On Site Remediation of Micropollutants from Stormwater for Reuse

By

Thamer Mohammed Ahmed Mohammed

A thesis submitted to fulfil the requirements of the degree of
Philosophy of Doctorate of Engineering

University of Technology, Sydney
Faculty of Engineering and Information Technology

Australia, 2012

CERTIFICATE

I certify that this thesis has not already been submitted for any degree and is not being submitted as part of candidature for any other degree.

I also certify that the thesis has been written by me and that any help that I have received in preparing this thesis, and all sources used, have been acknowledged in this thesis.

Signature of Candidate

…………………………………………………

(Thamer Mohammed Ahmed Mohammed)

Acknowledgement

It was not easy work, but both stressful and fun during my doctoral research at The University of Technology, Sydney. It would not have been possible to achieve this doctoral research without the help and support of the people around me and therefore they need a special mention here. I am highly appreciative to people for their help and support during my research. My first thanks and gratitude goes to my principal supervisor Prof. Saravanamuthu Vigneswaran. He was a source of inspiration, motivation and strength throughout my research. I would like to show my deep gratitude to my co-supervisors A.Prof. Jaya Kandasamy, and Dr. Rupak Aryal and a special thanks also to Dr. Paripurnanda Loganthan for his help and support. My particular thanks to my best friend Akram Sukar who I spent and enjoyed some of my best time with at UTS. My thanks also go to A. Prof. Huu Hao Ngo for his valuable effort in the environmental laboratory with appropriate instruction. It is a pleasure to thank Rami Hadad and David Hooper for their help and support. I would also like to thank my colleagues and mates Johir, Ben, Chinu, Javeed, Ibrahim, Ghausul, Yousuf, and Monami. I had a wonderful time with these guys.

I would like to show my gratitude to Prof. Ravi Naidu, Managing Director of Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC-CARE) and Mr. Andrew Beverage for the financial support. I owe my thanks to the academic and technical support of the University of Technology, Sydney and its staff, especially Phyllis for all my academic support. Above all, I would like to thank my Mother, my wife, my children Ali, Zaid and Sumaya and the whole Hanoun family for their personal support and great patience at all times. My family was always with me during the accomplishment of this doctoral research. Thanks very much every one.

Finally, I would like to forward all my appreciation to ALAH who guided those people who supported and helped me through my research.

Published papers arising from this research

Journal Papers:

Thamer Mohammed, Saravanamuthu Vigneswaran and Jaya Kandasamy, 2011, Biofiltration as pre-treatment to water harvesting and recycling, Waste Water Technology, vol. 63, no10, pp. 2097-2105.

Thamer Mohammed, Saravanamuthu Vigneswaran, Paripurnanda Loganathan, Jayakumar Kandasamy, Rupak Aryal, 2012. “Removal of inorganic contaminants from simulated stormwater by three sorbents in columns under intermittent runoff condition,” Accepted to appear in the Journal of Separation Science and Technology.

Thamer Mohammed, Paripurnanda Loganathan, Andrew Kinsela, Saravanamuthu Vigneswaran, Jayakumar Kandasamy,2012, Enrichment, inter-relationship and fractionation of heavy metals in road-deposited sediments of Sydney, Australia. Soil Research, vol 50, pp229-238.

Aryal, R., Vigneswaran, S., Loganathan, P., Kandasamy, J.K. & Mohammed, T.M.2012, 'Hydrous iron oxide for removal of inorganic contaminants in simulated stormwater: A batch sorption kinetics study', Korean Journal of Chemical Engineering, vol. 28, no. 8, pp. 1706-1712.

Thamer Mohammed, Rupak Aryal, Saravanamuthu Vigneswaran, Paripurnanda Loganathan, Jaya Kandasamy & Ravi Naidu, 2012, 'Removal of heavy metals in stormwater by hydrous ferric oxide', Institution of Civil Engineers.Proceedings.Water Management, vol. 165, no. WM3, pp. 171-178.

Wang Guen Shim, Javeed Mohammad Abdul, Thamer Mohammad, SaravanamuthuVigneswaran, HuuHao Ngo, Jaya Kandasamy. 2012, Biofilter in leachate treatment processes, Desalination and Water Treatment, vol. 41 pp. 249–257.

Conference papers

Thamer Mohammed, Paripurnanda Loganathan, Andrew Kinsela, Saravanamuthu Vigneswaran, Jayakumar Kandasamy, Heavy metal levels and solid phase speciation of road-deposited dusts in Sydney, Australia. CESE 2011, Challenges in Environmental Science and Engineering 25 - 30 September 2011 Tainan City, Taiwan

Rupak Aryal, Thamer Mohammed, Saravanamuthu Vigneswaran, Jaya Kandasamy, Ravi Naidu, Hydrous iron oxide media for stormwater treatment, batch equilibrium and kinetics. 3rd International site remediation conference 27 - 30 September 2009 Adelaide Australia.

Table of Contents

List of figures

CHAPTER 1

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

CHAPTER 7

List of Tables

CHAPTER 1

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

CHAPTER 7

Nomenclature

A = Surface area (m^2)

AC = Activated Carbon

ANZECC = Australian and New Zealand Environment and Conservation Council

ASTM = American Standard Testing and Methods

BV = Bed Volume

BMP = Best Management Practice

BOD = Biological Oxygen Demand

BOM = Biodegradable Organic Matter

C_b = The concentration of particles in a feed water

COD = Chemical Oxygen Demand
Da = Dalton

DOC = Dissolved Organic Carbon

DOM = Dissolved Organic Matter
DMF = Dual media filter

EF = Enrichment Factor

EfOM = Effluent Organic Matter

GAC = Granular Activated Carbon

EPS = Extracellular Polymeric Substances

FAO = Food Agriculture Organisation for the United Nation

h = hour

HFO = Hydrous Ferric Oxide

HPSEC = High Pressure Size Exclusion Chromatography
IE = Ion Exchangers
kPa = Kilo Pascal
MFI = Modified Fouling Index

MWD = Molecular Weight Distribution
MF = Microfiltration
MFI-UF = Modified fouling index by using ultra filter membrane
MFI-NF = Modified fouling index by using nano filter membrane
MWCO = Molecular Weight Cut-off
M_w = Weight Average Molecular Weight
M_n = Number Average Molecular Weight
NF = Nanofiltration
NOM = Natural Organic Matter
NTU = Nephelometric Turbidity Unit
PAC = Powdered Activated Carbon
PI = Pullotion Index
R_m = Membrane resistance
RO = Reverse Osmosis
SEC = Size Exclusion Chromatography
SS = Suspended Solids
SWOM = Seawater Organic Matter
t = Filtration time (s)
THM = Trihalomethanes
TDS = Total Dissolved Solid
TMP = Trans-membrane Pressure
UF = Ultrafilter
ULPRO = Ultra Low-pressure Reverse Osmosis Membranes
V = Total permeate volume (l)
WHO = World Health Organisation
ZVI = zero-valent iron
ΔP = Applied trans-membrane pressure (Pa)
η = Water viscosity at 20^0C (N s/m^2)
α = The specific resistance of the cake deposited
ρ = Polydispersity
^{0}C = Degree Celsius

Abstract

Water scarcity due to persistent drought is forcing the countries around the world to explore alternative fresh water resources. Australia is the driest inhabited continent, and has one of the most variable rainfall intensities in the world. In the last one hundred years Australia has suffered six major droughts and fifteen less severe droughts. The drought that commenced in 2001 has encouraged the harvesting of stormwater and re-use of water in order to lower the demand placed on municipal water supplies. Urban and industrial stormwater runoff has high potential as a reusable water resource, although it requires treatment due to the presence of several types of contaminants including inorganic ones that have adverse ecological impacts on receiving waters. The main aim of this research was to focus on the identification of contaminants of concern in Australian stormwater and provide suitable remediation solutions with effective onsite treatment practices such as biofiltration and adsorption/ ion exchange column techniques.

Long term biofilter experiments were conducted with raw stormwater collected from a canal at Carlton, in Sydney. Anthracite and granular activated carbon (GAC) were used as a single filter media in biofilter columns. Media heights of 75 and 40 cm were used. The filter columns were operated at filtration velocities of 0.12 and 0.25 m/h. The removal efficiency for turbidity and DOC for the GAC filter media were found to be 75% and almost 100% respectively. The removal efficiency for the anthracite filter was much lower. Molecular weight distribution analysis showed an almost similar trend to the DOC removal. When compared to the anthracite filter media, the GAC biofilter removed a much larger range of organic compounds present in the stormwater. The GAC biofilter removed organic matter earlier as compared to the anthracite filter. Based on a limited sample of stormwater, the removal efficiency for phosphorus was upto 74% and that of nitrogen was up to 30%. In general, the GAC filter showed higher heavy metal removal efficiency than the anthracite filter. The removal of zinc, iron, lead and nickel were good, however, the concentration of heavy metals in the raw surface water sample was low.

In another study, Organic matter removal from a diluted synthetic landfill leachate was studied using a GAC biofilter. This filter with a depth of 35cm was found to remove a significant amount of organic matter from the diluted synthetic landfill leachate. The experiments were conducted at low (0.2 m/h) and high (2 m/h) flow velocity through the GAC filter to represent insitu and exsitu biofiltration. The results showed that organic matter can be removed in a consistent manner for a long period of time. GAC bio-filtration led to a consistent TOC removal even after a long period of operation without the need to regenerate the activated carbon. Even after 30-50 days of continuous running, the organic removal efficiency from the GAC bio-filter was approximately 40% and 60% when high (2 m/hr) and low (0.2 m/hr) filtration velocities were used. It should be noted that the performance can be enhanced by using a larger filter depth which is the case in real situations.

A study was conducted using three filters in series to evaluate the efficiency of removal of TOC, turbidity and nutrients from stormwater. The first filter system containing sand removed 70% turbidity and 6% TOC. The second filter system containing GAC removed 99% of the remaining TOC and 43% of the remaining turbidity. The use of a Purolite A520E filter media as the third stage filter was found to be capable of removing up to 89% of nitrate within 6 hours, however no phosphate removal was achieve. Therefore it is vital to have GAC and Purolite as a media in filtration system along with sand to achieve organic and nutrient removal.

Combined removal of a mixture of heavy metals (Cd, Cu, Ni and Zn) and an oxy anion of Se (predominantly selenate species, SeO4-) from a synthetic stormwater sample was investigated by their sorption on hydrous ferric oxide (HFO) (5%), HFO+Ca(OH)2 (6%), and HFO+Ca(OH)2+MnO2 (7%) in columns containing 93-95% anthracite, conducted under seven intermittent runoffs (wetting and drying) each of 8 h duration within a 40 h period. The contaminants removal behaviour varied between the ions and between the sorbents as well as with flow rate and time. The removal efficiency was greater at a low flow rate (0.75 m/h) than at a high flow rate (1.5 m/h). At the initial period when Ca(OH)2 produced elevated pHs, the HFO only column removed less heavy metals but more Se than the HFO+Ca(OH)2 columns. With increased time when the pH effect of Ca(OH)2 became insignificant, the MnO2 in the column increased the removal of all contaminants. The removal efficiencies (%) at the low flow rate for Cd, Cu, Ni, Zn by the HFO+Ca(OH)2+MnO2 column, and Se by the HFO column were 95-

100, 94-98, 88-99, 96-100, 92-94 for the 1st and 3rd runs and 61-76, 85-88, 51-69, 57-79, 82-88 for the 5th and 7th runs, respectively.

Urban road-deposited sediments (RDS) are potential heavy metal pollution sources of both terrestrial and aquatic environments. A study was conducted to determine the heavy metals enrichments, their possible sources and potential bioavailability and mobility in RDS from nine sites along major motorways of Sydney, the largest city with highest road traffic density in Australia. The results showed that the mean total concentrations of metals in the RDS decreased in the order, Fe > Mn > Zn > Cu > Cr >Pb> Ni> Cd. The corresponding order in the background soils (minimally contaminated from roads) was Fe >Mn > Zn ~ Ni > Cu ~ Pb > Cr > Cd. Both the pollution index (PI) and metal enrichment factor (EF), which are comparative measures between contaminated and uncontaminated sites were highest for Cu and Zn suggesting that Cu and Zn inputs to RDS were mainly the likely result of brake and tyre wear, respectively. Cluster and correlation analyses showed that while the concentrations of these two metals were related in the soil, they were not correlated in the RDS. Low PI and EF values as well as the close inter-relationships of Fe, Mn, Cr and Ni in both RDS and soils, would suggest that these metals were derived mainly from natural sources. Metal fractionation data showed that 50-95% of Cr and Fe in RDS were present in the immobile and bio-unavailable residual fraction, whereas 15-65% of Zn was contained in the exchangeable fraction which is considered to be mobile and bioavailable. Significant quantities of Mn, Ni, Cu, Pb and Cd were detected in all fractions, although the residual fraction contained the majority in all instances. Copper was the only metal appreciably present (5-25%) in the organic fraction.

CHAPTER 1

1. Introduction

1.1Background

Australia is the driest continent, and has one of the most variable rainfall intensities in the world. In the last one hundred years Australia has suffered six major droughts and fifteen less severe droughts (Windram, 2009). The drought that commenced in 2001 has encouraged the re-use of water in order to lower the demand placed on municipal water supplies.

The average annual volume of urban stormwater runoff in Australian cities is almost equal to the average annual urban water usages, of which at least 50% is for non-potable use (Mitchell et al., 1999). The high potential for the continued proliferation of organic and inorganic contaminants pose substantial challenges to the recycling and reuse of stormwater. As Australia is entering a recycling era of stormwater and wastewater, it is essential to identify the emerging contaminants of concern in urban stormwater for sustainable on-site remediation technology for large runoff volumes as well as appropriate on-site treatment methods.

Previously, stormwater used to be thought of as a waste product rather than as a resource to be harvested. This can be highlighted by the use of drainage systems, such as kerb and guttering, which have been implemented with the primary aim of transporting water from one location to another, as quickly and efficiently as possible. This frame of mind, as well as the effects of urbanisation, have upset and modified the natural water cycle on which all life forms depend (Dunphy, 2007).

The world's population living in urban areas is estimated to increase to two-thirds by 2050 (United Nations, 2008). This will consequently lead to an increasing imperviousness, which in turn will induce more total runoff volume, polluting waterways and leading to reductions in the groundwater recharge by blocking infiltration of water into the ground.

There are many pollutants in urban stormwater runoff. The major categories are: (i) total suspended solids (TSS), (ii) heavy metals, (iii) polycyclic aromatic hydrocarbons (PAHs) and (iv) nutrients (Aryal et al., 2010). Table 1.1 presents the common pollutants found in urban stormwater, their likely sources and the effects of the pollutants on our waterways. Table 1.1 shows contaminants are emitted from diverse sources. Typical ranges of urban water quality data for Australian catchments are presented in Table 1.2. This is compared with corresponding water quality standards.

Table 1. 1 Possible sources of pollutants in stormwater runoff and their effects on the waterway. (Modified from CSIRO, 1999).

Pollutant	**Effect**	**Urban source**
Sediment	Reduces the amount of light in the water available for plant growth and thereby reducing the supply of food for other organisms. Can clog and damage sensitive tissues such as the gills of fish. Can suffocate organisms which live on or in the bed of lakes and streams by forming thick deposits when this suspended material settles out.	• Land surface erosion • Pavement and vehicle wear • Building and construction sites • Organic matter (for example leaf litter, grass) • Car washing • Weathering of buildings/structures • Atmospheric deposition.
Nutrients	An increase of nutrients in water stimulates the growth of aquatic plants. Causes excessive growth of aquatic weeds and algae that may choke lakes and streams and lead to dramatic daily fluctuations in dissolved oxygen levels.	• Organic matter • Fertiliser • Sewer overflows, septic tank leaks • Animal faeces • Detergents (car washing)
Oxygen demanding substances	Oxygen is used up more quickly than it can diffuse into the water from the atmosphere. The resulting drop in oxygen levels may then be sufficient to kill fish and other aquatic organisms. If all the oxygen in the water is used up, unpleasant odours can result.	• Organic matter decay • Atmospheric deposition • Sewer overflows, septic tank leaks • Animal faeces • Spillage, illegal discharges.
pH acidity	Increased acidity damages plants and animals	• Atmospheric deposition • Spillage, illegal discharge • Organic matter decay
Micro-organisms	Contain very high numbers of bacteria and viruses. Some of these organisms can cause illnesses, including hepatitis and gastroenteritis.	• Animal faeces • Sewer overflows, septic tank leaks • Organic matter decay.
Toxic organics	Can poison living organisms or damage their life processes.	• Pesticides, Herbicides • Spillage, illegal discharge • Sewer overflows, septic tank leaks.
Heavy metals	Poison living organisms or damage their life processes in some other way. Persists in the environment for a long time.	• Atmospheric deposition • Vehicle wear • Sewer overflows • Weathering of buildings, • Spillage, illegal discharges.

