed significantly from each other, pairwise comparisons of the differences in mean rank were then performed using the Mann-Whitney U test with a Bonferonni adjustment. Data were screened for outliers prior to the analysis and only one data point for total Pb at the hospital (passive) carpark (storm event 19) was found to be an extreme outlier and was removed from the dataset.

Relationships among total metals were assessed for each carpark using Pearson correlation. Scatter plots were used for initial visual inspection to confirm the presence of a linear relationship. Metal to metal species ratios (i.e. TZn to TCu, TCu to TPb) were calculated for each metal to understand wear and tear from smaller and heavy commercial vehicles for each carpark.

Total and dissolved metals concentrations were also compared for each carpark using Pearson's correlation. Percentage partitioning was calculated to assess the dominant phase of each metal (dissolved vs particulate).

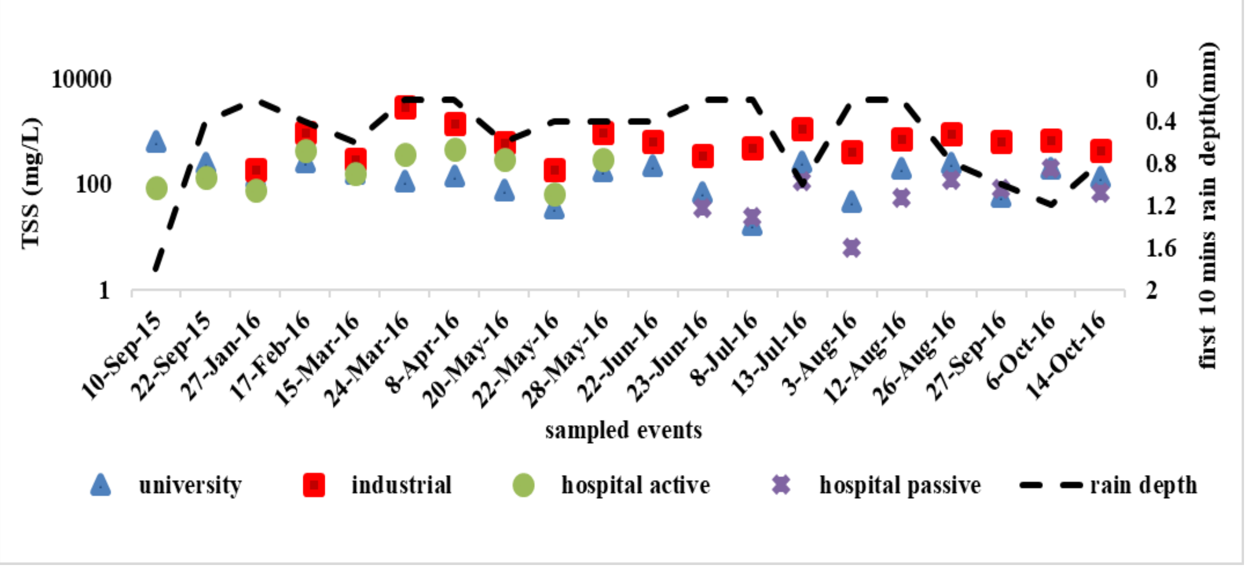
Pair wise comparisons of TSS and metals were used to identify if particular carparks differed significantly between wet and dry seasons.

4.4 Results

4.4.1 Overview of event-based pollutant concentrations from urban carparks

The concentration of TSS and heavy metals from the three different urban carparks varied over the twenty storm events monitored (Figure 4.1). The industrial carpark had significantly higher pollutant concentrations over all the storm events for TSS and total metals (Zn, Cu and Pb, Table 4.1). The university and hospital carparks mean pollutant concentrations were not statistically different.

The variation of pollutants at the university and industrial carparks was influenced by rainfall characteristics. Low positive correlations were found at the university carpark for TSS and first 10 mins initial rainfall intensity ($r = 0.49$, $p < 0.005$) and TSS and initial 10 mins rain depth ($r = 0.471$, $p < 0.005$). At the industrial carpark, TCu was positively correlated with ADD ($r = 0.470$, $p < 0.005$) and initial 10 mins rain depth ($r = 0.509$, $p < 0.005$). TPb was also positively correlated with ADD ($r = 0.503$, $p < 0.005$). The Hospital carpark did not show any correlation with rainfall characteristics.



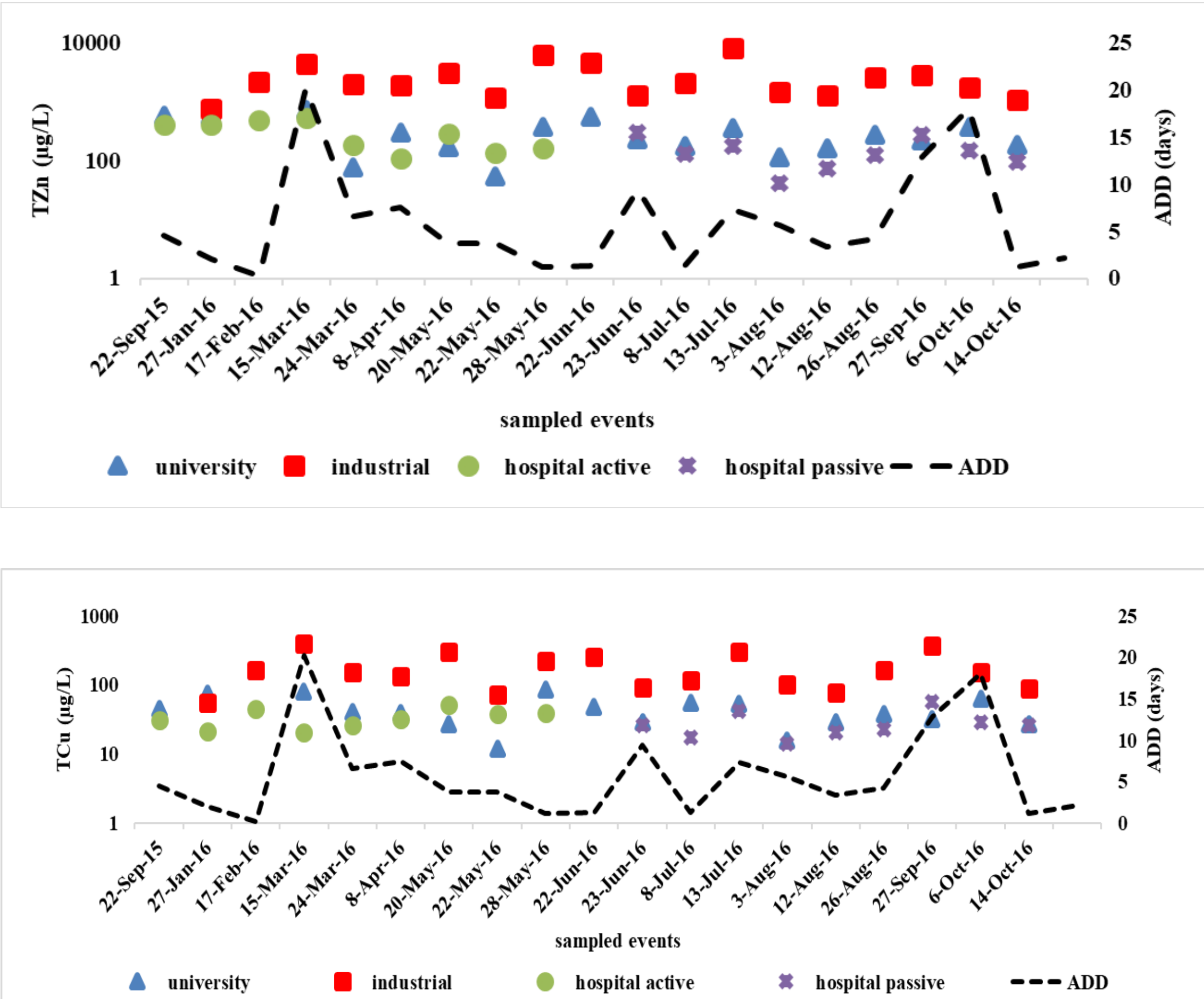


Figure 4-1: First flush pollutant concentrations in urban carpark runoff from 20 different storm events - the rainfall characteristics of each date were similar for the carparks (the industrial carpark was not monitored for storm 1 and storm 2 and the hospital carpark was not monitored for storm event 11). Heavy metals were not analyzed for storm 1

Mean concentrations of TSS were higher for the wet season (June-Sep) at the university carpark and mean concentrations of heavy metals were higher for the dry season (Oct-May) at the industrial carpark. Statistically seasons had no influence on carpark runoff quality. The hospital carpark was not included in this analysis since the hospital was not operational (passive) after the dry season.

Table 4.1: Pairwise comparison of TSS and total metals from carparks: a post hoc significance test using Mann-Whitney U test

Pairwise combination of car park types	Bonferonni adjustment			
	TSS	**Total Zn**	**Total Copper**	**Total Lead**
University-hospital (active carpark)	0.215	0.646	0.13	0.23
University-hospital (passive carpark)	0.010ˣ	0.02ˣ	0.02ˣ	0.18
University-industrial	<0.001ˣ	<0.001ˣ	<0.001ˣ	<0.001ˣ
Hospital (active carpark)-industrial	<0.001ˣ	<0.001ˣ	<0.001ˣ	<0.001ˣ
Hospital (active carpark)-hospital (passive carpark)	0.004ˣ	= 0.05ˣ	0.214	0.021ˣ
Hospital (passive carpark)-industrial	<0.001ˣ	<0.001ˣ	<0.001ˣ	<0.001ˣ

ˣ **denotes a statistically significant result. The significance level is 0.05**

4.4.2 Carpark runoff concentrations

Total Suspended Solids

TSS concentrations between carparks were significantly different from each other (X^2 (2) = 34, p <0.001, Kruskal-Wallis Test). In addition, a post hoc analysis for pair wise comparisons identified that TSS for all the carparks were statistically different except for the university-hospital active carpark (Table 4.1). TSS concentrations in first flush from the industrial carpark were higher than in the first flush from the two other carparks (Figure 4.2). Mean and median TSS values for the hospital active carpark was found to be four times higher than (Table 4.2) for the passive hospital carpark.

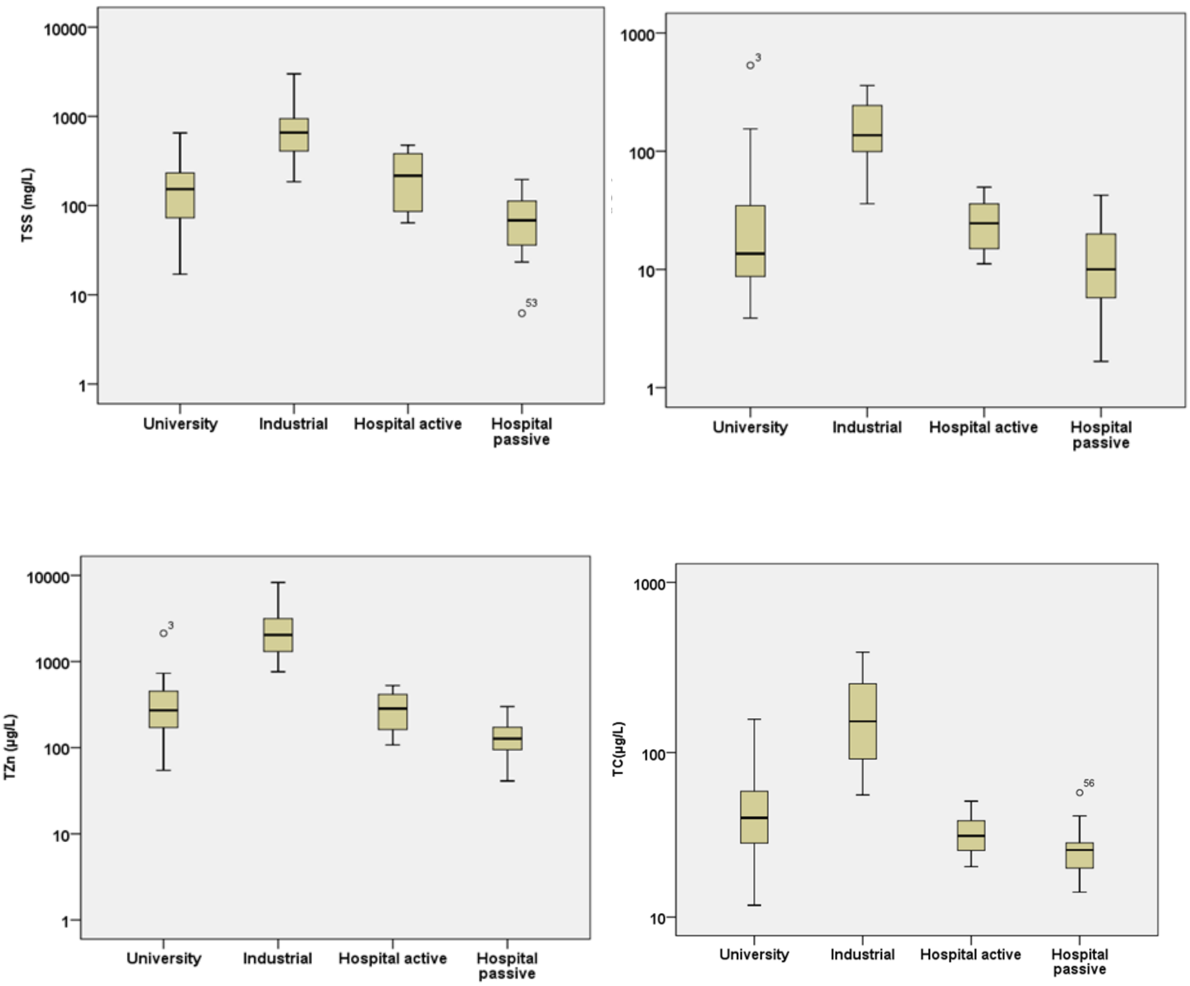


Figure 4-2: First flush pollutant concentration at each carpark ***(° denotes outliers' ± 1.5x Inter Quartile Range)***

Table 4.2: Mean, median, range, and mean rank of TSS and total metals (Zn, Cu, Pb) concentrations from different carparks, and mean ranks from Kruskal-Wallis test

Carpark type	TSS (mg/L)	TZn (µg/L)	TCu (µg/L)	TPb (µg/L)
	mean, median (range) **mean rank**			
University	174, 154 (17 - 651) **22**	401, 272 (55 - 2128) **22**	50, 41 (12 - 157) **24**	58, 14 (4 - 532) **21**
Hospital (active)	237, 196 (64 - 476) **28**	332, 236 (108 - 997) **20**	34, 32 (21 - 51) **17**	27, 25 (11 - 50) **24**
Hospital (passive)	63, 62 (6 - 120) **9**	151, 126 (41 - 300) **11**	28, 26 (14 - 58) **13**	16, 11 (2 - 42) **12**
Industrial	781, 657 (185 - 3002) **46**	2716, 2035 (761 - 8277) **46**	178, 153 (56 - 390) **45**	171, 137 (36 - 359) **44**

Total heavy metals (TZn, TCu and TPb)

TZn (X^2 (3) = 36, p <0.001), TCu (X^2 (3) = 35, p <0.001) and TPb (X^2 (3) = 29, p <0.001, Kruskal-Wallis analysis) concentrations for each carpark were found to be significantly different from each other. A post hoc analysis for pair wise comparison identified that TZn, TCu and TPb concentrations for each carpark were statistically different except for the university-hospital active carpark (Table 4.2). Pollutant concentrations at the hospital active-hospital passive carparks were also statistically different except for TCu concentrations.

The highest TZn concentrations were observed at the industrial carpark (mean and maximum of 2716 µg/L and 8277 µg/L). TZn from the industrial carpark runoff was generally at least an order of magnitude higher than from the other carparks studied (Figure 4.2). The hospital and the university carparks had similar mean concentrations despite differences in land use characteristics. TZn concentrations were reduced by half following the hospital carpark shut down. This clearly shows that metal concentrations decrease with concurrent decrease in vehicular activities, however, it will take a significant amount of time to flush off from carpark surfaces. Similarly, the industrial carpark produced the highest concentrations of TCu and TPb (mean, maximum: 178 µg/L, 390 µg/L and 171 µg/L, 351 µg/L) respectively. TCu was an order of magnitude higher than in the university and hospital carparks and surprisingly had similar mean and max values for the hospital operational and non-operational carpark.

Metal sources and vehicular wear and tear

In each carpark, linear relationships were observed between each metal (TZn and TCu, TCu and TPb, and TPb and TZn) with exceptions for the hospital (both operational and non-operational) carpark. Pearson correlation was performed to confirm the relationship between each metal for all of the carparks. The industrial carpark had the highest TZn to TCu (15:1) indicating higher wear and tear from larger commercial vehicles. The university and the hospital active carparks had similar and lower TZn to TCu ratios indicating consistent wear and tear from small vehicles.

4.4.3 Fractionation of heavy metals

A linear relationship was observed between TZn and dissolved Zn (dZn) for all the carparks except for the industrial carpark. Strong positive correlations were found between TZn and dZn concentrations for the university carpark ($r = 0.95$, $p < 0.001$), and moderate positive correlations were found at the hospital operational carpark ($r = 0.67$, $p < 0.001$) and the hospital non-operational carpark ($r = 0.66$, $p < 0.001$). A moderate positive correlation was found for TCu and dissolved Cu (dCu) for the university carpark ($r = 0.595$, $p < 0.005$). In contrast, strong positive total metals to particulate metals relationship were found for the industrial carpark (Zn: $r = 0.99$, $p < 0.001$, Cu: $r = 0.98$, $p < 0.001$, Pb: $r = 1$, $p < 0.001$). The highest percentage of dZn was 70% at the hospital operational carpark, followed by the university (65%) and the hospital non-operational carpark (62%) (Figure 4.3). The industrial carpark exhibited a lower percentage of dZn (15%) and higher percentage of particulate metals (pZn, pCu and pPb) as compared to the other two carparks studied. dCu ranged from 18% to 45%. A smaller percentage (below 9%) of dPb was measured for all sites. A large variation on % metal partitioning between the events was seen for the carparks. Even though the hospital operational carpark had the highest percentage of dissolved metals as compared to the two other carparks, mean, and maximum dissolved metal concentrations were found to be higher at the industrial carpark (Table 4.3).

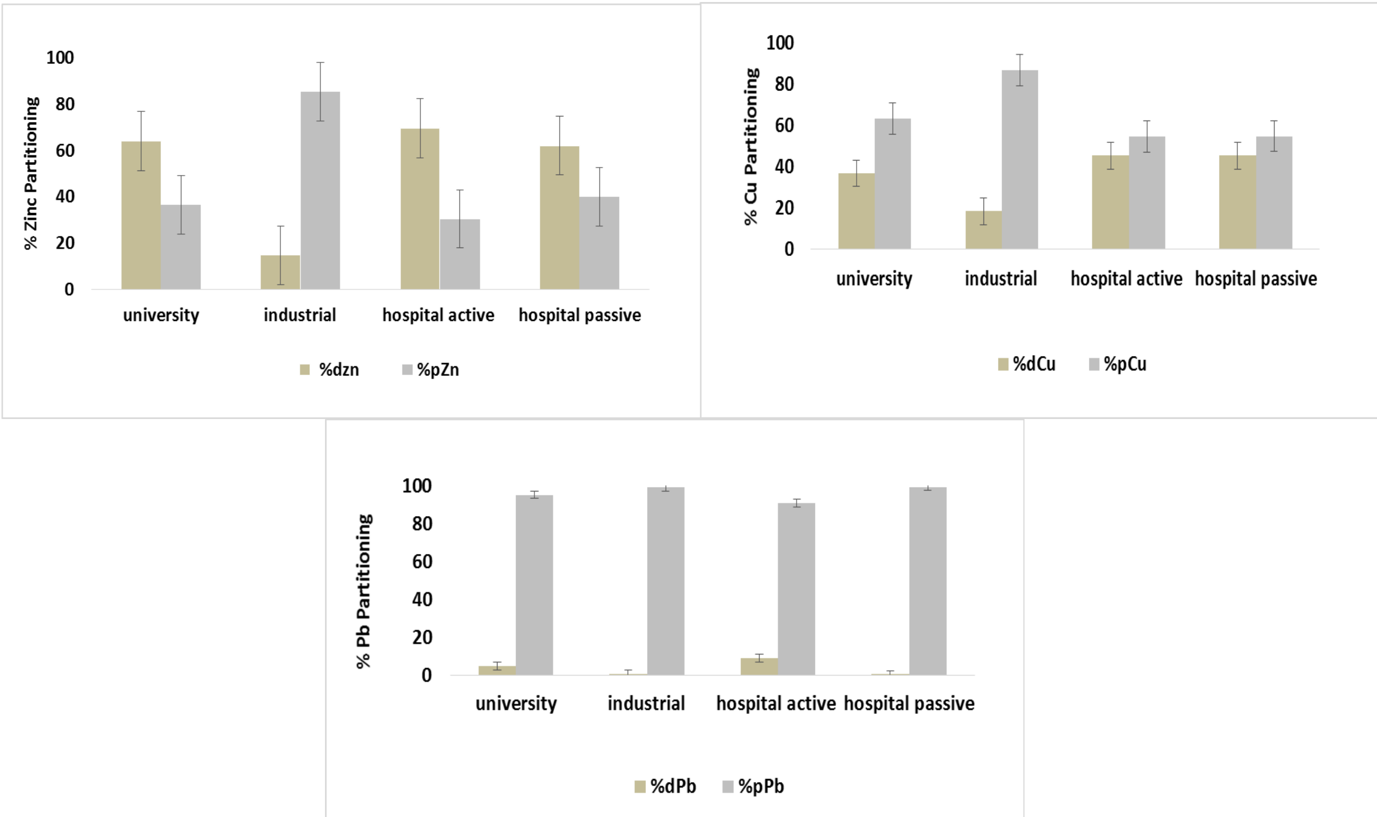


Figure 4-3: Dissolved (dZn, dCu, and dPb) and particulate (pZn, pCu, and pPb) metal partitioning for each carpark studied, + / - 1 Standard Deviation

Table 4.3: Mean, median and ranges of particulate and dissolved metals (Zn, Cu and Pb) concentrations

Carpark type	pZn(μg/L)	dZn(μg/L)	pCu(μg/L)	dCu(μg/L)	pPb(μg/L)	dPb(μg/L)
			mean, median (range)			
University	144, 104 (0-528)	256, 118 (31-2175)	31, 22 (0-115)	19, 16 (6-43)	56, 12 (0.1-32)	3, 1 (0.14-32)
Hospital (active)	92, 84 (0-240)	302, 231 (54-1001)	19, 15 (6-32)	15, 15 (9-22)	24, 23 (10-49)	2.3, 2 (0.40-11.1)
Hospital (passive)	57, 32 (0-212)	94, 62 (45-325)	15, 12 (2-50)	13, 12 (7.8-23)	14, 10 (1.19-35)	0.5, 0.5 (0.10-0.9)
Industrial	2315, 1481 (93-8123)	400, 283 (88-944)	145, 105 (34-326)	33, 27 (8-72)	170, 135 (35-359)	1.3, 1.4 (0.15-2.7)

4.5 Discussion

4.5.1 Discharge of Total suspended solids

The three urban carparks differ widely according to their land use activities (such as traffic pattern, size of vehicles, and its wear and tear). The differences in TSS concentrations between the three carparks are most likely due to carpark characteristics and surrounding land use (Gunawardana et al., 2012, Herngren et al., 2005). Higher TSS concentrations observed at the industrial carpark are influenced by the higher wear and tear from larger commercial vehicles (Garg et al., 2000, Smolders and Degryse, 2002) and the influence from rainfall parameters such as ADD and initial rain depth to some extent. TSS builds-up at the industrial carpark at a higher rate resulting in higher TSS concentrations during first flush. The industrial carpark had higher traffic counts as compared to the other two carparks studied with an average daily traffic of >1000 of which 20% were 16-wheeler commercial trucks. The higher mean TSS concentrations at the industrial carpark suggest that depending upon a frequency and nature of a vehicle, TSS concentrations can be many times higher than road runoff (Gobel et al., 2007). Similarly, median TSS at the university carpark runoff was found to be higher than road runoff reported by Charters et al. (2015) for the similar catchment. Although, vehicle count at the hospital carpark was lower than at the university, mean and median TSS concentrations were higher for the hospital operational carpark. This is probably due to contribution from atmospheric deposition and wind transport (Bourcier et al., 1980; Helmreich et al., 2010) apart from vehicular traffic. The hospital carpark was located in the foothills (Port Hills) which might have influenced TSS deposition on it. In addition, several other factors such as visiting and parking hours, the rate of manoeuvring and size of the vehicles were consistent throughout the years at the hospital carpark whereas at the university traffic was more irregular as the university closed during the semester break, team break as well as at the end of years so, it is likely that the despite the larger drainage area and higher traffic count, these other factors contributed to a difference in TSS concentrations between these two carparks.

The size of the drainage area did not have an effect on the first flush concentrations, when the ratio of the drainage area to traffic count is considered (Lau et al., 2009, CH2MHILL, 1998). In this study, drainage area ranged from (1752-5036 sq m). The ratio of the drainage area (m^2) to traffic count was high at the university carpark (5.6:1) and less for the industrial and the hospital carparks (3:1). Even though the industrial and the hospital carparks had similar ratios, mean TSS concentrations were three times higher at the industrial carpark. This finding reinforces that apart from vehicular traffic and drainage area, mode of driving (speed turning and wheel movement) and size of vehicles are also likely to influence on TSS loadings substantially.

4.5.2 Discharge of total metals

The high Zn concentrations observed at the industrial carpark are likely to be contributed from large vehicular wear and tear. Tire wear is a major contributor of Zn (Kennedy and Sutherland, 2010). Vehicle tires have a different weighted average ZnO in the thread (the part exposed to wear). Zn loads from trucks (2.1%) are higher than cars (1.2%) (Smolders and Degryse, 2002, Murphy et al., 2014). Similarly, Cu emitted from brakes pads ranged from 5.1 mg/mi to 14.01 mg/mi for small cars to large trucks respectively (Garg et al., 2000). The higher Zn and Cu at the industrial carpark is also likely due to the frequent braking and acceleration as almost half of the area of the industrial carpark is connected to a road which follows to the carpark. The TZn to TCu ratios at the university and the hospital active carparks are lower and consistent with small vehicle wear and tear.

The similar mean Cu concentrations for both hospital active and passive carparks is likely due to lower desorption property of Cu which remains longer on carpark surfaces (Gunawardana et al., 2015).

A recent study on atmospheric deposition of heavy metals in urban runoff (Murphy et al., 2015 and Charters et al., 2016) in the same geographic location found average TZn concentrations of 26.3 µg/L, TCu concentrations of 7.9 µg/L, and TPb concentrations of 2.2 µg/L, suggesting a small contribution of total metals in urban runoff from atmospheric deposition as compared to urban carparks. This result indicates the contribution of metals from atmospheric deposition is minimal as compared to vehicular activities in the study area.

4.5.3 Operational (active) vs non-operational (passive) carparks

A significant decrease in TSS and metal concentrations at the hospital passive carpark further suggest that, vehicular traffic is the main contributor of TSS and heavy metals build-up. A similar TCu concentration at the operational and non-operational carparks suggest that metals (especially Cu) will remain in the environment for a longer period as not all storm events completely clean carpark surfaces. Even when the carpark was non-operational, it takes a significant amount of time to flush off metals from the hospital carpark especially in a low-intensity rainfall climate.

4.5.4 Implications for treatment of TSS, particulate and dissolved metals

Results from TSS and heavy metals concentrations (both dissolved and particulate) indicate the industrial carpark had the highest concentrations of pollutants. Removal of TSS from the industrial carpark significantly reduces the concentration of heavy metals since the majority of metals were in particulate form. Despite this, the industrial carpark still had a significant amount of dissolved metals which need to be addressed while designing stormwater treatment systems. Poor correlation of total heavy metals with dissolved fractions in other carparks indicated that reduction of total heavy metals could not help in the reduction of dissolved metals. Many of the stormwater treatment systems are designed to remove particulate matter such as TSS including particulate heavy metals through filtration and sedimentation. Significant differences in the pollutant concentrations between the industrial and other two carparks suggest land use based treatment systems are essential. A similar concentration of pollutants at the university and hospital carparks suggest similar treatment systems could be employed whereas, treatment systems at the industrial carpark should be given priority to reducing dissolved metals in runoff treatment programs.

In New Zealand and elsewhere, BMPs such as retention ponds and constructed wetlands are preferred in the treatment of non-point source pollutants. Various studies show stormwater treatment systems such as retention basins can remove high percentage of coarse particles and particulate bound contaminants; however, they tend to be less effective in removing dissolved contaminants (Borne et al, 2013). Though these designs are considered low-cost solutions to stormwater contaminant removal (Westholm et al., 2014), they require large land areas (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 filtration systems for their ability to remove both particulate and dissolved contaminants from urban stormwater in areas with restricted space (Hipp et al., 2006).

Hence, for the industrial carpark, commercial treatment devices (with good filtration system) can be retrofitted directly to carpark sump before entering to nearby waterways.

The findings also indicate that stormwater treatment systems that capture or treat the initial portion of stormwater discharge from these carparks are likely to provide long term environmental benefit. Different first flush estimation criteria such as the first 12.7 mm of runoff per impervious area (Schueler, 1987), or volume of runoff by a 19 mm rainfall (State of California, 2001) or removal of at least 50% of the constituent mass in the first 25% of the runoff volume (Wanielista and Yousef, 1999) are all overly conservative for the carparks analyzed in this study where average rain depth was 5.4 mm with a maximum of 12.6 mm. For these carparks, treating the first flush runoff from a small portion of the event runoff volume is considered a more economical approach for reducing pollutants (Barco, 2008). The treatment of first flush runoff can lead to overall improvements in the performance of the treatment systems (Li et al., 2008). However, several factors need to be considered when designing/ implementing land use based suitable treatment systems such as sizing, cost-effectiveness, trapping as well as treatment efficiency of pollutants of concern.

4.6 Conclusions

This chapter quantifies potential differences in first flush pollutants from three different urban carparks. The major findings were enumerated as follows:

1) Urban carpark runoff quality varies significantly with carpark characteristics. The differences in the quantity of pollutants between the carparks were largely influenced by traffic count and the size of the vehicles. Despite smaller drainage area and lower traffic volume, the hospital carpark had similar pollutant concentrations as compared to the university carpark, which was attributed to its local topography and irregular traffic patterns. The correlations between each metal at the university and the industrial carparks indicated that metals originate from similar sources. In addition, the higher ratios of different heavy metals at the industrial carpark indicated relatively higher wear and tear from larger commercial vehicles.

2) Rainfall characteristics mainly ADD, initial 10 mins rainfall intensity and rain depth had a little influence (a low positive correlation) over pollutant concentrations at all the carparks suggesting that vehicular activities are likely to be the dominant source of deposited pollutants.

3) Application of treatment strategies should aim to remove large portions of dissolved metals from each carpark. Although some Best Management Practices (BMPs) such as swales, rain garden, filter strips and wetlands are proven to be efficient in the removal of a larger portion of pollutants, they require extra space as well as additional space burden to already existed carparks. Consideration of the total pollutants concentrations is necessary for the selection of suitable stormwater treatment systems for individual carparks. In addition, understanding of pollutant loads during steady-state is necessary from these carparks to facilitate the suitable treatment options.

CHAPTER 5

Influence of low-intensity rainfall and traffic characteristics on pollutant yields from steady-state stormwater runoff

5. Influence of low-intensity rainfall and traffic characteristics on pollutant yields from steady-state stormwater runoff

Substantial degradation of water quality in urban aquatic ecosystems can occur when stormwater runoff from impervious surfaces is channeled directly into local waterways as occurs in Christchurch and other cities around New Zealand. Stormwater runoff washes pollutants such as nutrients, heavy metals, hydrocarbons, pathogens and other organic chemicals from industrial, commercial and residential areas and discharges them directly to urban waterways (Bannerman et al., 1993). The sources and concentrations of these pollutants and their contributions to urban stormwater runoff are heavily dependent on land use and rainfall characteristics (Hatt et al., 2004). Various factors such as land use and rainfall conditions play important roles in influencing the pollutant build-up and wash-off process during steady-state conditions (Loucks, 1998; Ball et al., 2000; Lee and Bang, 2000). Pollutant wash-off increases with rain depth as more pollutants are removed by the sheer stress imparted by surface flow (Vaze and Chiew, 2002) and is also likely to continually increase with duration of rainfall as pollutants will be removed throughout the rain event, unless availability of pollutants on the surface is depleted (Opher and Friedler, 2010).

Monitoring studies on different impermeable surfaces have shown that pollutant concentrations are substantially higher during the initial period of the runoff hydrograph, commonly known as the first flush phenomenon (Charters et al., 2015; Deletic and Maksumovic, 1998; Gupta and Saul, 1996). However, depending upon land use and rainfall conditions, total pollutant loads during steady-state might be higher than those in the first flush. For example, pollutant concentrations might be lower in the steady state period, but the duration of this flow is much longer than that of first flush thus resulting in higher loads. Therefore, it is important to characterize and quantify pollutant loadings both from first flush (Chapter 4) and a steady-state in order to establish the benefit and efficiency of suitable stormwater treatment options for individual land use. Furthermore, most studies considered roof, road (highways) and larger catchment to analyze the effect of land use mainly in high and moderate intensity (≥5 mm/h) rainfall conditions. There is a dearth of knowledge on how low-intensity rainfall (≤5 mm/h, as reported by NIWA 2011) effect pollutant loads in smaller catchments such as impervious carparks. In addition, the role of ADD, rain depth and rain intensity on pollutant loads in urban carparks are not well understood, particularly in steady-state flows following the first flush. By understanding the factors that influence pollutant loading in carparks during steady-state runoff, suitable stormwater treatment systems can be implemented.

5.1 Objectives

This chapter presents untreated carpark runoff quality results undertaken during 21 rainfall events. The key objectives of this chapter are as follows:

1. To understand differences in TSS and heavy metal loadings (dissolved and particulates) for various impervious carparks during steady-state as a function of traffic characteristics (such as traffic patterns, nature of vehicles and other factors such as surrounding topography.

2. To understand the relationship between pollutant loadings (yield/m^2) with rainfall characteristics (rain depth, rain duration and antecedent dry days).

5.2 Methodology

5.2.1 Overview

A detailed description of sampling sites, layout, lab analysis and statistical analysis are provided in Chapter 3 (section 3.3, 3.4, 3.5.2). In this study, three automatic samplers (ISCO 6712 compact portable, Teledyne Isco, USA) were used to collect samples from three different land uses (university, hospital and industrial). These samplers were the primary means of collecting samples for steady-state runoff. Each sampler used 24 bottles each with 500 ml capacity. Samples were categorized as period 1 (first 40 mins, samples from first 8 sampling bottles), period 2 (41-80 mins after rain event which collect the samples from 9-16 sampling bottles and the remaining was categorized as period 3 (81 to 120 mins, from 17-24 sampling bottles). For all the carparks, separate turbidity tests were carried out for each sampling bottle to understand suspended sediments trends. Then, composite samples were made with respect to each period (1, 2, and 3) for analysis. Untreated steady-state runoff samples were collected from 21 storm events from September 2015 to October 2016 from three urban carparks. All steady-state samples were analyzed for TSS, total and dissolved metals (Zn, Cu and Pb) and also for Polycyclic Aromatic Hydrocarbons (PAHs). Due to a lower concentration of PAHs, further analysis of PAHs in sump sediment was carried out. The PAH values were found to be lower for sump sediments too and thus, no further analysis was carried out. Due to sampling logistics, not all the carparks were sampled for every storm event. The number of samples collected and analyzed per site is presented in (Table 5.1).