Table 1. 2 General characteristics of urban stormwater quality data in Australia (Singh et al., 2012)

Parameter	Unit	Sydney Range of Pollutant Concentration^{A}	Australia Range of Pollutant Concentration	Australian Standards
Nutrients				
Total Nitrogen	mg/L N	0.39-9.5	0.6-8.6	<0.1-0.75
Nitrate	mg/L N	0.38-7.9		
Nitrite	mg/L N	0.069-0.97		
Ammonia	mg/L N	0.4-1.15	0.01-9.8	<0.02-0.03
Total Phosphorous	mg/L P	0.021-0.36	0.12-1.6	<0.01-0.1
Orthophosphate	mg/L P	0.02-0.026		
Physical and Chemical				
TSS	mg/L		20-1,000	<10% change
pH	-	6.68-7.28		
TOC	mg/L	4.25-8.96		
Turbidity	NTU	1.5-90		
True Colour	PtCo	18-270		
Bicarbonate	mg/L $CaCO_3$ equivalent	30-95		
Water Hardness	mg/L $CaCO_3$ equivalent	22-145		
Metals				
Aluminium	mg/L	0.028-0.188		
Arsenic	mg/L	0.001-0.005		
Cadmium	mg/L	0.0009-0.001	0.01-0.09	0.0002-0.002
Chromium	mg/L	0.002-0.002	0.006-0.025	0.01
Copper	mg/L	0.008-0.049	0.027-0.094	0.002-0.005
Iron	mg/L	0.05-2.55		
Manganese	mg/L	0.001-0.024		
Nickel	mg/L	0.003-0.10	0.014-0.025	0.015-0.15
Lead	mg/L	0.001-0.022	0.19-0.53	0.001-0.005
Selenium	mg/L	0.001-0.004		
Zinc	mg/L	0.016-0.123	0.27-1.10	0.27-1.10
Biological				
Faecal Coliform	cfu/100ml		4000-200000	150 (PR) 1000 (SR)

* PR: primary recreation - SR: secondary recreation, ^{A} data measured in Carlton, Kogarah

Urban Stormwater and stormwater management is based on the following three principles CSIRO, 1999);

- Avoiding pollution wherever possible through appropriate control of the pollutant source.
- Minimising stormwater pollution by in-transit measures.
- Managing the effects in receiving waters as a last resort

In order to achieve environmental management objectives, these principles can be employed in series as it is illustrated in Figure 1.1.

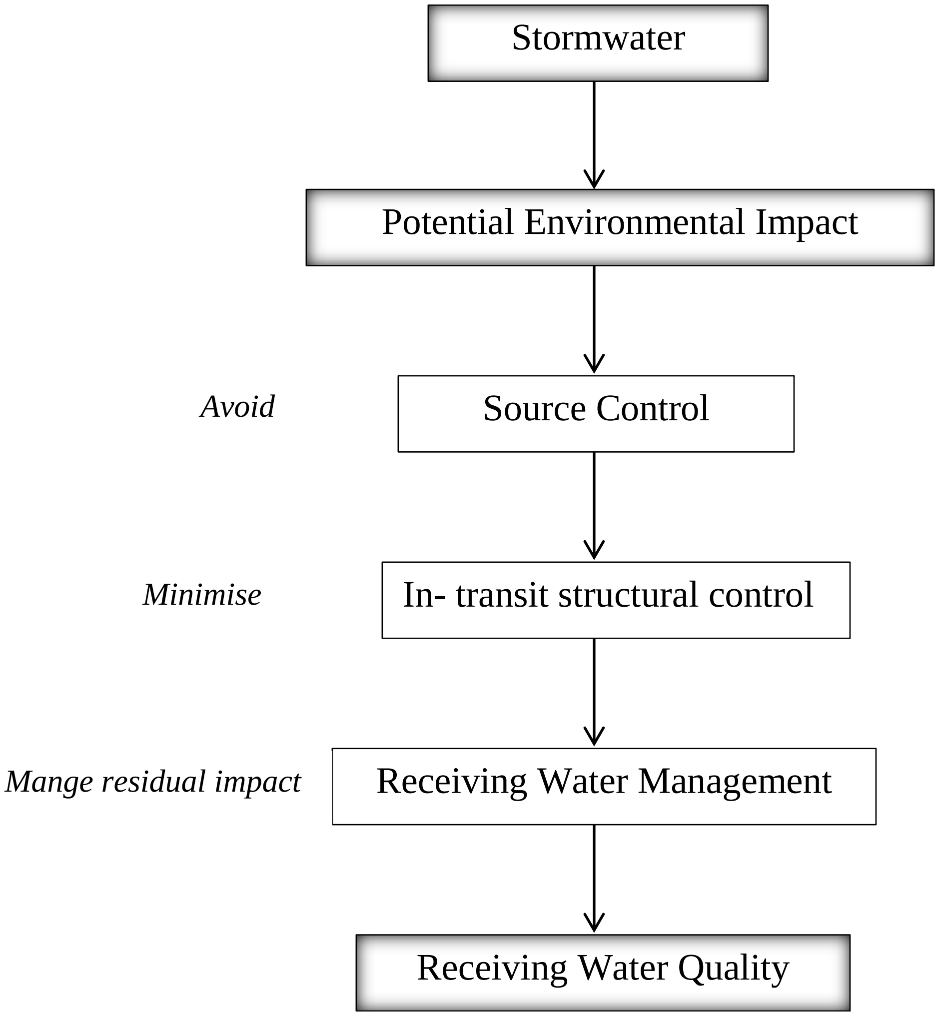


Figure 1. 1 Principles and framework of stormwater management (adapted from CSIRO, 1999)

Water sensitive urban design; Measures to conserve, treat and harvest stormwater runoff have been investigated, with the aim being to integrate sustainable water management with urban development. These measures are broadly referred to as ‘Water Sensitive Urban Design’ (WSUD). WSUD is a catch-all term for environmentally sustainable water resource management in urban areas. There has been a rapid development of WSUD planning and design materials in most Australian states (Mouritz, 1996; Evangelisti, 1998).

There has also been a considerable research effort by many organisations. As a result of the efforts of these groups there is now a vast array of WSUD/sustainable water management planning and technical resources available to organisations and practitioners wishing to plan, design and develop or retrofit more water sensitive urban environments. (Dahlenburg, 2005)

Pollutants and Treatments; The target pollutants in stormwater treatment are litter, coarse/fine sediments and nutrients. Treatment measures can be classified into non-structural measures, which aim to reduce pollution through public education, regulation and operational practices, etc., and structural measures. When assessing structural treatment measures for the removal or reduction of pollutants, there are three subsets which describe the type of treatment measure and type of pollutants which are to be removed or reduced. These are:

- Primary treatment; This removes gross pollutants and coarse sediments and any nutrients, or hydrocarbons attached on particulates larger than 1.25 mm. The removal method is through entrapment of litter/debris and sedimentation of coarser particles. Typical devices include, litter racks, sediment traps, gross pollutant trap (GPT), litter booms, and oil/grit separators. A description and comparison between different treatments used in stormwater are given in Chapter 2, Table 2.1.
- Secondary treatment; Secondary treatment consists of sedimentation of finer particles or filtration techniques to remove fine particles and attached pollutants. This can be achieved with pre-entrance treatments which uses filtration techniques to separate entrained sediment prior to its entry into the drainage network. Some common examples of pre-entrance treatments are filter or buffer strips and grass swales. Infiltration is also promoted in one of two ways; either by stormwater flowing over vegetated land enhancing infiltration, or through the use of purpose built structures such as porous pavements and infiltration trenches. In-transit secondary treatment systems

entrain pollutants flowing through the stormwater system. A typical example is a bio-retention system. These systems remove particulates and soluble contaminants by passing stormwater through vegetation and a filter medium. The vegetation can consume (bio-logical uptake) nutrients detained in the filter.

- Tertiary treatment; This treatment is for constructed wetland systems which are shallow, extensively vegetated water bodies that use processes of extended detention and, fine filtration and biological pollutant uptake to remove pollutants from stormwater.

Detailed examples on these three treatments are given in Chapter 2.

1.2Research Question, Objectives & Scope

It is important to explore sustainable measures of improving urban stormwater quality to meet water quality objectives for harvesting and/or discharge to surface waters. Onsite remediation is a confined system designed so that all treatment processes take place within the system, and adequate treatment occurs prior to the release of stormwater to the surrounding environment or to the conventional drainage system. This is done by restricting or limiting water and pollutant movement to a certain area. Systems can be physically and/or biochemically confined

This research was focused on;

(i) The identification of contaminants of concern in Australian stormwater and
(ii) Providing suitable remediation solutions with effective onsite treatment practices such as a) adsorption b) biofiltration and c) adsorption/ Ion exchange columns.

The content of the research is broadly divided into four sections as given below.

a) Water quality

Stormwater consists of suspended solids, poly aromatic carbons (PAHs), heavy metals and biodegradable organics (BOD). In this study we analysed and compared them with Australian water quality standards. We focused mainly on total organic matter (as a surrogate matter instead of PAHs), heavy metals, solids and nutrients.

The most investigated heavy metals in literatures were Cu, Zn, Pb, Cd, Cr, V, Ni and Hg. The sources of heavy metals in soil, sediment and runoff vary from location to location and are catchment specific.

The heavy metal concentrations in solid and aqueous phases in stormwater runoff were studied.

b) Biofilter for solids (sediments) and organic removal

It is sustainable technology to treat the stormwater through the consumption of organic matter by living microorganisms.

In this study long term biofilter experiments were conducted with raw stormwater collected from a canal at Carlton, in Sydney, with anthracite and granular activated carbon (GAC) as filter media in biofilter columns. The filter columns were operated at low filtration velocities of 0.12 and 0.25 m/h to simulate the natural infiltration conditions. The removal efficiency was studied in terms of turbidity and dissolved organic matter (DOC). Molecular weight distribution analysis of organic matter was also studied as well as the heavy metal removal efficiency. Although the concentrations of heavy metals in raw stormwater samples were low, their removal was also studied. The nutrient removal was studied by passing the stormwater through a Purolite ion exchange medium.

Iron based media can be more efficient in removing the heavy metals from stormwater. Also stormwater events are intermittent.

c) Alternative adsorption media for heavy metal removal

Three combinations of sorbents (Hydrous ferric oxide (HFO), hydrous ferric oxide + calcium hydroxide ($CaOH_2$), and hydrous ferric oxide + calcium hydroxide + manganese oxide (MnO_2)) were tested for their capability in removing heavy metals under intermittent runoff conditions.

The experiments showed that the mixture of HFO, $Ca(OH)_2$ and MnO_2 are effective sorbent/filter media in removing both cationic (Cd, Cu, Ni, Zn) and oxy anionic (Se) contaminants from stormwater over a long period of time. The intermittent condition of runoff was simulated by operating the filter for the duration of 8 hours followed by a 40 h no-flow period (wetting and drying condition). The purpose of the study was to determine whether this system is capable of removing heavy metals under conditions that mimics field conditions.

d) Heavy metals in road deposited sediments (RDS)

Heavy metals are one of the main categories of contaminants. The concentrations of eight heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in RDS from nine sites along major motorways of Sydney, were measured and compared with those in the background soils using the enrichment factor (EF) and pollution index (PI). The concentrations of the different chemical forms of these metals in RDS were also measured using a 3-step sequential extraction method. The heavy metal removal capacity was also studied through batch experiments. It should be noted that organic matter such as poly aromatic hydrocarbons (PAHs) are also major contaminants in RDS. However they were not studied in this research.

A review of the PAHs and their typical concentration levels are presented in the literature review (Chapter 2).

CHAPTER 2

2. Literature Review

This review provides a general overview of stormwater quality and quantity and current stormwater management practices and possible treatment methods. A detailed review on the water quality and different treatment methods such as biofiltration and adsorption are given in chapter 3, 4, 5, 6 and 7.

2.1Stormwater Treatment Measures-WSUD

The management of stormwater runoff in traditional urban developments has been driven by a concept that reflects the view that stormwater runoff has no meaningful value as a useful resource, is environmentally benign and adds little to the amenity (aesthetic, recreation, education, etc) of an urban environment. Consequently, conventional urban stormwater management has focused on providing highly efficient drainage systems to rapidly collect and remove stormwater runoff using a combination of underground pipes and linear "engineered" overland flow paths (often located along the back fence line of properties to keep them out of sight). These systems kept stormwater runoff "out of sight" and consequently "out of mind".

The increased rates of stormwater runoff associated with traditional urban development coupled with a dramatic increase in stormwater runoff volume and associated contaminants such as litter, sediments, heavy metals and nutrients has caused significant degradation of the natural environments (Wong, 2006).

Changes to the water cycle resulting from conventional stormwater drainage systems and urbanisation have been observed across all regions and have been specifically identified in North America and urban areas within South-Eastern Australia (Walsh et al., 2004).

In Australia, WSUD is gaining prominence as a contemporary approach for managing urban stormwater to minimise the impact of urban development on waterways and estuaries.

2.1.1 What is 'water sensitive urban design'?

WSUD seeks to minimise the extent of impervious surfaces, treating stormwater runoff and mitigate changes to the natural water balance through on-site reuse of the water as well as through temporary storage. An integrated approach to stormwater management is the key to WSUD. This integrated approach regards stormwater as a resource rather than a burden and considers all aspects of run-off within a development, including implementation of water quality/quantity controls, maximising water reuse, conservation and preservation of amenities and environmental values within the catchment (see Figure 2.1).

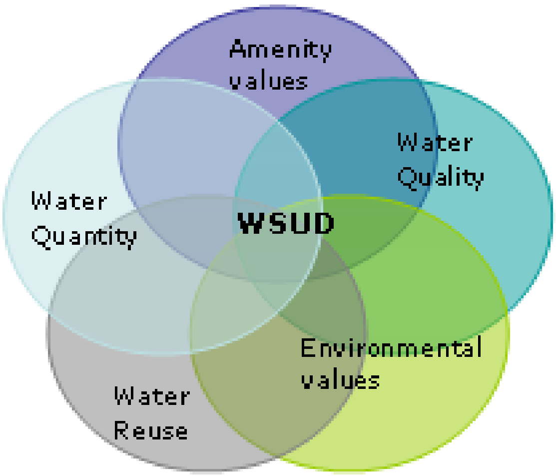


Figure 2. 1 WSUD Conceptual Model

2.1.2 Water Sensitive Urban Design Treatment

Water Sensitive Urban Design is used to preserve water and remove pollutants from stormwater before it reaches downstream drainage systems. Applying Water Sensitive Urban Design is most successful when it is considered early in a site and building's design. Table 2.1 describes briefly the stormwater treatment methods, techniques and, their advantages and disadvantages. As an example, instead of designing roof and paved areas to drain directly to a storm water pipe, the water is directed to Water Sensitive Urban Design for treatment or reuse before it reaches the storm water drain. Most of the Water Sensitive Urban Design elements described below incorporate landscape design.

Table 2. 1 Stormwater treatment methods and techniques and their advantages and, disadvantages (Begum et al., 2008)

Treatment Measures	Description	Advantages	Disadvantages
Litter Baskets and Pits	A wire or plastic 'basket' installed in a stormwater pit to collect litter from a paved surface (litter basket) or within a piped stormwater system (litter pit).	a) Can be retrofitted in existing areas with high litter loads b) Low downstream maintenance c) Installed underground to minimise visual impacts. d) Litter baskets are applicable for small areas (<1–2 ha) and pits can be used for larger catchments (150 ha)	a) Potential for litter pits to aggravate upstream flooding if blocked by litter and vegetation b) Potential for litter baskets to reduce pit inlet capacity if located close to an inlet c) Hydraulic head loss occurs for litter pits d) Potential loss of pit inlet capacity due to litter basket on steeper slopes
Trash / Litter Racks	Litter racks (or trash racks) are a series of metal bars located across a channel or pipe to trap litter and debris.	a) Can be used to trap litter upstream of other stormwater treatment measures b) Appropriate for retrofitting into existing areas c) Low downstream maintenance d) Applicable for areas between 8 and 20 ha	a) Racks have a tendency to be blocked by debris b) Collected litter can move upstream along a tidal channel due to tidal sway c) Potential odours and health risk to workers when handling litter d) Possible safety risks when installed in channels and difficult to clean/ maintain

Treatment Measures	**Description**	**Advantages**	**Disadvantages**
Sediment Trap	Sediment traps (known as sediment basins or sediment fore bays) are designed to trap coarse sediment and can take the form of a ‘tank’ or a less formal pond.	a) Trap coarse sediments upstream such as a wet basin or constructed wetland b) Reduce coarse sediment loads to stormwater systems or receiving waters c) Can be installed underground d) Applicable for areas greater than 5 ha	a) Limited removal of fine sediment, and pollutants can be re-mobilised b) Above ground sediment traps can be visually unattractive c) Trapping of excessive sediment can result in downstream channel erosion d) Potential for mosquito breeding
Gross Pollutant Trap	A gross pollutant trap (GPT) is a sediment trap with a litter (or trash) rack, usually located at the downstream end.	a) GPTs trap coarse sediments before they enter into the waterway b) Collect litter at a single location for removal c) Appropriate for retrofitting into existing urban areas d) Traps can be located underground, minimizing visual impacts e) Suitable for catchments greater than 6–8 ha	a) Litter rack has a tendency for blockage b) Potential to aggravate upstream flooding c) The appearance of the trap and litter can be obtrusive d) Potential odours and health risk to workers when handling litter e) Possible safety risk when installed in channels f) Difficult and expensive to clean

Treatment Measures	Description	Advantages	Disadvantages
Oil/Grit Separators	Oil/grit separators, also known as water quality inlets, generally consist of three underground retention chambers designed to remove coarse sediment and hydrocarbons.	a) Appropriate for treating stormwater from areas expected to have significant vehicular pollution (e.g. parking) b) Can also trap litter c) Can also be used for treating stormwater from areas storing or handling petroleum products d) Can be appropriate for retrofitting into existing areas	a) Limited removal of fine or soluble pollutants b) When turbulent stormwater enters the chambers, this action may resuspend particulates or entrain floating oil c) Trapped debris is likely to have high concentrations of pollutants, possibly toxicants d) Needs to be regularly cleaned with safety
Green Gully	Green Gully is a road gully that collects water from stormwater or rain, makes it suitable for irrigation and offers an automatic network to irrigate land and water plants.	a) Diverts stormwater from the roadways to the diverter channel by filtering litter b) Waters roadside plants with stormwater collected from the diverter channel c) Provides an automated road network system to irrigated land and water roadside plants d) Suitable for urban and rural areas	a) Only traps floating litter and debris b) Limited removal of fine sediment or soluble pollutants c) Possible safety risk when installed in roadside d) Needs to be regularly cleaned to maintain work performance

2.1.3 Rainwater tanks to collect roof water

There are many studies on the rainwater system and the saving for consumption of a potable water supply. A study was conducted on the rainwater tank in Ringdansen, Sweden (Villarreala and Dixon, 2005) which identified that 20% of household water use in Sweden was used for flushing toilets, 15% for laundry, and 10% for car washing and cleaning. The performance of a rainwater system is best described by its water saving efficiency (WSE). Therefore the greatest benefits come from plumbing rain water tanks to internal toilets to achieve water saving and help protect the local creeks and water catchments.

2.1.4 Gross pollutants traps

While reducing litter is the best solution, litter still exists. A GPT is a treatment device designed to capture coarse sediment, trash and vegetation matter in stormwater. GPTs are often used as the first treatment element in a stormwater treatment train (Allison and Pezzaniti, 2005), see Table 2.1. They are fitted inside storm water pits or near drainage outfalls. There are many different types of GPTs suitable for use in an urban catchment. Litter collection baskets, trash racks, floating booms and, sediment trap basins are some examples of gross pollutants trap devices.

2.1.5 Bioretention systems

Bioretention systems also known as biofiltration systems are a very effective way to collect sediments and filter pollution from the stormwater. Filtered water is collected by a perforated pipe at the bottom of the bioretention system that is connected to the normal storm water drain. These bioretention systems collect the water runoff from the footpath and road as shown in Figure 2.2.

Examples of the filtration media are sand, gravel, peat and compost. Engineered soils, including granulated activated carbon (GAC), zeolite, perlite and other compounds, may also be used.

According to Blecken et al 2009a and Blecken et al 2009b, in general, the removal of heavy metals from stormwater in tested biofilters of all designs used in the study was very high. Substantial loads (mostly >95%) of metals such as lead (Pb) and Zinc (Zn) were removed from the stormwater. Due to this high overall removal capacity, biofilters are a good management device to reduce concentrations of heavy metals in stormwater discharges.

They work best in fertile, porous soils that will support healthy vegetation and allow adequate infiltration.

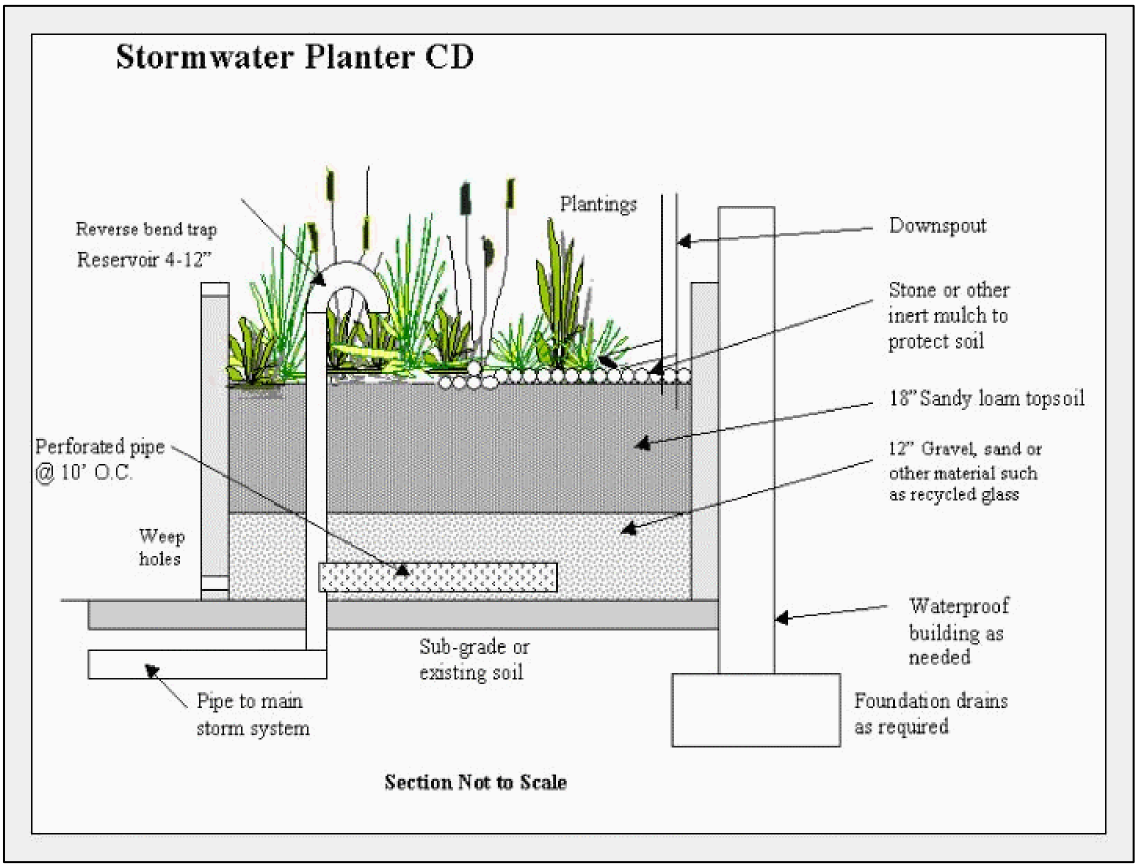


Figure 2. 2 Schematic of bioretention system, adapted from Water sensitive urban design element. STEPS, Moreland city council.

2.1.6 Infiltration

Infiltration filters the water through soil before it percolates to the surrounding soils and the groundwater. Water flows into the infiltration prepared area before moving through the topsoil. There is no pipe to collect the filtered water.

They are typically categorised into four categories (Dierkes et al., 2002).

1) Without storage (e.g. over vegetated soils, swales, permeable and porous pavements)

2) With on-ground storage (e.g. infiltration basins)

3) With subsoil storage (e.g. infiltration trenches, soakaways, infiltration pipes)

4) Combinations of one to three of the above

Infiltration without storage

Swales

Grassy swales are long, narrow channels that are used to filter and infiltrate stormwater from parking lots, sidewalks, streets, and other impervious surfaces. Swales are usually planted with grass as in Figure 2.3. While often used instead of kerb and channel, they can also be used in private landscaping. They collect sediments and filter water but are not as effective at removing pollutants as bioretention systems. Filtered water can be collected through a perforated pipe that is connected to the normal storm water drain.

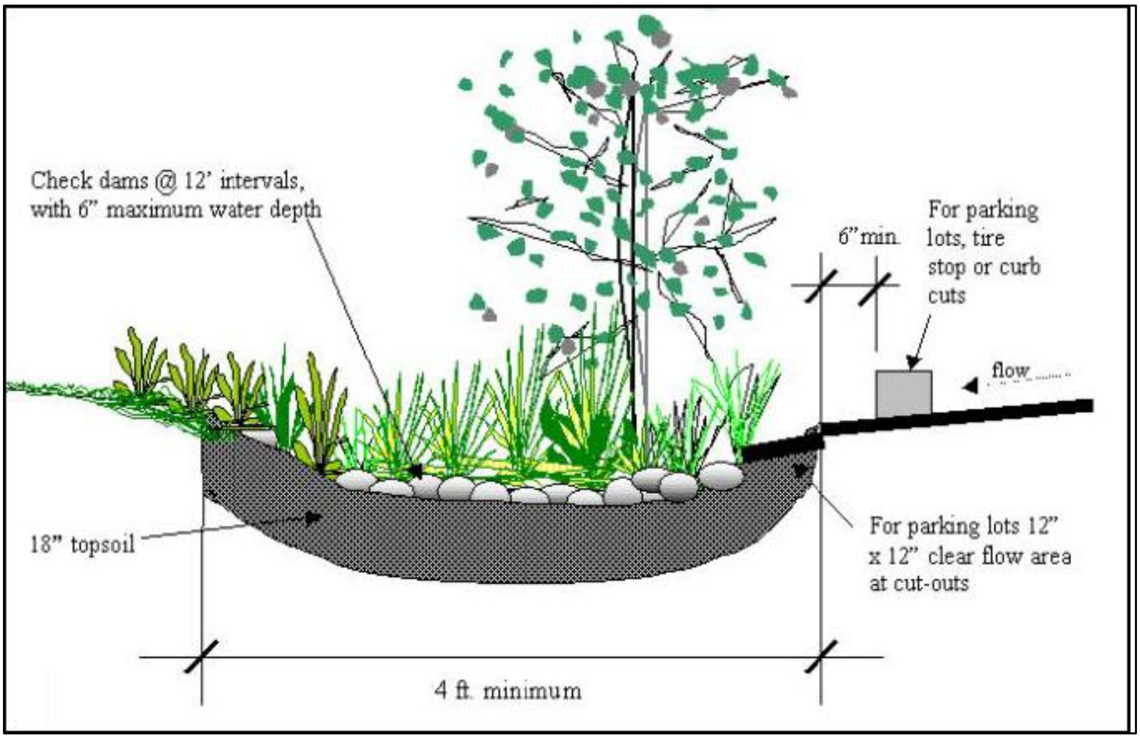


Figure 2. 3 Typical section through a swale, Adapted from Water sensitive urban design element. STEPS, Moreland city council

Vegetation strips

A vegetated strip treats sheet flow and is placed parallel to the impervious surface. Vegetation strips can be planted with grass or other vegetation (Figure 2.4). They can encourage soil infiltration and they can be used for pre-treatment in combination with other Water Sensitive Urban Design devices (for example, the bioretention planter strip shown in the photograph below). Vegetation soaks up and slows down the flow of water distributing the water evenly, protecting the stream bank, if located adjacent to stream and traping pollution.

Figure 2. 4 Adapted from a citizen guide to Stormwater Management in Maryland

Green Roof

A green roof also known as vegetated roof is one of the only sustainable technologies that are multi-functional (Castleton et al., 2010):

- They help to reduce the "urban heat island" effect and cool buildings.
- They reduce the impact of increased urban temperatures.
- They store rainwater and therefore minimise the impact of stormwater runoff, consequently reducing the burden on antiquated stormwater drainage systems.
- They can provide valuable wildlife habitats in urban areas.
- The plants on green roofs absorb carbon dioxide (CO_2) as part of the process of photosynthesis.

The two main classifications of Green Roof are the Extensive Garden Roof and the Intensive Garden Roof.

Extensive Garden Roof; Extensive green roofs are not intended for recreational use (Figure 2.5). It is ideally suited for locations that will receive little or no maintenance or human intervention once it is established and where structural capabilities are a concern. Recommended plants used in such gardens include sedum, herbs, grasses and other vegetation that can withstand harsh growing conditions. The soil mixture, composed primarily of mineral materials mixed with organic medium, can be very shallow (as little as eight centimetres). The entire system is very light, weighing little more than a traditional ballast roof, allowing for safe installation on almost any existing roof (Tobias Emilsson, 2008).

Figure 2. 5 Ballard Library - Seattle, WA adapted from www.hydrotechusa.com.

Intensive Garden Roof; An intensive green roof could be used for recreation (Figure 2.6) and incorporates plants that require regular maintenance, such as watering, fertilizing and mowing. The variety of plants possible is numerous, including sod grass lawns, perennial and annual flowers, shrubs, and even small trees that require a deeper substrate of >20cm and more horticultural maintenance (Jim and Tsang 2011). In contrast to extensive green roofs, intensive green roofs are heavier and require a higher initial investment and more maintenance over the long term than extensive roofs. They generally require more structural support to accommodate the weight of the additional growing medium and public usage.

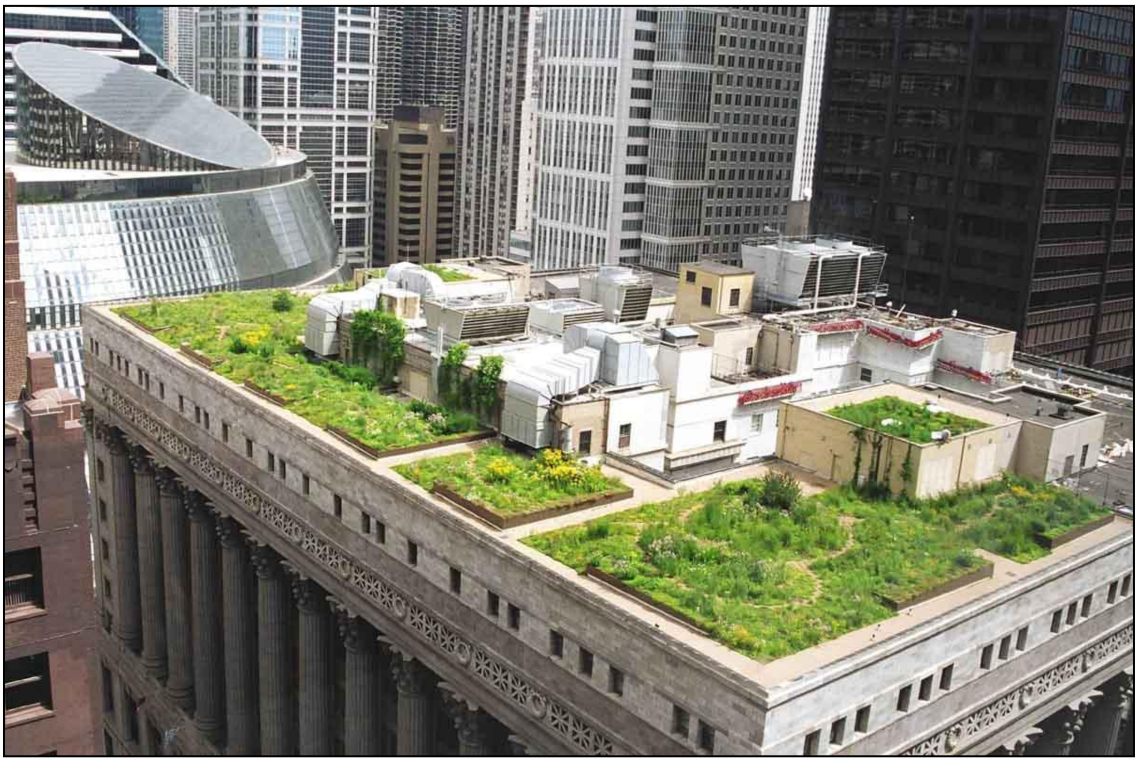


Figure 2. 6 Chicago City Hall adapted from garden roof, www.nationalroofingusa.com

Infiltration with on Ground Storage

Infiltration basins;

Infiltration Basins are open earthen impoundments designed to retain stormwater and allow it to infiltrate into the soil and to groundwater. The design should include an inlet settling basin to remove coarse materials prior to flowing into the infiltration basin, high soil permeability and the water table and bedrock should be situated well below the soil surface, as shown in Figure 2.7. Infiltration basins reduce stormwater pollutants through volume reduction, filtration and settling and are also effective in removing bacteria, suspended solids, insoluble nutrients, oil and grease, and floating wastes (David Bingham 1993; Argue and Pezzaniti, 2005).

According to Barraud et al., 1999; Pitt et al., 1999 and Dechesne et al., 2004 despite these advantages, long-term sustainability of infiltration basin systems is not certain over time. Two major problems are encountered over time: clogging and the eventual contamination of the underlying soil and groundwater systems. Clogging affects hydraulic capacity and can result in loss of flood protection. Eventual contamination of soil and groundwater may occur if basins do not trap pollutants effectively.

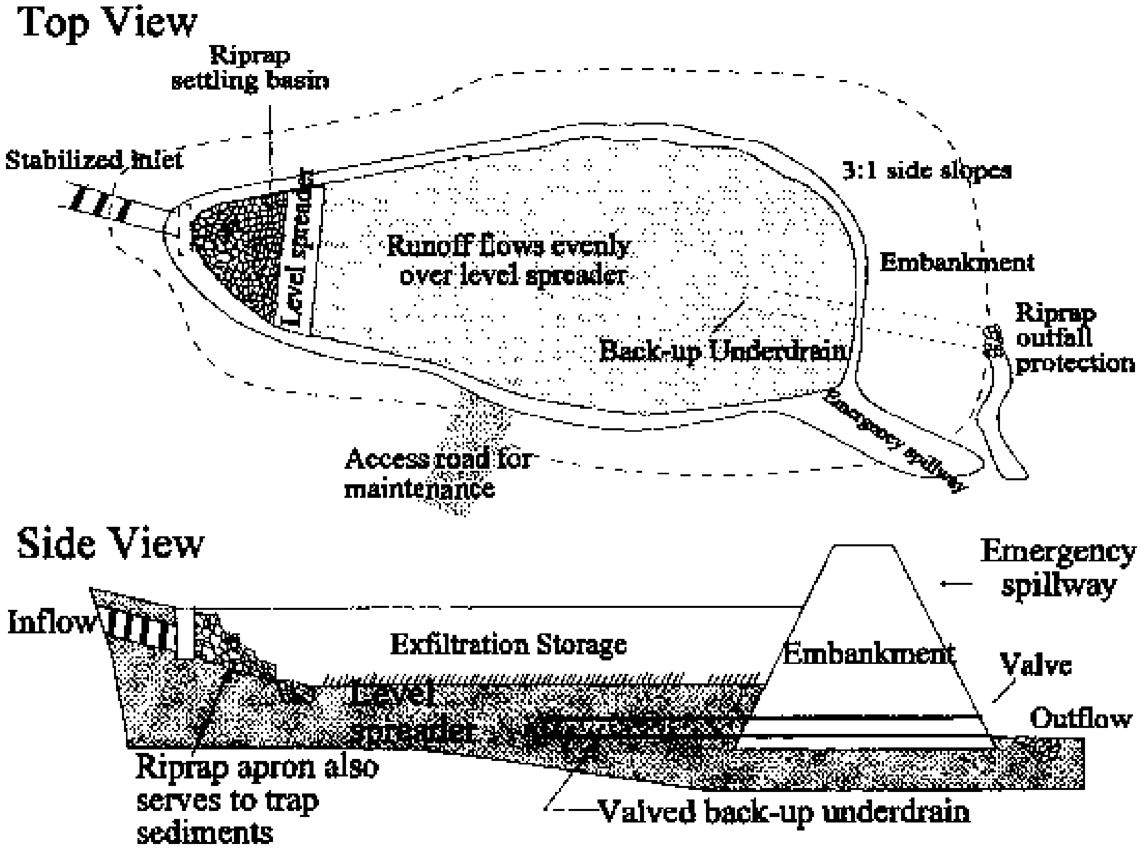


Figure 2. 7 Top and side view of an infiltration basin design, Source: Schueler, 1987.