Table 5.1: Number of samples collected for TSS and heavy metals during steady-state periods

Steady-state	University	Hospital (operational)	Hospital (non-operational)	Industrial	Total samples analyzed
TSS	46	15	20	34	115
Heavy metals	276	90	120	204	690

Prior to the statistical analysis, pollutant concentrations were converted into yield (load) per square meter to enable a normalized comparison between each carpark. Pollutant loads in each carpark during each steady-state period (period 1: first 40 mins after a rainfall event, period 2: 41-80 mins after rainfall event and period 3: 81-120 mins after rainfall event) were multiplied by rain depth of each steady-state period and respective drainage area of each carpark (eqn 1). Total runoff volumes were calculated for each period and multiplied with pollutant concentrations to achieve total yield per square meter for each carpark (eqn 2).

$$\text{Volume (v)} = \text{rainfall depth (mm)} \times \text{area of carpark (sq. m)} \qquad (1)$$

$$\text{Pollutant yield} = \text{volume} \times \text{pollutant concentration} \qquad (2)$$

Note: (Pollutant yield = pollutant yield (mass)/the area of the respective carpark)

Volume (m^3) is the volume of runoff from each carpark, rainfall depth (mm) is total rain depth for each steady-state period, and area (m^2) is drainage area for each carpark.

Following assumptions were made while calculating pollutant yields:

1) Time of concentration is zero (time of concentration would not have much impact in smaller catchments)

2) All rainfall becomes rainfall (carpark surfaces were all impervious, hence neglecting loss from other processes such as percolation)

5.2.2 Statistical analysis

Statistical analysis was done using IBM®'s SPSS® Statistics (Release 23.0) software.

Comparison of differences across three carparks

Initially, a Shapiro- Wilk test (Charters, 2016) was done to assess the distribution pattern of the steady-state data. The distribution was not normal and thus non-parametric tests were selected. A Kruskal-Wallis test was performed to ascertain whether statistically significant differences in TSS and total metal loads exist between the three carparks (refer Chapter 4 for a detailed explanation of the selection of the Kruskal-Wallis test). Pairwise comparisons were then performed with a post hoc significance test using the Mann-Whitney U test. These multiple comparisons were used to identify which carparks differed significantly from each other.

Relationship between TSS and heavy metals (dissolved metals)

A Pearson correlation analysis was performed to identify the strength of the relationship between TSS and total metal yields for all of the carparks. Scatter plots were used to confirm the linear relationship between TSS and heavy metals. Data were screened for outliers prior to the correlation analysis. The data were log-transformed for normality and confirmed with a Shapiro-Wilk analysis and Q-Q plots.

Ratios of total Zn to total Cu

The relationship among total metals was compared for each carpark to analyze the proportionally dominant metals in each carpark. Metal to metal species ratios were calculated. These ratios can be used to identify the origin of metals (i.e. small or heavy commercial vehicles) for each carpark.

Relationship of pollutants with ADD and rain depth

The data were divided into three categories (ADD <3 days, 3-6 days and >6 days) to investigate the relationship of ADD with total pollutant load. The strength of the relationship was examined using Pearson's correlation analysis. The data were log-transformed for normality and confirmed with Shapiro-Wilk analysis and Q-Q plots. Similarly, to investigate the relationship between rainfall depth and pollutant yields, data were categorized as rain depth <2 mm, 2-5 mm and >5 mm. The strength of the relationship was examined using Pearson's correlation analysis. Normality was checked prior to Pearson's correlation analyses.

5.3 Results

5.3.1 Pollutant yields in stormwater runoff from urban carparks

There were significant differences in TSS and metal yields between different urban carparks and within different periods of storm events. The Kruskal-Wallis analysis among each carpark and steady-states showed that, pollutants differ significantly (TSS (X^2 (11) = 49, p <0.001), TZn (X^2 (11) = 57, p <0.001), TCu (X^2 (11) = 36, p <0.001), and TPb (X^2 (11) = 54, p <0.001) To further analyze which carpark and steady-state periods differ significantly, a pairwise comparison of TSS and total metals from each carpark using a post hoc significant Mann-Whitney U test was performed.

A post hoc analysis for pair wise comparisons (Table 5.2) between the carparks and within the different steady-state periods identified that TSS, TZn, TCu and TPb yield were statistically different for period 1 beween university-industrial and hospital-industrial carparks. For all carparks, pollutant yields were not statistically different for period 2 and period 3 for all of the pollutants and were not presented in the (Table 5.2). As expected, First flush pollutant yields were found to be higher than the corresponding steady-states (period 1, period 2 and period 3) yields for all of the carparks sampled. There was a subsequent reduction in mean pollutant yields from period 1 to period 3 (Table 5.3). However, at the university carpark, mean pollutant yields were higher during period 2 as compared to period 1. This is likely due to the sampling layout of the university carpark, which is discussed in Chapter 3.

Table 5.2: Pairwise comparison of TSS and total metals from each carpark: post hoc significance test using Mann-Whitney U test

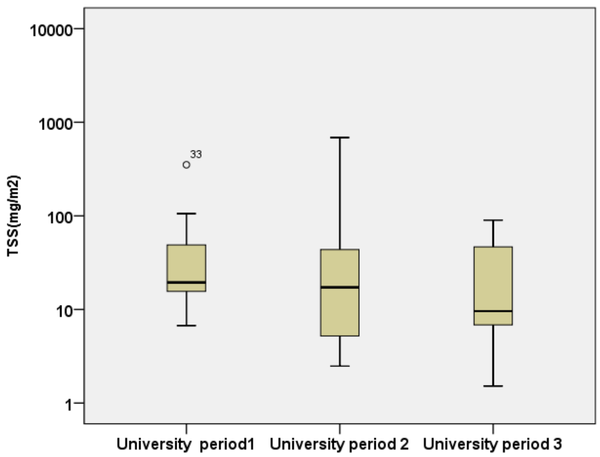
Pairwise comparison of carpark type	p values with Bonferonni adjustment			
Pairwise combinations of car parks during period 1	**TSS**	**Total Zn**	**Total Copper**	**Total Lead**
University-hospital (active carpark)	0.68	0.1	0.76	0.36
University-industrial	<0.002 ˟	<0.001˟	<0.002˟	<0.001˟
Hospital (active carpark)-industrial	<0.012˟	<0.001˟	<0.01˟	0.08

˟ denotes a statistically significant result. The significance level is 0.05.

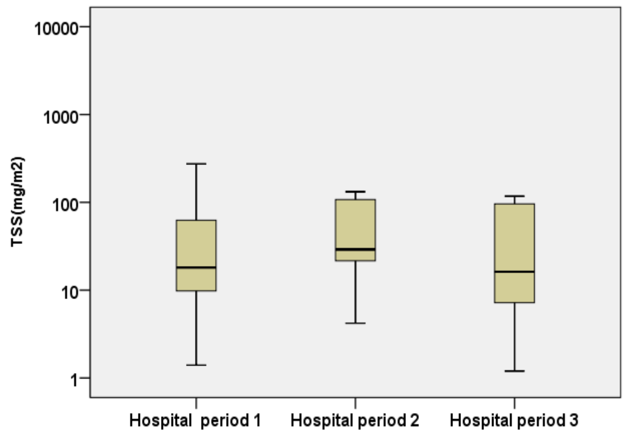
Similarly, steady-state pollutant yield between each period was not statistically different (except for the industrial period 1 and period 3) for all of the carparks.

Table 5.3: Mean, median and (min-max) of TSS and total metals (TZn, TCu, TPb) yield for different carparks and within the different periods, and mean ranks from Kruskal-Wallis test

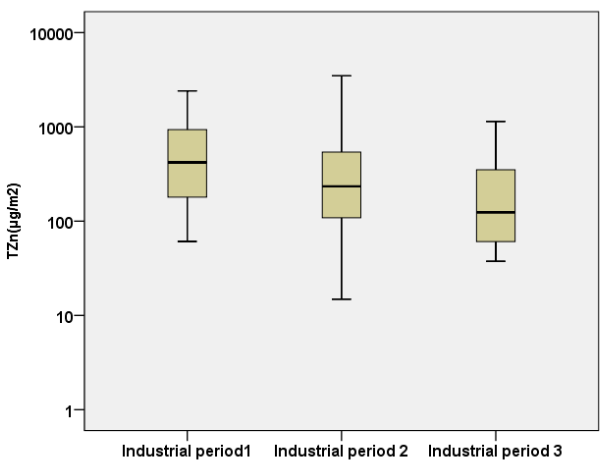
Urban Carparks	Pollutant yield	First Flush	Period 1	Period 2	Period 3
		mean, median, *std error* (range) **mean rank**			
University	TSS (mg/m^2)	125, 45, *57* (3 - 1172) **78**	50, 19, *20* (7 - 352) **60**	67, 17, *42* (2 - 686) **51**	28, 10, *9* (2 - 90) **42**
	TZn (µg/m^2)	170, 109, *47* (15 - 851) **65**	152, 101, *42* (18 - 699) **65**	195, 89, *83* (12 - 1295) **59**	82, 64, *20* (14 - 260) **47**
	TCu (µg/m^2)	23, 14, *5* (3 - 68)**72**	16, 12, *3* (1 - 64) **59**	20, 12, *6* (1- 90) **59**	14, 10, *5* (2 - 59) **50**
	TPb (µg/m^2)	26, 9, *12* (1 - 231) **73**	5, 3, *2* (0.26 - 27) **48**	9, 3, *4* (0.25 - 64) **49**	4, 1, *2* (0.46 - 18) **37**
Industrial	TSS (mg/m^2)	310, 227,*66* (38 - 1121) **121**	233, 116,*73* (14 - 829) **106**	163, 36, *94* (3 - 1056) **77**	45, 18, *20* (5 - 185) **55**
	TZn (µg/m^2)	1347, 711, *449* (152 - 8277) **125**	823, 420, *230* (61 - 2406) **112**	648, 234, *315* (15 - 3486) **91**	315, 124, *136* (38 - 1138) **77**
	TCu (µg/m^2)	81, 58, *19* (11 - 305) **114**	112, 48, *50* (5 - 705) **106**	42, 21, *17* (2 - 159) **81**	23, 12, *7* (3 - 62) **68**
	TPb (µg/m^2)	81, 49, *21* (7 - 359) **121**	45, 29, *13* (4 - 155) **105**	36, 11, *17* (0.74 - 179) **86**	17, 6, *6* (2 - 50) **79**
Hospital (active carpark)	TSS (mg/m^2)	99, 95, *18* (15 - 180) **96**	59, 29, *25* (4 - 132) **56**	33, 36, *10* (9 - 62) **71**	36, 36, *32* (4 - 68) **56**
	TZn (µg/m^2)	123, 83, *32* (22 - 317) **64**	95, 20, *30* (42 - 209) **43**	76, 56, *29* (17 - 166) **57**	43, 43, *11* (32 - 53) **45**
	TCu (µg/m^2)	13, 13, *3* (4 - 31) **59**	20,20, *4* (10 - 31) **56**	22, 14, *52* (5 - 52) **81**	14, 14, *1* (13 - 15) **61**
	TPb (µg/m^2)	11, 8, *3* (2 - 25) **75**	14, 14, *5* (2 - 26) **69**	6, 5, *3* (2 - 16) **79**	3, 3, *1* (2 - 4) **53**



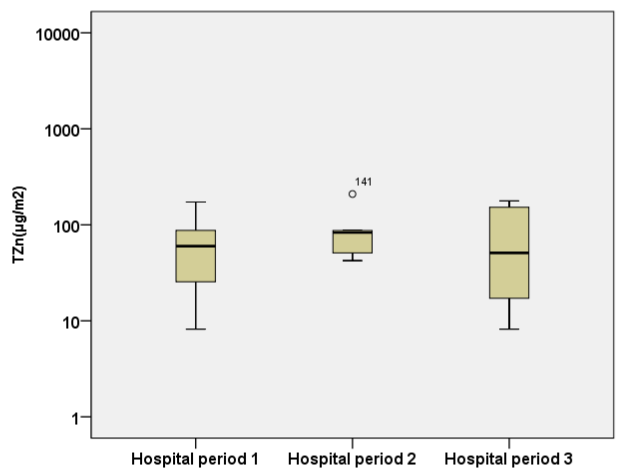
TSS(mg/m2)
10000
1000
100
10
1
33
University period1
University period 2
University period 3



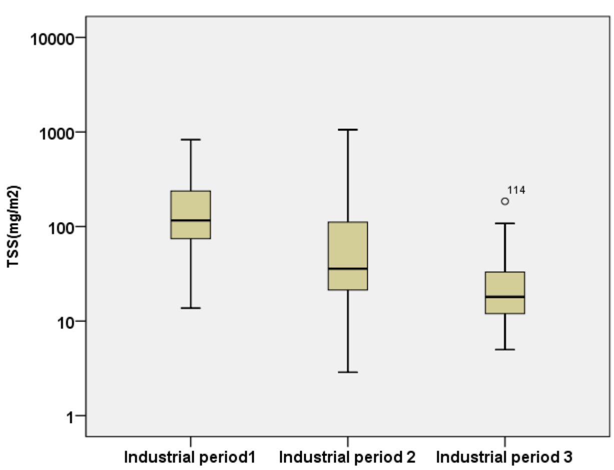
TSS(mg/m2)
10000
1000
100
10
1
Hospital period 1
Hospital period 2
Hospital period 3



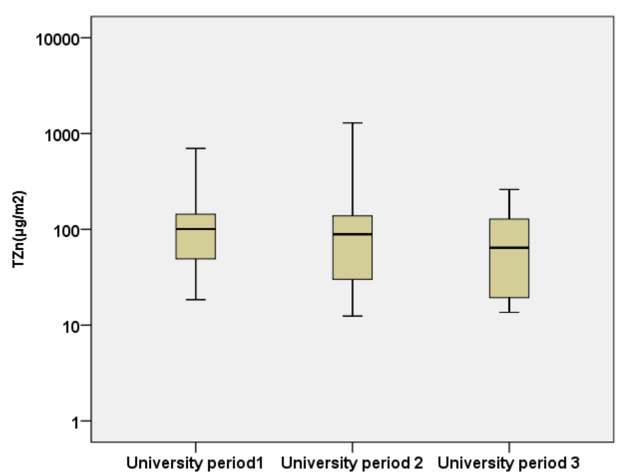
TZn(µg/m2)
10000
1000
100
10
1
Industrial period1
Industrial period 2
Industrial period 3



TZn(µg/m2)
10000
1000
100
10
1
141
Hospital period 1
Hospital period 2
Hospital period 3



TSS(mg/m2)
10000
1000
100
10
1
114
Industrial period1
Industrial period 2
Industrial period 3



TZn(µg/m2)
10000
1000
100
10
1
University period1
University period 2
University period 3

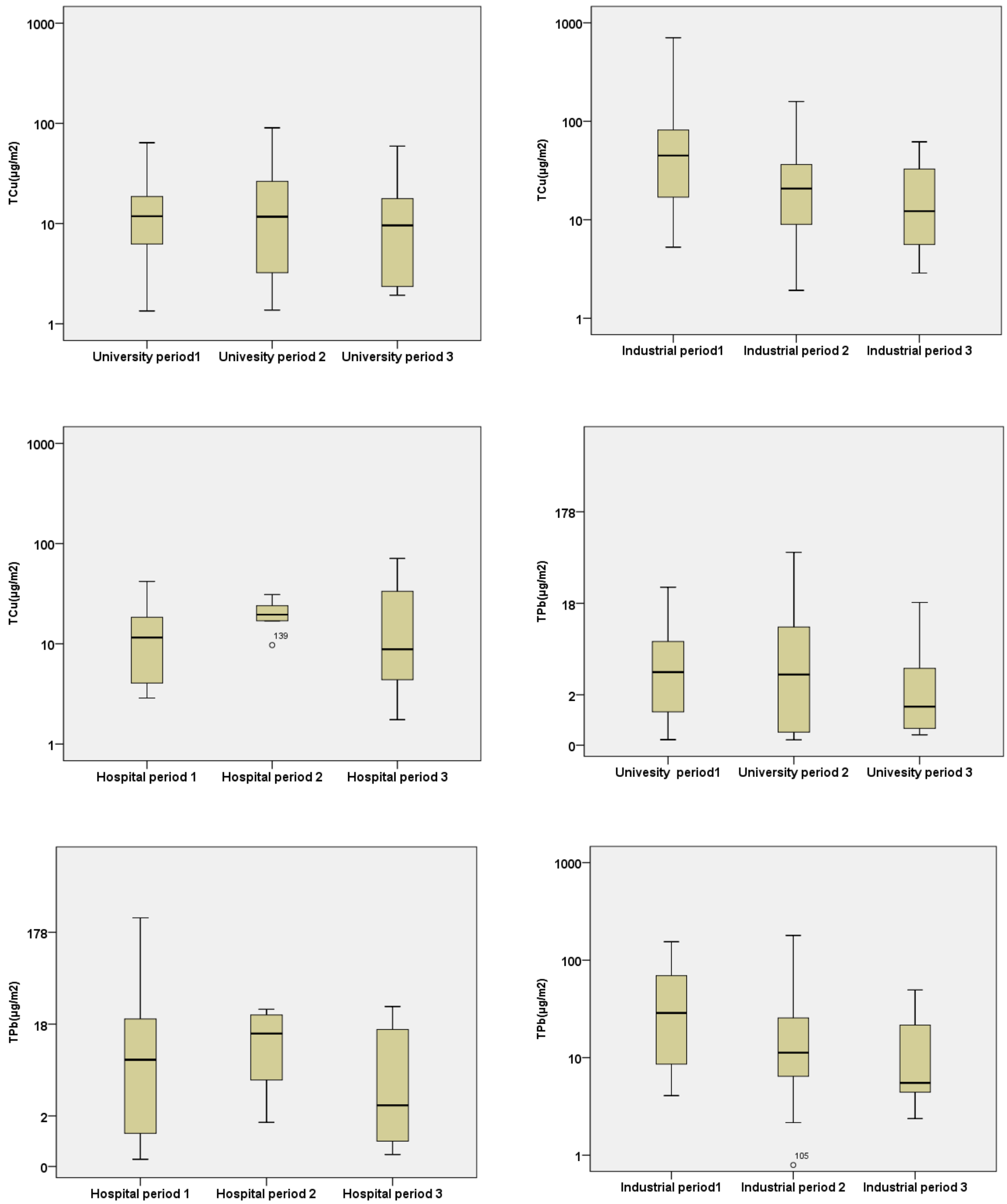


Figure 5-1: Distribution of TSS and heavy metals yield for each carpark at different steady-states (° denotes outlier's ± 1.5x Inter Quartile Range (IQR), * denotes outlier's ± 3x IQR). Note the varying unit for TSS (mg/m^2) and metals ($\mu g/m^2$)

A visual inspection of data in (Figure 5.1) showed that median metal yields were similar at the university carpark for all the steady-state periods whereas subsequent reduction in pollutant yields at different steady-state periods were noted at the industrial carpark. Relative median metal yields were higher during period 2 at the hospital carpark.

Based on a post hoc significance test using the Mann-Whitney U test, significant differences in TSS were found between the university and industrial carparks and between industrial and hospital carparks during period 1. Pb was only the metal which was significantly different during period 3 in each carpark.

5.3.2 TSS and heavy metals relationship

A Pearson correlation analysis was performed to identify the strength of the relationship between TSS and total metal yields for the carparks. TSS and total metals were significantly correlated at the university (except for Zn for periods 1 and 2) and the industrial carparks. The hospital carpark showed a strong positive correlation ($r = 0.9$, $P < 0.05$**) for total Pb during period 1 (Table 5.4). However, no correlation was found for TZn and TCu at the hospital carpark.

Table 5.4: Pearson correlations between TSS and total metal yield for carparks and between different periods of storm events

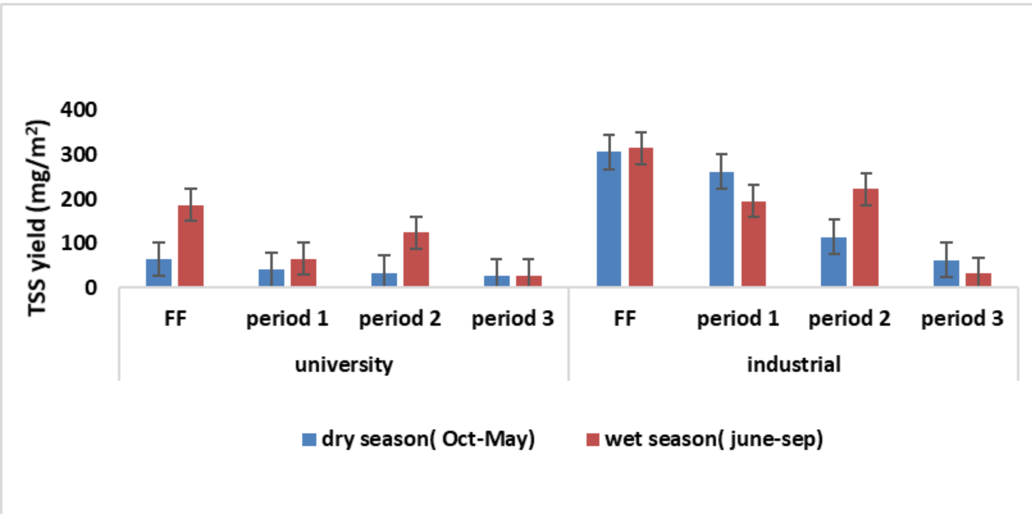
Pearson correlation between TSS and total metal yields/m^2			
Total Metal yield/m^2	**Period 1**	**Period 2**	**Period 3**
		University carpark	
Total Zinc	r = 0.65, p = 0.004**	r = 0.87, p <0.001**	r = 0.81, p <0.001**
Total Copper	r = 0.70, p <0.001**	r = 0.92, p <0.001**	r = 0.84, p <0.001**
Total Lead	r = 0.72, p <0.001**	r = 0.89, p <0.001**	r = 0.88, p <0.001**
		Industrial carpark	
Total Zinc	r = 0.91, p <0.001**	r = 0.95, p <0.001**	r = 0.87, p <0.012**
Total Copper	r = 0.81, p <0.017*	r = 0.91, p <0.001**	r = 0.79, p <0.049*
Total Lead	r = 0.83, p <0.001**	r = 0.94, p <0.001**	r = 0.82, p <0.037**
		Hospital active carpark	
Total Zinc	r = 0.84, p <0.06	r = 0.90, p = 0.03	r = 0.9, p = 0.10
Total Copper	r = 0.58, p = 0.30	r = 0.70, p = 0.18	r = 0.02, p = 0.98
Total Lead	r = 0.97, p <0.05**	r = 0.91, p <0.02**	r = 1, p <0.02**

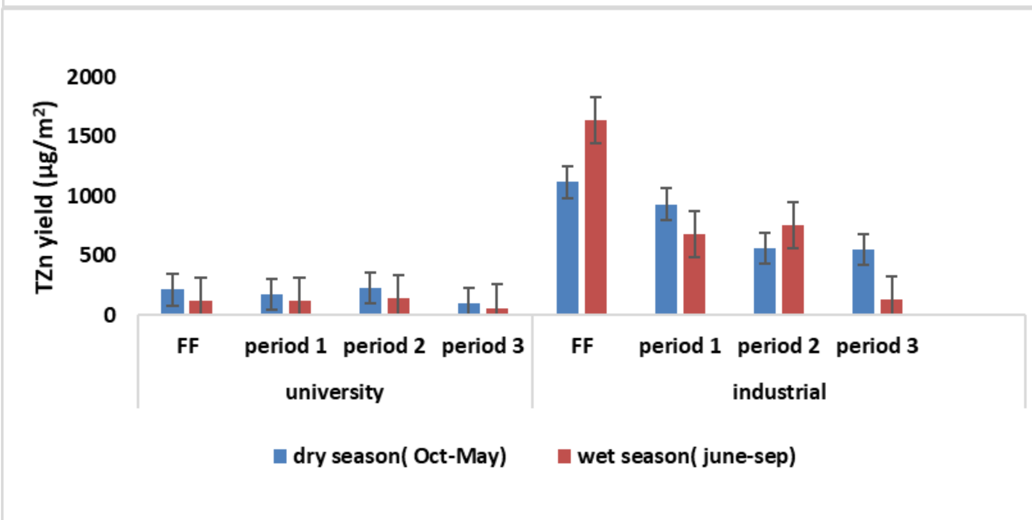
*** Denotes statistically significant result. The significance level is 0.05**

**** Denotes statistically significant result. The significance level is 0.01**

5.3.3 Seasonal variations in pollutant yields from three carparks

Seasonal variation in pollutant yields was analyzed to identify the influence of the wet (June to September) and dry (October to May) seasons on pollutant build-up and wash-off. There was a fair amount of variation between the carparks and within the different steady-state periods (Figure 5.2). Mean TSS yields were higher during the wet season at the university carpark but similar for the industrial carpark. There were no obvious differences in mean metal yields during the wet and dry seasons in both carparks. These visual results (Figure 5.2) were further confirmed with a pairwise *t*-test. The average 10 min intensity, average 10 mins rain depth, and average intensity were higher during the wet season as compared to dry season. Longer duration and larger ADD were also observed during the wet season as compared to dry season. The differences in rainfall during the wet and dry season were presented in Appendixes.





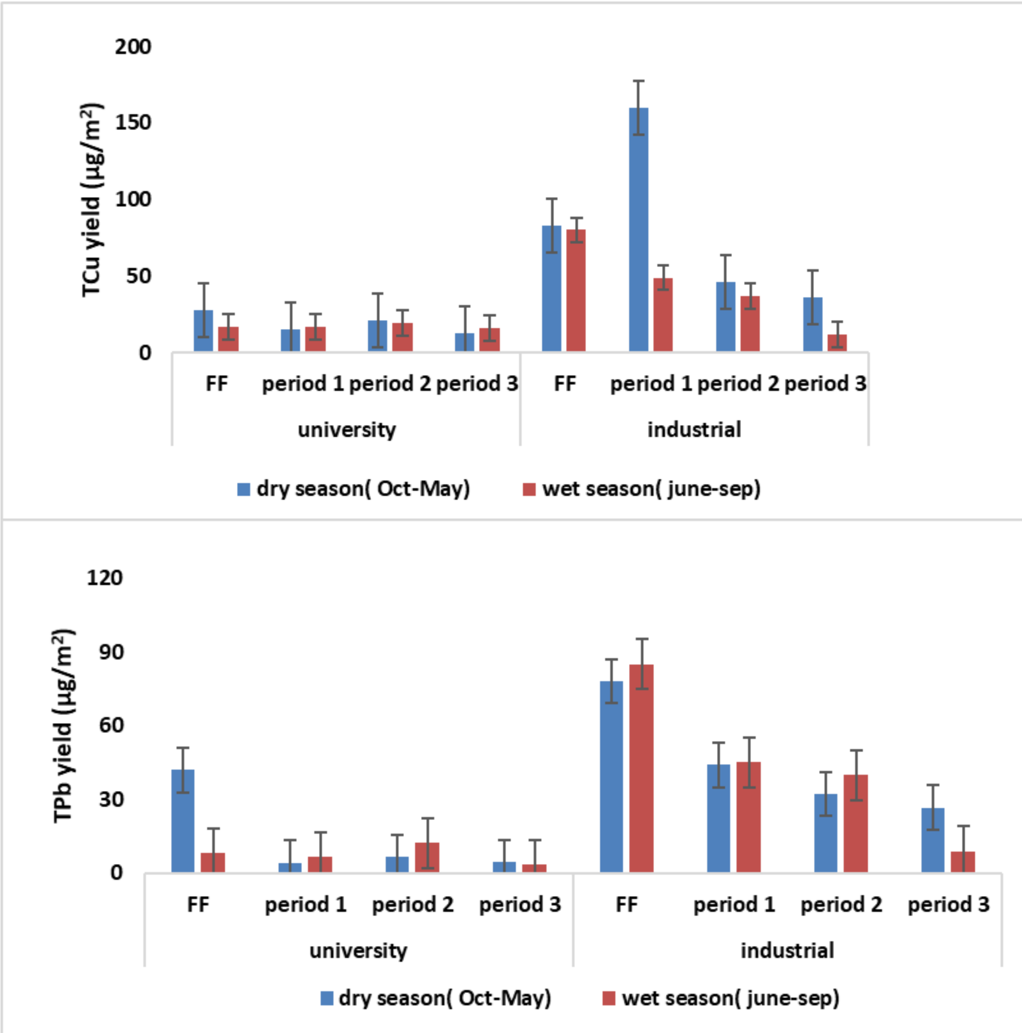


Figure 5-2: Seasonal variations during dry (blue) and wet (red) months.The hospital carpark was non-operational from mid-June and was not included for the comparison.

5.3.4 Metal species ratios

TZn to TCu ratios were higher at the industrial carpark (7:1, 15:1 and 14:1) during period 1, period 2 and period 3 respectively. The university carpark had higher TZn to TCu ratios as compared to the hospital active carpark. Except for the industrial carpark, metal species ratios tend to decrease over the steady-state periods. TCu to TPb ratios were relatively homogenous all each carpark.

5.3.5 Active (operational) vs passive (non-operational) carparks

There was a significant difference ($p < 0.005$) between the operational and non-operational carparks during the first flush period. Mean pollutant yields were reduced by half in the non-operational (passive) carpark during first flush (Table 5.5). The pollutant yields between the active and the passive carparks were similar during steady-state (period 1), but drastically declined in the subsequent periods. A visual examination of the box and whisker plots also demonstrates that there is a fair amount of variation among the pollutants in different flow durations (Figure 5.3). Overall, there was a consistent reduction in pollutants in the passive carpark as storms progressed. Elevated pollutant yields were observed through first flush to period 1 in the passive carpark.

Table 5.5: Mean, Median, Std Error and ranges of TSS and total metals (TZn, TCu, TPb) yield for the active and the passive carparks during the first flush and between the different steady-state periods

Urban Carparks	Pollutant yield	First Flush	Period 1	Period 2	Period 3
		mean, median *std error* (range)			
Hospital active	TSS (mg/m^2)	99, 95 *18* (15 - 180)	60, 29 *25* (4 -132)	33, 36 *10* (9 - 62)	36, 36 *32* (4 - 68)
	TZn (µg/m^2)	123, 83 *32* (22 - 317)	95, 83 *30* (42 - 209)	76, 57 *29* (17 - 166)	43, 43 *11* (32 - 53)
	TCu (µg/m^2)	13, 13 *3* (4 - 31)	20, 20 *4* (10 - 31)	22, 14 *52* (5 - 52)	14, 14 *1* (13 - 15)
	TPb (µg/m^2)	11, 8 *3* (2 - 25)	14, 14 *5* (6 - 26)	6, 5 *3* (2 - 16)	3, 3 *1* (2 - 4)
Hospital passive	TSS (mg/m^2)	47, 16 *16* (1 - 118)	58, 18 *32* (1 - 274)	4, 4 *2* (0.48 - 11)	4, 5 *1* (0.1 - 9)
	TZn (µg/m^2)	67, 60 *17* (8 - 173)	79, 52 *25* (8 - 176)	12, 11 *3* (5 - 21)	22, 13 *11* (4 - 75)
	TCu (µg/m^2)	14, 12 *4* (3 - 42)	21, 9 *9* (2 - 71)	3, 3 *1* (1 - 8)	5, 3 *3* (2 - 19)
	TPb (µg/m^2)	39, 7 *22* (0.3 - 256)	8, 2 *4* (0.5 - 28)	0.4, 0.9 0.*1* (0.18 - 1)	0.4, 0.4 *0.04* (0.2-0.6)

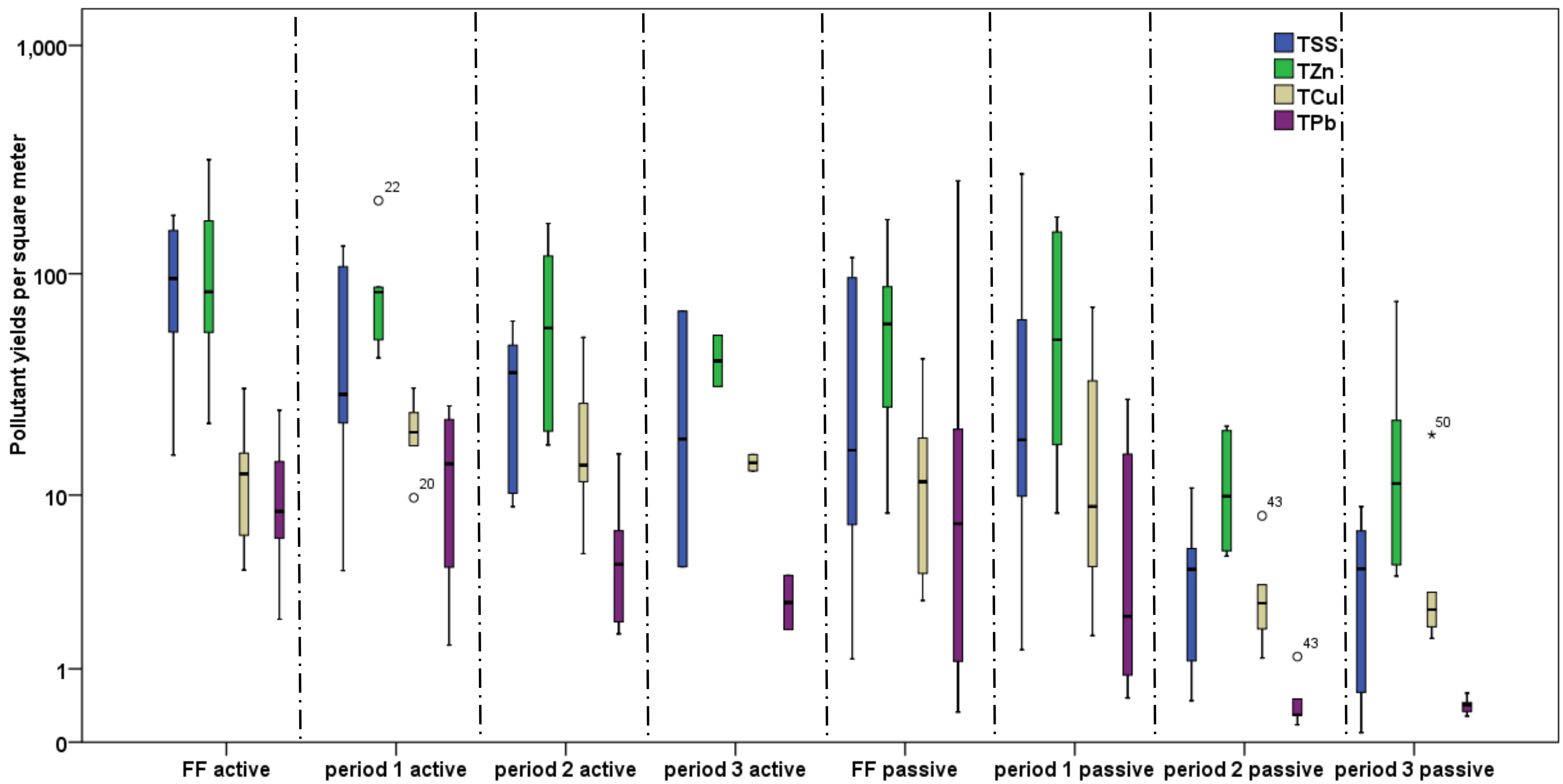


Figure 5-3: Variability in TSS and heavy metals (Zn, Cu and Pb) yield in the operational (active) and the non-operational (passive) carparks. The box represents the 25 th (lower) percentile, median, and 75 th (upper) percentile. Note the varying scales for each pollutant.

5.3.6 Pollutant yields and percentage reduction on each period during different flow periods

Mean pollutant yields were higher for period 2 as compared to period 1 at the university carpark whereas mean pollutant yields were consistently lower as the storm progressed during each sampling period (i.e first 40 mins, 41-80 mins and 81-120 mins after rain started) at the industrial carpark. Pollutant loads peaked at 0-40 mins after rain started at the industrial and the hospital carparks whereas, it reached a maximum during 41-80 mins before it moderates at the university carpark. The increased rain duration resulted in a decrease in pollutant load from each carpark surface. Paired t-tests identified a significance difference within each period at the industrial carpark. Whereas, there were no significance differences between each steady period at the university carpark, which is likely due to the carpark layout (detailed in Chapter 3). There is also a gradual reduction in % load in each steady-state period (Figure 5.4).

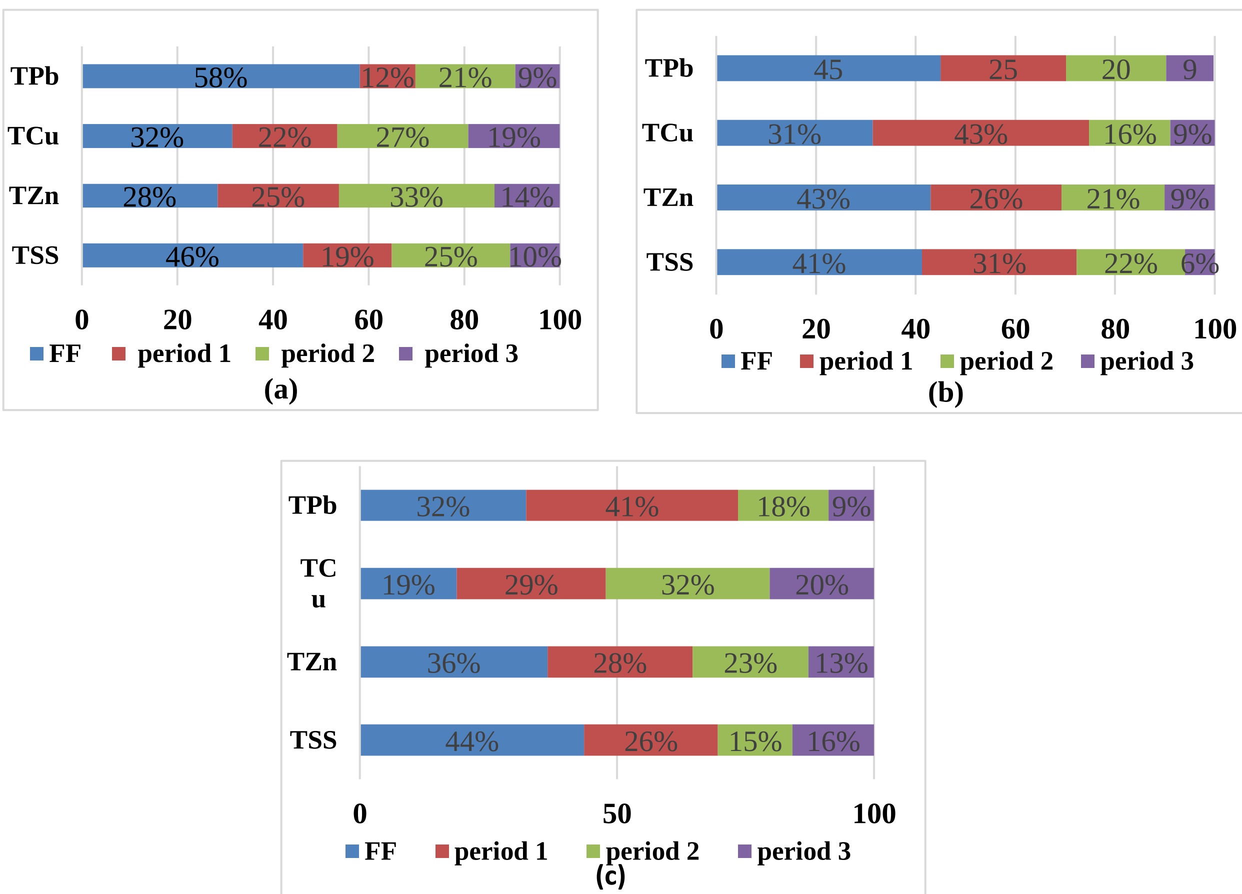


Figure 5-4: Percentage reduction in each steady-state; a) university carpark, b) industrial carpark c) hospital carpark

5.3.7 Effect of traffic on metal partitioning

The highest percentage of dissolved Zinc (dZn) and dissolved Copper (dCu) was found at the university carpark (100%) during period 1 (Figure 5.5) with the hospital carpark having(Zn: 86%-90% and Cu: 65%-75%). The industrial carpark exhibited the lowest percentage of the dissolved metals. Pb was predominately found to be in particulate form at the university and the industrial carparks.

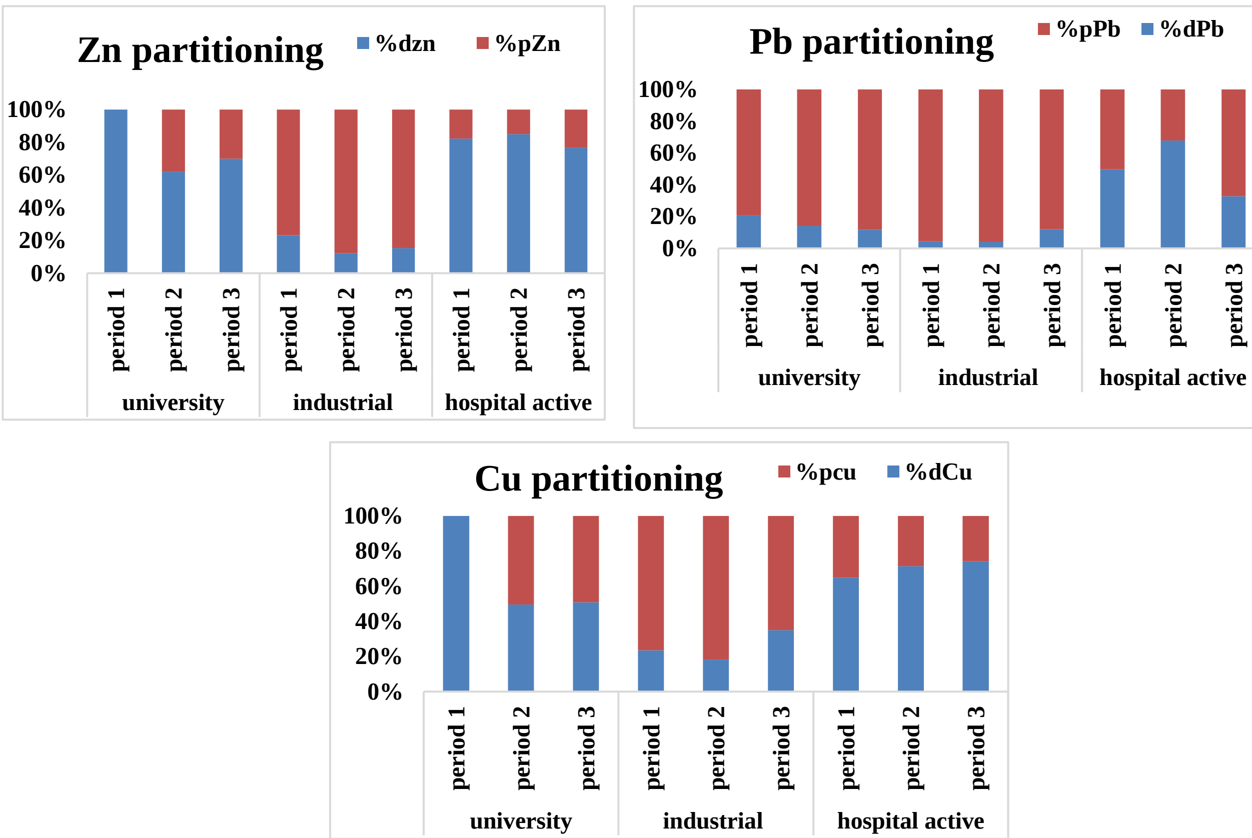
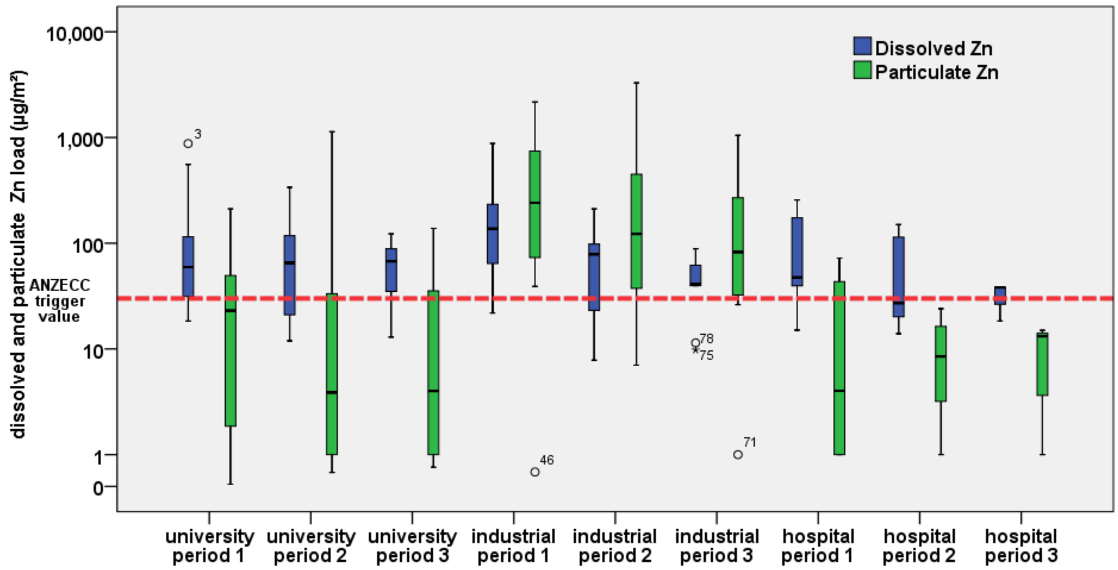
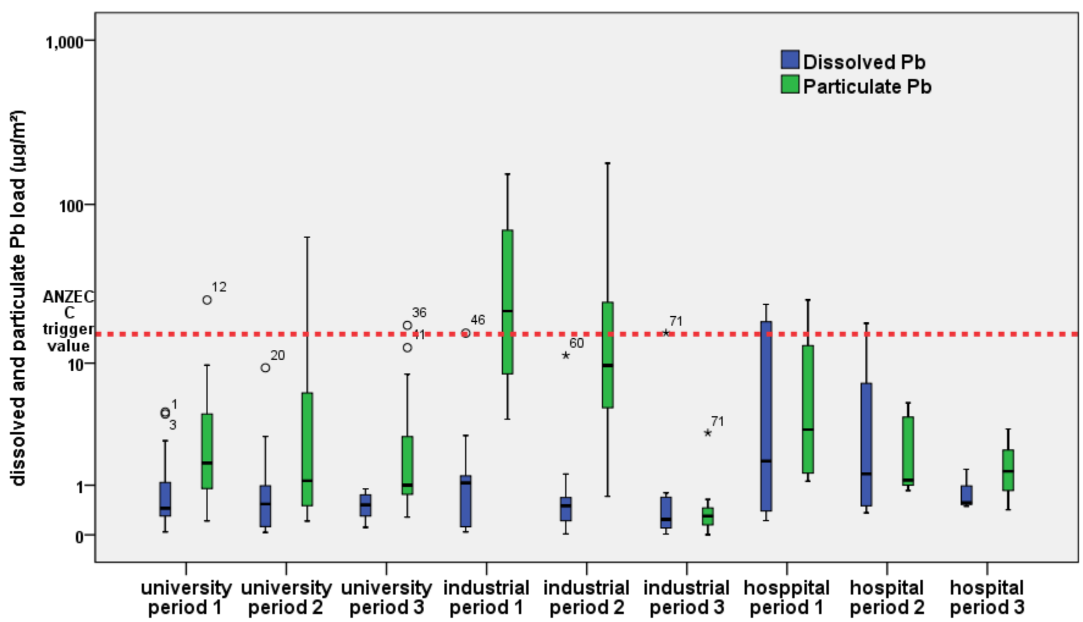


Figure 5-5: Average Zinc, Copper and Lead partitioning between dissolved and particulate forms from each carpark

Median dissolved Zn and Cu yield were found to be higher at the university and the hospital carparks for all the steady-state periods (Figure 5.6). Though the percentage of particulate metals was higher at the industrial carpark, the total dissolved metal yields were higher at the industrial carpark as compared to the other two carparks studied. Particulate Pb was one order of magnitude higher at the industrial carpark.


Dissolved Zn
Particulate Zn
dissolved and particulate Zn load (µg/m²)
10,000
1,000
100
10
1
0
ANZECC trigger value
university period 1
university period 2
university period 3
industrial period 1
industrial period 2
industrial period 3
hospital period 1
hospital period 2
hospital period 3


Dissolved Pb
Particulate Pb
dissolved and particulate Pb load (µg/m²)
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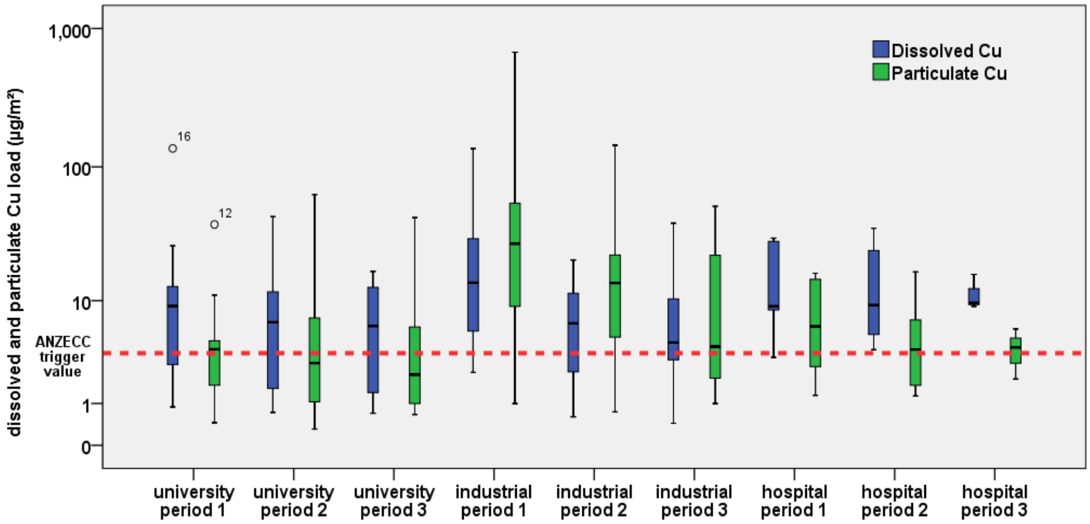


Figure 5-6: Distribution of dissolved and particulate Zn Cu and Pb yields for each carpark (° denotes outliers ± 1.5x Inter Quartile Range (IQR), * denotes outliers ± 3x IQR). The interquartile range represents the middle 50% of the data. The median is represented by the line in the box. The whiskers represent the range from the 25% to the 75% of the data, excluding outliers. ANZECC 80% trigger value for dissolved Zn (31 µg/L), Cu (2.5 µg/L) and Pb (9.4 µg/L) were presented by red dotted line in the graph.

5.3.8 Total metals vs dissolved

Linear relationships between total and dissolved metal yield were observed at the university and the hospital carparks. No correlation was found between total and dissolved metals at the industrial carpark (Figure 5.7) and thus it was not included in this graph. Strong positive correlations were found for the total and dissolved Zn and Cu loadings at the hospital and the university carparks for all the steady-state periods except for period 3 for the hospital carpark. For total and dissolved Pb, only the hospital carpark was found to have a statistically significant correlation ($r = 0.920$, $p = 0.009$ (Table 5.6).

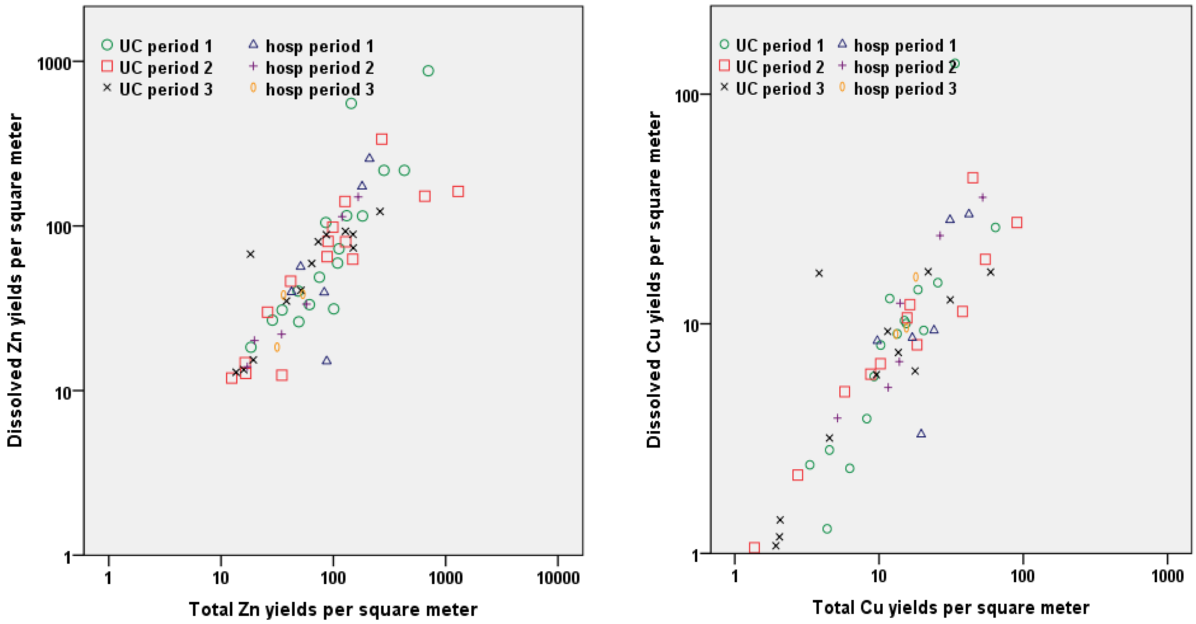


Figure 5-7: Total versus dissolved Zn and Cu yields at the university (UC) and the hospital (hosp) carparks

Table 5.6: Pearson correlation between total and dissolved metal yields

Carpark		**Total Zn to dissolved Zn**	**Total Cu to dissolved Cu**
University	Period 1	r = 0.828, p <0.001**	r = 0.48, p = 0.05*
	Period 2	r = 0.482, p = 0.06	r = 0.787, p <0.001**
	Period 3	r = 0.846, p <0.001**	r = 0.677, p = 0.01*
Hospital	Period 1	r = 0.926, p = 0.008**	r = 0.851, p = 0.03*
	Period 2	r = 0.989, p <0.001**	r = 0.965, p = 0.02**
	Period 3	r = 0.670, p = 0.53	r = 0.908, p = 0.276

***Correlation is significant at the 0.05 level (2-tailed)**
****Correlation is significant at the 0.01 level (2-tailed)**

5.3.9 Role of rainfall on TSS and metal yields from urban carparks

Rainfall depth

All the sampled events were classified into three groups on the basis of rain depth, <2 mm, 2-5 mm and > 5 mm (Table 5.7 and Figure 5.8). Larger rain events had relatively greater pollutant yield than smaller rain events. A Pearson correlation was therefore undertaken to further quantify the relationship for each rain depth category with pollutant yields (Table 5.7). A linear relationship between pollutants and rainfall depth

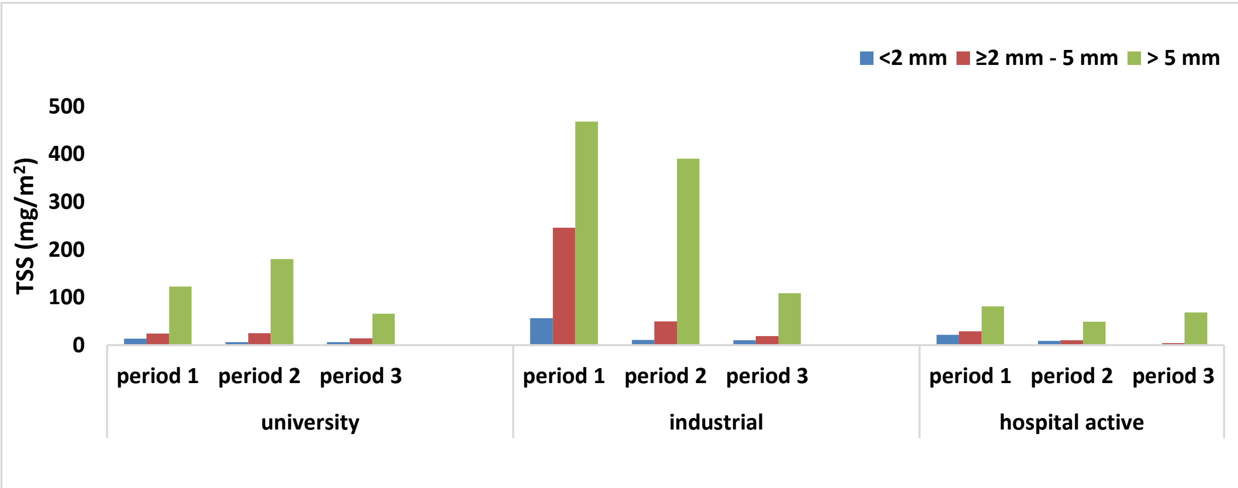
>5 mm was generally consistent for the pollutants at the university and the industrial carparks. Strong positive correlations were found for depth (>5 mm) with TSS (period 2 and 3), TZn (period 2) and TCu (period 1 and 2) yield at the university carpark. Similarly, the industrial carpark also showed strong statistical positive correlations between depth (>5 mm) and TSS (period 2 and period 3), TZn (period 1 and period 2 and TCu (period 1 and period 2). The hospital carpark was not included for a Pearson correlation analysis since half of the storm events were monitored when the carpark was non-operational.

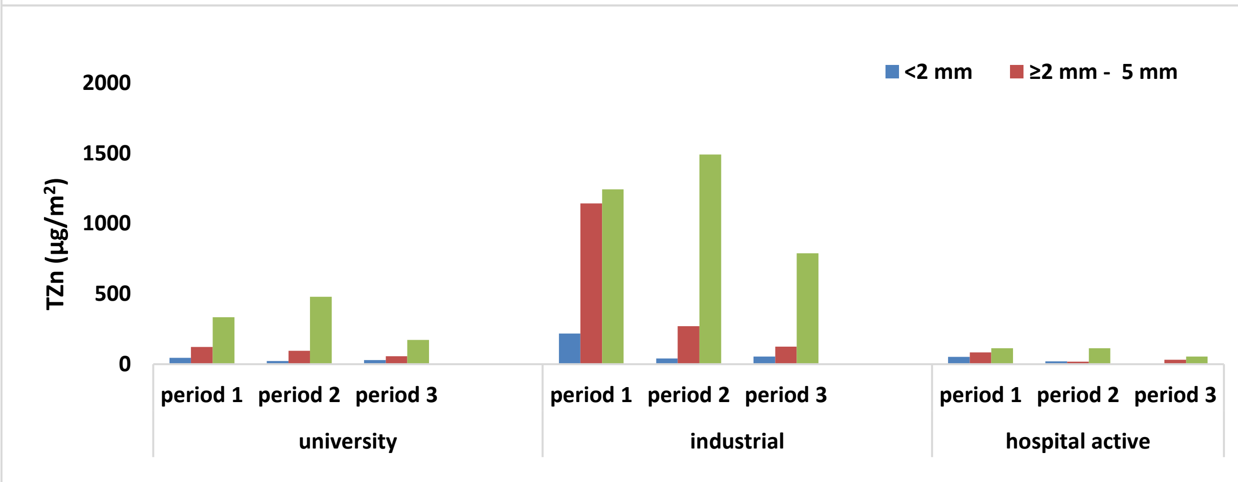
Table 5.7: r- values for correlations (p <0.05) among different rain depths (< 2 mm, 2-5 mm and > 5 mm) and pollutant yields (TZn, TCu and TPb) for each storm event

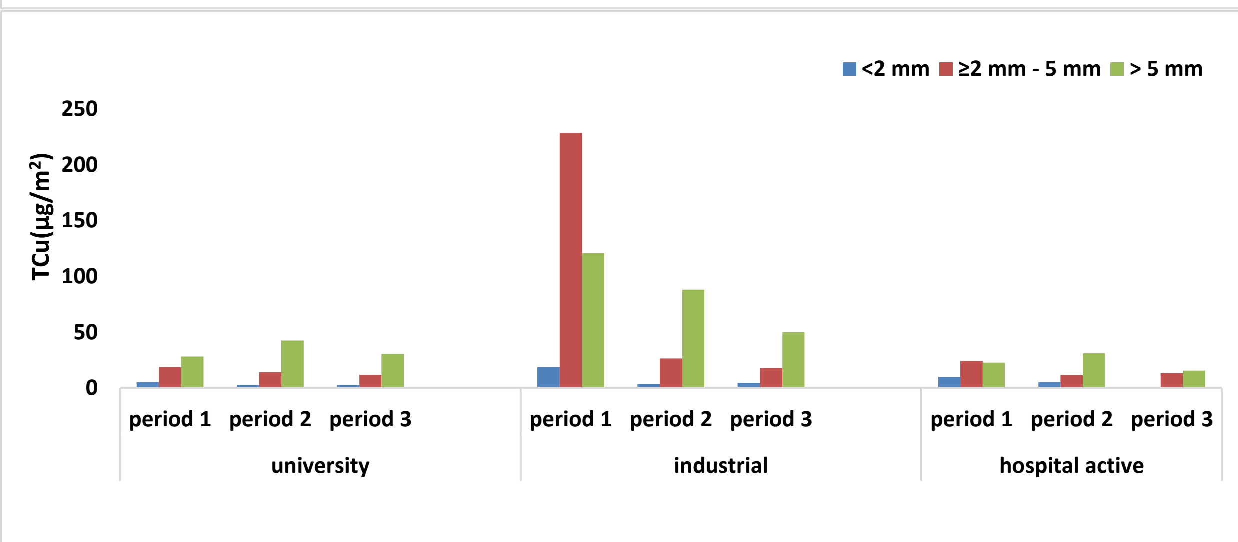
Total TSS, TZn and TCu yield		Period 1	Period 2	Period 3
			University carpark	
TSS:				
	< 2 mm	r = -0.3, p =0.9	r = 0.99, p <0.001**	r = 0.66, p = 0.33
	2 - 5 mm	r = 0.1, p =0.8	r = 0.8, p = 0.06	r = 0.58, p = 0.41
	> 5 mm	r = 0.7, P = 0.06	**r = 0.86, p <0.02****	**r = 0.9, p <0.05****
TZn:				
	< 2 mm	r = 0.68, p = 0.13	r = 0.9, p = 0.03**	**r= 0.9, p = 0.005****
	2 - 5 mm	r = 0.54, p = 0.34	r = -0.2, p = 0.74**	**r = 0.8, p = 0.05****
	> 5 mm	r = 0.23, p = 0.65	**r = 0.57, p = 0.02****	r = -0.8, p = 0.17
TCu:				
	< 2 mm	r= 0.61, p = 0.19	r = 0.9, p = 0.01**	**r = 0.9, p = 0.01****
	2-5 mm	r = 0.5, p = 0.36	r = 0.7, p = 0.13	r = 0.8, p = 0.08
	> 5 mm	**r = 0.8, p = 0.05****	**r = 0.99, p <0.001****	r = 0.2, p = 0.74
			Industrial carpark	
TSS:				
	< 2 mm	r = -0.15, p = 0.98	r = -0.84, p = 0.35	r = 0.39, p = 0.74
	2 - 5 mm	r = 0.38, p = 0.52	r = 0.13, p = 0.86	r = 0.93, p = 0.23
	> 5 mm	r = 0.46, p = 0.53	**r = 0.9, p = 0.03****	r = 0.86, p = 0.33
TZn:				
	< 2 mm	r = -0.21, p = 0.97	r = -0.26, p = 0.82	**r = 0.9, p = 0.05****
	2 - 5 mm	r = 0.48, p = 0.40	r = 0.2, p = 0.79	r = 0.97, p = 0.14
	> 5 mm	**r = 0.9, p = 0.02****	**r = 1, p = 0.009****	r = 0.18, p = 0.87
TCu:				
	< 2 mm	r = 0.05, p = 0.46	r = 0.95, p = 0.02**	r = 0.91, p = 0.26
	2 – 5 mm	r = 0.31, p = 0.30	r =-0.09, p = 0.8	r = 0.91, p = 0.26
	> 5 mm	**r = 0.9, p = 0.03****	**r = 0.9, p = 0.03****	r =-0.69, p = 0.51

**** Denotes statistically significant result. The significance level is 0.05**

Pollutant yields with varying antecedent dry days







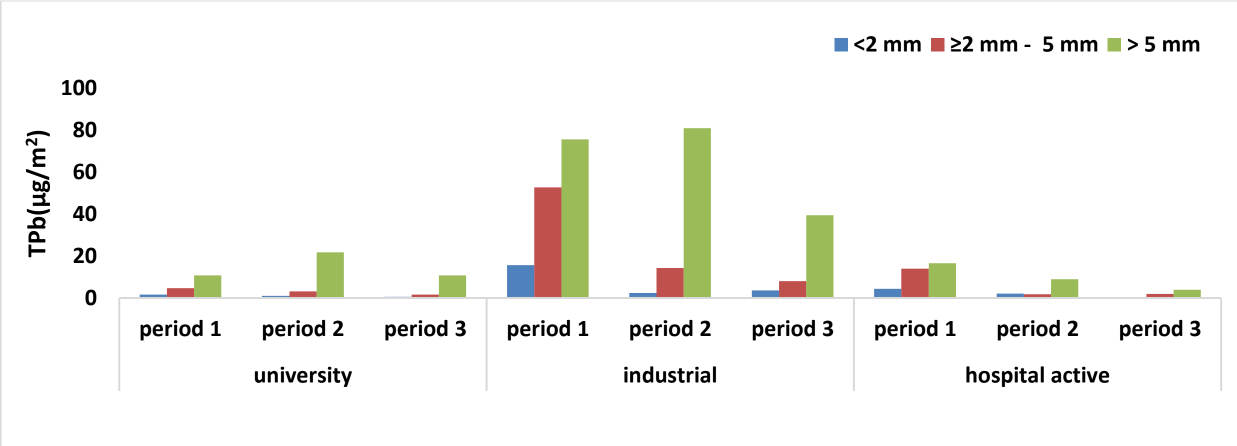


Figure 5-8: Mean TSS and metals yield from three carparks in different rain depths (< 2 mm, 2 – 5 mm and >5 mm)

Data were further analyzed and categorized into three different groups: ADD <3 days, 3-6 days and >6 days. Average pollutant yields were found to be relative maximum for 3-6 antecedent dry days after storm events (Figure 5.9). The data indicated that build up over the dry days occurs relatively quickly after a rain event, reached a relative maximum at 3-6 antecedent dry days and moderates after 6 days. To further identify the strength of the relation, a Pearson correlation was performed for each ADD group with pollutant yields (Table 5.8). Strong positive correlations were found for ADD (3-6 days) at the university carpark for TSS, TZn, TCu (period 1 and period 2) and TPb during period 1 and the industrial carpark for TSS (period 1 and 2), TZn, TCu and TPb for period 1 and period 2) (Table 5.8). A significant difference in pollutant yields for different rain depths during a storm event was confirmed in this study.