Infiltration with Subsoil Storage

Infiltration trenches

An infiltration trench (Figure 2.8) is a shallow excavated trench, 0.9 to 3.7 meters (3 to 12 feet deep), backfilled with a coarse stone media, and lined with filter fabric (Schueler et al., 1992). It can be utilised to capture and allow infiltration of stormwater runoff into the surrounding soils from the bottom and sides of the trench and it performs well for the removal of fine sediment and associated pollutants. The use of an infiltration trench is feasible only when soils are permeable and the groundwater table is well below the bottom of the trench. Pre-treatment using buffer strips, swales, or detention basins is important for limiting the amounts of coarse sediment entering the trench which can clog and render the trench ineffective.

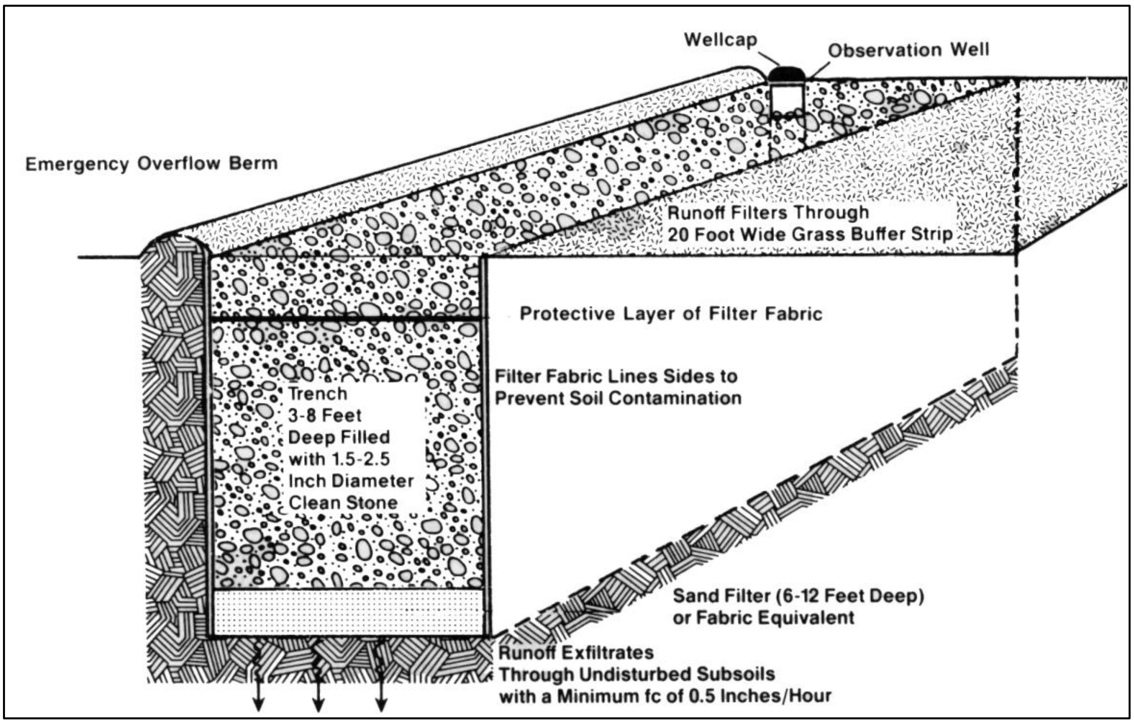


Figure 2. 8 Typical Infiltration Trench Design, Source: Schueler, 1987.

2.1.7 Constructed Wetlands

Constructed wetlands (also referred to as *stormwater wetlands*) are widely used to control polluted urban stormwater discharges. They are shallow water bodies that contain large amounts of vegetation (Figure 2.9) designed to both treat urban stormwater and control runoff volumes (Greenway, 2005). Wetlands are among the most effective stormwater practices in terms of removal of sediment and pollutants and in addition they can contribute to flood mitigation, aesthetic values and wildlife habitat (Dallmer, 2002; Wong and Breen, 2002 and Georgia Stormwater Management Manual). Constructed stormwater wetlands differ from natural wetland systems in that they are engineered facilities designed specifically for the purpose of treating stormwater runoff and typically have less biodiversity than natural wetlands both in terms of plant and animal life. However, as with natural wetlands, stormwater wetlands require a continuous base flow or a high water table to support aquatic vegetation.

Figure 2. 9 Fresh Water Creek, Chullora NSW, sourced from www.wsud.org

The stormwater management system discussed above occupies large areas, so is not suitable in urban areas. In urban areas and high density settlements, high rate treatment sand as granular becomes important.

2.2 Granular Media Filtration in stormwater management

Filters packed with different granular media can be used to remove the suspended solids and associated organic and inorganic matter. Some media can also be used to adsorb organic and inorganic pollutants.

According to the Water Desalination Technical Manual, Department of Army, USA (1986) three types of media filtration set up can be used for pre-treatment; single media, dual media and sometimes mixed media filtration. These types of media are commonly used to treat water;

- Single media: Single media filters generally consist of one medium of sand, anthracite, GAC, etc. Some of the desalination pre-treatment systems also use green sand to remove iron and manganese compounds.
- Dual media: Dual media filters consist of two media with different specific gravities such as sand and anthracite. Usually, less dense media are placed on the top of the filter and dense media at the bottom. The use of dual media filters provides larger quantities of filtered water and less headloss during operation.
- Mixed media: Consists of more than two media such as silica sand, garnet and anthracite. Mixed media filters provide a better coarse to fine filtration arrangement and create a media flow pattern to achieve a very low Silt Density Index (SDI).

When choosing the right media some consideration should be taken to achieve the best effluent quality such as retaining the maximum quantity of solids, ensuring minimum head loss and correct maintenance of the system.

The design of rapid filters depends on the quality of water to be treated. General filter characteristics according to the Water Desalination Technical Manual, Department of army, USA (1986), is given in Table 2.1.

Table 2. 2 Characteristics of rapid filters

Characteristics	Sand filter	Anthracite filter
Filtration rate, m/h	10-20	10-20
Depth of bed, cm	80	80
Particle size, mm	0.35-0.5	0.7-0.8
Max headloss (gravity Filter), m	5	5
Max headloss (pressure filter), KPa	200-400	200-400
Backwash rate, m/h	40-50	40-50

The following subsections provide an overview of some of the media commonly used in water and wastewater treatment.

2.2.1 Sand

It is well established that sand filters are recognised as being effective at removing suspended particles and particulate bound contaminants from water and wastewater. Therefore it is widely used around the world for on-site and small communities' wastewater treatment. However, they are generally not considered effective at removing dissolved constituents (Sansalone, 1999). The size of the particles and the depth of the filter influence its effectiveness. According to Rodgers et al. (2004), particle size is one of the key parameters to guarantee treatment efficiency as well as the reliability and durability of the system. As the biggest operational problem is the clogging phenomena, due to excess biofilm development and surface deposit, the load applied needs to be well established to guarantee sufficient porosity free to water and gas transfers.

The removal of metals can be enhanced if the sand is coated with iron oxide, which is able to bind metals of all sizes strongly to the sand surface. The enhanced capacity is due to the increased specific surface area (SSA) and amphoteric surface charge the coating provides.

Breakthrough investigations were undertaken by Sansalone (1999) and it was found that the capacity of silica sand was negligible for zinc, cadmium, copper and lead at both a pH of 6.5 and 8. When the sand was coated with iron oxide, the capacity of the sand was significantly improved due to the increase of amphoteric media of high surface area from (0.01 to 0.5m^2 g^{-1}) to (5 to 15m^2 g^{-1}).

2.2.2 Hydrous Ferric Oxide (HFO)

A large number of metal oxides have been utilised in the last few decades for various separation and adsorption processes due to their high surface area and their affinity to adsorb several heavy metals (Ambe, 1987; Abdel-Samad and Watson, 1998; Toledo et al., 2000). The interest in these materials has grown mainly due to their innocuous, inexpensive, and readily available nature. Furthermore, some of these metal oxides show high selectivity for certain cations, offering a convenient means for many difficult separations (Trivedi et al., 2001).

Hydrous ferric oxide (HFO) is environmentally significant because its abundance and capacity to immobilize metals or ligands through sorption.

Hydrous ferric oxides (HFO) are efficient sorbents for inorganic and organic pollutants and therefore have great potential in environmental science and engineering applications. Hydrous ferric oxides (HFO) are poorly crystalline, highly porous solids with large specific surface areas, ranging from (200 to 750 m2 g^{-1}) (Hofmann et al., 2004).

The focus of the current study is on such a medium alone and in combination with calcium and manganese salts. The details are given in chapter 6.

2.2.3 Activated Carbon

According to Vinod et al. (2000) and Cimino et al. (2005) Activated Carbon (AC) is the most commonly used and most effective adsorbent. Activated carbon comes in different forms, including powdered activated carbon (PAC) and granulated activated carbon (GAC).

According to Clark and Pitt, (1999) activated carbon can be produced by charring or burning high carbon content materials such as coconut, almond and walnut shells, other woods, peat, lignite and coal. The charred particles are then activated by exposure at high temperatures to an oxidising gas. This activation process makes the particles significantly porous which creates a large internal surface area available for adsorption. Most carbonaceous materials have an internal surface area of approximately 10 $m^2.g^{-1}$. The activation process significantly expands the internal surface structure and as a result an internal surface area of around 1,000 $m^2.g^{-1}$ is obtained (Allen, 1996).

Powdered and granular activated carbons are used in waste and potable water treatment, air emission cleaning, chemical processes such as solvent recovery and decolourisation, and general domestic applications such as odour removal. Nevertheless, its application is restricted due to its high cost. The use of low-cost wastes and agriculture by-products to produce activated carbon has been shown to provide an economical solution to this problem (Cimino et al., 2005; Ioannidou et al., 2006).

According to Srivastava et al., (2005) the cost associated with the activation and regeneration of the carbon, as well as its disposal, are clear problems associated with the use of this material. To avoid/or reduce the regeneration, activated carbon can be used as a biofiltration. This is discussed in section 2.3.

2.2.4 Ion Exchange Resins

Ion exchange resin is an insoluble resin that has the capability of removing pollutants with either positive or negative charge from a solution and releasing other ions of equivalent charge into the solution without changing the structure of the resin. For such a process to occur, the solution must be an ionised solution separated into cations with a positive charge and anions with a negative charge. The exchange resins are organic polymer beads with a particle size range of 0.3 to 1.2 mm diameter and a specific gravity of 1.3 to 1.4.

Ion exchange resins can be utilised in water treatment to remove specific anions such as nitrate, arsenic and cations such as heavy metals, calcium and magnesium (Della Rocca et al., 2007; Martin et al., 2009).

According to Della Rocca et al., (2007), Amberlite IRA900, Amberlite IRA996, Duolite A126 and Purolite A520 can be utilised for nitrate adsorption.

Purolite is an effective nitrate selective ion exchanger used by many researchers to reduce nitrate concentration in wastewater (Samatya et al., 2006a; Samatya et al., 2006b).

A variety of adsorbents have been used for nitrate removal, such as Purolite A520E (Samatya et al., 2006a), Purolite A300 (Primo et al., 2009), etc., for in batch column studies.

Purolite A520E is a macroporous strong base anion resin which is specially designed for the removal of nitrates from water for potable process. The macroporous matrix and the special ion exchange group functionality imparts ideal nitrate selectivity to Purolite A520E making this resin particularly suitable for nitrate removal even when moderate to high concentration of sulphates are present. (Purolite, 2010)

A variety of adsorbents have also been developed for phosphate removal, such as aluminium oxide, iron oxide, zirconium oxide, ion exchange resin and, hydrotalcite, etc (Chouyyok et al., 2010).

Zeolites are microporous, aluminosilcate minerals commonly used as commercial adsorbents. Zeolites are minerals that are recognised for their ability to adsorb a broad range of compounds. Zeolite is also considered as ion exchange.

Due to its porous structure, it can adsorb a wide range of cations, such as NH_4^+, Na^+, K^+, Ca^{++}, Mg^{++} and others (Jorgensen and Weatherley 2003). These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Some of the more common mineral zeolites are analcime, chabazite, clinoptilolite, heulandite, natrolite, phillipsite, and stilbite.

Zeolites are also referred to as molecular sieves as they are the aluminosilicate members of this family of microporous solids. There are hundreds of naturally occurring zeolites as well as human-made compounds. Compared with activated carbon, the pore size of zeolite is uniform (Clark et al., 1997).

2.2.5 Peat

Peat is plentiful, inexpensive and readily available. It also possesses several characteristics that make it an effective media for the removal of dissolved metal pollutants. Formed from dead plant remains preserved by water, peat is created from partially decomposed organic material, (excluding coal) that is slowly oxidized by micro-organisms. This is the biochemical stage of metamorphosis which occurs normally in the first few meters of earth.

According to Brown et al., (2000), peat accepts a wide range of effluent compositions and it removes a multitude of heavy metals. It is particularly effective at removing hydrocarbons from water.

The adsorption ability of peat appears to generally increase as the degree of decomposition increases. The actual physical structure and chemical composition of peat is dependent on the type of vegetation (such as mosses, sedges and other wetland plants) from which it is formed (Clark and Pitt, 1999).

2.3 Biological filtration

Biological filtration or biofiltration is considered one of the most important separation processes that can be employed to remove organic pollutants from air, water, and wastewater, as well as treating odours from waste gases (Nanda et al., 2011). Although, it has been used for over a century, it is still difficult to theoretically explain all the biological processes occurring in a biofilter (Chaudhary et al., 2007)

According to Xie et al, (2009) a biofiltration system was able to remove the petrochemical odorous pollutants from the wastewater. The removal rate of H_2S, NH_3 and VOCs reached 98%, 91% and 90%, respectively at an empty bed retention time (EBRT) of 120 s after being in operation for one month.

Biofiltration although simple as a treatment method, involves a number of removal mechanisms. It involves the activities of micro-organisms that are immobilised on the supporting media. Therefore, the filter media and the relevant factors in the development of micro-organisms affect the performance of biological filters. The growth of the microbial community in a biofilter is affected by the influent characteristics such as nutrients, toxin and pH levels as well as temperature. Operational conditions such as the backwashing technique, and empty bed contact time (EBCT) will also affect the performance of biological filtration in water treatment.

Biological filter functions rely mainly on the activities of the micro-organisms community attached onto the filter media. The activities of the microbes determine the performance of biological filtration.

The formation of a biofilm results from attachment and metabolism of biological matter, which includes micro-organism and macro-organism. Biofilm is defined as a surface accumulation, which is not necessarily uniform in time or space that comprises cells immobilized at a substratum and frequently embedded in an organic polymer matrix of microbial origin (Xie et al., 2009). Once bacteria attaches to the filter media (Figure 2.10), it multiplies to produce extracellular polymeric substances (EPS), which develops into a viscous slimy gel. The biofilm formation process can be divided into five stages: the formation of conditioning film, bacteria transport, reversible and irreversible adhesion, biofilm development and accumulation, and bio-film detachment (Characklis and Marshall 1990).

The biological filtration using granular activated carbon (GAC) is an efficient process in drinking water treatment. Many studies showed that GAC biological filters have a great potential in removing disinfectant by-products, biodegradable organic matter and synthetic substances (McKay, 1996). It has been found effective in biologically degrading the organic matter found in wastewater. The detail on the biofilter is discussed in chapter 5.

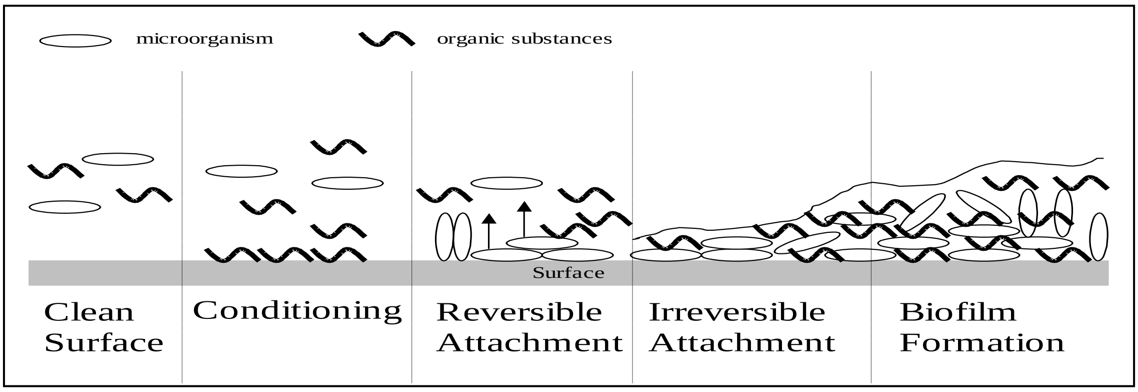


Figure 2. 10 Formation of biofilm (Adapted from Sheikholeslami, 2007)

2.4 Major pollutants in stormwater.

There are many pollutants in urban stormwater runoff. The major categories are: (i) total suspended solids (TSS), (ii) heavy metals, (iii) polycyclic aromatic hydrocarbons (PAHs) and (iv) nutrients (Aryal et al., 2010). Table 1.1 presents the common pollutants found in urban stormwater, their likely sources and the effect of the pollutant on our waterways

Pollutants originate from either point or non-point sources. Point sources are specific identifiable locations where stormwater pollution originates. These could include a discharge pipe from a factory or sewage plant. Non-point pollution has been considered to be one of the major sources of pollution in developed urban areas and it is comparatively difficult to identify and control (Drapper et al., 2000; Ngabe et al., 2000). It may be the results of natural processes such as rainfall or snowmelt or originate from human activities such as litter, use of fertilisers and more. Without appropriate stormwater treatment devices, the waterways quality will be compromised and the outcome could be devastating, not only for aquatic ecosystems but also for community values such as aesthetics, recreation and economics and for the health of receiving water bodies.