Table 5.8: r- values for correlations among different antecedent dry days (ADD) (<3 days, 3-6 days, >6 days) and pollutant yields (TZn, TCu and TPb) for each storm event, NED: not enough data to run a Pearson correlation analysis separately

Total TSS, TZn and TCu yield/m^2		First Flush	Period 1	Period 2	Period 3
				University carpark	
TSS	<3 days,	r = 0.20, p = 0.61	r = 0.20, p = 0.66	r = 0.05, p = 0.90	r = -0.22, p = 0.71
	3-6 days	r = 0.37, p = 0.45	**r = 0.9, p = 0.02****	r = -0.14, p = 0.85	r = -0.70, p = 0.28
	>6 days	r = 0.49, p = 0.32	r = 0.86, p <0.02	**r = 0.96, p = 0.009****	**r = 0.97, p = 0.03****
TZn	<3 days	r = -0.93, p = 0.82	r = 0.13, p = 0.07	r = -0.25, p = 0.57	r = 0.32, p = 0.59
	3-6 days	**r = 0.9, p = 0.02****	**r = 0.8, p = 0.04****	r = -0.16, p = 0.83	r =-0.36, p = 0.96
	>6 days	r = 0.78, p = 0.06	r = 0.94, p = 0.01	r = 0.84, p = 0.07	r =-0.10, P = 0.89
TCu	<3 days	r = 0.05, p= 0.99	r = 0.01, p = 0.82	r = -0.53, p = 0.22	r = -0.23, p = 0.7
	3-6 days	**r = 0.92, p= 0.02****	**r = 0.8, p = 0.04****	r = -0.14, p = 0.85	r = 0.77, p = 0.22
	>6 days	r = 0.05, p = 0.15	r = 0.46, p = 0.42	**r = 0.9, p = 0.02****	r = -0.2, p= 0.79
TPb	<3 days	r = -0.65, p = 0.08	r = 0.29, p = 0.52	r = -0.48, p = 0.27	r = -0.11, p = 0.7
	3-6 days	**r = 0.92, p = 0.02****	**r = 0.9, p = 0.03****	r = -0.18, p = 0.81	r = 0.23, p = 0.76
	>6 days	r = 0.77, p = 0.07	r = 0.77, p = 0.12	**r = 0.9, p = 0.05****	r =-0.86, p = 0.13
				Industrial carpark	
TSS	<3 days	r = 0.43, p = 0.33	r = 0.33, p = 0.57	r = 0.31, p = 0.68	NED
	3-6 days	**r = 0.9, p = 0.02****	**r =1, p = 0.002****	r = 0.85, p = 0.34	r = 0.72, p = 0.48
	>6 days	r = 0.33, p = 0.51	r = 0.15, p = 0.85	r = -0.34, p = 0.66	r =-0.72, p = 0.27
TZn	<3 days	r = 0.22, p = 0.63	r = 0.59, p = 0.28	r = 0.18, p = 0.81	NED
	3-6 days	**r = 0.9, p = 0.02****	**r = 0.9, p = 0.05****	r = 0.76, p = 0.4	r = 0.76, p = 0.44
	>6 days	**r** = -0.64, p = 0.90	r = 0.05, p = 0.94	r =-0.81, p = 0.91	r = 0.62, p = 0.37
TCu	<3 days	r = 0.58, p = 0.16	r = 0.92, p = 0.78	r = 0.21, p = 0.78	NED
	3-6 days	r = 0.79, p = 0.11	**r = 0.90, p = 0.03****	r = 0.37, p = 0.75	r = 0.85, p = 0.34
	>6 days	r = -0.12, p = 0.81	r = -0.70, p = 0.93	r =-0.11, p = 0.88	r =-0.62, p = 0.37
TPb	<3 days	r = 0.52, p = 0.23	r = 0.15, p = 0.80	r = 0.35, p = 0.64	NED
	3-6 days	**r = 0.87, p = 0.05****	r = 0.92, p = 0.72	r = 0.66, p = 0.53	r = 0.78, p = 0.42
	>6 days	r = 0.14, p = 0.78	r = -0.08, p = 0.91	r =-0.06, p = 0.93	**r = 0.99, p = 0.001****

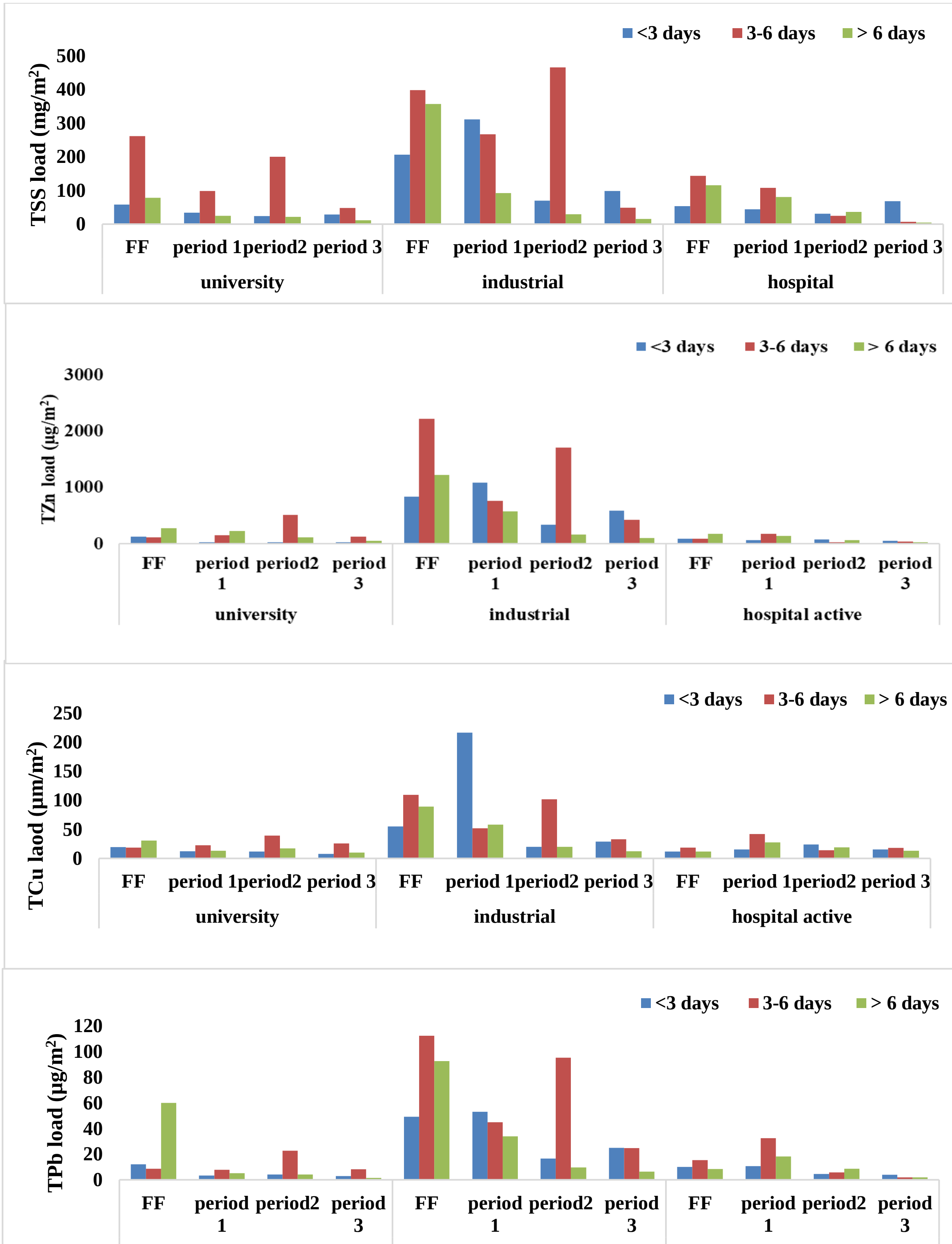


Figure 5-9: Mean TSS and metals yield from three carparks in different antecedent dry days (<3 days, 3-6 days and >6 days)

5.4 Discussion

5.4.1 Influence of carpark characteristics on steady-state stormwater quality

Total suspended solids sources during steady-state

The sources of sediments were specific for each carpark and were influenced by many factors such as atmospheric deposition due to surrounding topography, number and size of vehicles, the wear and tear of brake pads and tires and as well as sampling layout at each carpark. For each carpark, vehicles are one of the major sources of pollutants, both directly and indirectly, in runoff (Hahn and Pfeifer 1994).

Pollutant loads are influenced by several other factors such as the size and frequency of vehicles. The relatively higher steady-state TSS yield at the industrial carpark is the result of the highest traffic volume (>1000 vehicles/day) and size of vehicles (mainly 16-wheeler commercial trucks). The substantial TSS inputs were from vehicular wear and tear, abrasion of wheels with carpark surfaces and wash off from automotive parts as well as asphalt wear during storm events. At the industrial carpark, vehicular derived TSS builds up during the antecedent dry periods but is also continuously contributed during storm events from ongoing vehicular activities as half of the carpark area is connected to road resulting in a higher steady-state TSS yield than other two carparks studied. In addition, despite the differences in the drainage area and frequency of vehicles at the university and the hospital carparks, there were no significant differences in TSS loadings between these carparks. The hospital carpark was located at the base of a hill and experienced higher dry deposition rates, unlike the university which was on flat terrain.

Carpark sampling layout also affects TSS loadings to some extent. Samples were directly collected from carpark surfaces at the hospital carpark whereas, at the university, all the sumps were connected to underground stormwater pipes networks and discharged to the main manhole where the samples were taken (detailed sampling layout is presented in Chapter 3). These sumps and manholes provide ample opportunity for the settling of coarse sediments during the course of discharge and resulting low TSS loadings during steady-state despite the larger drainage area and higher traffic volume as compared to the hospital carpark. Initial TSS loadings (%) were also lower at the university carpark as compared to the hospital carpark.

In addition to sampling layout, pollutant loadings are also influenced by seasonal variations. Mean pollutant values were multiple times higher in winter than in warm seasons (Helmreich et al., 2010). Similar results were found at the university carpark during the wet seasons and no obvious seasonal variations noticed at the industrial carpark.

Influence of vehicular activities on heavy metals yield during steady-state runoff

The differences in metal species ratios for each carpark suggested that build-up of metals was influenced by many factors in addition to vehicles. TZn to TCu ratios from steady-state sampling at the industrial carpark were found to be two times higher than in road runoff (Moores et al., 2009). The university carpark had higher TZn to TCu ratios as compared to the hospital carpark. The difference in the ratios was likely to be influenced by different traffic behaviours or secondary sources such as atmospheric deposition. Other studies have also discussed and identified the importance of vehicular activity to pollution loads (Chu-Fang et al., 2005; Conko et al., 2004; Hjortenkrans et al., 2007; Sternbeck et al., 2002). Mean metal loads decrease over the different steady-state periods at the industrial carpark (i.e exhibiting flush first phenomenon) whereas, at the university carpark, mean values were relatively higher as the storm progressed suggesting that the wash off process for heavy metals from the university is likely influenced by mixed runoff contribution from the roof as well as carparks surfaces. Sampling layout also affects the metal loadings in the subsequent flow periods. Mean total Zn was 6 times higher at the industrial carpark as compared to the university carpark during initial steady-state (period 1). Besides vehicles, other secondary factors such as connecting roads to the carpark, different braking conditions (ranging from no brake required to moderate), varying traffic frequency, vehicle size (private small car to 16-wheeler commercial truck) are expected to accelerate metal pollutants in each carpark.

For example, tire wear is a major contributor to Zn (Kennedy and Sutherland, 2008). Vehicle tires have different weighted average for ZnO in the thread (the part exposed to wear) for a car (1.2%) and a truck (2.1%), it was assumed that the Zn loads from trucks would be higher than cars (Smolders and Degryse, 2002, Murphy et al., 2014). Similarly, Cu emitted from brake pads ranged from 5.1 mg/mi to 14.01 mg/mi for small cars to large pickup trucks, respectively (Garg et al., 2000). Therefore, the rate of wear and tear influenced the release of these heavy metals onto carpark surfaces. Higher Pb loads were seen at the industrial carpark, which is likely due to loss of wheel weights from vehicles resulting in a contribution to stormwater through solubilization of lead on the wheel weight surface (Kennedy and Sutherland, 2008). Brake pad and tire wear are also considered minor contributors to Pb loads.

In addition, there was a strong correlation between TSS and total metals at the university and industrial carpark revealing that metals and TSS had the same origin. Not all the metals during each steady-state period were correlated at the hospital carparks suggesting that vehicles were not the only contributing factors as the hospital. Since the carpark is located closer to the hills, it is likely to be contributed by wind transported atmospheric deposition.

5.4.2 Fractionation of heavy metals in carpark runoff

Heavy metals such as Zn, Cu and Pb in carpark runoff can adversely affect receiving waterways by bioaccumulating in the food chain. Runoff from urban land uses often contains significant loads of metal elements both in particulate and dissolved form. The site to site variation in the partitioning of heavy metals is shown in Figure 5.8. Zn was predominately found in the dissolved form. During the initial steady-state (period 1) at the university carpark, 100% of Zn and Cu were in the dissolved form followed by the hospital carpark (70%). Pb was predominately particulate bound for all of the carparks (Morrision et al., 1984; Pitt, 1995). The industrial carpark exhibited lower dissolved % but the total dissolved loadings were higher than other two carparks. Although there are significant differences in carpark characteristics and metal properties, a large fraction of the dissolved metals load at the university and the hospital carparks were associated with suspended solids (Florea and Busselberg, 2006; Hatje, 2003). TSS was statistically correlated with the total and the dissolved metals at the university and the hospital carparks, and TSS was correlated with particulates metals at the industrial carpark. Metal partitioning at the industrial carpark is likely to be influenced by traffic characteristics (Sansalone and Buchberger, 1997 b). In addition, there was no relationship with rainfall and runoff pH (plot not shown) with the dissolved metals for the carparks. The study also revealed that the dissolved metal loadings were higher during initial steady-state as compared to later runoff and tend to reduce as the duration of storm increases.

5.4.3 Influence of rainfall characteristics on stormwater quality

Rain depth

For all carparks, TSS, TZn and TCu showed a positive significant relationship with storm events with rain depths greater than 5 mm except for TSS and TZn during the initial steady period at the university carpark. Higher rain depth is associated with a higher intensity suggesting the greater mobilization of particulate matter during heavier rainfall (Kayhanian et al., 2003).

The influence of rain depth was more prominent during period 1(0-40 mins) and period 2 (41-80 mins). Pollutant loadings can be expected to decrease as the duration of rainfall events increases, reflecting the greater dilution of pollutants by longer durations. This suggested that at the beginning of a rain event the rate of pollutant wash off was at its highest and slows as the duration of the rain event increased (Murphy et al., 2015). TPb loading was significantly lower as compared to other pollutants and was not included in the statistical analysis.

In addition, the condition and the type of carpark surface can be expected to influence pollutant yields through their effects on both the generation of runoff and the extent to which the transport of pollutants may be inhibited (Murphy, 2015). Contrary to the findings, since all the carparks surfaces were asphalt have not had any influence on the total loadings.

Antecedent dry days

ADD was found to be one of the factors which significantly influence pollutant build up in all of the carparks studied. Average pollutant yields were found to be higher for 3-6 days after the pervious event. A strong statistically significant relationship was found between pollutants during first flush and initial 40 mins of storm events for both the university and the industrial carparks. As the storm progressed the effect of ADD on pollutant loadings declined. Surprisingly, this result was similar to the findings by (Gunawardena et al., 2011; Wicke et al., 2010; Murphy et al., 2015) for atmospheric deposition. They found that pollutant build-up increased asymptotically with ADD, which ultimately plateaued after 6 days. The similar findings are likely due to the fact that the carparks surfaces were not further disturbed by other factors such as street sweeping, vacuum cleaning (Hewitt and Rashed, 1992; Pitt et al., 1995; Shinya et al., 2003; Westerlund et al., 2003; Moores et al., 2010;). Kayhanian et al. (2003) found that higher pollutants are associated with longer ADD prior to an event reflecting the greater accumulation of pollutants.

Pollutant loadings also reflect site to site influences on accumulation rates. In particular, variations in traffic patterns, frequency, size and nature of vehicles at different points in a carpark can influence accumulation rates. Muschack (1990) reported that higher pollutant loading in runoff derived from zones of braking and acceleration as well as while manoeuvring the vehicles. One of the important factors which may influence is nature and type of vehicles. Depending on the number of wheels, wear rates of brakes and tires have been reported to be up to 7 and 31 times greater for heavy commercial vehicles like trucks as compared to passenger cars (Kennedy et al., 2002).

5.4.4 Implications for treatment approaches

Many of the available stormwater treatment systems utilize filtration and sedimentation, therefore emphasizing the removal of particulates. The findings in this research implied that the relative reduction in TSS at the industrial carpark resulted in a significant reduction in particulate heavy metals, especially during the initial period of steady- state period. In addition, relative removal of total heavy metals reduced appreciable dissolved metals at the university and the hospital carparks. Addition mechanism is recommended to treat the dissolved metal loads in the carparks.

5.4.5 National guidelines

Average concentrations (µg/l) of dissolved Zn, Cu and Pb were compared with the relevant effects-based Eco toxicological thresholds for safeguarding 80% of freshwater species (Table 5.9) (ANZECC, 2000).

Table 5.9: Average concentrations (TSS: mg/L and dissolved metals: µg/L) in carpark runoff from each land use compared with the 80% ANZECC eco toxicological guidelines.

Pollutants	Guideline value*	University	Industrial	Hospital
		Period 1, Period 2, Period 3		
TSS (mg/L)	25	35, 27, 21	139, 71, 36	63, 20, 11
dZn (µg/L)	31	120, 78, 69	200, 105, 73	108, 33, 28
dCu (µg/L)	2.5	9, 8, 11	17, 10, 10	15, 12, 13
dPb (µg/L)	9.4	1, 1, 3	2, 3, 2	7, 3, 1

*__Recommended values for TSS and trigger values for heavy metals__

TSS values exceeded the ANZECC threshold at the industrial carpark for all of the flow periods and only for initial steady periods at the hospital and university carparks. Dissolved Zn and Cu ecotoxicological thresholds were exceeded by the industrial and the university carparks for the steady-state periods and at the hospital carpark during the steady-state period (period 1), indicating that at least 20% of aquatic species would be adversely affected by the carpark runoff except for the later steady-state period at the hospital carpark. Dissolved Pb values were not exceeded at any of the carparks; therefore, dissolved Pb runoff from the carparks will not be harmful to over 80% of aquatic species according to guideline values.

5.5 Conclusions

This chapter quantified differences in steady-state pollutant yield in runoff from three different carparks. Relationships between pollutants yield and rainfall parameters were established. Some of the major findings from this chapter are as follows:

1) TSS and heavy metals yield were statistically different during period 1 between the university and the industrial carparks and between the hospital and industrial carparks. There was a reduction in mean pollutant yields from each subsequent period in the industrial and hospital carparks. This shows that the increased rain duration resulted in a decrease pollutant wash off from each of those carparks.
2) Linear relationships between total and dissolved metal yield at the university and the hospital carparks suggest that removal of total metals will reduce dissolved metal yields.
3) No significant seasonal pollution variations were observed for the samples obtained in period 1 to period 3.

4) The mean pollutant yields between the operational and the non-operational hospital carpark were similar for period 1 but drastically declined in the subsequent periods (period 2 and period 3) for the non-operational carpark. This result suggests that wash-off process is relatively weak in a low-intensity rainfall condition.
5) Larger rain events had relatively greater pollutant yield than smaller rain events.

Average pollutant yields were found to peak at 3-6 antecedent dry days. Management options including carpark sweeping and routine clean-up activities are recommended to reduce coarser particles. Alternative treatment systems are necessary for the removal of fine particles and heavy metals (dissolved and particulates).

Chapter 6

Particle size distribution in urban carparks runoff

6. Particle size distribution in urban carpark runoff

6.1 Introduction

The management of urban waterways would be incomplete without the proper study of sediment characteristics. Sediment discharge from urban carpark runoff is a major contributor of key pollutants such as heavy metals, pathogens, organic matter, and nutrients. The sources of sediment are mainly traffic (including the wear and tear of vehicles and road materials, abrasion of brakes and tires (Gunawardana et al., 2012; Herngren et al., 2006; Thorpe and Harrison, 2008; Westerlund, 2005) and direct atmospheric deposition (Murphy et al., 2014). The type of traffic and atmospheric deposition (in addition to topography, land use and prevailing rainfall conditions) will influence the size and composition of particle size in carpark runoff. Fine particles can contribute disproportionately turbidity and heavy metal transport, which can, in turn, affect aquatic flora and fauna. (Frumai et al., 2002). Suspended solids load with a varied particle size distribution can pose a long-term threat to aquatic organisms. For example, finer particles tend to occur at the surface since they don't settle and may pose more of a threat to the respiratory organs of fish and other invertebrates whereas coarser particles tend to occupy deeper zones and are less threating as compared to fine particles (Schindle et al., 2005, Greig et al., 2005).

Few studies have compared the distribution patterns of particle sizes in stormwater runoff from different land use. There is particularly little information about the effect of rainfall and seasons on the distribution pattern of particles from urban carpark runoff. Charters et al. (2015) analyzed particle size distributions (PSDs) of various surfaces in a similar geographical location and observed substantial inter-event variation for each surface studied. Selbig et al. (2013) reported large differences in PSD within and between various land uses and reported that concentrations of metals and PAHs generally increased with decreasing particle size. The size of the particle is influenced by source area runoff as well as catchment characteristics. A study by Shaheen (1995) reported that 58% of particles deposited on highways were larger than 250 µm whereas Sansalone et al. (1998) indicated that 20% of particles were from 600 to 1000 µm and 30% were from 1000-10,000 µm for various land uses.

Information on particle size distribution and the factors that influence the PSD is crucial when selecting and designing the most appropriate treatment systems to mitigate sediment and heavy metals transport from source to sink (waterways). Inaccurate representation of particle size distribution in urban runoff can lead to under and oversized best management practices (BMPs) designs, rendering them either ineffective or unnecessarily costly. To select the most appropriate BMP for stormwater pollution management, accurate characterization of PSD in urban runoff is increasingly important. The treatment of stormwater runoff is usually accomplished through flocculation, sedimentation and filtration (Lawler, 1997). However, the design and performance of the stormwater treatment systems are largely affected by particle size distribution, as the size has a major influence on the settling velocity of particles and the concentration of adsorbed metals depends on particle size (Gulliver et al., 2010, Clifford et al., 1995).

6.1.1 Objectives

This chapter aims to identify and understand variations in PSD from different carparks within a similar geographical location.

The specific objectives are as follows:

- Assess whether there are significant differences in PSD between first flush and steady-state conditions between the carparks
- Assess the relationship between turbidity and particle size distribution
- Identify the relationship between rainfall characteristics (first 10 mins rainfall intensity, rain depth, ADD, first 10 mins rain depth and average intensity) and the PSD
- Describe how PSD affects the selection of stormwater treatment systems
- Compare the results with other urban carparks PSD profiles

6.2 Methodology

A general description of the sampling sites, sampling layout, field sample collection techniques, laboratory analyses, and statistical analysis approaches related to the study of PSD are presented below (a detailed description is provided in Chapter 3). A review of suitable PSD sampling techniques is also presented.

6.2.1 Overview of sample collection

First flush (Nalgene TM stormwater first flush samplers, 1 L HDPE) as well as automatic sampling (ISCO 6712C) were deployed in sumps within the three urban carparks to collect the carpark runoff for PSD analysis. A HORIBA LA 950 (EPA approved) particle size analyzer was used to analyze the carpark runoff samples (Figure 6.1). Untreated carpark runoff samples were collected from 21 stormwater events (total of 188 samples were analyzed: Table 6.1) from September 2015 to October 2016 from three different carparks (university, hospital and industrial). Nine storm events were sampled under similar rainfall conditions from all three carparks to analyze the effect of rainfall on particle size distribution from the individual carpark. The hospital carpark located in the foothills was closed after mid-June 2016. Nevertheless, sampling continued to investigate the effect of limited traffic on pollutant loads. Samples from active (operational) and passive (non-operational) carparks were also compared under different rainfall conditions. To understand the contribution of wind transported sediments from hills towards the city, a loess soil sample was taken from a Port hill facing south towards Christchurch City.

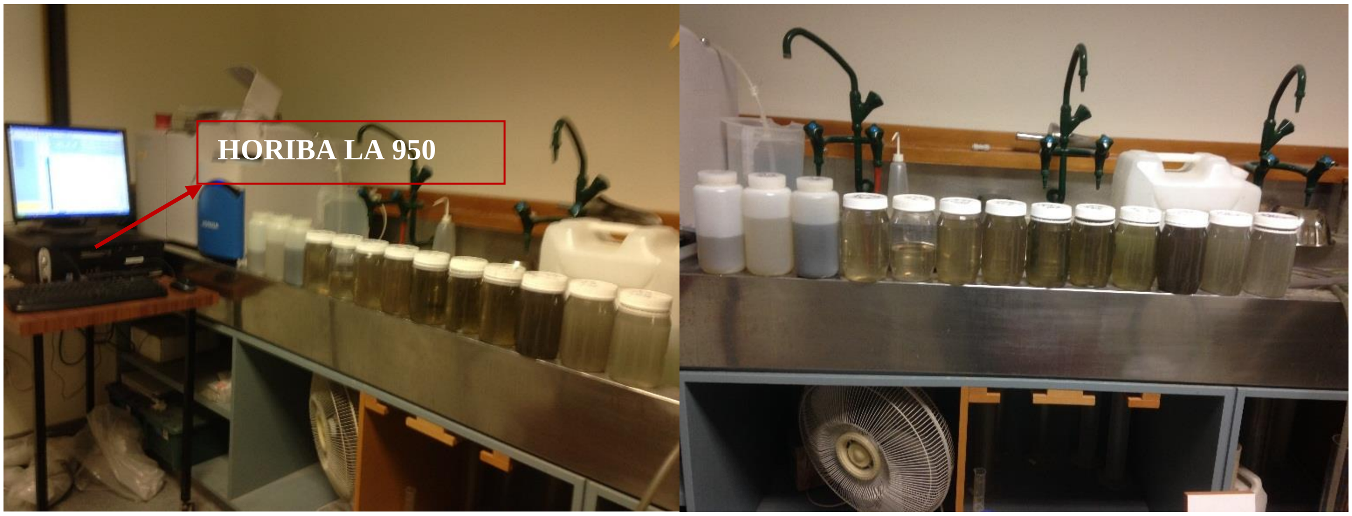


Figure 6-1: HORIBA LA 950 particle size analyzer and untreated runoff samples

Table 6.1: Number of samples collected for PSD analysis during first flush and steady-state periods from different carparks

Urban Carpark	University	Hospital (active)	Hospital (passive)	Industrial	Total samples analyzed
First Flush	17	9	7	14	47
Steady-state	51	27	21	42	141

6.2.2 Selection of suitable particle size analyses techniques

Sieving, coulter counter, and laser diffraction are the most common methods for quantifying particle size distribution. Each of these methods has limitations and may result in different PSD estimates. Selection of the most appropriate particle sizing technique is therefore crucial for the accurate characterization of PSD.

Stormwater contains both organic as well as inorganic substances. Due to the heterogeneity of particles in stormwater, an accurate determination of PSD can be challenging. Various techniques and instruments have been adopted to achieve accurate PSD outcomes. A comparative analysis was carried out by Goossens (2008) using 10 different instruments as shown in (Table 6.2). The instruments were divided into four categories depending upon their working principles. Out of these selected instruments, four of the instruments used the laser diffraction technique, which included the HORIBA LA 950, two other techniques were based on sedimentation, one was based on impedance measurements and the last three used optical techniques. The complexity of the measurement protocol, the complexity of the calculations, the amount of sediment required for measurement and the time necessary to perform a measurement were used as criteria to evaluate each method. The laser diffraction instruments produced the best results for the various criteria considered in the study.

A laser diffraction particle size analyzer reported by Andrew et al. (2010) was found to be the most accurate and reliable technique for measuring PSD in environmental samples of mixed compositions. In this technique, a particle will scatter light at an angle determined by that particles' size. Larger particles will scatter at small angles and smaller particles scatter at wide angles. A collection of particles will produce a pattern of scattered light defined by intensity and angle that can be transformed into a particle size distribution (HORIBA Manual, 2015). Furthermore, the advantage and limitations of particle sizing techniques to characterize stormwater runoff are summarized in (Table 6.2) (Grant et al., 2003).

Table 6.2: Summary of the comparative analysis of ten instruments for the study of PSD using wet samples (adapted from Goossens, 2008)

Name of Instruments	**Malvern Mastersizer S, Coulter LS 200, Fritsch Analysette 22 (version C), Horiba Partica LA - 950**	**Sedigraph 5100, Atterberg cylinder**	**Coulter Multisizer 3,**	**EyeTech, image analysis software Histolab and CIS-100**
	Criteria for the comparison of the techniques			
Working Principle	laser diffraction	sedimentation	impedance measurement	optical techniques
Reproducibility	higher reproducibility (the diffraction patterns are created by an accumulation of a very large number of individual grains). Small variations in the grain size distribution of a sample will create only small differences in the diffraction pattern	the experimental protocol of the Atterberg technique is complex	low level of reproducibility	low level of reproducibility (these methods measure the individual particles, the presence of only a few or sometimes single, coarse grain in a sample may substantially affect the behavior of the grain size curve near the course end of the spectrum)
Analysis time	few seconds	two hours for atterberg cylinder and few minutes for the sedigraph	rapid result	rapid result
Analytical range µm	0.05-900, 0.375-2000, 0.1-1250, 0.01-3000 respectively for the above instruments	0.1-300, 0.1-65 respectively	0.4-1200	0.7-6400, depends on microscope ised, 0.1-3600
Resolution of analysis (number of grain size classes)	64, 92, 62, 93 respectively	220, 6 respectively	256	NA (data are for individual particle, NA, 600
Extra data processing	If volume data are requested, no extra processing is needed for this technique	If desired, transformation of mass percentage to volume percentage (grain density data required)	Analysis of different steps may be necessary	None if desired classes are pre-selected except in Histolab, which is very time consuming

Advantages and limitations of particle sizing techniques to characterize stormwater runoff are summarised in (Table 6.3) as reported by (Grant et al., 2003).

Table 6.3: Measurement of particle properties (adapted from Grant et al. 2003)

Particle's (*P*'s) property measured	**Aspects measured**	**Advantages**	**Limitations**	**Sample instruments**
Transport property: sedimentation	Gravity	Directly applicable results to sedimentation basin design.	Slow	MICROMERITICS Sedigraph
Electrical property: differential resistance	Voltage pulse (proportional to *P*'s Volume)	Directly applicable results to sedimentation basin design.	Carrier fluid influence (e.g., coagulation); May disrupt fragile flocs	COULTER Multisizer 2
Light obscuration: (blockage)	Voltage pulse (proportional to *P*'s maximum cross-sectional area)	Change of particles in subsize region has no effect elsewhere. Results are not affected by *P*'s shape, nature, gravity, and refractive Index	May disrupt fragile flocs	NICOMP AccuSizer780 PACIFIC SCIENTIFIC INSTRUMENTS Model 9703
Light diffraction property: light intensity	Light intensity	Change of particles in the sub-size region has no effect elsewhere. Results are not affected by *P*'s, nature, gravity, and refractive index. Optical analogue of resistive pulse technique but without electrolyte.	Concentration of the solution has great influence on results	SEQUOIA LISST-100 MASTERSIZER S Laser Particle Size Analyser
Dynamic light scattering property: Time or spatial fluctuations in scattering intensity	Hydrodynamic effect—photo pulse signal	Do not require calibration step. Good for small particle till 1 nm.	Need long time to get stable	NICOMP PSS 170

6.2.3 Rainfall characteristics

Weather data from a Campbell weather station, situated at the University of Canterbury's Department of Civil and Natural Resources Engineering building were used for analysis. The weather station data were compared against meteorological records from the National Institute of Water and Atmosphere's (NIWA) weather station to verify accuracy. Data between stations were similar and therefore the University's weather data, which was closest to the carparks, were used for this research. Samples collected from 21 storm events were used to analyze seasonal PSD from three carparks. Nine storm events were sampled concurrently from three carparks in similar rainfall conditions.

Event average rainfall intensity, antecedent dry days (ADD), rain duration and total rain depth were monitored for all 21 storm events (Table 6.4).

Table 6.4: Rainfall characteristics of sampled events

Storm Event (SE)	Date and time	10 mins rain depth (mm)	10 mins initial rain intensity (mm/h)	average intensity (mm/h)	rain depth (mm)	rain duration (h)	antecedent dry days (day)
SE1	9/10/2015 15:45	1.8	10.8	10.8	1.8	0.16	4.49
SE2	9/22/2015 20:10	0.4	2.4	0.91	2.2	2.42	1.1
SE3	1/27/2016 15:10	0.2	2.4	2.96	10.6	3.6	0.25
SE4	2/17/2016 16:05	0.4	4	2.81	7.6	2.7	20.18
SE5	3/15/2016 14:50	0.6	3.6	1.24	3.2	2.58	6.61
SE6	3/24/2016 0:10	0.2	1.2	2.05	10.6	5.17	7.5
SE7	4/8/2016 5:15	0.2	1.2	2.4	2	0.9	3.75
SE8	5/20/2016 18:05	0.6	3.6	3.3	7.8	2.3	3.76
SE9	5/22/2016 20:30	0.4	2.5	1.1	4	3.5	1.15
SE10	5/28/2016 1:00	0.4	2.5	3.23	7.8	2.4	1.3
SE11	6/22/2016 1:00	0.4	2.5	0.65	0.6	0.92	9.4
SE12	6/23/2016 8:05	0.2	1.25	0.91	1.7	1.9	1.26
SE13	7/8/2016 0:30	0.2	1.25	0.81	4.2	5.2	7.3
SE14	7/13/2016 20:50	1	6.25	6.87	12.6	1.8	5.6
SE15	8/3/2016 7:45	0.2	1.25	1.09	1	0.9	3.4
SE16	8/12/2016 21:25	0.2	1.25	0.39	4.6	11.8	4.2
SE17	8/26/2016 11:05	0.8	5	1.97	4.6	2.3	12.9
SE18	9/6/2016 4:25	0.2	1.25	1.1	1	0.9	0.63
SE19	9/27/2016 3:05	1	6.25	6.25	1	0.16	1.93
SE20	10/6/2016 15:45	1.2	7.5	4.6	5	1.1	1.24
SE21	10/14/2016 15:05	0.8	5	1.6	3.2	2	2.12
	Average	**0.54**	**3.5**	**2.3**	**5.4**	**3**	**6**
	(Min-Max)	**(0.2 - 1.8)**	**(1.2 - 10.8)**	**(0.39 - 6.87)**	**(1 - 12.6)**	**(0.9 - 11.8)**	**(0.25 - 20.18)**

6.3 Statistical analysis

Statistical analysis was conducted using SPSS software. D50 (the size at which 50% of particle pass i.e, median particle size), D10 (the size at which 10% of particle pass) and D90 (at which 90% of particle pass) were used as major particle size classes used during the statistical analysis. The percentage of sand (>63 µm), coarse silt (20-63 µm), medium to fine silt (20-2 µm) and clay (≤2 µm) were further classified based on ISO 14688 International Soil Classification.

The key particle size matrices were analyzed using the Shapiro-Willis test. Since the results were mixed (data were non-normal with few exceptions), a Mann-Whitney U test was performed to determine the differences between the particle size during the wet and the dry seasons. The wet season was from June to Sep (SE 11, SE 12, SE 13, SE 14, SE 15 and SE 19) and the dry season was from October to May (SE 2, SE 3, SE 4, SE 5, SE 6, SE 7, SE 8, SE 9 and SE 10, SE 20, SE 21).

Data were then log transferred to meet the assumption of normality when required. The assumption of non-normality is quite common in stormwater quality analyses (Buren et al., 1996). A one-way ANOVA test was performed to determine if a significant difference existed between the key particle sizes during first flush and consecutive steady-state periods within the carparks and between the carparks.

A Pearson's correlation was performed to establish the relationship between rainfall parameters with key PSD metrics.

6.4 Results

6.4.1 Particle size fractions (D10, D50 and D90) distribution from 21 storm events

Key particle size metrics D10, D50 and D90 were used to analyze the distribution pattern using Boxplots for each carpark (Figure 6.2).

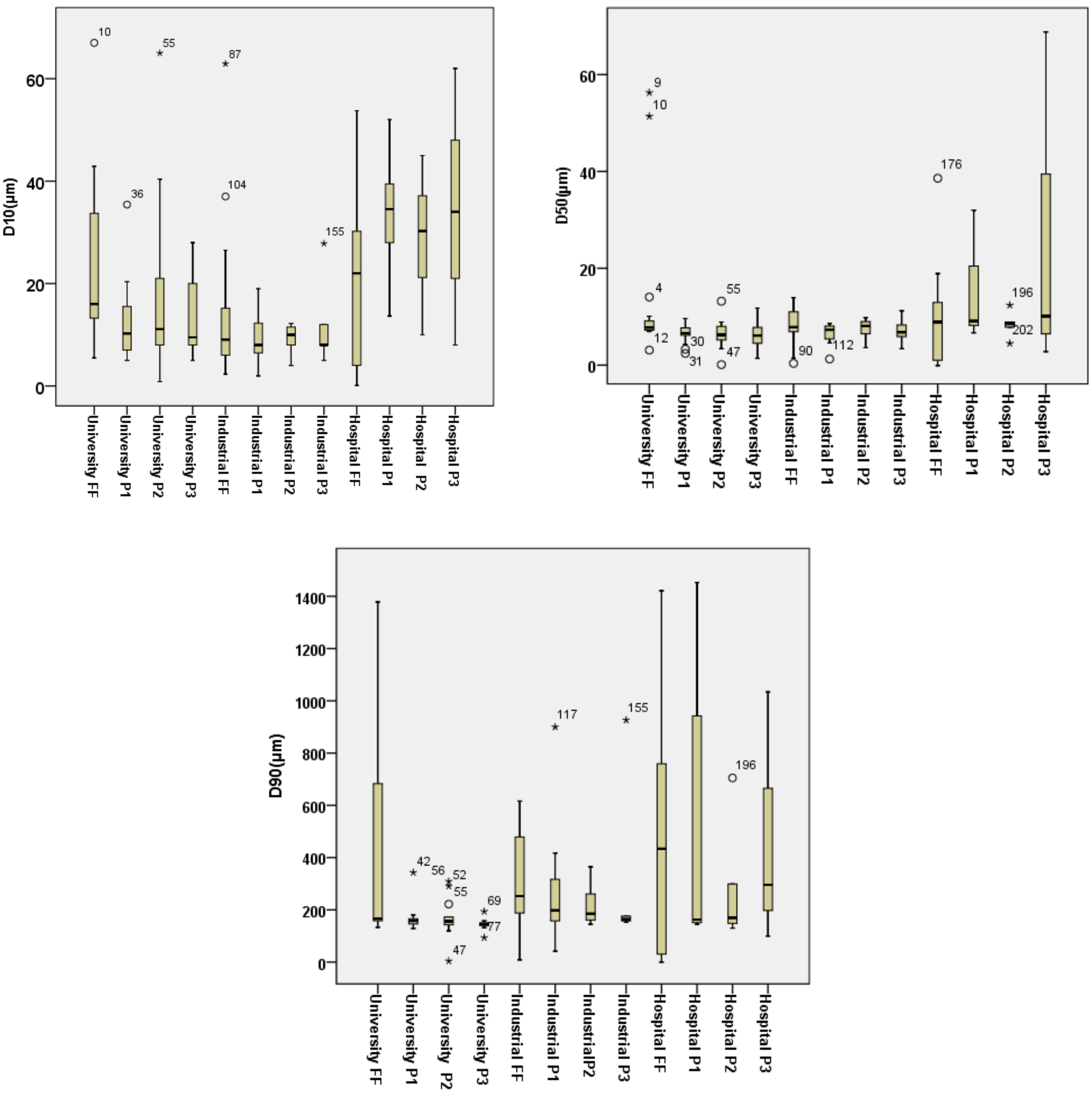


Figure 6-2: Boxplots of observed D10, D50 and D90 values from 21 storm events sampled (12 samples in each storm event, total 188 samples were analyzed) during September 2015 to October 2016 from three different carparks. Boxplots for each carpark show the range from the first to third quartiles, with the median value indicated by a line and whiskers showing the range of observations excluding outliers. (° denotes outlier's ± 1.5x Inter Quartile Range (IQR), * denotes outlier's ± 3x IQR).