Suspended solids and sediments;

Urban runoff contains a wide range of particulate matters ranging in size from smaller than 1µm to greater than 10,000µm (Sansalone et al., 1998).

Sediment pollutant levels can be measured as Total Suspended Solids (TSS) and/or turbidity. The term suspended solids (SS) refers to the mass (mg) or concentration (mgL^{-1}) of inorganic and organic matter, which is held in the water column of a stream, river, lake or reservoir by turbulence. It is well established by many researchers all over the world in the last 50 years or more that suspended solids (SS) is one of the major reasons for water quality deterioration downstream of urban areas leading to aesthetic issues, higher costs of water treatment, and serious ecological degradation of aquatic environments (Borchardt and Sperling, 1997; Bilotta and Brazier, 2008).

Suspended solids in runoff are enriched with several types of organic and inorganic pollutants and during wet weather they are washed off along with associated pollutants. These suspended solids can play an important role in transporting and partitioning chemicals in the aquatic ecosystem.

Heavy metals

Many different definitions have been used to define heavy metal. Some have been based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity. In urban environments, the term heavy metal usually refers to toxic metals that originate from anthropogenic activities. Some metals are naturally found in the human body and are essential to human health. Iron, for example, prevents anaemia, and zinc deficiency in human beings that would otherwise result in growth failure, immune disorders affecting T helper cell 1 (Th1) functions, decreased interleukin-2 (IL-2) production, and cognitive impairment (Prasad et al., 2001). Therefore human and living organisms require some metals in trace amounts to function properly. However excess levels of these heavy metals can damage human health and ecosystems. The heavy metals of most concern in the environment are chromium (Cr), nickel (Ni), zinc (Zn), copper (Cu), lead (Pb), vanadium (V), cobalt (Co), cadmium (Cd) and mercury (Hg). Due to their toxicity, heavy metal discharge to the environment has been regulated by laws throughout the world. The restriction level varies between types of heavy metals and from country to country. Researchers have been investigating heavy metals level in road and soil particles, rivers, lakes, coastal sediments and in urban runoff.

Ellis and Revitt, (1982) studied several heavy metals in the sediment on street surfaces as a function of sediment particle size. The distribution pattern of Pb, Cd, Cu and Zn was related to the level and type of traffic densities. Their study showed that concrete motorways had particles less than 250 μm whereas other locations having asphalt surfaces exhibited varying degrees of wear, which provided a considerable amount of free coarse materials. Heavy metals occurred in the ranges reported in Table 2.3. Further detailed discussion on heavy metals in road runoff is presented in chapter 7.

Table 2. 3 Heavy metals range (Ellis and Revitt 1982)

Sediment Size (μm)	**Pb ($\mu g\ g^{-1}$)**	**Cd ($\mu g\ g^{-1}$)**	**Mn ($\mu g\ g^{-1}$)**	**Zn ($\mu g\ g^{-1}$)**	**Cu ($\mu g\ g^{-1}$)**	**Fe ($\mu g\ g^{-1}$)**
<250	40-1690	0.72-4.2	766-855	119-2133	42.6-640	6780-22700
>250	111-2296	1.3-6.8	694-1244	91.6-1760	27.2-212	4195-22850

Hydrocarbons

Several types of hydrocarbons have been found in urban dust and runoff. They were found to be from natural and anthropogenic origin (Ngabe et al., 2000). Polycyclic aromatic hydrocarbons (PAHs) were one of the first atmospheric pollutants to be identified as being carcinogenic. In the last few decades, considerable attention was given to the possible adverse impact of the toxic compounds in the atmospheric environment on human health (Baek et al., 1991). These compounds are abundant in the urban atmosphere and have consequently undergone considerable scrutiny.

The hydrocarbons include simple aliphatic hydrocarbons to polycyclic aromatic hydrocarbons (PAHs). According to Benner et al., (1989), nearly 35% of the total PAHs input was from road related activities. These PAHs have low degradability and possible carcinogenicity or mutagenicity. Consequently, the USEPA has identified 16 species of PAHs as priority pollutants in the Clean Water Act (Schnelle et al., 1995). Figure 2.11 shows the 16 USEPA PAHs.

Latimer et al., (1990) studied sources of petroleum hydrocarbons in urban runoff with four different landuse types. Their results indicated that in all four landuse types, hydrocarbons were primarily from used crankcase oil, with a small amount of fuel oil detected at industrial sites. They further reported that only a small amount came from the natural source surveyed, and the majority of this oil probably would have come from: (1) oil drops within the driving lanes on the road surface or deposits in parking areas and/or (2) direct dumping of waste crankcase oil into storm drains.

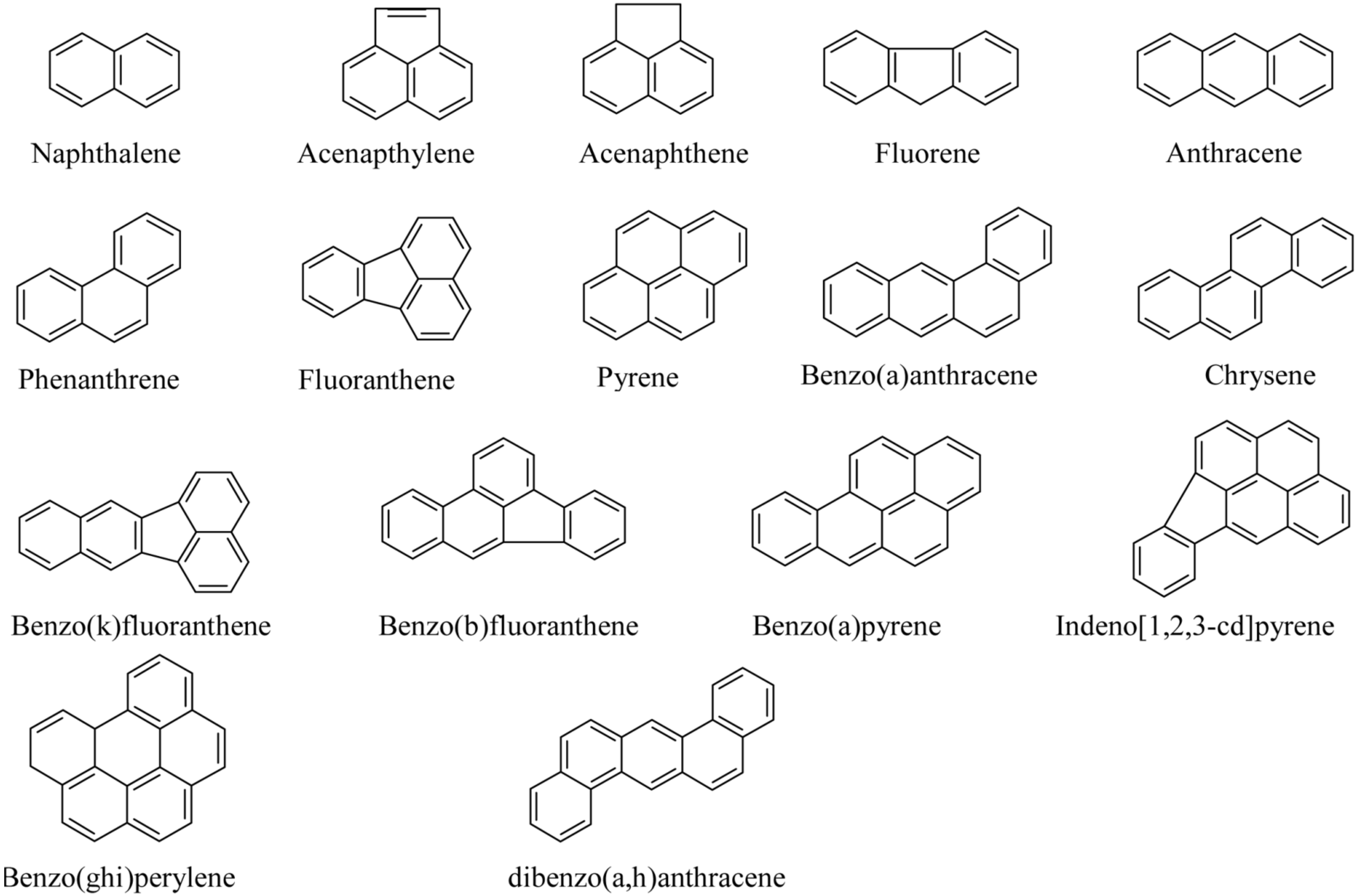


Figure 2. 11 The 16-USEPA PAHs.

Nutrients

Nutrients (nitrogen and phosphorus) are essential elements in all aquatic ecosystems. However, an excessive level of these nutrients is often responsible for eutrophication. Eutrophication associated effects can have an adverse impact on aquatic ecosystems; one example is the growth of plants and blue-green algae that, upon decaying, deprive the waters of life-sustaining oxygen (Environmental Protection Agency 1992, 1993).

Common sources of these nutrients are chemical fertilizers which were applied to agricultural land, lawns, gardens, golf courses, landscaped areas, and gardens (Cooper and Lipe, 1992). Cherkauer and Zager, (1989) studied the impact of urbanization on water quality during a flood in small catchments in the urban areas of Milwaukee, USA. They reported the significant response of pollutants to the rain in urban basins compared to rural catchments. Several studies have also identified urban stormwater as a major contributor to nitrogen and phosphorus loading of surface waters, second only to agriculture (King et al., 2007). Furthermore, urbanised coastal catchments of Western Australia (WA) have been linked to nutrient enrichment of ground and surface waters (Gerritse et al., 1990).

Point sources of nutrients are also major contributors to nutrient enrichment. A study in the South West region of Western Australia found that a single piggery contributes 24% of the Serpentine River's phosphorus (P) load to the Peel-Harvey estuarine system (Weaver, 1993).

2.5 Road – deposited sediments

One of the main sources of stormwater is runoff from road – deposited sediments (RDS). As RDS contain elevated concentration of heavy metals arising from vehicle activity, the stormwater runoff from RDS may contain high concentrations of heavy metals that can end up in water bodies and pollute the aquatic environment. Studies have been conducted to determine the heavy metal concentration and enrichment with respect to the neighbouring sites and source apportionment. This section briefly reviews important literature on these aspects. The detailed discussion on RDS is discussed in chapter 7.

2.5.1 Metal concentration in RDS

Metal concentration in RDS can be of high variability as shown in Table 2.4. However it is clear from Table 2.2 that urban metal loading often exceed those found on motorways, and therefore there is the possibility of heavy metal loading from sources other than vehicles such as soils. According to Shaheen, (1975) this may also relate to the different composition of the road surfaces, such as the concrete surface which can release high level of Pb and Zn compared with asphalt surfaces.

Table 2. 4 Heavy metal concentration ranges in road deposited and stormwater runoff (Ellis and Revitt, 1982)

Metal	**Location type**	**Road sediments levels (ug/g)**	**Stormwater runoff (total) (mg/L)**	**Stormwater runoff (soluble) (ug/L)**
Pb	Motorway	130 - 10 000	0.000 - 14.73	< 3 - 1 200
	Urban/Residential	128 - 8 300	0.25 - 26	10 - 1 800
	Rural	5 - 3 900	0.1 - 1.0	16
Zn	Motorway	44 - 480	0.01 - 22	< 15 - 1 200
	Urban/Residential	13 - 1 110	0.008 - 4.6	
	Rural	7.5 - 710	0.15 - 1.10	
Cd	Motorway	0.22 - 2.2	0.0005 - 13.73	< 0.5 - 5
	Urban/Residential	0.0034 - 10.1	0.0008 - 0.008	
	Rural	0.02 - 5.4		
Cu	Motorway	22 - 200	0.003 - 0.38	4 - 200
	Urban/Residential	25 - 3 170	0.007 - 1.41	
	Rural	33 - 150	0.02 - 0.12	
Fe	Motorway	21 000	0.67 - 440	0 - 500
	Urban/Residential	1 400 - 128 000	1.0 - 85	
	Rural	13 000 - 43 000	20 - 62	
Mn	Motorway	370	0.04 - 0.64	170
	Urban/Residential	100 - 1 450	0.007 - 3.4	
	Rural	210 - 860		

2.5.2 Metal enrichment methods

The source of the metals in RDS can be classified into geogenic (natural) and anthropogenic origins. The geogenic is derived from the parent material of soils which has varied pollutant elemental concentration. The anthropogenic sources are roads, industry, buildings and other activities in the vicinity of the roads. The contribution of the roads can be assessed by comparing the pollutant concentrations in RDS with those in soils away from the roads. If the concentrations in RDS are higher than those in the soils, it is assumed that roads are the major contributor to the pollutant enrichment in RDS.

Several methods have been used to quantify pollutant enrichment in RDS. These methods are similar to those used in contamination evaluation of sediments in water reservoirs (Loska and Wiechuła, 2003; Lu et al., 2009). The common methods used in pollutant enrichment in RDS are listed below.

2.5.2.1 Geoaccumulation index

Geoaccumulation index (I_{geo}) is defined as (Faiz et al., 2009; Lu et al., 2009; Wei et al., 2009)

$$I_{geo} = \log_2 (C_n/1.5B_n)$$

where C_n represents the measured pollutant concentration in RDS and B_n is the geochemical background value of the pollutant which is generally taken as the background content of pollutant in soil. The constant 1.5 is introduced to minimise the effect of possible variations in the background values due to lithological variations.

2.5.2.2 Pollution Index

The Pollution Index (PI) is defined as the ratio of the heavy metal concentration in RDS to the corresponding heavy metal background concentration in the nearby soils. The PI of each heavy metal was calculated and classified as either low ($PI \leq 1$), medium ($1 < PI > 3$) or high ($PI > 3$) (Faiz et al., 2009; Lu et al., 2009).

2.5.2.3 Integrated pollution index

Integrated pollution index (IPI) (Faiz et al., 2009) is defined as the mean value of the PI of a pollutant.

2.5.2.4 Enrichment factor

The Enrichment Factor *(*EF) is determined by a similar method as that used for the PI, with the exception that the measured metal concentrations in RDS and background soils are normalised against a reference metal. The EF is calculated using the following equation:

$$EF = [C_x / C_{ref}]_{Sample} / [C_x / C_{ref}]_{Background}$$

where; C_x is the concentration of the examined heavy metal in the sample and the background (soil) reference, and C_{ref} is the concentration of the reference element in the sample and the background soil. Five contamination categories are recognised on the basis of the enrichment factor; an EF of less than 2 shows deficiency to minimal enrichment, an EF of between 2 and 5 shows moderate enrichment, an EF of between 5 and 20 shows significant enrichment, an EF of between 20 and 40 shows very high enrichment, and an EF of greater than 40 shows extremely high enrichment (Lu et al., 2009; Yongming et al., 2006). As the composition of soils is inherently variable, the pollutant concentrations are normalised using a reference metal which is often characterised by its low occurrence variability natural origins. Common metals used as reference include Al, Fe, Mn, Si and Ti (Joshi et al., 2009; Lu et al., 2009; Yongming et al. 2006).

2.5.3 Metal apportionment

Research on identification and apportionment of the pollutant sources is proven to be vital in adopting the suitable pollution control and management measures. For example, when the source of Pb was identified predominantly from leaded fuel, steps were taken to remove Pb from leaded fuel and new regulations were implemented to use unleaded fuel. Source apportionment has been conducted for the important organic and inorganic pollutants in many countries. The methods used in these studies were based on matching the pollutant concentration distribution pattern of the possible sources with those of RDS. Because several sources and pollutants are involved, advanced statistical methods such as principal component analysis, cluster analysis and multiple regression analysis have been generally used to determine the source apportionment of the pollutants. The main sources of contaminants to RDS are shown in Table 2.5.

Table 2. 5 Sources of contaminants to RDS (Taylor, 2007).

Contaminant	**Source**
Pb	Petrol combustion, paint, smelters, coal combustion
Zn, Cd	Tyre wear, galvanized roofs, abrasion of vehicles, lubricating oil, alloys
Cu	Brake linings, alloys, metal industry
Fe	Car exhaust particulate, corrosion of vehicle body work, background geology
Mn	Tyre wear, brake linings, background geology
Cr	Engine wear vehicle plating and alloys, road surface wear
Ni	Engine wear, metal industry, background geology
Asbestos	Break clutch linings
Cl, Na	Road salt
PGEs (Pt, Pd, Os)	Catalytic convertor
Pesticide/ herbicide	Garden application
PCBs	Biomass burning, petroleum combustion
Bacteria	sewage treatment works, animal faeces
Pharmaceutical compound	Sewage treatment works

2.5.4 Remediation methods to reduce pollution from RDS

As previously mentioned, RDS can have a major adverse impact on waterbodies due to its high level of heavy metals, making the management of RDS an important component of urban pollution control. One of the most effective ways of reducing RDS and consequently reducing the heavy metals is the sweeping and the proper disposal of RDS. Conventional sweeping is effective in removing heavy metals associated with particle sizes greater than 250 µm. However, most heavy metals are associated with smaller particles, particularly fine particles (Ellis and Revitt, 1982). These can be transported to waterbodies in stormwater runoff. Methods discussed in section 2.14 to 2.2 are used to remove these heavy metals.