Overall, the D50 value shows the least variation at the university and the industrial carparks. D90 values were relatively consistent at the university steady-state periods. The hospital carpark shows a wide range of variation for the metrics (D10, D50 and D90) analyzed. D10 and D90 values of particle size distribution display high variability for all three carparks (Figure 6.2). Boxplots also illustrated that differences in median values for D10, D50 and D90 particle size for the university and the industrial carparks were relatively small as compared to the hospital carpark. The higher variation of median particle size at the hospital carpark can be attributed to the contribution of wind-deposited particles, as the hospital carpark is closer to the foothills, in addition to differences in traffic characteristics and the diversity of pollutant generating activities. The differences in mean, median and (min-max) values were relatively narrow for each of the carpark when compared to 21 storm events (total storm event sampled) and 9 storm events (all the carparks were sampled concurrently) (Table 6.5).

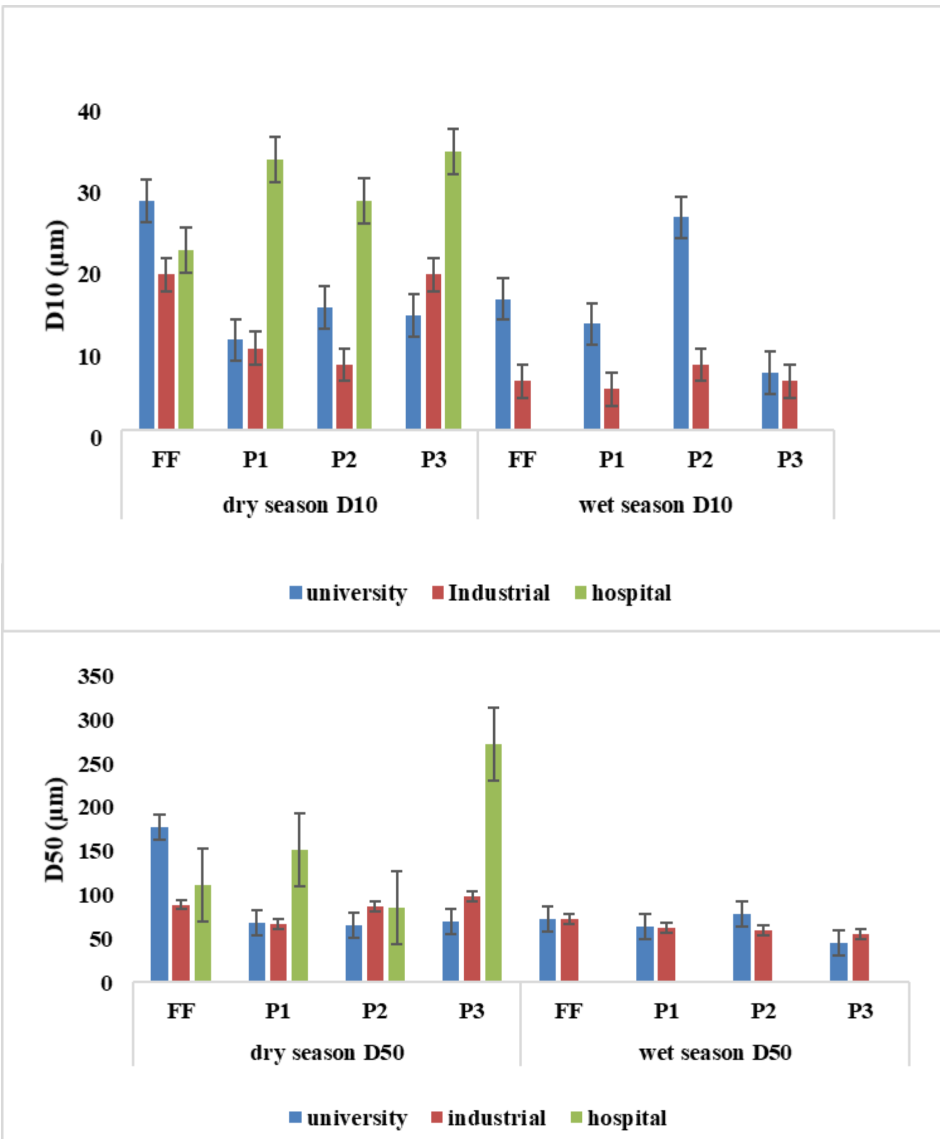
Table 6.5: Mean, Median and (Min-Max) of D10, D50 and D90 particle size value for each carpark from 21 storm events (total storm events sampled) and 8 storm events (all the carparks were sampled concurrently)

	Mean		**Median**		**Min -Max**	
	21 storm events	**8 storm events**	**21 storm events**	**8 storm events**	**21 storm events**	**8 storm events**
			D10 (µm)			
University FF	24	24	16	16	5-67	11-67
University Period 1	13	10	10	9	5-35	5-20
University Period 2	18	17	11	11	0.85-65	0.85-65
University Period 3	13	14	10	10	5-28	5-28
Industrial FF	15	19	9	10	2-63	2-63
Industrial Period 1	9	12	8	11	2-19	6-19
Industrial Period 2	9	14	10	10	4-12	4-50
Industrial Period 3	12	13	8	10	5-28	5-28
Hospital Period FF	23	23	22	20	0.08-54	0.7-51
Hospital Period 1	34	38	35	38	14-52	25-52
Hospital Period 2	29	27	30	26	10-45	10-45
Hospital Period 3	35	35	34	34	8-62	8-62
			D50 (µm)			
University FF	135	124	78	76	32-564	32-515
University Period 1	66	66	67	67	25-97	34-89
University Period 2	66	64	63	55	2-133	2-133
University Period 3	63	64	62	62	15-119	15-119

Industrial FF	83	102	79	86	5-140	5-260
Industrial Period 1	66	75	74	83	14-87	47-106
Industrial Period 2	77	86	82	84	37-99	37-165
Industrial Period 3	72	81	69	77	35-113	35-123
Hospital Period FF	111	96	90	95	0.12-387	3-190
Hospital Period 1	151	206	92	205	38-321	92-321
Hospital Period 2	85	75	86	89	46-125	46-90
Hospital Period 3	273	273	102	102	29-689	29-689
			D90 (μm)			
University FF	434	423	166	164	133-1378	133-1378
University Period 1	167	171	158	153	129-343	129-343
University Period 2	169	179	156	157	4-309	4-309
University Period 3	145	143	145	143	94-194	94-194
Industrial FF	312	367	253	252	9-616	9-809
Industrial Period 1	272	340	198	356	42-900	101-900
Industrial Period 2	215	231	185	201	145-365	145-365
Industrial Period 3	315	354	164	170	153-926	153-926
Hospital Period FF	467	374	434	305	0.16-1421	5-882
Hospital Period 1	564	873	162	942	145-1453	155-1453
Hospital Period 2	270	156	170	157	130-705	130-182
Hospital Period 3	476	476	296	296	99-1034	99-1034

6.4.2 Seasonal variation in median particle size distribution in three carparks

The seasonal variation of D10, D50 and D90 particle sizes were analyzed to identify the influence of wet and dry seasons on PSD for the carparks. The hospital carpark was not included in the comparison, as this carpark was non-operational after the dry season. The distribution pattern of D50 during the wet and the seasons are relatively similar except for the dry first flush at the university carpark (Figure 6.3). D10 particle size is relatively high at the university carpark as compared to the industrial carpark during the wet season and D90 particle size is relatively high during the dry season at the industrial carpark. The hospital carpark displayed consistently higher mean particle size during the dry season. No consistent trend was observed during the dry and the wet seasons between the different sampling periods (FF, P1, P2, P3) and within each carpark.



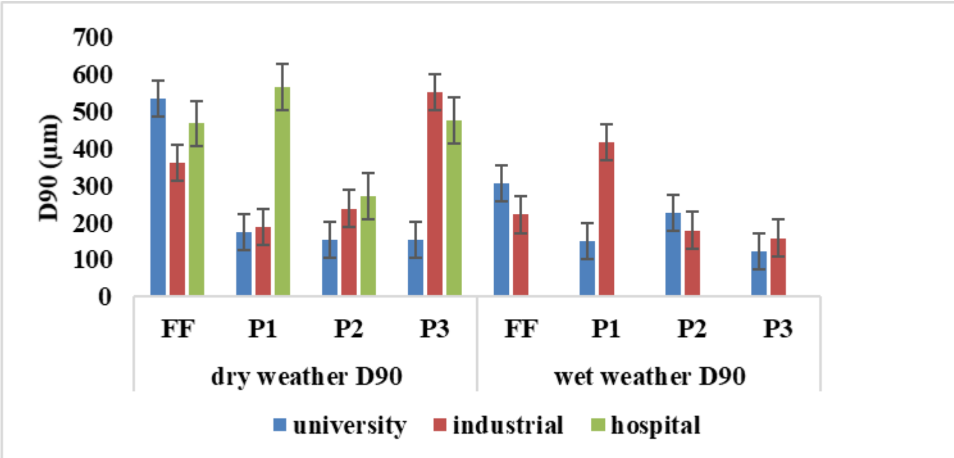
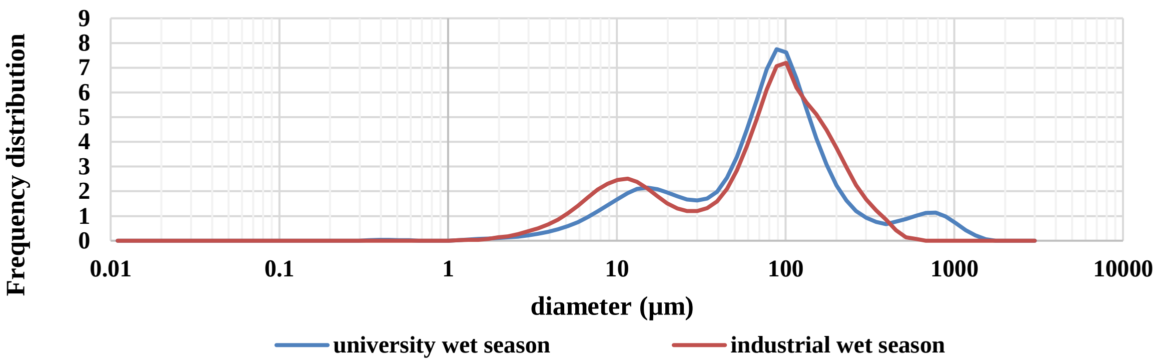


Figure 6-3: Mean D10, D50 and D90 particle size during the wet and dry seasons from three urban carparks FF, P1, P2, P3 are sampling periods: First flush, period 1 (first 40 mins of sampling period), period 2 (41 to 80 mins) and period 3 (81 to 120 mins). FF samples from hospital carpark during the wet season were not included as the carpark was non-operational during that period.

The traffic characteristics and drainage area can also result in differences in sediment deposition and hence PSD. The variability evident in the particle size distribution at the hospital carpark further confirms the influence of surrounding topography (influencing atmospheric deposition) and surrounding land use characteristics along with traffic. These visual representations were further confirmed by using the Mann-Whitney U test between each surface type and flow periods (period 1, period 2 and period 3). A Mann-Whitney U test revealed no significant differences in each flow period and between each period of the dry and the wet seasons except for first flush and period 1 during the dry season at the university carpark for D50, first flush and period 3 during the dry and the wet seasons for D90 and first flush and period 1 for the dry season for D10. No significant differences were noted at the industrial carpark during each flow period and between the dry and the wet seasons. Since there were no differences between each flow period, a representative particle size distribution curve was developed for each carpark.



Frequency distribution
9
8
7
6
5
4
3
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0
0.01
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1
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100
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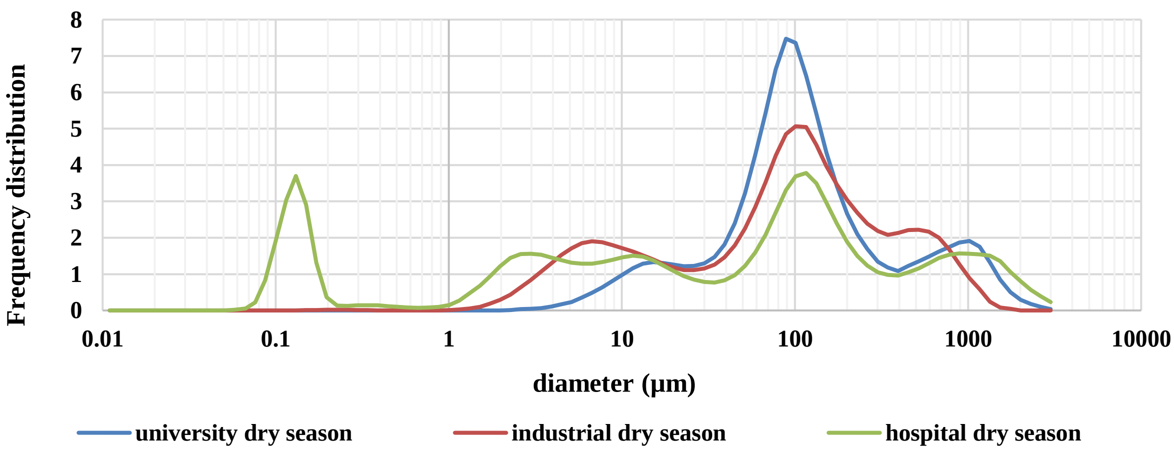
10000
diameter (μm)
university wet season
industrial wet season

(a)



Frequency distribution
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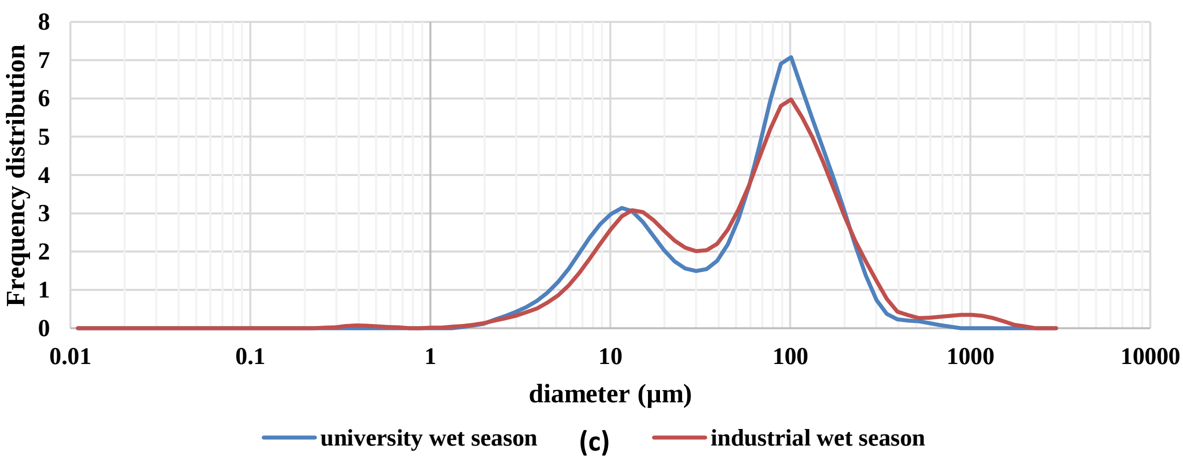
diameter (μm)
university dry season
industrial dry season
hospital dry season

(b)



Frequency distribution
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diameter (μm)
university wet season
industrial wet season

(c)

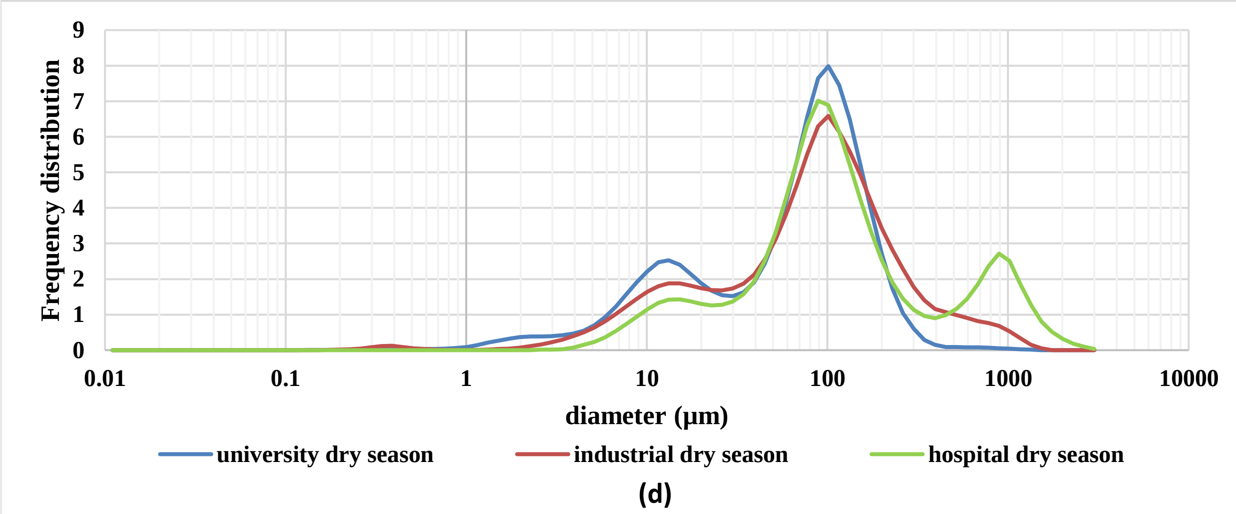


Figure 6-4: Average (P1, P2 and P3) seasonal mean frequency PSD for three carparks during first flush and steady-state periods. Wet season was considered from June to Sep (SE 11, SE 12, SE 13, SE 14, SE 15 and SE 19) and dry season was considered from October to May (SE 2, SE 3, SE 4, SE 5, SE 6, SE 7, SE 8, SE 9 and SE 10, SE 20, SE 21) : a) wet season first flush, b) dry season first flush, c) steady-state wet season and d) steady-state dry season

During the wet season, the university first flush carpark runoff (while averaging all PSDs from each season) was found to have a poly-model distribution with three distinct peaks around 10-11 µm, 80-100 µm and 500-1000 µm whereas the industrial carpark was found to have bi-model distribution with peaks around 9-11 µm and 80-100 µm. On the other hand, during the dry season (Figure 6.4) variations in size distribution within the three carparks with more than three distinct peaks were noticed. First flush hospital carpark showed the highest variations in PSD across all the storm events during the dry season as compared to steady-state periods. Notable peaks were seen around 0.1-0.2 µm (clay particles) during the dry first flush period which was likely contributed from a single storm event sampled on January 2016.

6.4.3 Variation of PSDs with and without traffic at the hospital carpark

The variation of PSD is mainly influenced by traffic volume and atmospheric deposition (Gidhagen et al., 2004). The highest variation was seen during the first flush (active) carpark with more than two notable peaks as compared to the (passive) carpark. As the storm progressed, the influence of traffic on particle size distribution decreased. However, the strength of the relationship between traffic and PSDs and contribution of wind-deposited particle sizes have not been investigated due to lack of continuous traffic and wind direction/speed data during the sampling period.

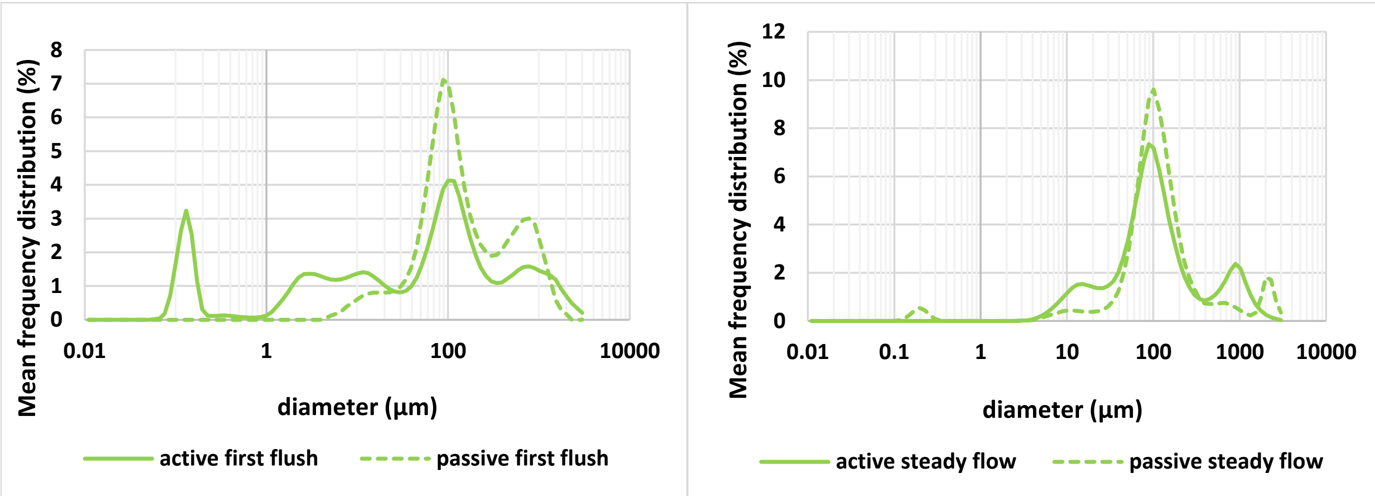


Figure 6-5: PSD profile (an average of storm events 2, 3, 4, 5, 6 and 10 for active carpark and storm events 12, 15, and 18 for passive first flush (left) and steady-state runoff (right) from hospital carpark.

6.4.4 Particle size distributions across the three carparks

A one-way analysis of variance (ANOVA) between groups was conducted to explore the difference in D10, D50 and D90 values across the three carparks and within each flow period. Three carparks did not differ significantly from each other. Despite no significant differences, the mean value for the hospital carpark was quite high as compared to the university and the industrial carparks (Table 6.6). The median diameter D50 in the three carparks ranged from 79-162 µm, lower at the university carpark and higher at the hospital carpark. The results showed that the particle size from all three carparks was predominantly sand particles (sand >63 µm) with the highest at the hospital carpark and lowest at the university carpark followed by fine silt (20-2 µm). The industrial carpark had the highest variation in the particle size categories followed by the university carpark.

Table 6.6: Summary statistics for representative D10, D50 and D90 values (Mean, Minimum and Maximum) for three carparks

Land use	Number of samples analyzed (n)	D10 µm (Mean, Min-Max)	D50 µm (Mean, Min-Max)	D90 µm (Mean, Min-Max)
University	34	16, (5-45)	79, (21-214)	229, (90-556)
Industrial	33	15, (4-40)	86, (31-164)	323, (102-750)
Hospital	14	31, (11-53)	162, (43-323)	470, (97-888)

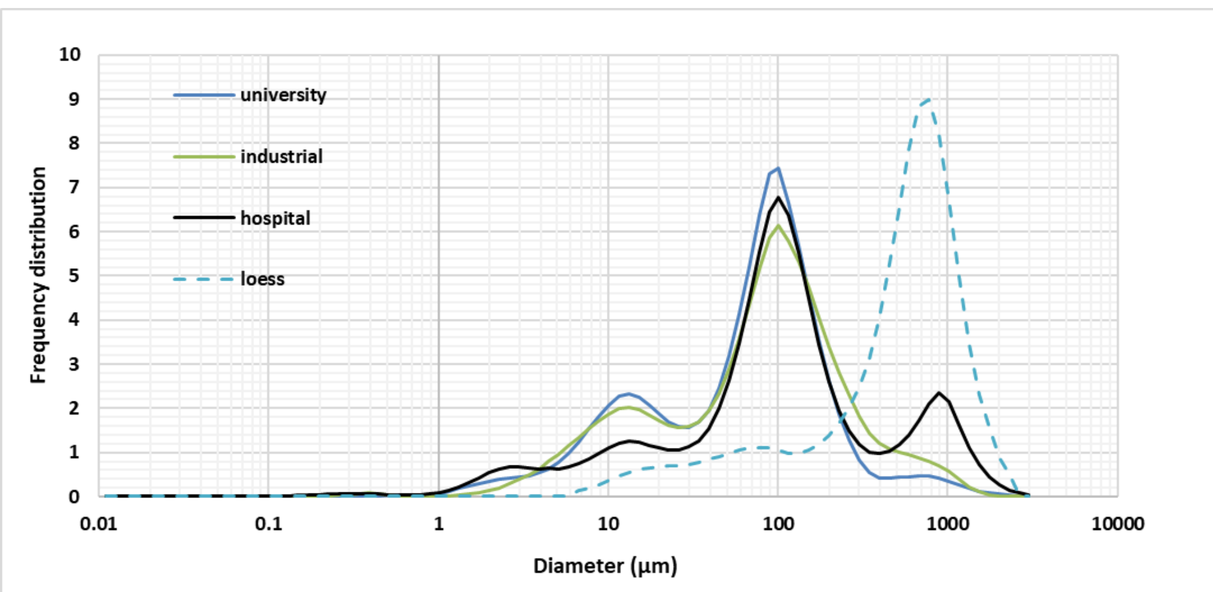
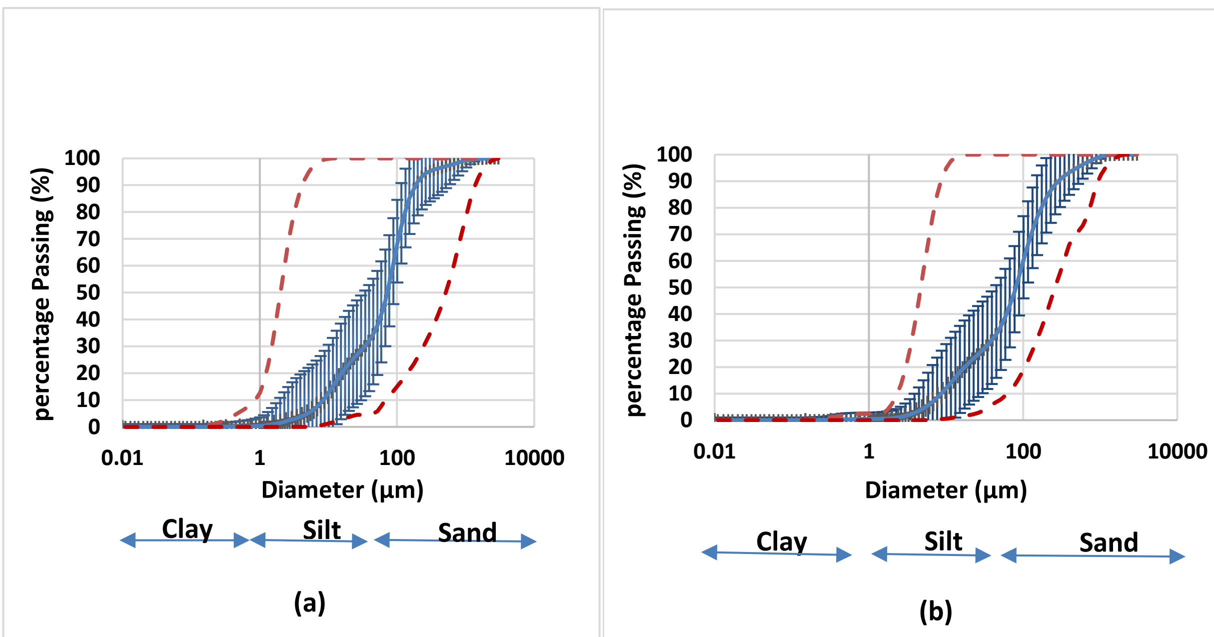


Figure 6-6: Mean frequency PSD for the three carpark surfaces compared to mean representative soil taken from an adjacent hill.

Since there were no significant differences between D10, D50 and D90 particle size for each period, typical PSD profiles for the three carparks were developed based on the mean value for each size fraction from nine storm events and from both first flush and steady-state periods (period 1, period 2 and period 3) which were sampled concurrently under the same rainfall conditions. University and industrial carparks were found to have a bi-modal distribution, with a peak centered at 10-11 µm and 80-110 µm (Figure 6.6). At the hospital carpark, poly-modal distribution was observed with minor peaks centered around 1-2 µm and 10-11 µm and significant peaks around 80-110 µm and 800-1000 µm. The hospital carpark PSD profile showed the highest variation in PSD across all samples. The samples were compared with loess samples collected from hills adjacent to the hospital carpark to observe any influence from wind transported particles. Furthermore, % of sand, silt and fine were assessed with percentage passing curve at different particle sizes profile as shown in (Figure 6.7). There was a slight difference in the cumulative percentage of the particle size between the industrial and the university carparks. The hospital carpark exhibited a wide variation across the storm events.



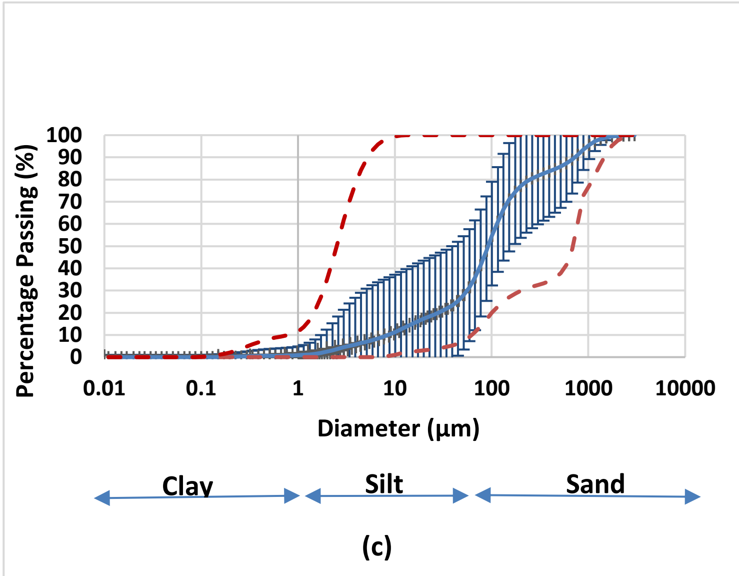


Figure 6-7: Mean cumulative PSDs (solid lines) +/- 1 S.D. and maximum and minimum (dotted lines) for three carparks: a) university carpark, b) industrial carpark and c) hospital carpark

Table 6.7: Summary statistics for representative % of sand, silt and clay (Mean, Maximum and Minimum) for three carparks (average from 9 storm events)

Carparks	**Sand** >63 µm (%)	**Coarse silt** 20-63 µm (%)	**Medium to fine silt** 20-2 µm (%)	**Clay** ≤2 µm (%)
		mean%, (max% - min%)		
University	60, (92 - 20)	19, (28 - 3)	22, (58 - 4)	2, (49 - 0)
Industrial	59, (86 - 0)	17, (45 - 0)	21, (100 -2)	1, (9 - 0)
Hospital	74, (91 - 31)	15, (31 - 6)	15, (65 - 3)	2, (35 - 0)

For all carparks, the sand fractions are the dominant size fraction observed (Table 6.7). The clay and medium to the fine silt ranged from 2% to 22% at the university carpark. The decrease in clay and silt is accompanied by an increase in sand particles. The percentage of sand was 74% at the hospital carpark with less fine size fractions sediments.

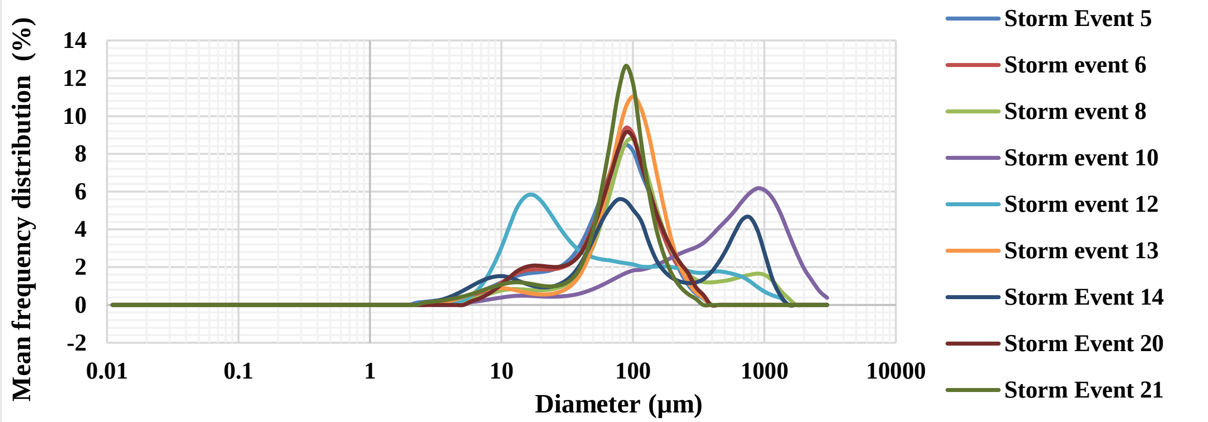
In addition, suspended solids concentrations and % of sand, silt and clay from FF as well as steady-state (Table 6.8) illustrates the constant decrease of TSS concentrations as the storm progressed. However, there was no clear trend over the % distribution of particle size fractions over the duration of sampling periods. Although the % of coarser particles tend to decrease from first flush through later runoff at some sites, it says little about the general trend of distribution pattern.

Table 6.8: Mean TSS and mean % sand, silt and clay for three carparks (FF as well as from steady-state runoff from 21 storm events)

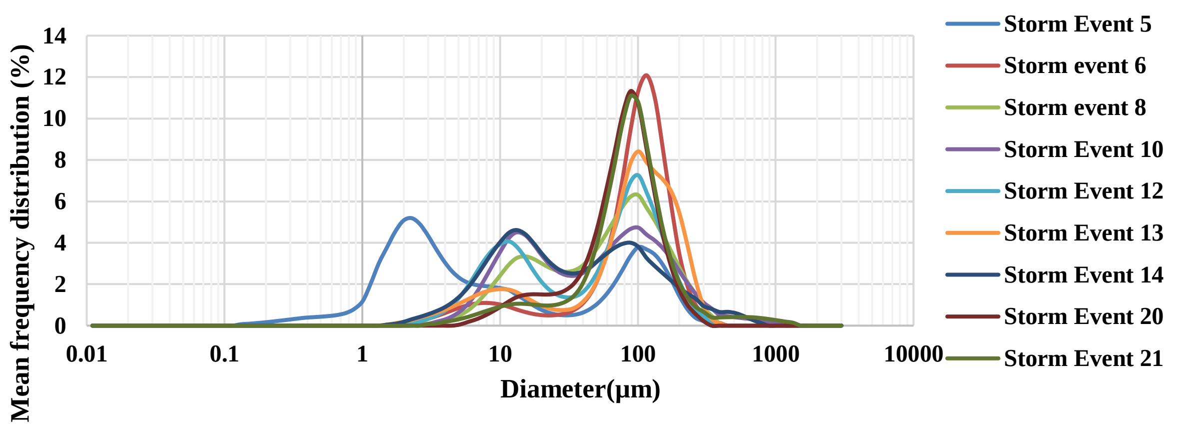
Carpark runoff at the different time phase	**TSS** (mg/L)	**Sand** >63 μm (%)	**Coarse silt** 20-63 μm (%)	**Medium to fine silt** 20-2 μm (%)	**Clay** ≤2 μm (%)
University FF	174	67	20	13	0
University period 1	33	56	18	25	0.15
University period 2	27	62	18	23	5
University period 3	21	52	20	27	0.15
Industrial FF	781	53	12	25	0.14
Industrial period 1	139	58	21	20	0.5
Industrial period 2	71	64	17	17	1
Industrial period 3	36	58	19	22	0.5
Hospital FF	237	78	13	23	9
Hospital period 1	58	81	13	6	0
Hospital period 2	19	66	21	14	0
Hospital period 3	14	67	15	17	0

6.4.5 Intra event variations on PSD from three carparks

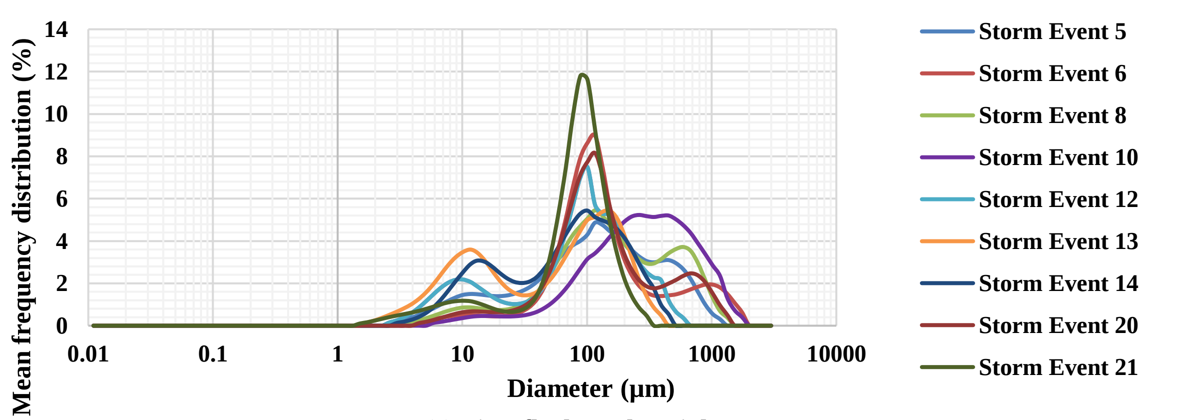
Variations in particle size distribution were observed between first flush and steady-state periods across the same event at each carpark. Except for the first flush storm events 10, 12 and 14 at the university carpark, distribution patterns were found to have a similar trend, with a minor peak around 1.7 μm to 13 μm and major peak around 70-110 μm (Figure 6.8) for all the carparks studied. A similar trend in PSD was observed for first flush and steady-state at the industrial carpark except more coarse particle existed during the first flush. The hospital carpark did not show any clear trend with high variability among each storm events, especially during first flush. The frequency distribution curve during storm 6 (Figure 6.8 e) at the hospital first flush was found to be finer, this was a random case.



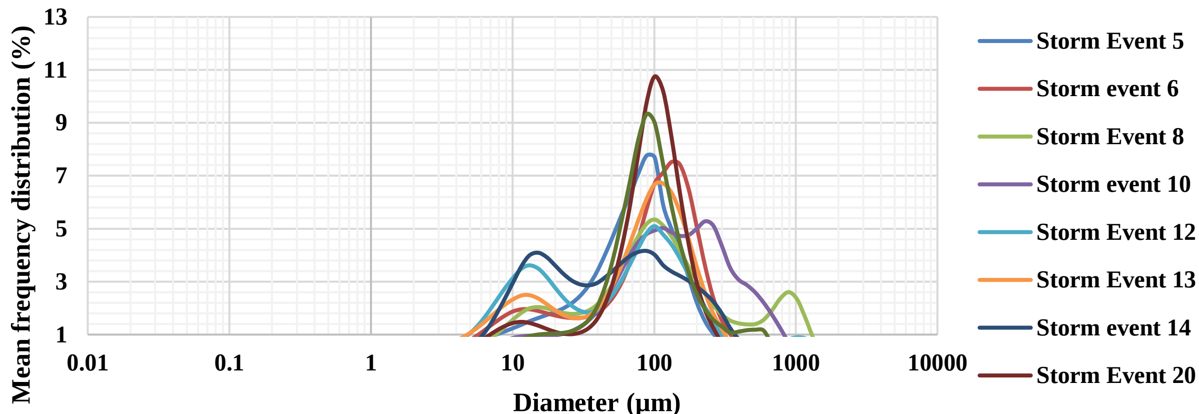
(a) First flush: University



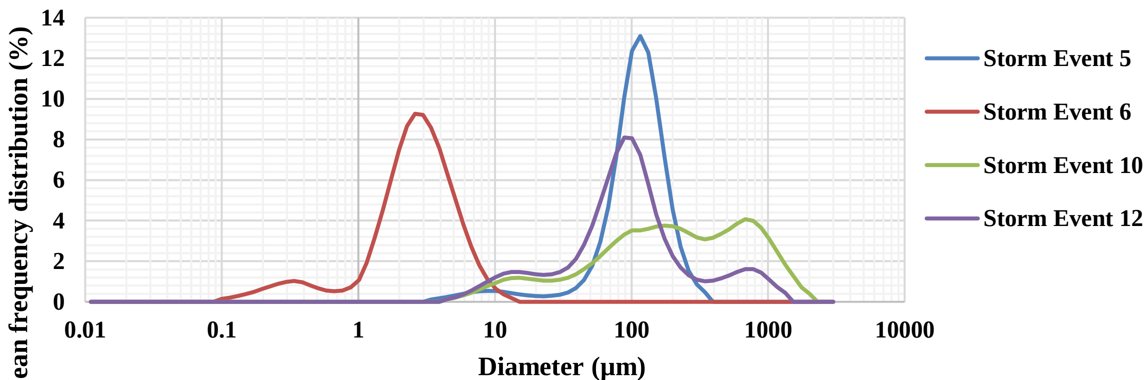
(b) Steady-state: University



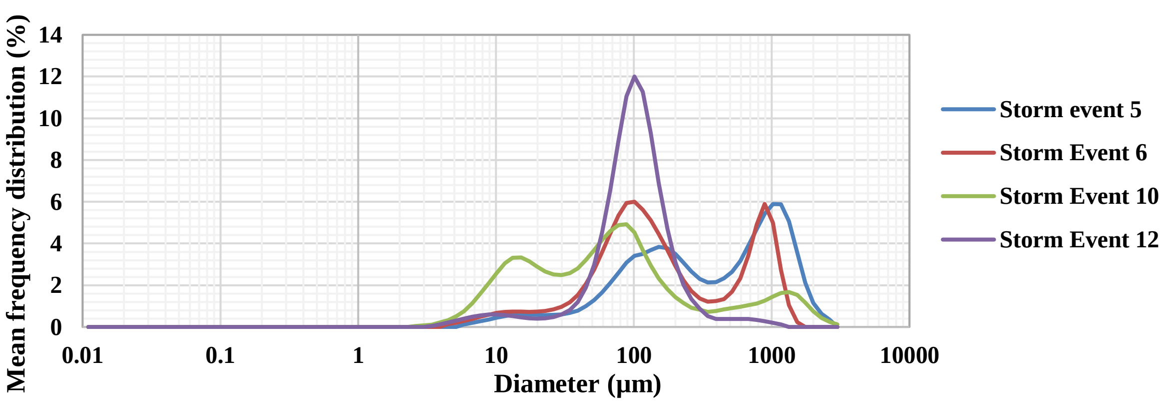
(c) First flush: Industrial



(d) Steady-state: Industrial



(e) First flush: Hospital



(f) Steady-state: Hospital

Figure 6-8: Mean frequency distribution for three carparks during first flush and steady-state periods. a) first flush: university, b) steady-state: university, c) first flush: industrial, d) steady-state: industrial e) first flush: hospital, f) steady-state: hospital. 9 storm events were sampled concurrently from the university and the industrial carparks during same rain conditions and 4 storm events were sampled from the hospital carpark

6.4.6 Role of rainfall characteristics on particle size in different land use

A Pearson correlation was conducted between D10, D50 and D90 with various rainfall parameters, namely initial rain depth, antecedent dry days, initial rain intensity and first 10 mins rainfall intensity (Table 6.9). The findings showed that only D50 and D10 particle sizes were significantly correlated to various rainfall parameters. In all the carparks, PSD metrics (D10, D50 and D90) were significantly correlated to each other. None of the PSD metrics were significantly correlated with rainfall parameters at the university carpark. Overall, very little influence from rainfall parameters on PSD matrices was noted for the other two carparks.

Table 6.9: Correlation analysis between D50, D90 and D10 with rainfall characteristics from 21 storm events

Carpark	**Correlation with D50**	**Correlation with D90**	**Correlation with D10**
University FF	D90 (r = 0.69, p <0.01), D10 (r = 0.63, p <0.01)		
University SF	D90 (r = 0.79, p <0.01), D10 (r = 0.76, p <0.01)	D10 (r = 0.58, p < 0.01)	
Industrial FF	D90 (r = 0.96, p <0.01), D10 (r = 0.71, p <0.01), ADD (r = -0.53, p <0.05)	D10 (r = 0.72, p < 0.01)	
Industrial SF	D90 (r = 0.66, p <0.01)		IRD (r = 0.43, p <0.05), IRI (r = 0.41, p <0.05)
Hospital FF	D90 (r = 0.99, p <0.01), D10 (r = 0.96, p <0.01), IRD (r = 0.68, p <0.05),	D10 (r = 0.95, p < 0.01)	IRD (r = 0.69, p <0.05)
Hospital SF	D90 (r = 0.86, p <0.01), D10 (r = 0.76, p <0.01),		

IRD = Initial rain depth (first 10 mins rain depth), ADD= antecedent rain days, IRI= initial rain intensity (first 10 mins rainfall intensity)

6.5 Discussion

6.5.1 Role of PSD in heavy metals and sediments transport: comparison with published papers

Heavy metals such as Zn, Cu and Pb are predominately transported with suspended solids to urban waterways. Knowledge of total and dissolved metal concentrations (as discussed in chapters 4 and 5) are not always enough to explain the potential impacts of heavy metals on urban waterways. The concentration of heavy metals is significantly affected and associated with the particle size distribution (Tuccill, 2006), with increased metal concentrations associated with smaller particle sizes (Zanders, 2005; Sansalone and Buchberger, 1997b). Stormwater management treatment options are designed to improve water quality and therefore largely depend upon pollutant removal by settling or filtering of sediments. Sand size particle fractions will settle readily, but fine particle such as clay and silt may be discharged into waterways with runoff flow because of their lower settling velocities (Pitt et al., 1995). The affinity of heavy metals with various size fractions was reviewed from the literature (Table 6.10). It was seen that generally heavy metals loads were associated with smaller size fractions (<63 µm)as compared to coarser particles. The smaller particles have a larger surface area which is dependent on mineral composition (Juracic and others 1980, 1982).

In this study separate size fraction analysis was not carried out for heavy metals, however, the overall particle size distribution in the three carparks showed that 26% to 40% were fine particles, which are expected to have the highest metal concentrations.

Table 6.10: Summary of dominant size fractions of various land use

Geographic locations	Reference	Land use	Dominate particle size fraction
Sydney, Australia	Brich and Scollen, 2009	urban, road runoff	<63 µm
Marie, Canada	Stone and Marsalek, 1996	river bottom sediment	<63 µm
Korea	Duong and Lee, 2009	road dust from industrial areas	<75 µm (varied from element to element)
Gela, Italy	Manno et al., 2006	urban, industrial, peripheral	medium size particles (12-63 and 63-40 µm)
Queensland state, Australia	Herngren et al., 2005	residential, industrial and commercial	<150 µm
LA, USA	Lau and Stenstrom, 2005	residential, industrial and commercial	100-250 µm
Lulea, Sweden	Viklander, 1998	city center and housing area (with varied traffic loads)	<75 µm
India	Singh et al., 1998	bed sediments	<37 µm
Beijing, China	Zhao et al., 2010	road-deposited sediment	<44 µm
Bejing, China	Li et al., 2014	road-deposited sediment	<150 µm
China	Yao et al., 2015	river sediment	<16 µm (78% - 82%) of total metal loadings

6.5.2 Turbidity and TSS in relation to particle size

Suspended solids consist of many different particles of varying sizes and thus have the ability to obstruct the transmittance of light in a water sample when TSS concentration increases, light scattering intensity decreases (Sadar, 1998). Turbidity is mainly defined as the optical property of the water sample that causes light to be scattered and absorbed rather than transmitted in straight lines (APHA, 2005) which are affected by suspended particles in water. In many studies, turbidity was used as a surrogate for measurement of suspended solids even though turbidity is not a direct measure of suspended particles in water. A strong positive relationship between suspended solids and turbidity will possibly assist environmental decision makers in the selection of the most economic option for estimating suspended solids concentration. However, there are many factors which could influence the turbidity of the water sample such as particle size distribution, which is often neglected during the decision-making process.

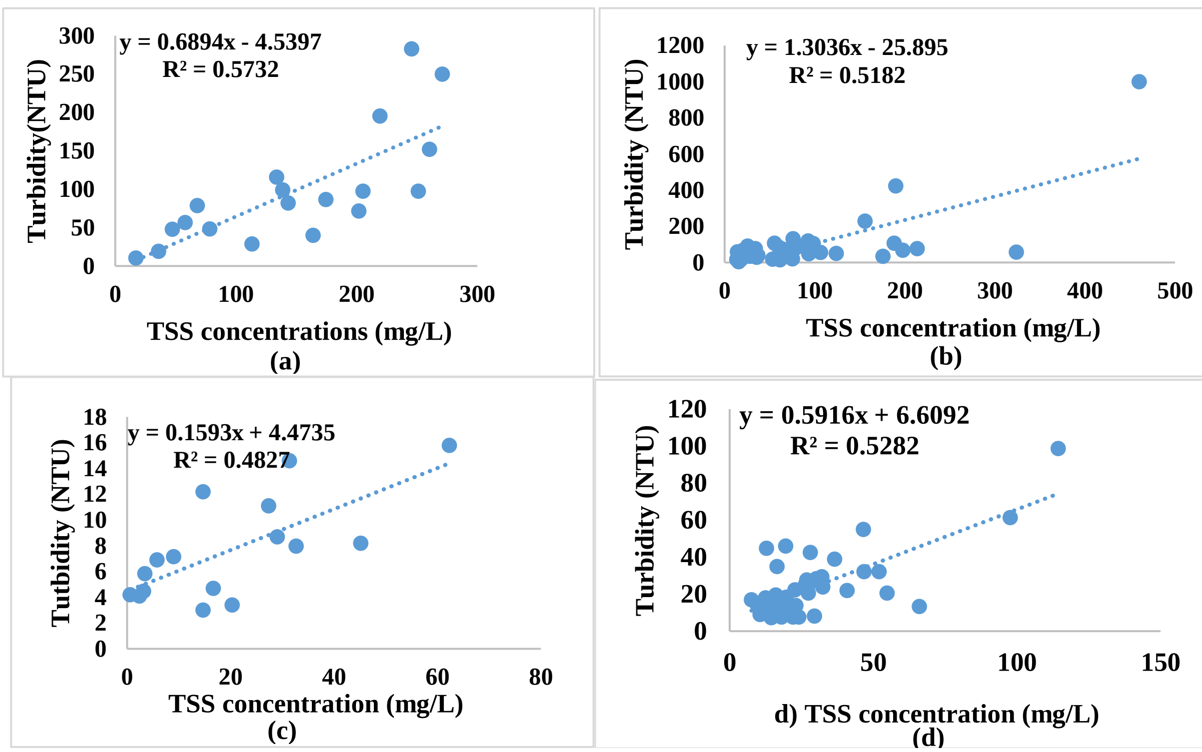


Figure 6-9: Correlation between Total Suspended Solids (TSS in mg/L) and Turbidity level (NTU) from left a) university first flush b) industrial steady-state c) hospital steady-state and d) university steady-state, which were analyzed from 21 storm events between Sep 2015 to Oct 2016

A moderate correlation (R^2 = 0.5) between TSS and turbidity was observed at all the carparks during first flush and steady-state (Figure 6.9). Although previous studies have found a strong correlation between TSS and turbidity (Packman et al., 1999, Gippel, 1995) across different land uses, particle size distribution also influences the turbidity measurement. Suspended solids consist of many different particles of varying sizes. Some of the particles are heavy enough (especially sand particles) and eventually settle and influence turbidity readings. The findings of this study show that approximately 60% of particles are sand (>63 µm) in the distributions and thus establishing a relationship between turbidity and TSS is problematic due to the dominance of larger particles (which have a higher settling rate). In addition, differences in size (Clifford et al., 1995; Gippel, 1988), color (Malcolm, 1985) and reflectivity of the particles **(**Bhargava and Mariam, 1991), could affect the light scattering of a suspension. For these carparks, using turbidity to serve as a surrogate for TSS measurement is not recommended without considering particle size distribution.

6.5.3 Factors influencing PSD in urban carpark: Land use, surrounding topography, rainfall characteristics (seasonal variations and rainfall parameters)

Incorrect assumptions about PSD in urban stormwater could result in the oversized or undersized design of treatment systems because particle size is a key contributing factor in the overall solids removal efficiency (Selbig, et al., 2016). Site-specific measurement of particle characteristics would provide the most accurate information for the design of stormwater treatment in terms of cost and long-term environmental benefit.

Results of this study show that median particle size (D50) at the university and the industrial carparks had a relatively similar value (closer to the fine particle) which were similar to the findings reported by Charters et al. (2016) from the same catchment for road runoff. The hospital carpark had a larger median particle size value (155 µm: sand-sized particles) during steady-state. However, the median particle sizes are larger during first flush than steady-state periods for all the carparks. This may be due to differences in sampling technique for first flush and steady-state periods. As first flush samples were directly collected from surface runoff before entered into the sampling sump or drainage network whereas steady-state samples were collected from autosamplers that had gone through the carpark internal drainage network at the university and sampling sumps at two other carparks. The larger median particle size at the hospital carpark may be due to the influence of the surrounding topography (hills). In addition, seasonal PSD's at the industrial and the university carparks showed only minor differences. A similar finding was reported by Selbig et al. (2016) for the study carried out for a residential and commercial parking lot.

Only small seasonal variations were observed at the university carpark and none of the other carparks exhibited any seasonal differences in D10, D50 and D90. The university carpark was not operational from November to early February as well as during the term breaks. The irregular traffic volume during the dry season might have impacted the particle size distributions as compared to the wet season as traffic rate affects PSD (Virtanen et al., 2006). The hospital (when operational) and industrial carparks, on the other hand, had a consistent traffic flow throughout the different seasons.

Three carparks had a minor peak of around 10-11 µm suggesting that these fine particles could be derived from wear and tear of vehicular parts such as tires and brakes linings. Similar findings were reported by (Charters et al., 2016) for a road runoff and (Cadle and Williams, 1978) for a particulate emitted from tires ranges in size from 0.01 to 30 µm. For the three carparks, particle size centralized around 80-105 µm (sand particles) and the findings were similar to those from Ball et al. (1998) and Miguntanna (2009).

6.5.4 Role of PSD in treatment performance

Though there were no significant differences between particle size distribution pattern during first flush and steady state, the intra event PSD distribution pattern suggests that stormwater treatment systems should target both fine and coarse particle size. Many of the treatments systems are designed to remove coarser sediments, however, findings from this study found that approximately 40% of the particle were below 63 µm. These particles need to be addressed when designing or implementing suitable proprietary devices in these carparks. Targeting the fine size particles would also assist in the removal of a significant amount of heavy metals from these carparks.

6.5.5 Comparison of findings to other national and international literature

While this study has helped characterize the PSD of urban carpark runoff in a similar geographical location using both grab and automatic sampling methods, there is uncertainty about the factors affecting the wide variability of particle size results reported by various researchers.

International literature was reviewed for PSD from carpark surfaces as a result of different traffic densities and drainage area. Characteristics of land use, analytical methods and median values were discussed in (Table 6.11).

Table 6.11: Comparison of median particle size in stormwater runoff from previous studies

Land use	Study area description	Sample method	Analytical method	d50 (µm)	Source
Urban road runoff	450 m^2 drainage area; asphalt-surfaced, 3,500 vehicles/day	event mean	wet sieving and filtration to 8 µm	26	(Brodie and Dunn, 2009)
carpark runoff	56 m^2 drainage area, concrete surface			33	
Carpark runoff	Multiple sites: 1) 1.3 ha drainage area, 2) 2.4 ha, 3) 0.4 ha, all asphalt surfaces	event mean	wet sieved to 32 µm, particle analyzer to 2 µm	54	(Selbig and Bannerman, 2011)
Roof runoff	commercial land use, 290 m^2 drainage area, flat, rubber surface	event mean		95	
Carpark runoff	commercial land use, 0.45 ha drainage area	event mean	particle analyzer	63-125	(Moores et al., 2012)
Carpark runoff	23876 m^2 drainage area, asphalt surface	event mean	wet sieved to 32 µm, particle analyzer to 2 µm	32	(Selbig, 2013)
Residential		autosampler, bed load sampler	wet sieved to 32 µm, particle analyzer to 2 µm	9-250	(Burton and Pitt 2002), (Selbig and Bannerman, 2007), (Selbig, 2015)
Carpark runoff		autosampler	Particle analyzer	46	(Fowler et al., 2009)
Carpark runoff		autosampler	wet sieved to 32 µm, particle analyzer to 2 µm	32-54	(Selbig and Bannerman, 2011), (Selbig, 2015)
Carpark runoff	University (5036 m^2), hospital (1752 m^2) and industrial (3042 m^2): asphalt surfaces	first flush/ autosampler	leser diffraction (0.001-3000 µm)	79 -162	This Study

The wide variations at the site and the catchment level indicate that urban runoff PSDs is influenced by a wide range of factors including local rainfall condition, topography and land use. The percentage of fine particles (<63 µm) in this study (except for the hospital carpark) was found similar to the findings reported by Charters et al. (2016) for road runoff in the same geographical region but a slight variation on D10, D50 and D90 particle size was observed for all the carparks. Similarly, Zanders (2005) investigated PSD profiles for street dust samples in Hamilton city and found that 23% of total solids were <63 µm and were consistent with other studies of street dust reported in the city. In Auckland city, the finest PSDs were particles entering stormwater treatment ponds in south Auckland, whereas the coarsest PSDs were reported by NIWA for solids collected in catch pits (Moores et al., 2009a and b, Leersnyder, 1993, Gadd et al., 2010), which included gross solids (i.e., >5 mm). Similarly, all carpark runoff PSDs in this study had higher coarse particles (median particle size: 79-162 µm) as compared to influent PSD profile investigated by Moores et al. (2012) (median particle size: 31-125 µm) and stormwater sampling undertaken by NIWA (Reed and Timperley, 2004; Timperley et al., 2004 b) for eight different land uses in the same region (median particle size range: 30-75 µm). The wide variations in PSDs within the country may be due to the intra-event variability, sample collection method, timing of the sample collection, land use (more importantly traffic count, nature and size of a vehicle), rainfall conditions as well as atmospheric deposition.

All carpark runoff PSDs reported in this study had similar median D50 particle size and were also within the range as compared to other carparks PSDs findings (Selbig and Bannerman, 2010): commercial land use, (Moore et al., 2012): commercial land use, (Burton and Pitt, 2002), (Selbig, 2015), (Selbig and Bannerman, 2007): residential land use. In general, all of the carparks from this study were within the range of PSDs profile reported internationally.

6.5.6 Importance of PSD in maintaining the overall health of urban waterways

The PSDs profile from three carparks showed a wider variability from fines to coarser particles in each storm event. The concentrations of TSS reduced over the runoff duration, while the percentage of particles size remained the same in each flow period. A significant portion (approximately 40%) of particles are fine sediments. Results showed that the causes of fine particles from runoff are associated with traffic-related pollutants. Accumulated particles increase turbidity of waterways which ultimately restricts oxygen availability to aquatic flora and fauna (Greig et al., 2005) compromising the growth and development of an aquatic organism. It has also been reported that generally heavy metals (such as Zn, Cu and Pb) loads were associated with smaller size fractions <63 µm as compared to coarser particles (Juracic and others 1980, 1982). Urban and industrial development contributes substantially to heavy metals contamination in aquatic organisms (Xia et al., 2011). Sediment removal treatment systems are generally designed for removing a large number of coarse particles but targeting finer particles through new or redesigned systems would eventually reduce bioaccumulation and increase the overall health of urban waterways.

6.6 Conclusions

PSDs from urban untreated carparks showed a similar distribution pattern, but slightly different median (D50) values for each of the carparks. Some other major findings from this chapter are as follows:

1) Median values for D50, D10 and D90 particle size values for the university and the industrial carparks were relatively smaller as compared to the hospital carpark.
2) No significant seasonal differences were observed for each flow period.
3) The university and industrial carparks were found to have a bi -modal distribution and the hospital carpark showed a poly-modal distribution. The highest peaks occurred between 80 and 110 µm. PSDs were largely affected by drainage area, traffic count, and nature of the vehicles and method of sampling during first flush and steady-state.
4) Around 32-40% of particles from the carparks were fine particles (<67 µm), which is a significant portion of the particles from untreated carpark runoff as compared to other published literature.
5) Rainfall parameters had a limited influence on PSDs at the university and the industrial carparks.
6) The industrial carpark exhibited higher TSS followed by the hospital and the university carparks and TSS concentrations decrease over time whereas PSD pattern did not show any specific trend over the rain duration.
7) A moderate positive correlation between turbidity and TSS was found during first flush and steady-state periods. Turbidity measurements to serve as a surrogate for TSS measurement for the carparks studied was not recommended without considering PSDs.

Most stormwater treatment systems are designed to remove coarser particles (>67 µm). Given the sampling results, systems that can remove significant portions of fine particles from runoff are necessary. Pollutant source reduction, as well as stormwater treatment system such as proprietary stormwater treatment systems, are desirable in these carparks to achieve maximum pollutant removal.

Chapter 7

Indicator bacteria in first flush urban stormwater runoff

7. Indicator bacteria in first flush urban stormwater runoff

7.1 Introduction

The contamination of urban waterways with fecal matter represents a significant risk to human health. During storms, runoff flows across impervious surfaces such as carparks, washes off pollutants including indicator bacteria such as total coliform and *E. coli*, and transports them to waterways. The polluted stormwater runoff contributes to the impairment of freshwater resources available for recreational use such as fishing and swimming (Haile et al., 1999, Marsalek and Rochfort, 2010). Indicator bacteria are found in highly varying concentrations due to their survival, die off or regrowth in the water phase. The concentration of these bacteria are highly dependent on ambient conditions such as temperature, pH and solar radiation and are largely influenced by land use characteristics (McFeters and Stuat, 1992). Higher concentrations of bacteria are contributed from mature catchments with abundant green vegetation and trees, as compared to newer developments with less vegetation (Desai and Rifai 2010; Tiefenthaler et al., 2011). The landscape of older developments with trees, vegetation and wetlands that attract birds and waterfowl, contribute significant concentrations of indicator bacteria to the surrounding environment. However, many studies have found that the amount and concentration of indicator bacteria are also influenced by the amount of impervious cover (McLellan and Salmore, 2003) such as rooftops and carparks which are found to harbor fecal coliforms levels as high as 1,00,000 colony forming units (cfu)/100 ml. Previous studies on the variations of indicator bacteria are presented in (Table 7.1).

The sources of indicator bacteria in urban carparks are mainly dogs, birds as well as waterfowl (if a carpark is close to a waterway). Carparks in an urban setting, especially in residential areas, experience high traffic of dogs which produce a daily fecal output of 100-200 g per dog (Whitlock et al., 2002) resulting in significant *E. coli* loads. Birds such as gulls produce an average of 3.7 x 10^6 fecal coliforms per gram of fecal material with the majority of fecal coliforms being *E. coli*. Similarly, mallard ducks can produce an average of 7.83 x 10^{10} most probable number (MPN) of fecal coliforms per gram (Devane et al., 2007). Whereas, typical feral pigeon densities (10 to 200) per flock can generate 0.5 x 10^6 MPN per gram and waterfowl which is quite common in urban waterways generate typical fecal coliform densities of 3.3 x 10^7 MPN per gram (Krometis et al., 2007). Hence the fecal indicator load may vary widely with species, habitat and geographical locations.

The concentrations of indicator bacteria are affected by several environmental factors (chemical, physical and biological) in urban stormwater runoff. One of the most important parameters for indicator bacteria is temperature (Medema et al., 1995). Coliforms grow best at temperate or warm temperatures compared to colder temperatures, but also depend upon the availability of nutrients and other external factors. Sunlight and other environmental factors such as pH, turbidity, sedimentation, and salinity also play a role in the overall variability of these indicator bacteria (Alkan et al., 1995; Davies et al., 2000; Whitman et al., 2007; Yan et al., 2000). Several rainfall parameters such as ADD and rainfall intensity were also found to be influential factors for the variation of E. coli during storm events (McCarthy et al., 2007).

Monitoring indicator bacteria from runoff is crucial because it is important to treat urban stormwater prior to discharging it to recreational waterways. Indicator bacteria are used to indicate the likelihood of contracting a disease by consuming or recreating in such waters. The primary concern with regard to bacterial contamination in urban waterways is incidental human ingestion of contaminated water during recreational contact with the water, resulting in illness. Hence, it is important to treat urban stormwater runoff effectively.

Table 7.1: Variation of *E. coli* concentrations according to land use

Land use type	Sampling description	Concentrations (MPN/100ml)	Reference
Mature land use - post 2000; Urban land use Christchurch, NZ	N/A	2-145 97	Brough et al., 2012 Williamson, 1993
Urban Catchment, Melbourne, Australia	First flush runoff	Median concentrations: 410-12000	McCarthy, 2008
Light industrial and medium density residential, Melbourne, Australia	Stormwater pipes	Mean concentration: 610-8950	McCarthy et al., 2007
Mixed land use (high-density residential to landscaped commercial), New Jersey, US	Municipal storm sewer system	1500-8500	Selvakumar and Borst, 2006
Residential land use, Sweden	Manual, stormwater runoff	3438	Galfi, 2014

7.1.1 Objective

This chapter aims to quantify indicator bacteria, specifically total coliforms and *E. coli*, in runoff from different carparks (university, hospital, and commercial) located within a similar geographical location. The chapter further aims to assess the seasonal variation of indicator bacteria, the role of various environmental conditions such as pH and suspended solids, as well as the influence of rainfall parameters such as intensity and ADD over time.

7.2 Methodology

Twenty-one storm events were sampled for indicator bacteria from September 2015 to October 2016. Nalgene™ stormwater first flush samplers (1 L HDPE bottles) were used for sampling runoff in sumps within each of the three urban carparks. A detailed description of sampling sites, sampling layout, and field techniques used for sample collection are provided in Chapter 3 (Figure 3.1, section 3.4 and 3.5). All first flush samples were stored at 4 ^{0}C for transport. The first two samples events were analyzed at the Environmental Science and Research Centre (ESR) due to logistics. The remaining event samples were analyzed at the University of Canterbury Environmental laboratory using the Colilert-18 method.

7.2.1 Analysis procedure

The Colilert-18 system, which is a US Environmental Protection Agency (EPA) approved method, was used for total coliform and *E. coli* detection (Figure 7.1). The method is based on IDEXX's Defined Substrate Technology (DST). When total coliform and *E. Coli* metabolize Colilert 18's nutrient indicator ONPG (o - Nitrophenyl- B-D- Galactopyranoside), the sample turns yellow. When *E. coli* metabolize the Colilert 18's nutrient indicator MUG (4-methylumbelliferyl-β-D-glucuronide), the sample also fluoresces (Colilert-18 Test kit, 2015). Colilert-18 can detect bacteria at 1 MPN/100 ml within 18 hours. A 1:100 dilution was chosen with the Colilert technique for the carpark runoff samples. This dilution factor was selected on the basis of typical *E. coli* concentrations found in stormwater runoff for various land use (McCarthy et al., 2007). *E. coli* concentrations were used without adjustment (i.e. >2,40,000 was used as 2,400).

Figure 7-1: (a) IDEXX quanti-Tray/2000 (with quanti tray sealer) and (b) incubated quanti tray)

7.2.2 Data analysis

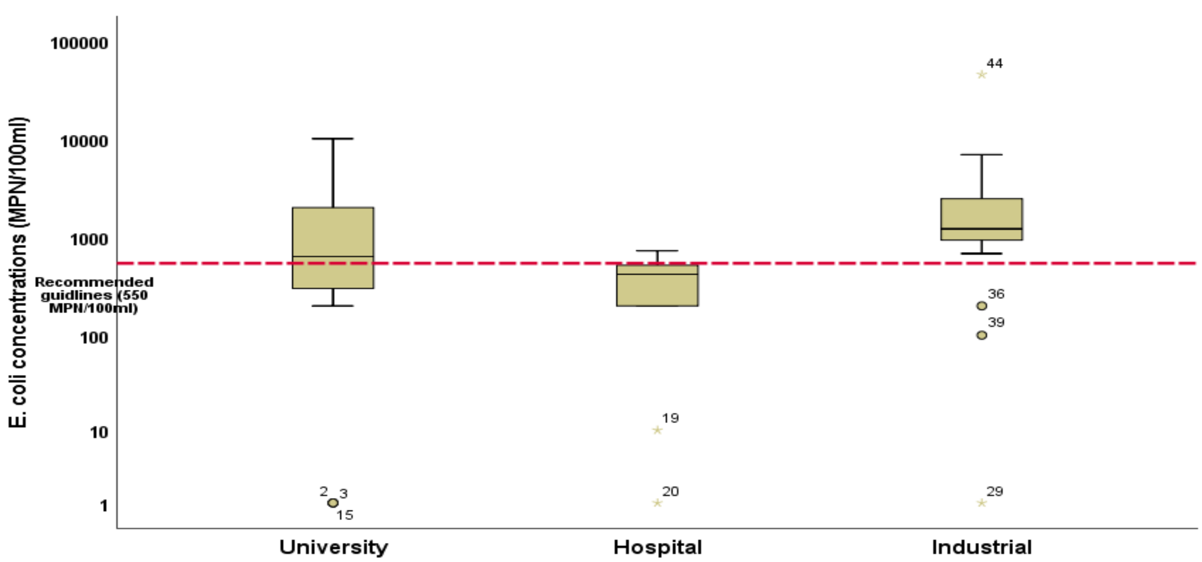
Data analysis was conducted using the IBM® SPSS® Statistics (23) software. *E. coli* concentrations from the three carparks were from independent storm events, and thus a Mann-Whitney U test was performed between each carpark to determine if significant differences existed in total coliform and *E. coli* concentrations. Further, the relationship between first flush TSS/turbidity/temperature and indicator bacteria (*E. coli* and total coliform) was evaluated using a Pearson's correlation. Differences in concentration during the wet and the dry seasons were also evaluated using the Mann-Whitney U test.

7.3 Results

7.3.1 Variation of indicator bacteria in three urban carparks

First flush *E. coli* and total coliform concentrations in urban carpark runoff from 21 different storm events were analyzed. The Mann-Whitney U test revealed significant differences in *E. coli* concentrations between the hospital and the industrial carpark ($p = 0.03$), but no other significant differences were observed. Boxplots (Figure 7.2) also revealed that median indicator bacteria concentrations in the industrial and at the hospital carparks were higher and lower, respectively, than the recommended guidelines (Ministry for Environment/Ministry of Health, 2003) >550 *E. coli*/100 ml; (Ministry for Environment/Ministry of Health, 2003) maximum >550 *E. coli*/100 ml).

The arithmetic mean, median, standard deviation and min/max values of water quality parameters of interest were also calculated for all the carparks (Table 7.2). Among the three urban carparks, the highest mean and median concentrations of TSS, turbidity, *E. coli* and total coliform were observed in the industrial carpark. The lowest levels of these parameters were found in the hospital carpark.