There are other types of pollution control methods that can also be implemented, such as swales, vegetation stipes etc.

CHAPTER 3

3. EXPERIMENTAL MATERIALS AND METHODS

3.1 Stormwater and synthetic water

Experiments were carried out using stormwater collected from the stormwater channel in Carlton, Sydney, Australia and synthetic water containing selected representative heavy metals.

3.1.1 Carlton stormwater

The sample collection and analysis of stormwater was conducted between September 2008 and March 2009. Results of the water characteristics are shown below in Table 3.1. The Carlton area is part of the catchment area of Kogarah, Sydney NSW, Australia.

Table 3. 1 General characteristics of the stormwater at Carlton

Parameters	**Unit**	**Date**
Nutrients		**10 Sep 08 - 20 Mar 09**
Total Nitrogen	mg/L N	
Nitrate	mg/L N	0.393 - 7.96
Nitrite	mg/L N	0.001 - 0.266
Ammonia	mg/L N	0.014 - 0.418
Total Phosphorous	mg/L P	
Orthophosphate	mg/L P	0.013 - 0.29
Traditional (physical & chemical)		
pH	-	6.8 - 7.8
TOC	mg/L	3.5 - 9.5
COD	mg/L	
Turbidity	NTU	6 - 168
Total Suspended Solids	mg/L	0.5 - 28
Conductivity (EC)	dS/m	0.17 - 1.16
True Colour	PtCo	18 - 270
Bicarbonate	mg/L CaCO3 equivalent	70 - 110
Total Dissolved Salts	mg/L	116 - 787
Water Hardness	mg/L $CaCO_3$ equivalent	103 - 135
Bacteriological		

Parameters	**Unit**	**Date**
Total Coliforms	cfu/100 ml	10 - 762
Faecal Coliforms	cfu/100 ml	9 - 500
Dissolved Salts		
Potassium	mg/L	3.3 - 18.2
Sodium	mg/L	14 - 126
Calcium	mg/L	11.1 - 32
Magnesium	mg/L	2.2 - 19
Sodium Absorption Ratio	mg/L	1 - 5.6
Chloride	Mg/L	19 - 241
Sulphate	mg/L SO_4^{2-}	13 - 86
Chloride/ Sulphate Ratio		1.4 - 4.9
Metals		
Aluminium	mg/L	0.028 - 0.188
Arsenic	mg/L	0.001 - 0.005
Cadmium	mg/L	0.0 - 0.001
Chromium	mg/L	0.002 - 0.002
Copper	mg/L	0.008 - 0.049
Iron	mg/L	0.053 - 2.6
Manganese	mg/L	0.001 - 0.024
Nickel	mg/L	0.003 - 0.1
Lead	mg/L	0 - 0.022
Selenium	mg/L	0.001 - 0.004
Zinc	mg/L	0.016 - 0.123

3.1.2 Synthetic stormwater preparation

Stormwater containing low concentrations of contaminants was collected from stormwater channels in a residential area south of Sydney, Australia. It was spiked with Cu, Cd, Ni, Se and Zn to produce desired concentrations of these contaminants using corresponding salts of these contaminants ($CuSO_4$, $CdCl_2$, $NiCl_2$, SeO_2, and $ZnSO_4$). All heavy metals were present mainly in the divalent cationic forms. Selenium was considered to be present predominantly as the selenate ion (SeO_4^{2-}) with low percentage as selenite (SeO_3^{2-}) because the stormwater was under aerobic conditions and the pH was close to neutrality (pH 6.8). The ratios of the contaminants were selected to represent those commonly occurring in stormwater (DEC, 2006). The ionic concentrations (mg/L) were higher than the upper limit of the stormwater analysed by many researchers: Cu 1.2 mg/L; Cd 0.1 mg/L; Ni 0.1 mg/L, Se 0.1 mg/L, and Zn 4.0 mg/L. The pH of the mixed solution was 5.4 but was adjusted to 6.8 by adding dilute NaOH solution to bring the pH to that of the field stormwater.

3.1.3 Diluted landfill leachate

Synthetic landfill leachate (SLL) prepared in the lab was also used in the biofiltration experiment. The composition of SLL was similar to the leachate used by Hrapovic et al., (2001) and is given in Table 3.2. It should be noted that we used diluted landfill leachate to represent the water contaminated by landfill leachate during a stormwater event. The leachate could contaminate the surface water or percolate through the soil and end up contaminating the ground water.

Table 3. 2 Composition of synthetic landfill leachate (SLL) (adapted from (Hrapovic, 2001)

Component	Per liter	Composition of trace metal solution (TMS)	
Acetic acid	7ml	FeSO4	2000mg
Propionic acid	5ml	H3BO4	50mg
Butyric acid	1ml	ZnSO4•7H2O	50mg
K2HPO4	30mg	CuSO4•5H2O	40mg
KHCO3	312mg	MnSO4•7H2O	500mg
K2CO3	324mg	(NH4)6Mo7O24•4H2O	50mg
NaCl	1440mg	Al2(SO4)3•16H2O	30mg
NaNO3	50mg	CoSO4•7H2O	150mg
NaHCO3	3012mg	NiSO4•6H2O	500mg
CaCl2	2882mg	96% H2SO4	1ml
MgCl2•6H2O	3114mg		
MgSO4	156mg		
NH4HNO3	2439mg		
Urea CO(NH2)2	659mg		
Na2S•9H2O	Titrate to Eh-120mv:-180mv		
NaOH	Titrate to pH=5.8-6.0		
Trace metal solution	1ml		
Distilled Water	to make 1L		

3.2Materials

3.2.1 Activated carbon and anthracite

Granular activated carbon (GAC) and anthracite were used as adsorbents/biosorbents to remove organics and heavy metals from Carlton stormwater.

In the last few decades, GAC was broadly employed in fixed bed adsorption for purifying liquid mixtures, especially industrial waste effluents (Aribike et al., 2008).

The physical properties of GAC and anthracite are shown in Table 3.3. The most important characteristics of GAC are its extremely large specific surface area (more than 1000 m^2/g GAC) and high porosity. GAC and anthracite were washed with distilled water, then dried at 103 ^{o}C and desiccated prior to their use.

Table 3. 3 Physical properties of Anthracite and GAC

Anthracite		**GAC**	
Specification	Estimated Value	Specification	Estimated Value
Effective Size (mm)	1.0-1.1	Nominal size, mm	0.3-2.38
Bulk Density (kg/m^3)	650	Bulk density, kg/m^3	300 to 500
Uniformity Coefficient	1.30	Iodine number, mg /(g.min)	Max 1000
Acid Solubility	1%	Specific surface m^2/g	1000

3.2.2 Hydrous ferric oxide (HFO)

A hydrous ferric oxide (HFO) (30-80 mesh) with the chemical formula of FeOOH obtained from Sigma Aldrich (USA) was also used as sorbent to remove the heavy metals and metalloids found in the synthetic stormwater. X-ray diffraction analysis (Appendix A) indicated that the HFO was amorphous with the presence of some nano-size iron oxides as reported for other HFO materials (Davies and Leckie 1978; Trivedi and Axe 2000).

3.2.3 Hydrous ferric oxide (HFO) and calcium hydroxide $Ca(OH)_2$

HFO described in 3.2.2 was used with $Ca(OH)_2$ as sorbents to test their ability to remove the contaminants from the synthetic water. Calcium hydroxide $Ca(OH)_2$, a finely divided powdery material, was obtained from a laboratory chemical supplier.

3.2.4 Hydrous ferric oxide (HFO), $Ca(OH)_2$ and MnO_2

Three materials namely, HFO, $Ca(OH)_2$ and MnO_2 were used as sorbents to remove the contaminants. The manganese dioxide (MnO_2) was obtained from Unilab Asia Pacific Chemicals, Australia. X-ray diffraction analysis (Appendix B) indicated that it was mainly pyrolusite.

3.3Experimental Apparatus/Equipment.

3.3.1 Jar Tester used for adsorption kinetics

A Jar tester was used for GAC adsorption kinetics experiments. The schematic of the Jar tester is shown in Figure 3.1. It consisted of six parallel vertical paddles attached to a horizontal shaft with screws. The paddles length could easily be adjusted with the screws. The jar tester had a speed controller knob (to control and fix the speed) and a speed display. The glass beakers containing GAC were placed at the bottom of a beaker holding the metal plate.

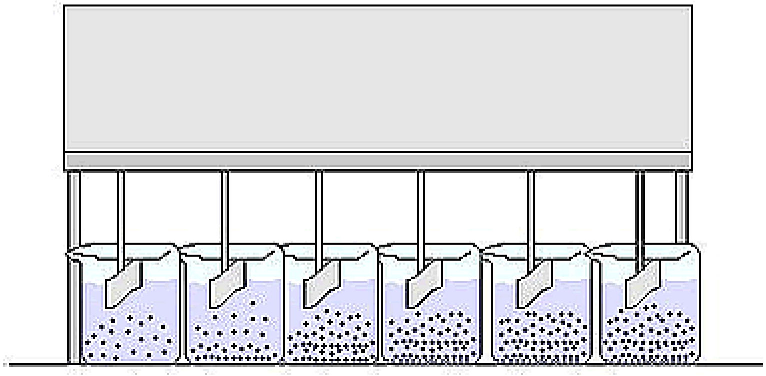


Figure 3. 1 Jar test apparatus

3.4Dynamic column experiment

3.4.1 Biosorption column experiment with GAC as adsorbent

Raw water was collected from a stormwater canal at Carlton, in Kogarah, Sydney. In this study, biofiltration experiments were conducted using transparent acrylic filter columns (Figure 3.2).

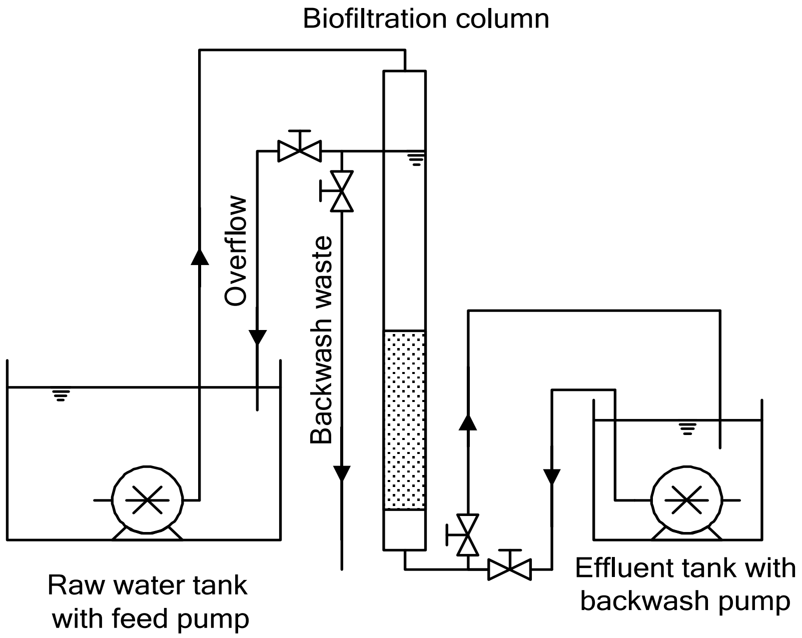


Figure 3. 2 Schematic diagram of biofilter column.

The filter columns used in the experiments had an internal diameter of 0.095 m and a length of 1.50 m. The columns were equipped with outlet pipes along its side and at the bottom of the columns. Anthracite and GAC were used as a single filter media in the biofilter columns. The prepared filter medium was packed in the columns up to a depth of either 75 or 40 cm. The columns were operated in down flow mode. Feed water was pumped from a feeding water tank to the top of the column and then passed through the filter bed. The filtrate was then collected at the bottom of the column for analysis.

In this study, the flow of stormwater through soil (acting as a biofilter system) was simulated, which typically occurs at a low rate. In stormwater, biofilters are used in situations where the hydraulic loading rate is low, typically in the upper part of the catchment near the stormwater source where the ratio of catchment areas to the biofiltration area is smaller. This meant the columns were operated at low and representative velocities of 0.12 and 0.25 m/h. These laboratory scale filters were backwashed occasionally for a period of 5 minutes to control excessive biofilm growth. This backwash/cleaning is not practised in proto-scale filtration systems because of the large surface area available.

3.4.2 Adsorption column experiments with HFO adsorbent

Three Perspex columns with an internal diameter of 3.2cm and a height of 30 cm (Figure 3.3) were used to remove the stormwater contaminants. These three columns were filled with 168 g of filter media consisting of (i) a mixture of 5% HFO and 95% anthracite, (ii) a mixture of 5% HFO, 1% $Ca(OH)_2$ and 94% anthracite, or (iii) a mixture of 5% HFO, 1% $Ca(OH)_2$, 1% MnO_2 and 93% anthracite. The anthracite used had an effective particle size of 1.0-1.1 mm. Anthracite was chosen as the filling material due to its inert property towards heavy metals and Se and its low cost. Low percentages of HFO, $Ca(OH)_2$ and MnO_2 were used to keep the water treatment operation costs to a minimum. The media were well mixed before packing in the column and the columns had ports for influent feeding, and effluent collection.

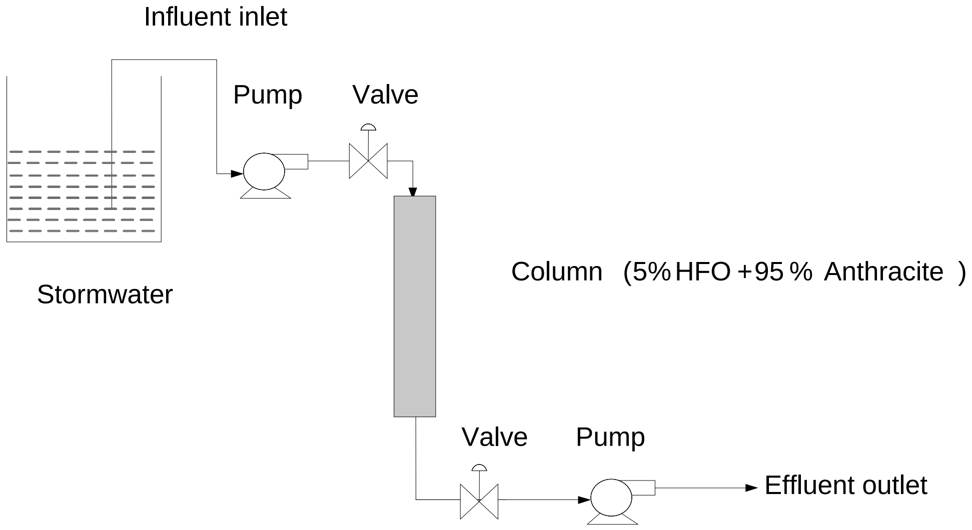


Figure 3. 3 Column Setup

The synthetic stormwater was passed through the column at pre-determined filtration velocities (0.75, 1, and 1.5 m/h) using a peristaltic pump (Masterflex) continuously for 8 hrs. The influents and effluents were collected at intervals of 10 min, 30 min and afterwards every 1 hour. The collected samples were filtered through 0.2 µm filter disks for heavy metal and metalloid analysis. Seven consecutive runs (runoff) each for 8 hrs duration were carried out to stimulate intermittent storm events and infiltration.

After each run, the column was leached for 3 hr by passing distilled water through and then dried by stopping the influent flow and opening the column valve for letting down the remaining solutions. The distilled water eluents were collected at 5 min, 0.5 hr, 1 hr and 3 hrs and analysed for the contaminant ions to determine the amounts of ions desorbed from the column. After each run, the column was kept for 40 h in room temperature (298 ± 1 K) and the next elution experiment was commenced after this period to mimic the intermittent runoff that occurs in field conditions. Of the seven runs, only the effluents of the 1st, 3rd, 5th and 7th runs were chemically analysed. The concentrations of the contaminant ions for the 2nd, 4th and 6th runs were calculated by taking the average of the ionic concentrations of the eluents immediately before and after the corresponding run. A Few samples collected on the 2nd, 4th, 6th and 8th days underwent chemical analysis to see whether they had the same trend of pollutant removal.

3.5 Field measurement

3.5.1 Flow rate measurement

The flow rate measurement of the influent water to the filter column was carried out manually by using a ‘clock and bucket’ method. The flow rate was maintained constant using a control valve.

3.5.2 Head loss

The headloss was measured using a calibrated manometer.

3.6 Analytical methods

3.6.1 Turbidity

Turbidity was measured in terms of NTU (Nephelometric Turbidity Units) using a 2100P turbidity meter, HACH, USA. The turbidity was measured approximately every hour from the beginning of each experiment period.

3.6.2 pH

The pH of the influent and the effluent was measured using a potable pH measurement meter (Model-920A, Orion).

3.6.3 Molecular Weight Distribution (MWD)

The MWD was measured using High Pressure Size-exclusion Chromatography (HPSEC, Shimadzu, Corp.,Japan) with SEC column (Protein-pak^{TM} 125, Waters, Milford, USA). The absorbance of elutes were detected at 254 nm UV responses. Standards of MW of various polystyrene sulfonates (PSS: 210, 1800, 4600, 8000, and 18,000 Da) were used to calibrate the equipment.

The number average molecular weight (M_n) and weight average molecular weight (M_w) distributions are generally calculated using the following equations:

$$M_w = \sum_{i=1}^{n} \left(N_i M_i^2\right) \Big/ \sum_{i=1}^{n} \left(N_i M_i\right)$$ Equation 3.1

$$M_n = \sum_{i=1}^{n} \left(N_i M_i\right) \Big/ \sum_{i=1}^{n} \left(N_i\right)$$ Equation 3.2

$\rho = M_w/M_n$ Equation 3.3

where, M_w = Weight average molecular weight, M_n= Number average molecular weight, ρ= Polydispersity, N_i is the number of molecules having a molecular weight M_i where i is an incrementing index over all molecular weight present.