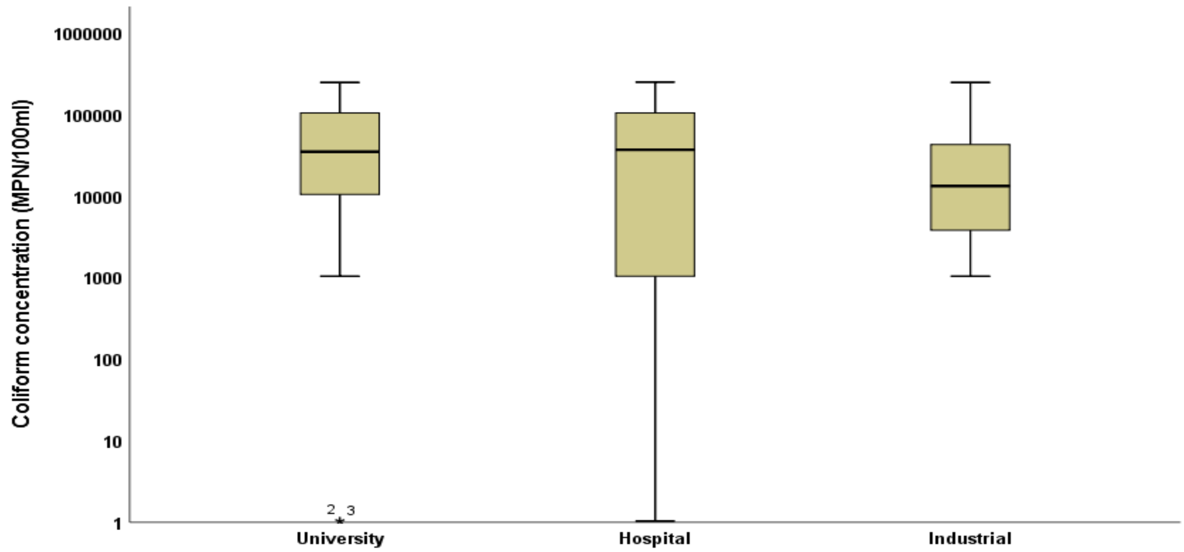


Figure 7-2: Distribution of *E. coli* (top panel) and total coliform (bottom panel) bacteria (MPN/100 ml) for each carpark during first flush period (° denotes outlier's ± 1.5x Inter Quartile Range (IQR), * denotes outlier's ± 3x IQR). Red dotted line shows recommended guideline which is 550 MPN/100 ml. The interquartile range represents the middle 50% of the data. The median is represented by the line in the box. The whiskers represent the range for the bottom 25% and the top 25% of the data value, excluding outliers.

Table 7.2: Site-specific statistics for the two indicator bacteria (total coliforms and *E. coli*) and other water quality parameters (TSS, Turbidity and pH) monitored in urban carpark runoff

	E. coli	**Total Coliforms**	**TSS**	**Turbidity**	**Temp (^oC)**
		University carpark			
Mean	1920	63360	63	88	12
Median	658	34340	42	80	12
Std. Deviation	2857	74735	65	61	3
Minimum	1	1	3	10	8
Maximum	10221	241960	271	250	20
		Hospital carpark			
Mean	371	72954	84	55	13
Median	425	36183	86	56	13
Std. Deviation	256	95620	61	27	4
Minimum	1	1	7	11	8
Maximum	737	244380	180	91	20
		Industrial carpark			
Mean	4315	39511	285	212	12
Median	1232	13554	176	137	12
Std. Deviation	10898	62250	268	195	3
Minimum	1	1011	38	89	8
Maximum	46110	241960	1121	884	20

7.3.2 Suspended solids and indicator bacteria variation in first flush samples

As noted before, stormwater runoff was monitored for first flush TSS, turbidity, temperature, total coliform and *E. coli* in three urban carparks during 21 storm events. The correlation between first flush TSS, turbidity, and temperature with *E. coli* and total coliforms was evaluated using the Pearson correlation method (Table 7.3). The hospital carpark yielded a moderate positive relationship between TSS and *E. coli*. In the other two carparks, no significant relationships were found between TSS and indicator bacteria. At the industrial carpark, a strong positive correlation was found between *E. coli* and total coliform.

Table 7.3: Pearson correlation with r- values between *E. coli*, total coliform, TSS, Turbidity and Temperature at three carparks

	E. coli	**TSS**	**Turbidity**	**Temp**
		University carpark		
Total Coliform	r = 0.050 p = 0.843	r = -0.240 p = 0.926	r = -0.960 p = 0.704	r = 0.287 p = 0.926
E. coli	1	r = -0.293 p = 0.234	r = -0.140 p = 0.956	r = 0.105 p = 0.678
		Hospital carpark		
Total Coliform	r = -0.187 p = 0.600	r = -.40 p = 0.252	r = -0.330 p = 0.338	r = 0.170 p = 0.638
E. coli	1	**r = 0.639** **p = 0.02**	r = 0.484 p = 0.157	r = 0.033 p = 0.927
		Industrial carpark		
Total Coliform	**r = 0.850** **p = 0.000**	r = 0.076 p = 0.780	r = -0.124 p = 0.648	r = 0.002 p = 0.995
E. coli	1	r = 0.090 p = 0.706	r = -0.930 p = 0.721	r = 0.183 p = 0.482

7.3.3 Seasonal variation of indicator bacteria in urban runoff

The seasonal variation of indicator bacteria was analyzed to identify the influence of the wet and the dry season on coliforms concentrations. A wide variation in total coliforms concentrations was observed for both the university and the industrial carparks (Figure 7.3) during the dry season. Mean total coliform concentrations were higher at the industrial carpark during both seasons (dry: October to May and wet: June to September) whereas mean *E. coli* was higher at the university during the wet season and lower at the industrial carpark during the dry season (Table 7.4). There was no obvious trend identified during the wet and dry seasons. These results were further confirmed with the Mann-Whitney U test which showed no significant differences in indicator bacteria during the wet and dry seasons. The hospital carpark was not included for the study of seasonal variations as the carpark was non-operational after the dry season.

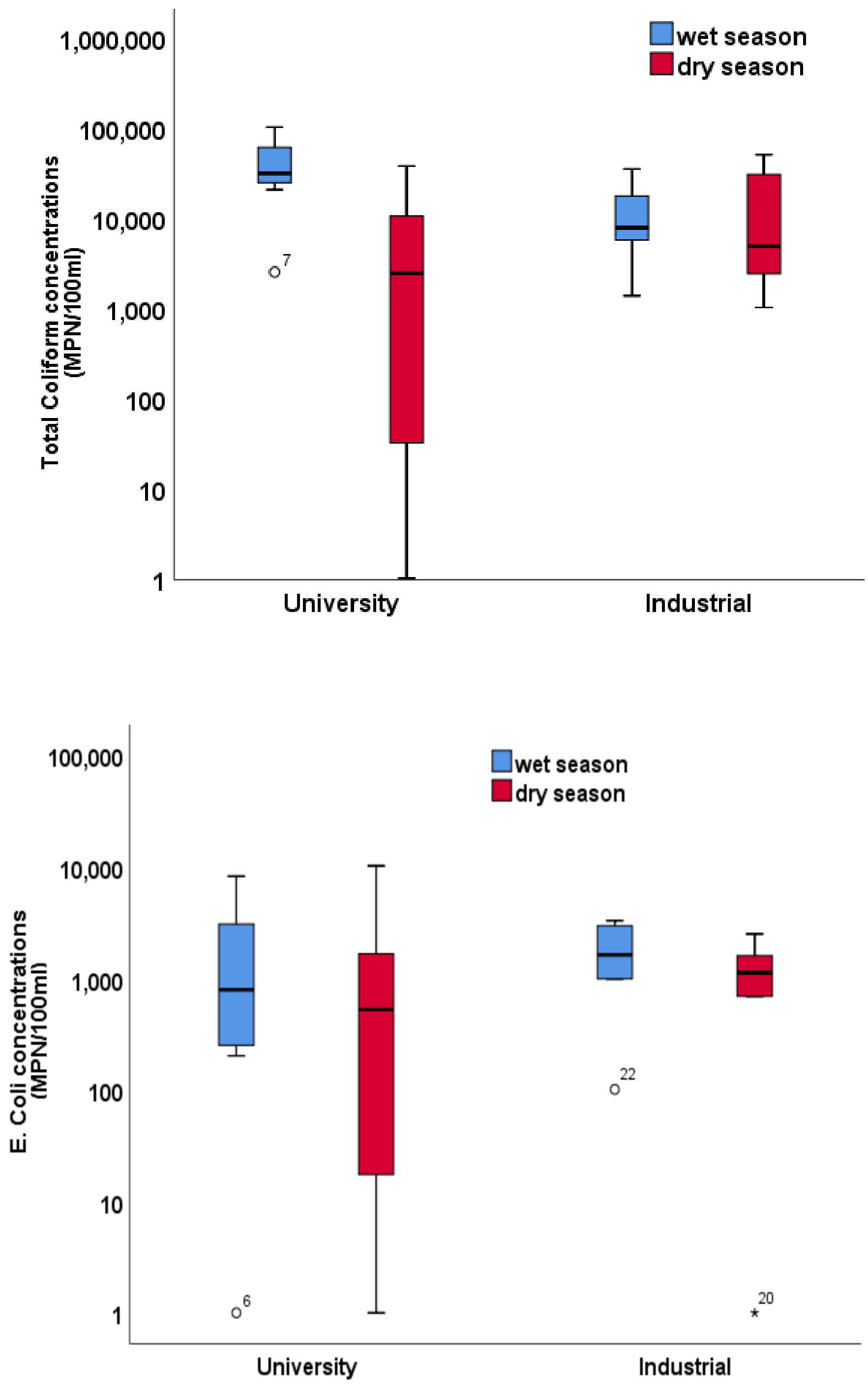


Figure 7-3: Distribution of total coliform (top panel) and *E. coli* (bottom panel) bacteria (MPN/100 ml) during the wet and the dry season for each carpark during first flush period (° denotes outlier's ± 1.5x Inter Quartile Range (IQR), * denotes outlier's ± 3x IQR). The interquartile range represents the middle 50% of the data. The median is represented by the line in the box. The whiskers represent the range for the bottom 25% and the top 25% of the data value, excluding outliers.

Table 7.4: Concentrations of indicator bacteria during the wet and the dry seasons

	Wet season (total coliform)	Dry season (total coliform)	Wet season (*E. coli*)	Dry season (*E. coli*)
		University		
Mean	43888	53974	2248	1710
Median	31068	10777	790	525
Std. Deviation	33520	75101	2964	2913
Minimum	2500	1	1	1
Maximum	102121	241960	8242	10221
		Industrial		
Mean	12477	55732	1791	5691
Median	7772	28149	1692	1190
Std. Deviation	12152	74811	1234	13541
Minimum	1364	1011	101	1
Maximum	34825	241960	3303	46110

7.3.4 Relationship between rainfall parameters and indicator bacteria

No correlation was found between any of the rainfall parameters with indicator bacteria. This suggests that indicator bacteria concentrations are highly variable.

7.3.5 Differences between operational and non - operational hospital carpark

The concentrations of *E. coli* were consistently below detection levels during the non-operational period. Only one storm event (storm event 19) was found to be higher (980 MPN/100 ml) at the passive hospital carpark. This is likely due to a random event like the presence of a dog or bird dropping in the carpark at the time of the sampling.

7.4 Discussion

7.4.1 Variation of indicator bacteria in urban carpark runoff

Results showed that the concentrations of indicator bacteria at the industrial and the hospital carparks were found to be statistically different. Similar findings were reported for urban land use by other researchers (Bannerman et al., 1993; Weiskel et al., 1996; Mallin et al., 2000). The highest mean concentrations were from the industrial carpark followed by the university carpark. Birds were more likely the primary source of indicator bacteria at the industrial carpark runoff whereas at the university carpark, dogs and rodents, in addition to birds, were another source of coliform bacteria since the university is located within a residential development. In addition, the latter carpark is located close to a public bar, outdoor dining, bar grease bins as well as food waste bins from university students which may attract vectors/rodents that contribute to indicator bacteria contamination in urban carpark runoff.

Many researchers have found that suspended solids are one of the vectors of bacteria transport (Galfi, 2014). A moderate positive correlation between suspended solids and *E. coli* was found in the hospital carpark. The other carparks did not show any correlation with TSS or with any other variable such as rainfall characteristics, drainage area, traffic count and vehicular activities. Although some trends have been identified, the data are too limited for further generalization. Additional research is necessary to understand the die off and wash off behaviours of indicator bacteria urban catchments. However, the data collected in this study gives an indication of average concentrations of indicator bacteria for treatment systems.

7.4.2 Treatment options for removal of indicator bacteria from stormwater runoff

Stormwater management practices (SMPs) are used to control and treat pollutants in stormwater. Conventional practices (infiltration, bio-retention, constructed wetlands, and vegetative swales) are not very effective in the removal of bacteria such as *E. coli* from urban carpark runoff, as they require a larger operating footprint, and have a risk of polluting the groundwater flow (Clark and Pitt, 2012). Stormwater treatment systems equipped with targeted media filtration have also been widely considered as an effective way of removing bacterial pollutants. Other studies, however, show that single filter media do not have a great adsorption capacity to remove signature pollutants (such as pathogen along with TSS and heavy metals) of concern from runoff (Dastgheibi, 2012, Wium-Anderson et al., 2012, Reddy, 2013, Reddy et al., 2014). The combination of more than one media is necessary to achieve optimum removal of bacterial pollutants.

Regarding the removal of indicator bacteria from the carparks studied, the industrial and the university carparks both exceeded the recommended recreational guidelines (Ministry for Environment/Ministry of Health, 2003) >550 *E. coli*/100 ml, (Ministry for Environment/Ministry of Health, 2003) maximum >550 *E. coli*/100 ml). These carparks runoff need to be treated with suitable media filter in order to remove the significant concentration of bacteria from carpark runoff. However, the bacteria contamination treatment for the hospital carpark is less necessary as the concentrations were consistently lower throughout the sampling period.

7.5 Conclusions

The concentrations of indicator bacteria exceeded national recreational water quality guidelines developed by the NZ Ministry for Environment. There was a correlation between total coliform and TSS but no correlation between total coliform and other water quality parameters. Runoff from the industrial and university carparks requires treatment with suitable filter media to remove *E. coli* and total coliforms before discharge into waterways. This is less need in the hospital carpark. Further, potential sources of these indicator bacteria can be determined by tracking their individual sources, which can be used to reduce their concentrations in urban runoff. Recommendations for additional steady-state runoff sampling of indicator bacteria are suggested for an in-depth understanding of their behaviour and nexus with other environmental factors.

Chapter 8

Conclusions and Recommendations

8. Conclusions and Recommendations

Carpark runoff is a significant source of pollutants to receiving urban waterways. The sources and concentrations of pollutants are largely dependent upon the type and extent of the activities taking place on these impervious surfaces and in the surrounding areas. However, it is still not common practice to select suitable stormwater treatment systems based on the characteristics of these activities and the surrounding land uses. There is a lack of information on the type and the quantity of the pollutants in stormwater discharged from different land uses under various rainfall conditions. This research has contributed to a greater understanding of runoff pollutants from urban carparks, which could inform the selection of the most adequate stormwater treatment systems for stormwater management for specific carparks.

8.1 Pollutant yields from different carparks during first flush and steady-state conditions

Pollutant yields: The most prevalent causes of water pollution in NZ in an urban carpark are suspended solids and heavy metals (dissolved and particulate). When implementing stormwater management strategies, it is crucial to target the area/land use where most pollution occurs. This research focused on three of the most common types of urban carparks to understand the dynamic nature of pollutant loadings (TSS, dissolved and particulate heavy metals, and *E. coli*) and particle size distributions. Results suggest that total suspended solids during first flush vary significantly with carpark characteristics. Constituent concentrations in runoff samples were higher during first flush than in the steady-state periods for all carparks. As a storm progressed, pollutant concentrations tended to decline, with the highest loads observed at the industrial carpark. The differences in the quantity of pollutants between the carparks during first flush were largely influenced by traffic count and the size of the vehicles. However, despite its smaller drainage area and lower traffic volume, the hospital carpark had similar pollutant concentrations as compared to the university carpark. This was attributed to the surrounding topography at the hospital and irregular traffic patterns at the university carpark.

Rainfall characteristics (mainly ADD, initial 10 mins rainfall intensity and rain depth) had little influence (a low positive correlation) over pollutant concentrations at the carparks suggesting that vehicular activities are likely to be the dominant source of deposited pollutants. The concentrations of *E. coli* during first flush were neither influenced by seasons (wet/dry) nor by land use activities. Though birds, rodents, and waterfowl have been identified as a common source of these bacteria in carparks, identifying the specific sources and individual’s contribution on total concentrations is challenging. *E. coli* concentrations at the industrial and the university carparks were consistently higher than recreational water quality criteria established by the NZ Ministry for Environment.

TSS and heavy metals yields during period 1 (first 40 mins of storm) of steady-state conditions varied significantly with carpark characteristics (traffic count, size of vehicle, drainage area and surrounding land use). The industrial carpark had the highest load of TSS and heavy metals among the three carparks studied. This is due to greater commercial vehicles movement in the industrial carpark. The hospital carpark had the smallest area and least vehicle movement but produced similar pollutant loads in the university carpark. The hospital carpark is located at the base of the Port Hills and a portion of the pollutant load is likely to be contributed by the surrounding topography through atmospheric deposition.

Regarding heavy metals (dissolved and particulate) loads, the industrial carpark had a higher load of heavy metals with a lower percentage of dissolved metals. Industrial carparks are hot spots for metal pollution; focusing stormwater management strategies on these carparks will provide significant water quality benefits to receiving waterways.

Source control: In urban carparks, traffic-related activities are the greatest contributors to stormwater runoff load. Source control structural and non-structural techniques can be used to reduce the amount of pollutants released to waterways. Structural techniques include the use of litter traps (appropriate for individual sumps to collect litter and coarser sediments) and stormwater treatment systems. Non-structural techniques include public education and outreach on stormwater impacts, solid waste management, street sweeping, etc.

Management strategies: The management of road runoff quantity and quality typically comes under the responsibility of local government. Urban carparks and connecting roads to carparks are often owned by private owners and businesses, many of whom are as yet unaware of the emerging need to control the quality of water discharging from their sites. The introduction of management practices is desirable to reduce the pollutant load from urban carparks into receiving waterways. Zn was one of the signature pollutants originating from traffic-related activities and its total concentrations were consistently higher than that of Cu and Pb in all the carparks studied. Therefore, effective management strategies to control the discharge of Zn can be achieved by preventing leaks (motor oil and hydraulic fluids: which have high Zn concentration), and frequent cleaning and vacuuming of carpark surfaces, as solid particles such as dust, soil, tree leaves, etc can soak up heavy metals. In some cases, frequent cleaning and maintaining downpipes and gutters may also reduce heavy metals, particularly Zn contained in suspended solids. Regarding bacterial contamination, the introduction of prevention practices that are effective at reducing bacteria concentrations is desirable instead of relying on stormwater treatment systems. Some of the practices include, tracking of bacteria from individual sources to understand the primary sources of *E. coli*, properly disposing of pet waste and litter in a timely manner, use of native vegetation and grass to cover and stabilize exposed soil to prevent sediment wash-off, and preventing carpark waste such as tree leaves and food residual (specially from university carpark) from entering stormwater facilities either by pick up or regular routine-cleaning of carpark surfaces.

8.2 Effect of rainfall on pollutants loads

The effect of a low-intensity rainfall on pollutant yield in urban carparks seemed to be less important as compared to traffic activities. ADD, initial rainfall intensity and rain depth had little influence over elevated first flush TSS concentration.

During steady-state conditions, a linear relationship between pollutant yield and rainfall depth >5 mm was generally consistent for the pollutants at the university and the industrial carparks. Average pollutant yields among the carparks were found to reach a maximum at 3-6 antecedent dry days after storm events. These findings suggest that build up over the dry days occurs relatively quickly after a rain event, reaches a relative maximum at 3-6 antecedent dry days, and slows down after 6 days. Various management strategies such as carpark sweeping and vacuuming would be useful prior to rain and after 3 days to reduce pollutants yield into waterways.

8.3 Size distribution of particulates from the urban carpark

The consideration of PSDs in designing stormwater treatment systems is important because it affects the removal of suspended solids and heavy metals in stormwater runoff. PSDs from urban untreated carpark runoff showed a similar distribution pattern, but slightly different median (D50) values for each carpark for both first flush and steady-state conditions. More centralized PSDs (80-110 µm) profile suggest that the influence of other external environmental factors was minimal at the studied sites. Around 32-40% of particles were fine particles (<67 µm) which is a significant portion from untreated carpark runoff as compared to other published literature. Metals in stormwater runoff adsorb most to fine sediment rather than to larger particles. A substantial portion of adsorbed metals can be removed by removing fine particles from carpark runoff.

Using particle size distribution in evaluating treatment unit performance is a more accurate and precise way of determining the actual performance. The differences in composition in particle size distribution can lead to variations in carpark runoff quality. Stormwater treatment systems designed only for treating coarser particles need to be reconsidered before implementing them at these carparks.

8.4 Selection of treatment systems

Despite differences in carpark characteristics and surrounding land use, the hospital and the university carparks had similar TSS loads. Overall results suggest that drainage area, traffic and land use activities had a similar effect at the university and the hospital carparks as there was very minimal difference in terms of total load and abundance of pollutants. Therefore, a similar type of stormwater treatment systems for TSS removal (based on PSDs) from stormwater runoff would be desirable at these carparks. However, the nature of vehicles involved, and traffic frequency has a greater influence on the discharge of pollutants at the industrial carpark. The industrial carpark needs more efficient treatment systems due to elevated TSS, metals (both dissolved and particulate) and *E. coli*. The specific treatment or management strategy most appropriate for a specific site depends on the need for removal of specific pollutants. From the observed pollutant loading in the carparks, treatment mechanisms for any given carpark may include more than one specific treatment or management option.

8.5 Recommendations

This research has provided an in-depth understanding of urban carpark pollutant loadings. The research outcomes can provide guidance for the selection of stormwater treatment systems for the individual carparks. However, there are still a number of areas that can be further explored and studied. The following are key research recommendations to further strengthen knowledge created.

8.5.1 Policy guidelines

Since this research has found that the quantity of pollutants concentration varies with carpark studied, a land use based treatment approach is recommended for each carpark. There is no clear information on national and local level guidelines suitable for use in different catchments with varied geomorphological and physical characteristics. Guidelines for the selection of treatment systems for different carparks are needed in order to better implement SMPs and stormwater management related policies.

8.5.2 Monitoring other carparks with different traffic conditions

It is recommended other types of carparks (such as commercial, office complexes, light industrial, etc.) with different traffic conditions be monitored. Although this research has increased the understanding of pollutants from the most common carparks in urban areas, knowledge on other carparks would enable wide understanding of the variability of the pollutant loadings.

8.5.3 Development of build-up and wash-off model

It is recommended that the information provided in this research be used to develop a land use based locally adapted model to understand the contribution of urban carpark load on stormwater runoff. The model would be user-friendly and freely available to the public via council website.

8.5.4 Testing of treatment systems in carparks

The evaluation of the performance of stormwater treatment systems is limited to laboratory and mainly been conducted by or on behalf of developers, manufacturers and distributors. There is minimal information on treatment system performance, particularly at the local level under natural rainfall conditions. It is envisaged that the testing of stormwater treatment systems in various carparks during rainfall would provide first-hand data for further improvement of such technologies in NZ.

8.5.5 Removal of multiple pollutants

Most stormwater treatment systems are targeted to reduce suspended solids, and total Cu and Zn concentrations to some extent in runoff. Removal of dissolved metals is poor in most BMPs. Therefore, further research on the use of filtration media in order to remove dissolved pollutants is recommended. In addition, further research is needed to address the removal of other key pollutants such as indicator bacteria in urban stormwater runoff.

8.5.6 Monitoring steady-state bacterial concentrations and source control for pathogens

This research was limited to the study of first flush bacterial concentration in urban runoff, however, further research on steady-state conditions is recommended to understand die off, growth and regeneration. The wash-off behavior of these bacteria can be influenced by the duration of rainfall. Identification of the most important sources and employing specific practices to address those bacterial sources are important in order to manage pathogen loads in urban stormwater runoff.

8.5.7 Research on metals partitioning behaviour

This study was limited to the monitoring of dissolved metals loads during first flush and steady-state conditions. The reason behind the higher dissolved loads at the university and hospital carparks is not well understood. It is recommended that analysis of the physical and chemical mechanisms involved in the partitioning of heavy metals be undertaken.

8.5.8 Other relevant recommendations for future work

- Heavy metal loads are dependent upon size fraction of particles. Further research is needed to understand heavy metal composition in respect to size fractions to estimate possible removal of heavy metals from urban carpark runoff when implementing stormwater treatment systems.
- The characteristics and amount of organic matter loading were not studied in this research. It is recommended that further investigation is undertaken to understand the amount of organic matter content in runoff, as degradation of organic matter can alter suspended solids characteristics and increase the bioavailability of heavy metals.
- The traffic count was carried out for the general estimation of traffic loads at the respective carparks. Event-based traffic count is recommended to predict the actual correlation between pollutant loads to number of vehicles.
- The fate and transport of pollutants from source (carpark) to sink (waterways) is important to understand any change in the physical, chemical and biological state of pollutants during transport as pollutant form and concentrations may change during transport from one point to another.

- The concentrations of PAHs were low during first flush runoff from all carparks. Monitoring of steady-state PAHs is recommended.

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Appendices

Chapter 2

Summary of findings on removal efficiencies of stormwater treatment devices: examples from New Zealand perspectives (Moores et al., 2014)

Comprehensive research was carried out to analyse the performance of the most commonly used stormwater treatment devices deployed for removing suspended solids, Cu and Zn from road runoff in the Auckland, New Zealand. Some of the important findings are as follows:

The filternator device achieved 65 % removal of total suspended solids (TSS). Removal rates for TSS during individual storm events varied between 39 % and 83%. The device removed between 50 % and 66 % of TCu and TZn, while removal rates for dissolved Cu were close to zero and those for dissolved Zn were negative (ie more dissolved Zn exited the device than entered it). Four out of 35 effluent samples exceeded the US Environmental Protection Agency water quality guidelines for acute exposure to dissolved Cu while there were no exceedances of the dissolved Zn guideline (Moores et al., 2012).

The Up-Flo device achieved an overall efficiency ratio for TSS removal of 17 % (range of 19 % to 53 % during individual storm events). The device removed between 26 % and 53 % of TCu and TZn and between 26 % and 83 % of dissolved Cu and Zn. One out of 36 effluent samples exceeded water quality guidelines for acute exposure to dissolved Zn while there were no exceedances of the dissolved Cu guideline.

The StormFilter achieved an overall efficiency ratio of 46 % for TSS removal (range of 148 % to 76 % during individual events). The device removed between 5 % and 25 % of TCu and TZn and between 12 % and 23 % of dissolved Cu and Zn. 34 out of 36 effluent samples exceeded water quality guidelines for acute exposure to dissolved Cu and dissolved Zn, respectively.

Overview of onsite stormwater treatment devices for stormwater management in New Zealand

There is a range of treatment devices available in New Zealand for treating stormwater runoff. These types of devices are also known as proprietary stormwater treatment devices. These devices are incorporate patented innovative technologies and typically manufactured and supplied by the owner of the patent or their licensed distributors.

These devices are best suited for treating runoff from roads with small catchments and low to moderate sediment loads. They are generally promoted for the removal of solids and associated particulate contaminants, although certain types of media are also targeted at removing hydrocarbons and dissolved contaminants including metals. The type and design of filters installed in a given location should take into account stormwater quality and quantity, catchment characteristics, treatment objectives, land availability, budget and ease of installation and maintenance (Moores et al., 2012).

There are two main processes by which stormwater treatment devices remove contaminants from stormwater:

1) Mechanical removal of the solids: occurs by trapping solids in the pore spaces between the filter media, and chemical sorption of dissolved pollutants onto the filter media. Sorption can occur though adsorption, ion-exchange and surface precipitation (Krauskopf and Bird, 1995).
2) Adsorption: a chemical process occurring on the solid surface that binds the pollutant through ion-exchange. In this process, an ion that is weakly bonded to the media (such as sodium or calcium) exchanges with a pollutant (such as zinc) to form a stronger bond and trap the pollutant. Surface precipitation occurs when solute species react with the filter medium to produce particles that can be filtered by the medium and are incorporated into the solid structure (Genc-Fuhrman et al., 2007).

Adsorption processes depends on three components: a) nature of the media (e.g. chemical composition, structure, particle size, surface area, pore size, method of preparation, age) b) quality of the influent water (e.g. temperature, type and concentration of ions present) and c) water retention time in the filter (related to the inflow rate, filter design and dimensions, and the hydraulic conductivity of the filter bed).

Filter media include natural and manufactured materials. Filtration products can be customized using different media to target site-specific pollutants. The selection of filter media reflects the target contaminants to be removed.

The most common filter media employed in New Zealand are as follows: **Sand:** effective for removing bacteria, suspended solids, particulate metals and nutrients, **Perlite (**naturally occurring puffed volcanic ash)**:** effective for removing TSS, oil and grease. **GAC (Granular Activated Carbon):** has a micro-porous structure with an extensive surface area to provide high levels of adsorption. It is primarily used to remove oil and grease and organics such as herbicides and pesticides. **Zeolite:** is a naturally occurring mineral used to remove soluble metals, ammonium and some organics. **CSF Leaf Media and MetalRx:** are created from deciduous leaves processed into granular, organic media. CSF is most effective for removing soluble metals, TSS, oil and grease, and neutralizing acid rain. MetalRx, a finer gradation, is used for higher levels of metal removal.

As mentioned above, there are different designs of media filtration available in New Zealand. Sand filter chambers, up-flow filters and radial filter cartridges are the most common media filtration available for treating stormwater.

There are three main suppliers of these devices in New Zealand: Humes, Hynds Environmental and Stormwater360. A summary of the devices available through these suppliers is given in (Table 2.1).

Table 1: Summary of media filtration stormwater treatment devices in New Zealand (Table adapted from (Moores et al., 2012))

Type	Product	Media	Principal configuration	NZ suppliers	Evaluated and approved in accordance with
Up-flow filters	Up-Flo	Sand, perlite, CPZ mix	Manhole	Hynds Environmental	ARCTP10, TARP, USEPA ETV
Radial filter cartridges	Filternator	Zeolite, perlite, GAC	Vault	Humes	ARCTP10, TARP, WDOE TAPE
	StormFilter	Zeolite, perlite, GAC (and ZPG mix).	Vault	Stormwater360	ARCTP10, TARP, USEPA ETV, WDOE TAPE

A summary of the performance of the devices, type of the products, NZ suppliers and advantages of the filter devices are presented in (Table 2.2).

Table 2: Summary of performance of the stormwater filter devices available in New Zealand

Type/ Product	NZ Supplier	Performance	Advantage
Up-Flo Filter	Hynds Environmental	▪ Removes >90% TSS with a mean particle size of 20 microns	Accepted by the ARC for 75% TSS removal Sized to treat >80% of all stormwater annually ▪ Low head requirements ▪ High flow rates ▪ Small footprint ▪ Removes sediments, floatables, oils and grease
Brief Description	The Hynds Up-Flo™ Filter is a high rate, modular system that combines a patented upward flow path with a unique drain down the system. Designed to meet the most stringent stormwater regulations by targeting a wide range of pollutants including gross debris, fine sediments, nutrients, metals, oils and grease. The multiple treatment capabilities of the Up-Flo™ Filter (settling, screening, and filtration) makes it one of the most effective and economical stormwater treatment systems available.		
Humes Sand Filter	Humes	▪ Total Suspended Solids Removal > 75% ▪ Maintenance frequency 6-12 months	ARC Approved > 75% TSS Removal
Brief Description	Humes Sand Filters are made of modular precast concrete units with factory pre-assembled internal fittings, all ready to be placed into the excavated ground and connected to the drainage system. Sand filters have demonstrated service life and consistent pollutant removal when properly maintained. Maintenance for sand filters is simple and inexpensive.		
Filternator	Humes	Total Suspended Solids Removal 80-88% Maintenance Frequency 6-12 months	ARC Approved > 75% TSS Removal

Brief Description of the Product	The Filternator is designed to remove total suspended solids, nutrients such as nitrogen and phosphorous, petrol and oil. It can be customized to remove a wide range of solid and soluble pollutants from stormwater runoff by adjusting the filter compounds.		
StormFilter	Stormwater 360	The targeted contaminants are TSS, heavy metals, oils-200 lits/hr.	ARC Approved > 75% TSS Removal Various filtration media available to target site-specific pollutants Cartridge-based system provides exact sizing; high durability due to uniform sediment loading
Brief Description of the Product	The StormFilter removes the most challenging target pollutants – including fine solids, soluble heavy metals, oil, and total nutrients using a variety of sustainable media.		