CHAPTER 4

4. Stormwater quality and characterisation

4.1Stormwater

4.1.1 Introduction:

Australia is the driest inhabited continent on the Earth, with the most variable rainfall patterns in the world. According to Ng et al., (2009) on a yearly basis only about 12% of rain fall over Australia actually ends up running off into streams and rivers or is retained as groundwater. The rest evaporates back into the atmosphere. As a consequence of this water shortages have always been a big issue for Australia. Australia has approximately 5% of the world's land area; however it only has 1% of the world's surface fresh water resources.

The recent drought and concerns about climate change have all highlighted the need to manage our water resources more sustainably. Furthermore, in some parts of Australia, the use of water resources is approaching, and in some areas exceeding the limits of sustainability (Hatt et al., 2006). Therefore expanding the use of stormwater runoff is vital to lowering the demand placed on municipal water supplies and reducing water pollution.

The focus of proposed national water conservation programs is the recycling of both treated wastewater and urban stormwater (Anderson, 1996; Coombes et al., 2002; Thomas et al., 1997). However, stormwater is usually of better quality than untreated sewage or industrial discharge (Mitchell et at., 2002), and most importantly has better public acceptance for utilisation and reuse. All of these factors make it a potentially valuable resource for water supply substitution (particularly for non-potable water applications).

The high potential for the continued proliferation of organic and inorganic contaminants poses substantial challenges for the recycle and reuse of stormwater. As Australia is entering recycling era of stormwater and wastewater, it is essential to identify the emerging contaminants of concern in urban stormwater for sustainable reuse.

Urban stormwater runoff consists of a number of micro-pollutants such as heavy metals, hydrocarbons, pharmaceutical care products and pesticides, which are derived from a variety of sources including building materials, vehicular movement, and human activities. Among these contaminants, inorganic contaminants such as heavy metals are commonly found to be in elevated concentrations high enough to cause toxicity to living organisms. Inorganic contaminants, unlike organic contaminants, are not biodegradable and therefore can accumulate in the environment for a long time. At elevated concentrations, they can cause both short-term (acute toxicity) and long-term damage (e.g. carcinogenic damages) to aquatic organisms as well the food chain to animals and humans (Aryal et al., 2011)

This chapter discusses the water quality of stormwater collected at Carlton, in Kogarah, Sydney. Water quality measurements in terms of physical, chemical and organic characteristics were undertaken and compared against drinking water standards.

4.1.2 Experimental Methods

The stormwater was collected from a stormwater channel at Carlton, in Kogarah, Sydney.

Detailed laboratory analyses were carried out on the stormwater to determine individual pollutants that exist in the stormwater. The pollutants analysed were heavy metals - aluminium, arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver and zinc and mineral salts - calcium, magnesium, chloride, potassium, sodium and sulphate. Other parameters measured were nitrate and nitrite, ammonia, total nitrogen, total phosphorous, orthophosphate, pH, conductivity, hardness, turbidity, total suspended solids, total dissolved salts, bicarbonate, faecal coliform and total coliform. The testing methods are summarised in Table 4.1 and the general characteristics of stormwater found during the study are shown in Table 4.2.

Molecular Weight Distribution

High pressure size exclusion chromatography (HPSEC, Shimadzu Corp., Japan) with a SEC column (Protein-pak 125, Waters Milford, USA) was used to determine the molecular weight distributions of stormwater. Standards of molecular weight of various polystyrene sulphonates (PSS: 210, 1800, 4600, 8000, and 18000 daltons) were used to calibrate the equipment.

Dissolved organic matter (DOC)

The organic concentrations of stormwater were measured in terms of Dissolved organic carbon (DOC) using a Multi N/C 2000 analyzer (Analytik Jena AG).

Table 4. 1 Water quality parameters and measurement methods (Eaton et al., 2005)

Parameter	**Measurement Method**
Heavy metals (aluminium, arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver and zinc	APHA 3120 ICPMS - Inductively Coupled Plasma - Mass Spectrometry
Chloride	APHA 4500-CL^{-} - G - Mercuric Thiocyanate Flow Injection Analysis
Nitrate	APHA 4500 NO3^{-}- F - Automated Cadmium Reduction Method
Nitrite	APHA 4500 NO2^{-}- B - Colorimetric Method
Mineral salts (calcium, magnesium, potassium, sodium &sulphate)	APHA 3120 ICPOES - Inductively Coupled Plasma - Optical Emission Spectrometry
pH	APHA 4500-H+ - Electronic Method
Ammonia	APHA 4500 NH3-H - Flow Injection Analysis
Orthophosphate	APHA 4500 P-G - Flow Injection Analysis for Orthophosphate
Conductivity	APHA 2510-B - Laboratory Method
Water hardness	Calcium & Magnesium Calculation
Turbidity	APHA 2130 - Nephelometric Method
Total suspended solids	GFC equiv. filter - APHA 2540 - D - Total Suspended Solids Dried at 103°c - 105°c
Total dissolved salts	Calculation using EC x 680
Bicarbonates	Total Alkalinity - APHA 2320 - Titration Method

Table 4. 2 General Characteristics of Stormwater during the study.

Parameters	**Unit**	**Date**					
		10/09/2008	**14/10/2008**	**11/11/2008**	**25/11/2008**	**2/12/2008**	**20/03/2009**
Nutrients							
Total Nitrogen	mg/L N						
Nitrate	mg/L N	2.039	0.393	7.955	4.929	7.861	4.321
Nitrite	mg/L N	0.004	0.006	0.005	0.029	0.266	<0.001
Ammonia	mg/L N	0.039	0.418	0.016	0.075	0.014	0.06
Total Phosphorous	mg/L P						
Orthophosphate	mg/L P	0.021	0.025	0.036	0.29	0.013	0.044
Traditional (physical & chemical)							
pH	-	7.28	6.79	7.4	7.76	7.55	7.29
TOC	mg/L	4.08	5.17	9.52	3.48	5.46	6.9
COD	mg/L						
Turbidity	NTU	6	168	15.5	56	148	59
Total Suspended Solids	mg/L	4	28	5	0.5	2	
Conductivity (EC)	dS/m	0.97	0.17	0.65	0.91	1.16	0.58
True Colour	PtCo	28	270	39	29	62	18
Bicarbonate	mg/L CaCO3 equivalent	95			110	100	70
Total Dissolved Salts	mg/L	658	116	445	617	787	397
Water Hardness	mg/L $CaCO_3$ equivalent	135		103			108
Bacteriological							

Total Coliforms	cfu/100 ml	<10		260	160	762	10
Faecal Coliforms	cfu/100 ml	<10	500	9	<10	410	<10
Dissolved Salts							
Potassium	mg/L	7.9	3.3	7.5	18.2	7.3	5.9
Sodium	mg/L	126	13.9	77.4	118.9		71.7
Calcium	mg/L	32.2	11.1	23.7	23.8	32.3	29.1
Magnesium	mg/L	13.3	2.2	10.6	6.4	18.5	8.5
Sodium Absorption Ratio	mg/L	4.7	1	3.3	5.6	5.1	3
Chloride	Mg/L	176.4	19.1	104.4	144.5	241	91
Sulphate	mg/L SO_4^{2-}	86.2	13.2	45.8	82.8	49.5	30
Chloride/ Sulphate Ratio		2	1.4	2.3	1.7	4.9	3
Metals							
Aluminium	mg/L	0.034	0.156	0.028	0.188	0.154	0.098
Arsenic	mg/L	0.002	0.001	0.001	0.005	0.002	0.002
Cadmium	mg/L	0	0	0.001	<0.001	<0.001	<0.001
Chromium	mg/L	0.002	0.002				
Copper	mg/L	0.009	0.019	0.049	0.024	0.011	0.008
Iron	mg/L	0.053	0.329	2.55	0.414	0.483	0.127
Manganese	mg/L	0.008	0.024	0.001	0.005	0.018	0.001
Nickel	mg/L	0.01	0.003	0.1			
Lead	mg/L	0	0.004	0.022	0.003	0.002	<0.001
Selenium	mg/L	0.004	0.001	0.001			
Zinc	mg/L	0.026	0.123	0.016	0.029	0.037	0.016

4.1.3 Results and Discussion:

A comparison of the concentration of pollutants from the stormwater samples collected from the stormwater channel at Carlton, in Kogarah, Sydney with the Australian Drinking Water Guidelines (ADWG) are shown in Table 4.3. The concentration of pollutants from the stormwater samples collected is complied with most of the heavy metals tested with the exception of iron, nickel and lead.

Aluminium, arsenic, cadmium, chromium, copper, manganese, mercury, selenium, silver and zinc concentrations were all under the Australian drinking water guideline (ADWG) limits. Iron, nickel and lead values were found in some tests up to nine, five and two times in excess of the limit of the ADWG 0.3, 0.02 and 0.01 mg/L respectively.

Mineral salts are a part of most of our daily dietary intake. The ADWG has not provided the maximum levels of these salts in our drinking water.

The World Health Organisation (WHO) and The Food Agriculture Organisation (FAO) recommends a minimum daily calcium intake of about 700 mg. The daily recommended intake is 150-500 mg and 2-3.5 g for magnesium and potassium respectively. The daily recommended sodium chlorine intake is 20 mg.

Although the intended reuse of the stormwater is for non-potable purposes, and therefore not for drinking, it was compared with the drinking water. To consume these quantities of mineral salts in the stormwater sampled in this study, more than 20L/day water is required to consume the equivalent calcium dosage, more than 10 litres for magnesium and more than 100 litres for potassium.

With regards to nitrate, nitrite and ammonia, all stormwater nutrient concentrations complied with the ADWG. Orthophosphate is being used around the world as a corrosion inhibitor in some potable water supplies, especially where it has been observed that high concentrations of copper exist in the potable water pipelines. According to Edwards et al, (2002) concentrations of orthophosphate are dosed at up to 1mg/L to generally decrease copper released in the water distribution pipes. All stormwater samples contained concentrations of orthophosphate at less than 1mg/L.

The pH analysis demonstrated that the stormwater pHs complied with the ADWG guidelines of between pH 6.5 and 8.5.

The Australian Drinking Water Guidelines (2004) state that there are no health guideline values for total hardness, but an aesthetic value is suggested at 200 mg/L $CaCO_3$ (which is reasonably hard water). Very hard water is likely to cause scale (insoluble calcium and magnesium compounds) to form on the inside of pipes and boilers. Water Hardness values were in the range of 70-110 mg/L $CaCO_3$ equivalent and therefore according to the ADWG it is considered good water quality.

The ADWG 2004 has a recommended limit of turbidity of 5 NTU. The turbidity in the stormwater was more than 10 times higher compared with the average of 5 NTU indicated in the ADWG.

Overall, the water samples collected from the stormwater generally complied with the standards for most parameters as proposed by the ADWG (Australian Drinking Water Guidelines) with the exception of a few individual parameters, (Table 4.3). The majority of parameters tested were comparable to potable water.

Table 4. 3 Comparison of Water Quality at Carlton, in Kogarah, Sydney with the AWDG (2004)

PARAMETER	AWDG (2004)	STORMWATER RANGE
pH	6.5 -8.5	6.68-7.28
CONDUCTIVITY (EC) (dS/m)	< 0.8	0.13-0.97
TOTAL DISSOLVED SALTS (mg/L)	Up to 500#	90-660
TOTAL SUSPENDED SOLIDS (mg/L)		24-35
TURBIDITY (NTU)	<5	2.5-40
WATER HARDNESS (mg/L $CaCO_3$ equivalent)	<200	103-109
ORTHOPHOSPHATE (mg/L P)		0.02-0.026
NITRATE (mg/L N)	<50	0.38-7.9
NITRITE (mg/L N)	<3	0.069-0.97
AMMONIA (mg/L N)	<0.5	0.014-0.418
SODIUM (mg/L)	<300	6.4-126
POTASSIUM (mg/L)		0.5-7.9
CALCIUM (mg/L)		7.2-32.2
MAGNESIUM (mg/L)		1.0-13.3
CHLORIDE (mg/L)	<400	19-241
SULPHATE (mg/L SO_4^{2-})	<400	13-86
ALUMINIUM (mg/L)	<0.2	0.028-0.188
COPPER (mg/L)	<2	0.008-0.049
IRON (mg/L)	<0.3	0.05-2.55
MANGANESE (mg/L)	<0.1 and <0.5*	0.001-0.024
LEAD (mg/L)	<0.01	0.001-0.022
ZINC (mg/L)	<3	0.016-0.123

*0.5 is for health and 0.1 is for aesthetic guidelines according to the AWDG 2004

according to the ADWG 2004 in major Australian reticulated supplies TDS values range from about 45 mg/L to 750 mg/L.

4.1.3.1 Molecular Weight Distribution (MWD) of organic compounds:

The molecular weight distribution of organic matter present in stormwater collected from the stormwater channel at Carlton, in Kogarah, Sydney is presented in Figure 4.1. From Figure 4.1, it is found that a wide range of organics with molecular weight (MW) 30000 Da to 670 Da are present in stormwater. The organic molecules of MW of 30000 Da are bio-polymer type substances such as protein and carbohydrate (retention time 8-11 minutes in the chromatograph). Whereas the molecular weight of humic substances are around 1100-1500 Da (retention time around 14-15 minutes) followed by low molecular acid and neutrals (MW of 730-670 Da; retention time from 16 minute to later). A comparison was also made between stormwater, tap water and milli-Q water in terms of organic matters by using MWD of organics (Figure 4.1). From Figure 4.1, it was found that stormwater contained higher biopolymer type substances (which results in higher UV intensity) than tap and milli-Q water. Furthermore, the stormwater also contained higher humic acid and lower molecular weight acid and neutral than tap water as well as milli-Q water.   In addition, these results also imply that tap water does not contain any bio-polymer type substances, whereas it contained humic acids as well as low molecular weight acid and neutrals. In addition, milli-Q showed almost zero UV intensity which implies that the no or very less organic matters were present in milli-Q water.

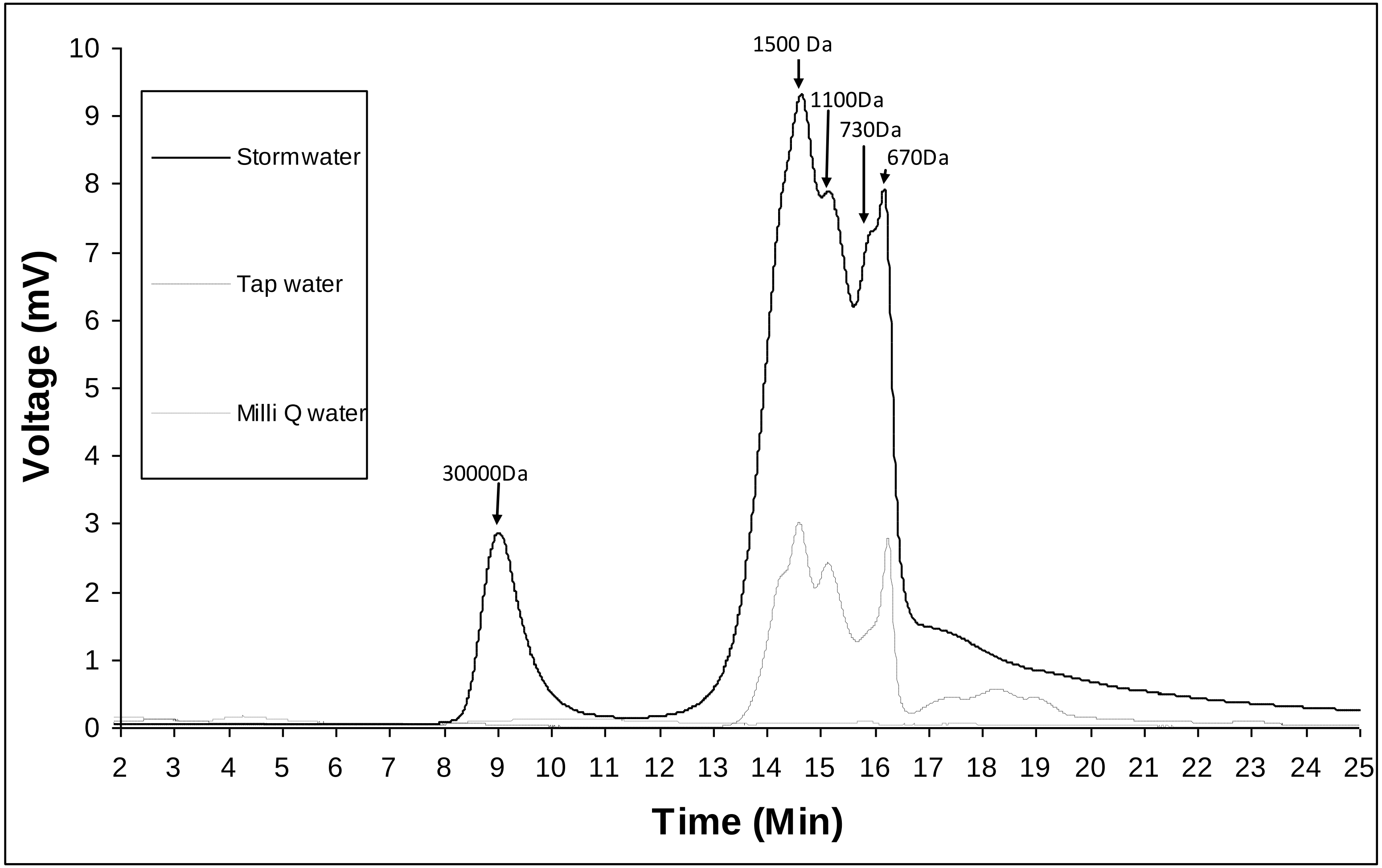


Figure 4. 1 Molecular weight distributions of organic matters in stormwater, Sydney tap water and milli Q water

4.2Road deposit

4.2.1 Introduction

Global urban road-deposited sediments (RDS) are increasing inline with an escalating rate of vehicle usage as a result of the rapid growth of urban populations. Currently over 50% of the world's population live in urban areas, and this is estimated to increase to two-thirds by 2050 (United Nations,2008). In Sydney, the largest and most populated city in Australia, the 2008 population of 4 million is estimated to increase to approximately 7.6 million by 2050 (Australian Bureau of Statistics, 2008). Despite improvements in vehicle manufacture, this rapid increase in urban population will eleveate current RDS loads. It is well known that urban RDS is strongly linked with vehicle exhaust emissions, degradation of vehicle tyres, body and brake linings, road surface erosion and nearby industrial activities (Taylor, 2007). This influence is often reflected by a high degree of inorganic and organic contaminant inputs such as heavy metals and polycyclic aromatic hydrocarbons to RDS. Heavy metals commonly found in the RDS include; Cd, Cr, Cu, Fe, Ni, Pb and Zn (Taylor, 2007; Weckwerth, 2001; Westerlund, 2001). The extent of contaminant input from traffic activities is generally determined by comparing the metal concentrations in RDS with those in nearby uncontaminated soils using different types of indices such as; a geoaccumulation index (I_{geo}) (Faiz et al., 2009; Lu et al., 2009; Wei et al., 2009), an enrichment factor (EF) (Lu et al., 2009), and a pollution index (PI)(Faiz et al., 2009; Lu et al., 2009; Wei et al., 2009). They are discussed in chapter 2 and chapter 7.