Chapter 4

Supplementary Information

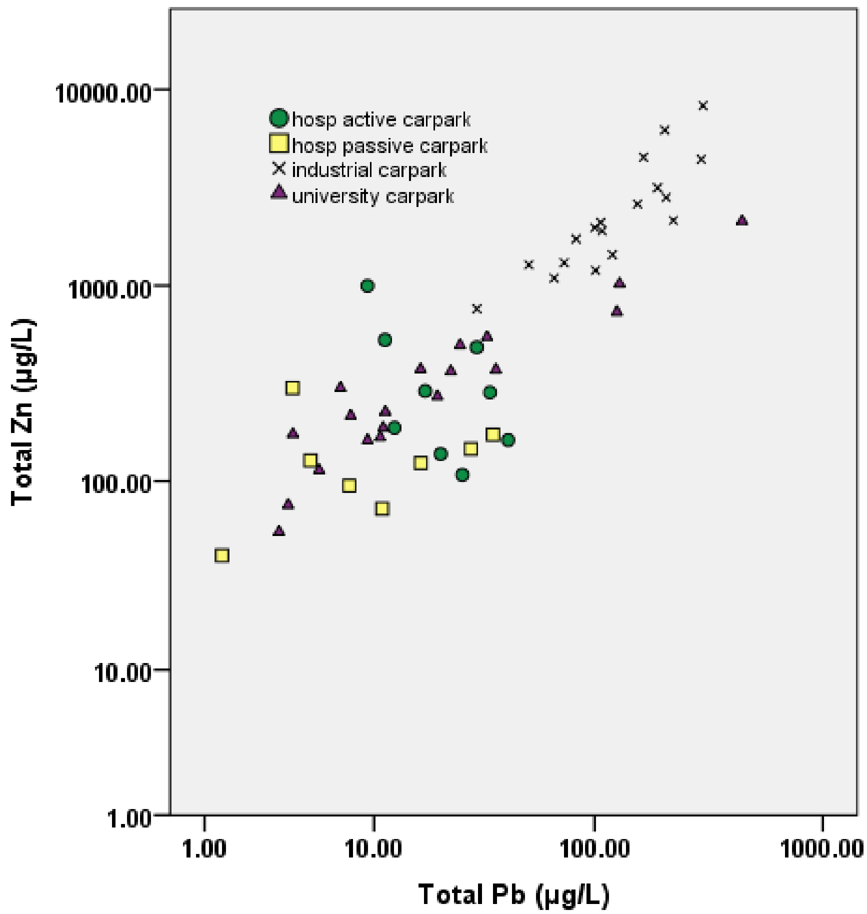
Table A: Summary of rainfall event characteristics from 21 storm events

Storm event	Date and time	10 mins rain depth(mm)	10 mins rain intensity (mm/hr)	average intensity (mm/hr)	rain depth(mm)	rain duration (hr)	antecedent dry days(day)
SE1	9/10/2015 15:45	1.8	10.8	10.8	1.8	0.17	4.49
SE2	9/22/2015 20:10	0.4	2.4	0.91	2.2	2.4	2.02
SE3	1/27/2016 15:10	0.2	2.4	2.96	10.6	3.6	0.25
SE4	2/17/2016 16:05	0.4	4	2.81	7.6	2.7	20.18
SE5	3/15/2016 14:50	0.6	3.6	1.24	3.2	2.58	6.61
SE6	3/24/2016 0:10	0.2	1.2	2.05	10.6	5.17	7.5
SE7	4/8/2016 5:15	0.2	1.2	2.4	2	0.9	3.75
SE8	5/20/2016 18:05	0.6	3.6	3.3	7.8	2.3	3.76
SE9	5/22/2016 20:30	0.4	2.5	1.1	4	3.5	1.15
SE10	5/28/2016 1:00	0.4	2.5	3.23	7.8	2.4	1.3
SE11	6/22/2016 1:00	0.4	2.5	2.5	0.4	0.17	9.4
SE12	6/23/2016 8:05	0.2	1.25	0.91	1.7	1.9	1.26
SE13	7/8/2016 0:30	0.2	1.25	0.81	4.2	5.2	7.3
SE14	7/13/2016 20:50	1	6.25	6.87	12.6	1.8	5.6
SE15	8/3/2016 7:45	0.2	1.25	1.09	1	0.9	3.4
SE16	8/12/2016 21:25	0.2	1.25	0.39	4.6	11.8	4.2
SE17	8/26/2016 11:05	0.8	5	1.97	4.6	2.3	12.9
SE18	9/6/2016 4:25	0.2	1.25	1.1	1	0.9	9.7
SE19	9/27/2016 3:05	1	6.25	6.25	1	0.2	18
SE20	10/6/2016 15:45	1.2	7.5	4.6	5	1.1	1.24
SE21	10/14/2016 15:05	0.8	5	1.6	3.2	2	2.12
	Average	**0.54**	**3.5**	**2.3**	**5.4**	**3**	**6**
	(Min-Max)	**(0.2 - 1.8)**	**(1.2 - 10.8)**	**(0.39 - 6.87)**	**(1 - 12.6)**	**(0.9 - 11.8)**	**(0.25 - 20.18)**

Table B: Person correlation between Total Zinc, Total Copper and Total Lead concentrations

Carpark characteristics	Total Zn to Total Cu	Total Cu to Total Pb	Total Zn to Total Pb
University	r = 0.90 p = 0.000**	r = 0.887 p = 0.00**	r = 0.971 p = 0.000**
Hospital active	r = -0.4 p = 0.295	r = 0.791 p = 0.006**	r = 0.48 p = 0.09
Hospital passive	r = 0.7 p = 0.04*	r = 0.82 p = 0.010*	r = 0.143 p = 0.73
Industrial	r = 0.7, p = 0.01**	r = 0.9 p = 0.00**	r = 0.8, p = 0.000**

*Correlation is significant at the 0.05 level (1-tailed)
**Correlation is significant at the 0.01 level (1-tailed)



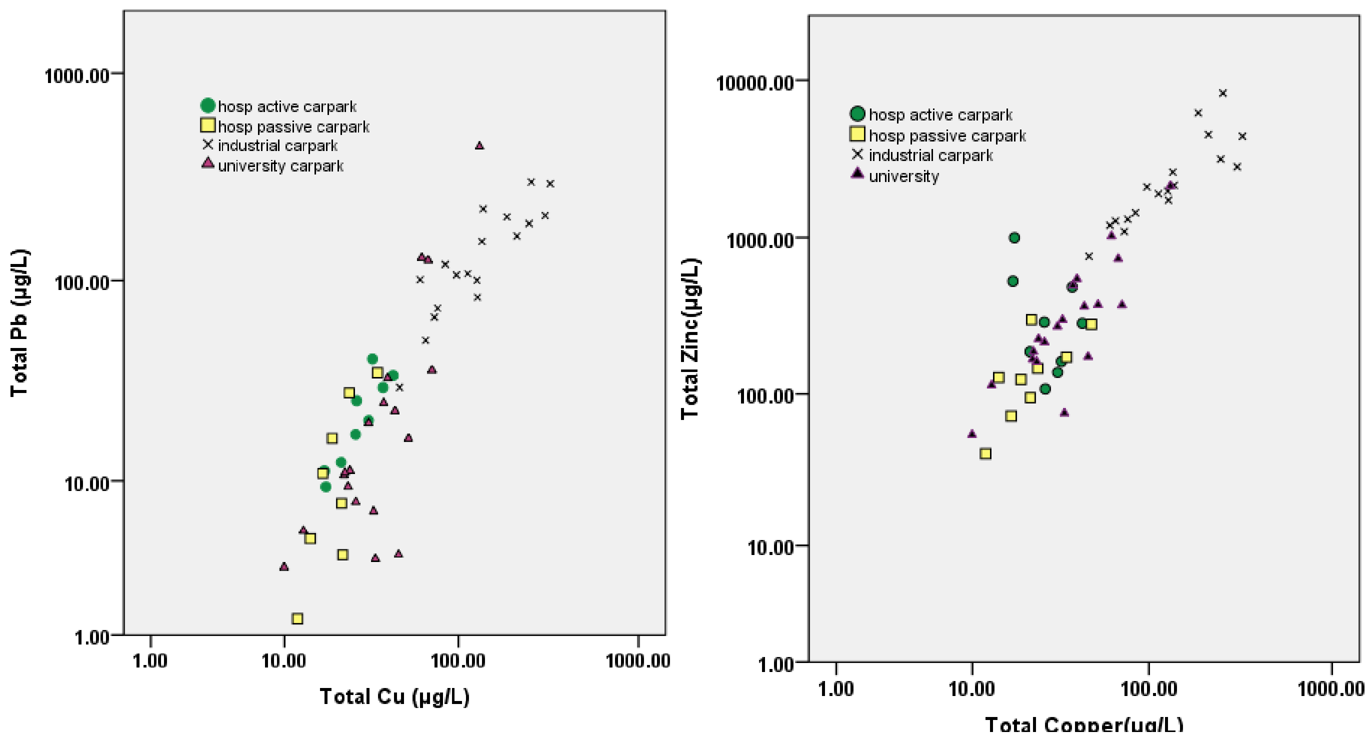


Figure B: Heavy metals relationship in three carparks

Table C: Average metal to metal ratios in each carpark

Metal to metal ratios	total Zn to total Cu	total Cu to total Pb	total Zn to total Pb
University	8:1	0.9: 1	7:1
Hospital active	9:1	1.3:1	11:1
Hospital passive	5:1	2:1	10:1
Industrial	15:1	1:1	16:1

*Correlation is significant at the 0.01 level

Table D: Pearson correlation between total and dissolved metal concentrations

Carparks	Zinc	Copper	lead
University	r = 0.97 p = 0.00*	r = 0.71 p = 0.01*	r = 0.15 p = 0.52
Industrial	r = 0.88 p = 0.7	r = 0.46 p = 0.05	r = 0.49 p = 0.85
Passive hospital	r = 0.7 p = 0.04*	r = 0.13 p = 0.7	r = 0.28 p = 0.5
Active hospital	r = 0.9 p = 0.001*	r = 0.63 p = 0.06	r = 0.26 p = 0.5

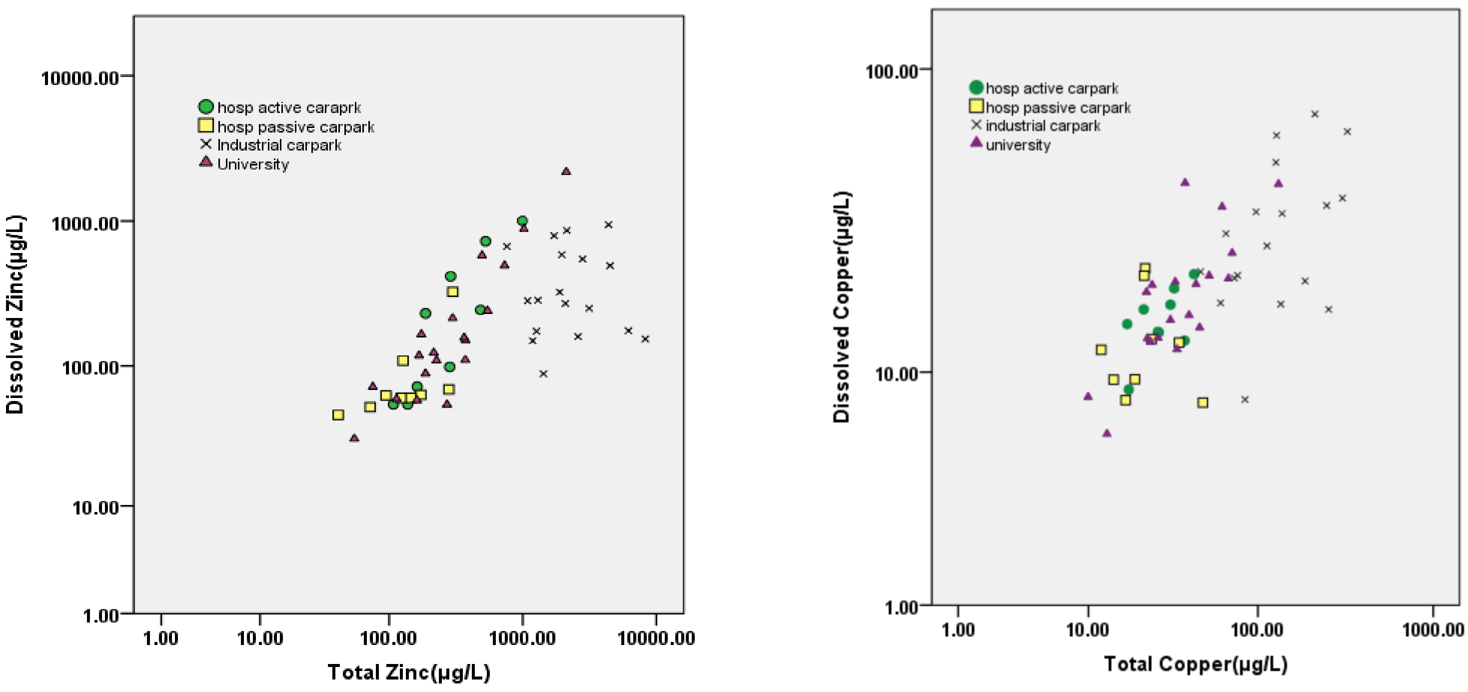
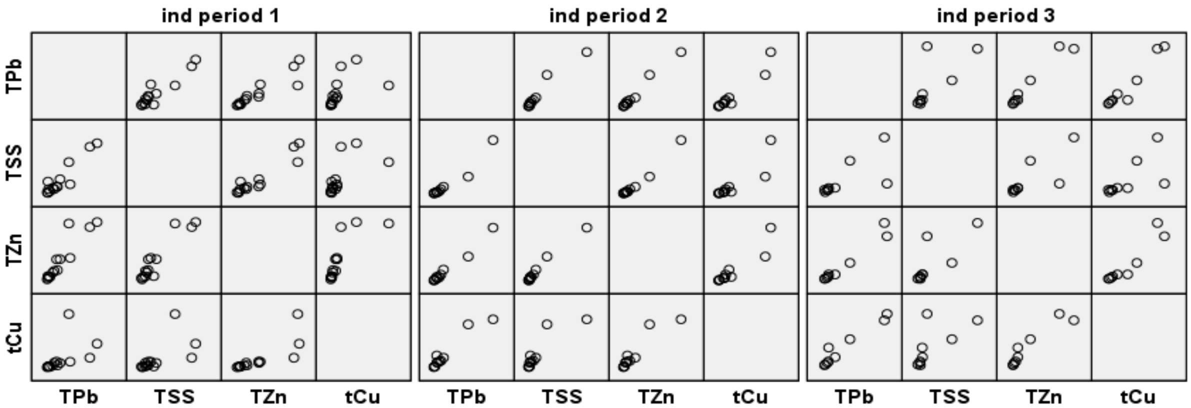


Figure D: Total vs dissolved metals concentrations

Table E: Average, minimum and maximum of % metal partitioning from three carparks

University		%dZn	%pZn	%dCu	%pcu	%dPb	%pPb
	Average	64	36.6	36.9	63.1	4.9	95.2
	Min	8.7	0.0	13.0	5.8	0.4	0.0
	Max	100.0	91.3	94.2	87.0	99.9	99.6
Industrial	Average	14.7	85.3	18.4	86.8	0.8	99.2
	Min	1.9	12.2	5.4	60.2	0.1	97.1
	Max	87.8	98.1	39.8	94.6	2.9	99.9
hospital (active)	Average	69.5	30.4	45.2	54.8	9.2	90.8
	Min	34.5	0.0	28.4	29.4	1.6	46.5
	Max	100.0	65.5	70.6	71.6	53.5	98.4
hospital (passive)	Average	62.1	40.0	45.3	54.8	0.3	99.4
	Min	24.5	0.0	13.5	15.2	0.8	0.0
	Max	100.0	75.5	84.8	86.5	18.0	99.2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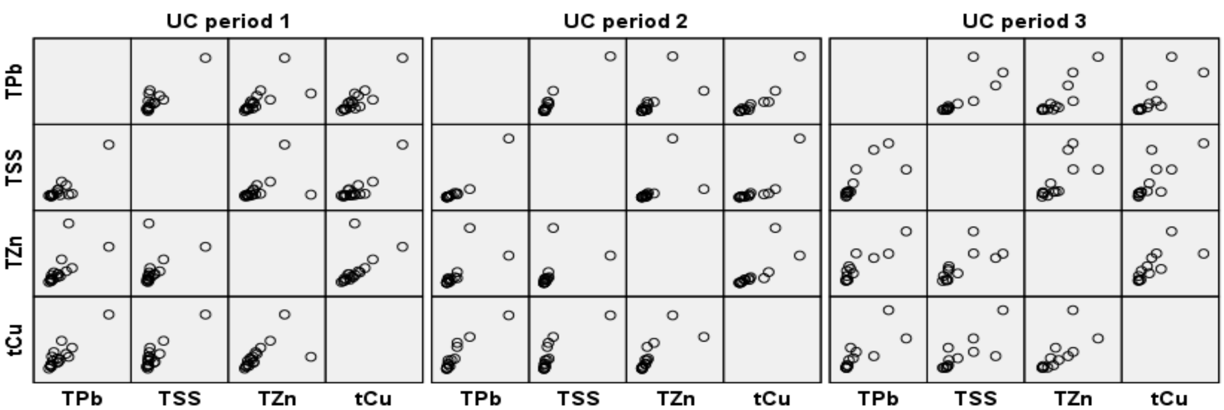
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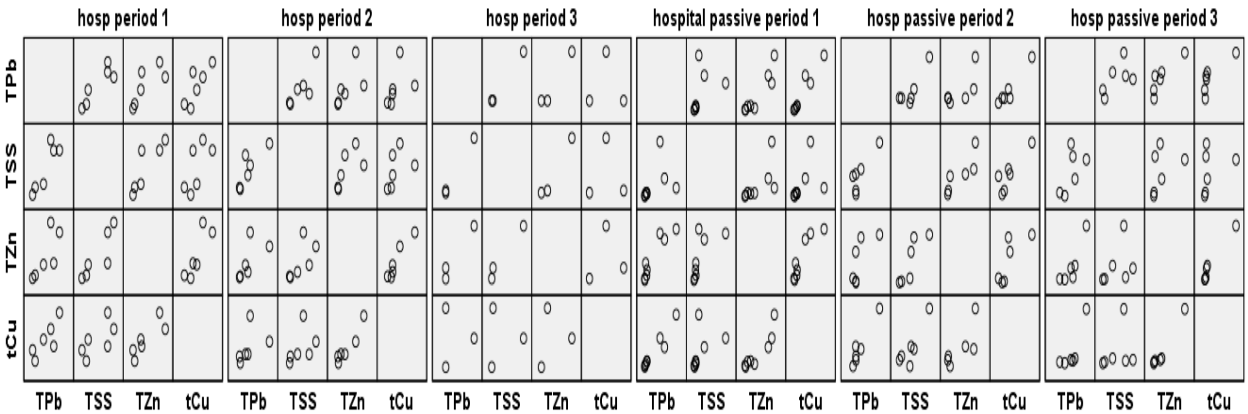


Figure: Correlation between various pollutants parameters in different steady-state (period1, period 2 and period 3)

Table 5.1: Dissolved and particulate heavy metals yield from the hospital carpark during different steady-state

Hospital dissolved and particulates	**period 1(Mean, Std Error, Min and Max)**	**period 2(Mean, Std Error, Min and Max)**	**period3(Mean, Std Error, Min and Max)**
dZn(µg/m2)	96, 39, 15-256	59, 24, 14-150	32, 7, 18-38
pZn(µg/m2)	21, 12, 1-72	10, 4, 1-24	10, 4, 1-15
dCu(µg/m2)	15, 5, 3-30	15, 5, 4-36	12,2, 9-16
pCu(µg/m2)	8, 3, 1-16	6, 2, 1-17	4, 1, 2-6
dPb(µg/m2)	8, 4, 0.22-24	5, 3, 0.36-18	0.9, 0.32, 0.49-2
pPb(µg/m2)	8, 4, 1-26	2, 0.8, 0.9-5	2, 0.87, 0.42-3

Table 5.2: Dissolved and particulate heavy metals yield from the Industrial carpark during different steady-state

Industrial dissolved and particulates	period 1(Mean, Std Error, Min and Max)	period 2(Mean, Std Error, Min and Max)	period3(Mean, Std Error, Min and Max)
dZn(µg/m2)	191,58, 22-876	80,21, 8-210	49, 9, 10-89
pZn(µg/m2)	632, 215 (0.54-2169)	568, 303, 7-3294	267,120, 1-1050
dCu(µg/m2)	26,9, (2-136)	8, 2, 0.61-21	9, 4, 0.44-39
pCu(µg/m2)	86,47, (1-675)	34, 16, 0.74-143	16, 7, 1-52
dPb(µg/m2)	2,1, 0.04-16	1, 0.9, 0.01-11	2, 2, 0.1-16
pPb(µg/m2)	43, 13, 4-153	34, 17, 0.71-179	0.6, 0.3, 0-3

Table 5.3: Dissolved and particulate heavy metals yield from the Universality carpark during different steady-state

Table 5.5

University dissolved and particulates yield/m2	period 1(Mean, Std Error, Min and Max)	period 2(Mean, Std Error, Min and Max)	period3(Mean, Std Error, Min and Max)
dZn(µg/m2)	152, 56, 18-876	87,22, 12-337	61,10, 13-122
pZn(µg/m2)	36, 12, 0.10-211	122,79,0.52-1132	26,12,0.68-138
dCu(µg/m2)	16, 8, 0.89-136	10,3, 0.73-43	8,2,0.70-17
pCu(µg/m2)	6, 2, 0.45-38	11,5, 0.31-63	7,3, 0.66-43
dPb(µg/m2)	1,0.34,0.04-5	1,0.6, 0.4 - 9	0.50,0.70, 0.11-0.90
pPb(µg/m2)	4, 1, 0.21-26	8,4, 0.21-63	3.8, 1.5, 0.28-17.64

The average 10 min intensity, average 10 mins rain depth and average intensity were higher during wet season as compared to dry season. Longer duration and larger ADD were also observed during the wet season as compared to dry season.

Table 5.4: Rainfall characteristics during the dry season (October to May)

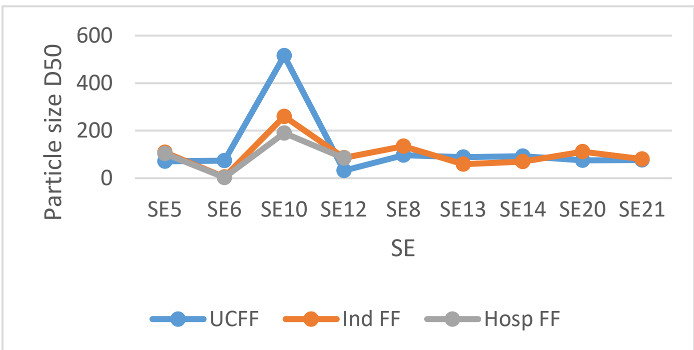
Storm event	**Date and time**	**10 mins rain depth(mm)**	**10 mins rain intensity (mm/hr)**	**average intensity (mm/hr)**	**rain depth (mm)**	**rain duration (hr)**	**antecedent dry days(day)**
SE3	27/01/2016	0.2	2.4	2.96	10.6	3.6	0.25
SE4	17/02/2016	0.4	4	2.81	7.6	2.7	20.18
SE5	15/03/2016	0.6	3.6	1.24	3.2	2.58	6.61
SE6	24/03/2016	0.2	1.2	2.05	10.6	5.17	7.5
SE7	8/4/2016	0.2	1.2	2.4	2	0.9	3.75
SE8	20/05/2016	0.6	3.6	3.3	7.8	2.3	3.76
SE9	22/05/2016	0.4	2.5	1.1	4	3.5	1.15
SE10	28/05/2016	0.4	2.5	3.23	7.8	2.4	1.3
SE20	6/10/2016	1.2	7.5	4.6	5	1.1	1.24
SE21	14/10/2016	0.8	5	1.6	3.2	2	2.12
	Average	**0.5**	**3.35**	**2.529**	**6.18**	**2.625**	**4.786**

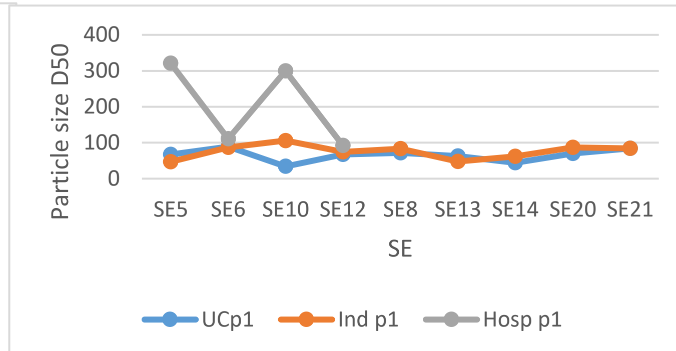
Table 5.5: Rainfall characteristics during the wet season (June to September)

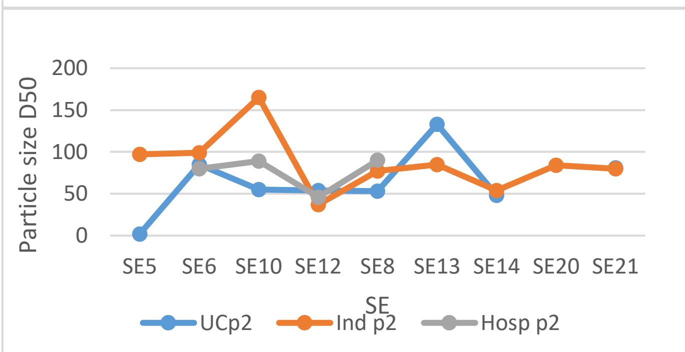
Storm event	Date and time	10 mins rain depth(mm)	10 mins rain intensity (mm/hr)	average intensity (mm/hr)	rain depth (mm)	rain duration (hr)	antecedent dry days(day)
SE1	42286	1.8	10.8	10.8	1.8	0.16	4.49
SE2	22/09/2015	0.4	2.4	0.91	2.2	2.42	2.02
SE11	22/06/2016	0.4	2.5	0.65	0.6	0.92	9.4
SE12	23/06/2016	0.2	1.25	0.91	1.7	1.9	1.26
SE13	8/7/2016	0.2	1.25	0.81	4.2	5.2	7.3
SE14	13/07/2016	1	6.25	6.87	12.6	1.8	5.6
SE15	3/8/2016	0.2	1.25	1.09	1	0.9	3.4
SE16	12/8/2016	0.2	1.25	0.39	4.6	11.8	4.2
SE17	26/08/2016	0.8	5	1.97	4.6	2.3	12.9
SE18	6/9/2016	0.2	1.25	1.1	1	0.9	9.7
SE19	27/09/2016	1	6.25	6.25	5	1.1	18
	Average	**0.6**	**3.6**	**2.9**	**3.6**	**2.7**	**7.1**

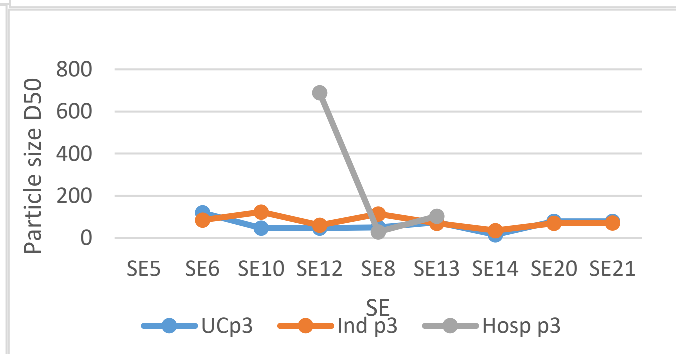
Chapter 6

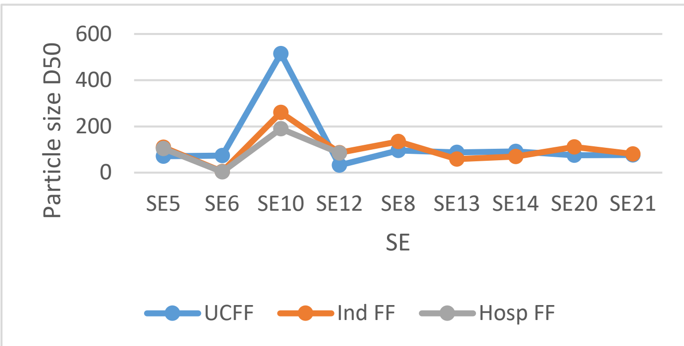
Comparison between 9 SE which were sampled during same rainfall conditions. Comparison of particle size D10, D50 and D90 during 9 Storm events at three different carparks.

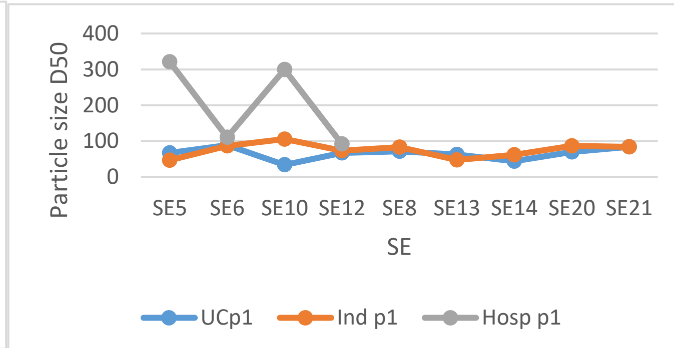


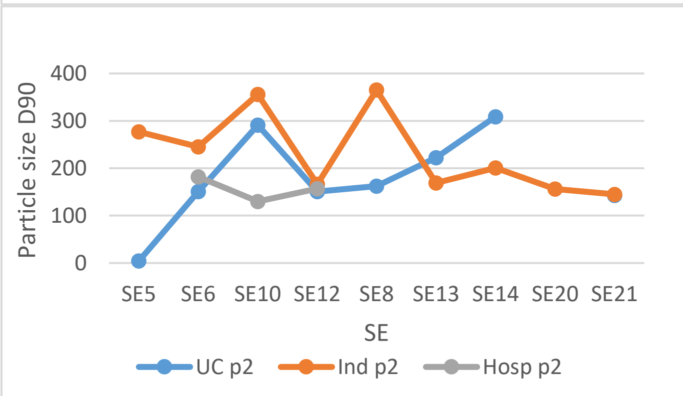


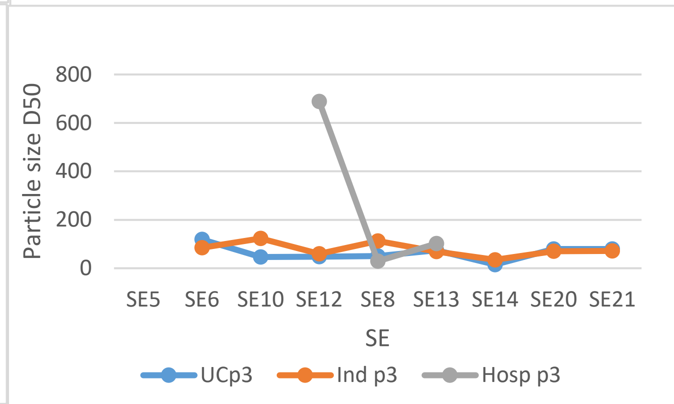


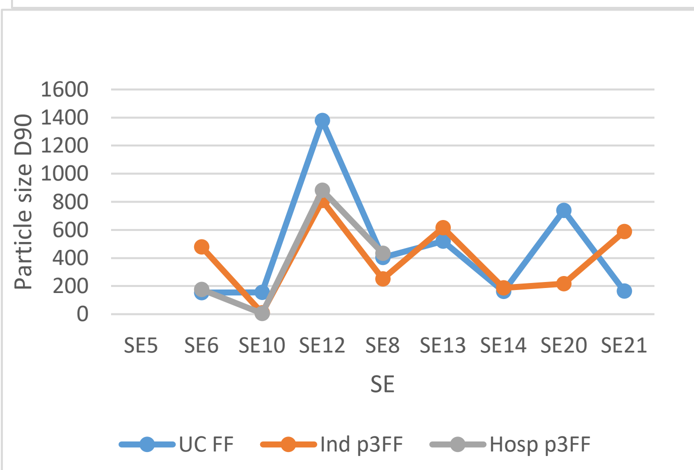


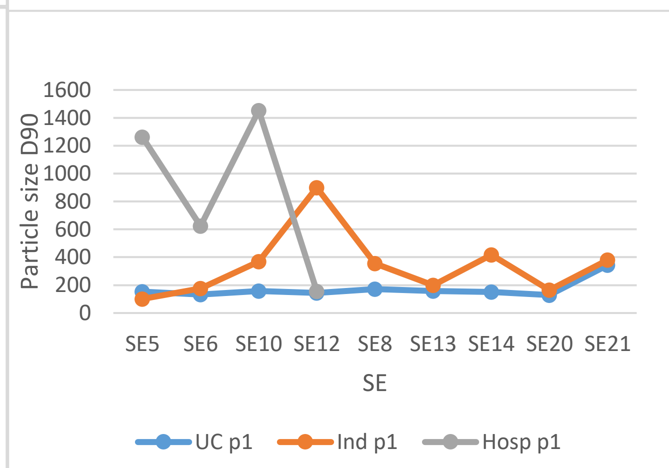

Particle size D50
600
400
200
0
SE5 SE6 SE10 SE12 SE8 SE13 SE14 SE20 SE21
SE
UCFF
Ind FF
Hosp FF

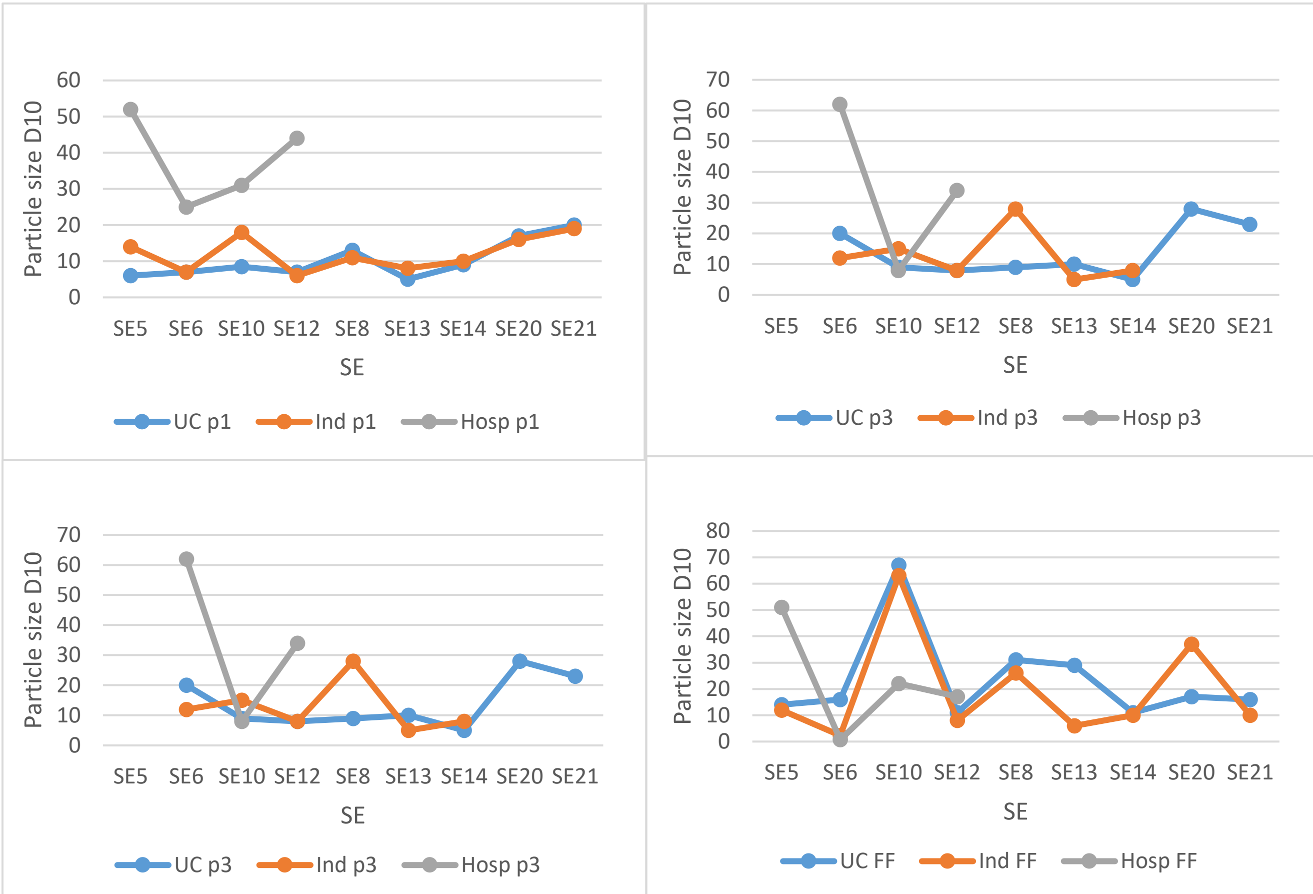

Particle size D50
400
300
200
100
0
SE5 SE6 SE10 SE12 SE8 SE13 SE14 SE20 SE21
SE
UCp1
Ind p1
Hosp p1


Particle size D90
400
300
200
100
0
SE5 SE6 SE10 SE12 SE8 SE13 SE14 SE20 SE21
SE
UC p2
Ind p2
Hosp p2


Particle size D50
800
600
400
200
0
SE5 SE6 SE10 SE12 SE8 SE13 SE14 SE20 SE21
SE
UCp3
Ind p3
Hosp p3


Particle size D90
1600
1400
1200
1000
800
600
400
200
0
SE5 SE6 SE10 SE12 SE8 SE13 SE14 SE20 SE21
SE
UC FF
Ind p3FF
Hosp p3FF


Particle size D90
1600
1400
1200
1000
800
600
400
200
0
SE5 SE6 SE10 SE12 SE8 SE13 SE14 SE20 SE21
SE
UC p1
Ind p1
Hosp p1


Particle size D10
SE
SE5 SE6 SE10 SE12 SE8 SE13 SE14 SE20 SE21
UC p1 Ind p1 Hosp p1
UC p3 Ind p3 Hosp p3
UC p3 Ind p3 Hosp p3
UC FF Ind FF Hosp FF