The mobile fraction of heavy metals in RDS can easily be dissolved in stormwater and have the potential to be transported into adjacent waterbodies. If concentrations of the mobile fractions exceed recommended guidelines (e.g. ANZECC, 2000a,b) the heavy metals can have adverse impacts on waterbody quality and human health (Lynam and Pfeifer, 1991; Scanlon, 1991; Trombulak and Frissell, 2000). Less mobile fractions of the heavy metals usually get deposited with the sediments in drainage channels and gully pots. However, they can also be mobilised if the biogeochemistry (pH, Eh, temperature) of the sediments or water changes during their transport. Therefore, it is important to understand the relative mobilities of heavy metals in RDS. Chapter 7 discusses this in detail.

The mobility of metals in RDS depends on the chemical forms in which the metals exist,rather than on their total concentration. The sequential extraction method is one method by which the readily mobile, less mobile and immobile fractions can be determined in RDS. Two general sequential extraction procedures have been used previously. The method of Tessier et al. (1979) is a five-step sequential extraction method which uses reagents to extract the following fractions in successive order of decreasing mobility: exchangeable, carbonate-bound, Fe/Mn oxide-bound, organic-bound and residual. The other sequential extraction method is a simpler three-step procedure developed by the Standards, Measurements and Testing programme of the European Union (Rauret et al., 1999; Sahuquillo et al., 1999). This method extracts exchangeable, reducible (Fe/Mn oxide-bound) and oxidisable (organic and sulphide-bound) fractions. The residual fraction is determined by subtracting the sum of these three fractions from the independently measured total metal concentration. In these methods, the exchangeable fraction is considered to be readily mobile and the residual fraction is the most immobile fraction. The residual fraction originates mainly from natural geological materials, whereas the more mobile fractions can be derived from anthropogenic sources such as industry, vehicles and road surfaces (Stone and Marsalek, 1996).

In Australia, only a limited body of work has been conducted on RDS, with the majority of these studies conducted on low-speed, city roads rather than on motorways (Birch and Scollen, 2003; Davis and Birch, 2011; Pathirana et al., 1994). On motorway roads the traffic density and speed are much higher and therefore, heavy metal pollution would also be expected to be elevated in a manner similar to that deduced by Duong and Lee (2011) on Korean highways. Furthermore, because of their relative isolation, it can be suggested that motorways display a lower likelihood of contamination from non-vehicular anthropogenic activities.

4.2.2 Road deposits analysis results

Nine RDS samples were collected along the city motorways. The total concentrations for each metal in RDS varied widely between sites (Table 4.4). As expected, overall concentrations of Fe were substantially higher compared to the trace heavy metals measured, which decreased in the order, Fe > Mn > Zn > Cu > Cr > Pb > Ni > Cd (Table 4.4). The total concentrations of the heavy metals for the nine sites are presented in Table 4.4.

Table 4. 4 Total metal concentration (mg.kg^{-1}) in motorways RDS of nine sites.

Metals	**Site number**									**Min**	**Max**
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**		
Fe (mg.kg^{-1})	48081	61660	22036	41435	103020	43023	355263	47132	45158	22036	355263
Mn (mg.kg^{-1})	669	1102	489	522	2651	565	3966	803	717	489	3966
Zn (mg.kg^{-1})	1498	1015	991	727	1161	557	2117	875	1038	557	2117
Cu (mg.kg^{-1})	730	595	468	314	401	480	674	544	687	314	730
Cr (mg.kg^{-1})	132	156	49	96	143	63	486	90	156	49	486
Pb (mg.kg^{-1})	379	119	40	97	36	68	130	155	49	36	379
Ni (mg.kg^{-1})	41	90	20	63	79	26	208	40	57	20	208
Cd (mg.kg^{-1})	1.39	0.74	0.24	0.65	0.56	0.35	1.72	0.53	0.35	0.24	1.72

Chapter 5

5. Biofilter

5.1Biofiltration as pre-treatment to water harvesting and recycling

5.1.1 Introduction

There are many media used in stormwater treatment to remove solids and organics associated with solids. In this study sand, GAC and Purolite A520E were used to remove turbidity, organics and nutrients, respectively.

Stormwater runoff is the main source of pollution of lakes and waterways. The chemical characteristics of stormwater are dependent on the nature of surfaces the runoff passes over such as roads, residential land uses etc. Best management practices (BMPs) such as filter strips and swales; infiltration systems (soakaways, infiltration trenches and infiltration basins); and storage facilities (detention basins, retention ponds, lagoons) are widely used as treatment of stormwater to reduce the urban runoff peak flows as well as the amount of stormwater based pollutants entering receiving waters. Studies have shown that a large number of pollutants, both organic and inorganic, may be present in stormwater (Eriksson et. al 2007), both in their dissolved and colloidal forms and associated with particles. Such discharges of urban stormwater may cause numerous adverse impacts including the export of heavy metals, organic compounds and pathogens to the receiving waters (Nogaro et al. 2007).

Filtration is an efficient solid-liquid separation process. However, the filtration alone cannot remove the dissolved organics present in the stormwater. On the other hand biological filtration or biofiltration may remove the dissolved organics. Biofiltration incorporates solid-liquid separation (filtration) with adsorption and biological processes. The mechanisms of biological organic removal in biofiltration have been studied by several researchers (Hoang et al., 2008; Chaudhary et al., 2003). Biofiltration is a complex system, which relies on the activities of micro-organisms that are attached to the supporting media such as granular activated carbon (GAC). Therefore the filter media and the following factors in the development of micro-organisms affect the performance of biological filters. The growth of microbial communities in biofilters is affected by the influent characteristics such as nutrients, toxics, pH and temperature. Operational conditions such as backwashing frequency and duration and empty bed contact time (EBCT) also affect the performance of biological filtration in water treatment.

Biological filtration or biofiltration is considered an important process in producing microbially safe and aesthetically pleasing drinking water (Urfer et al., 1997), that has attracted increased attention within the water industry. Generally, it is the most economical way to implement biological rapid filtration to achieve biodegradable organic matter (BOM) removal and particle removal within the same filter unit, i.e., single-stage biological filtration.

In this study, the performance of biofiltration using two different media, namely GAC and anthracite, was assessed at different velocities and media heights to determine the effectiveness of biofiltration in removing organic components from stormwater. The use of GAC as a biofilter medium has several advantages as it possesses an extremely large and irregular surface of the order of several hundred $m^2.g^{-1}$ of carbon that provides a large number of available sites for the adsorption of organic substrates and microorganisms (McKay, 1996). Anthracite by comparison is relatively inexpensive but does not have the high adsorption capacity as that of GAC.

5.1.2 Experimental Methods

Raw water was collected from a stormwater canal at Carlton, in Kogarah, Sydney. In this study, biofiltration experiments were conducted using transparent acrylic filter columns (Figure 5.1).

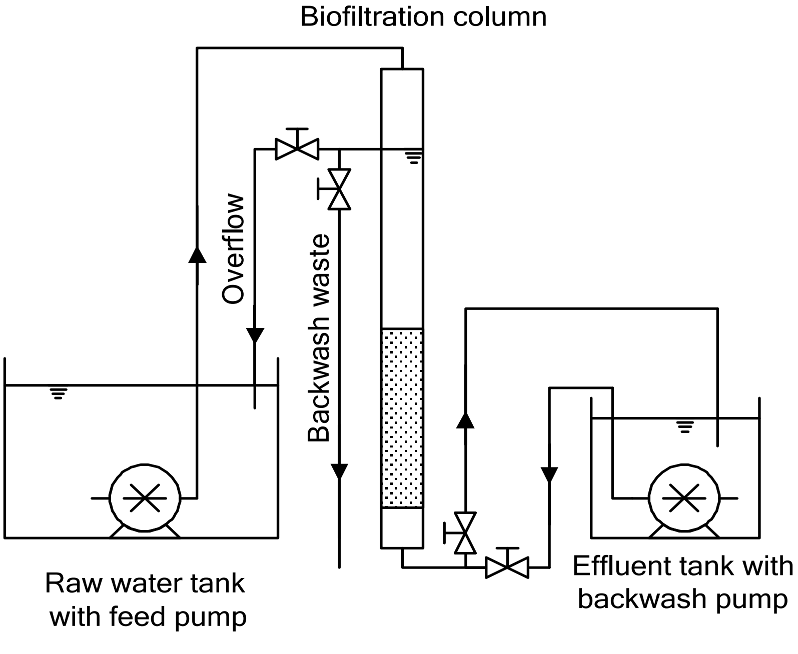


Figure 5. 1 Schematic diagram of biofilter column

Details of the materials and experiment methods are explained in detail in section 3.2.1 and 3.4.1 of chapter 3 respectively. The physical properties of GAC and anthracite are presented in Table 3.3. The organic concentrations of raw and treated stormwater were measured in terms of dissolved organic carbon (DOC) by using the Multi N/C 2000 analyzer (Analytik Jena AG). Detailed laboratory analyses were carried out to determine other individual pollutants. The pollutants analysed were heavy metals (aluminium, arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver and zinc), nitrate and nitrite, pH, ammonia, orthophosphate, conductivity, water hardness, turbidity, total suspended solids, and bicarbonate. The water quality parameter measurement methods are given in Table 4.1 in chapter 4.

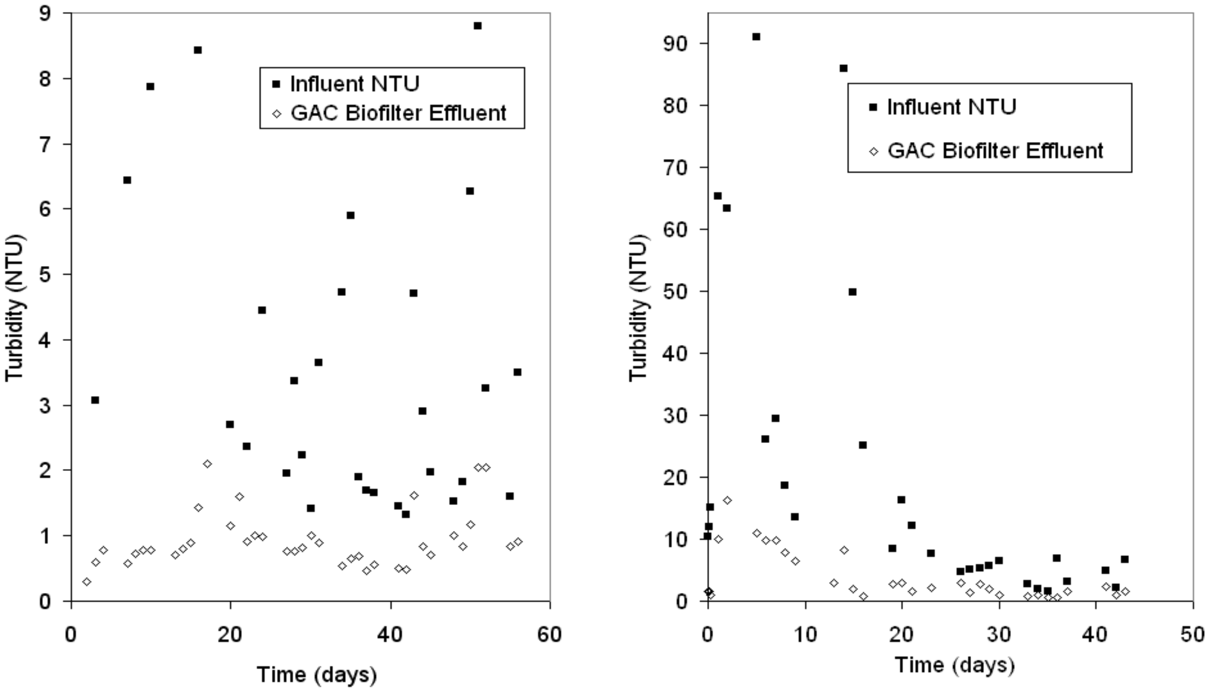
5.1.3 Results and Discussion

Physical and Chemical Characteristics: The influent stormwater had the following physical and chemical characteristics as shown in Table 5.1.

Table 5. 1 General characteristics of canal water used in this study

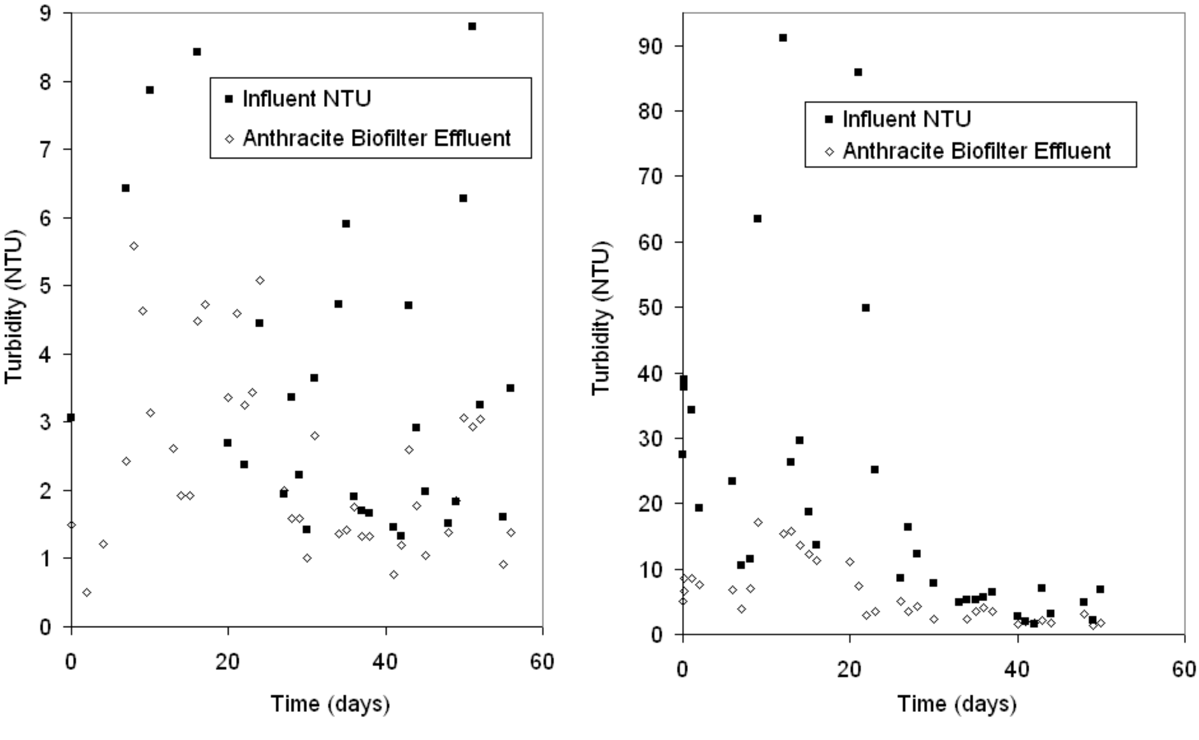
Parameter	Unit	Value
Nutrients		
Total Nitrogen	mg/L N	0.39-9.5
Nitrate	mg/L N	0.38-7.9
Nitrite	mg/L N	0.069-0.97
Ammonia	mg/L N	0.4-1.15
Total Phosphorous	mg/L P	0.021-0.36
Orthophosphate	mg/L P	0.02-0.026
Traditional (physical & chemical)		
pH	-	6.68-7.28
TOC	mg/L	4.25-8.96
Turbidity	NTU	1.5-90
True Colour	PtCo	18-270
Bicarbonate	mg/L $CaCO_3$ equivalent	30-95
Water Hardness	mg/L $CaCO_3$ equivalent	22-145
Metals		
Aluminium	mg/L	0.028-0.188
Arsenic	mg/L	0.001-0.005
Cadmium	mg/L	0.0009-0.001
Chromium	mg/L	0.002-0.002
Copper	mg/L	0.008-0.049
Iron	mg/L	0.05-2.55
Manganese	mg/L	0.001-0.024
Nickel	mg/L	0.003-0.10
Lead	mg/L	0.001-0.022
Selenium	mg/L	0.001-0.004
Zinc	mg/L	0.016-0.123

Turbidity removal: Figure 5.2 (a-d) shows the turbidity removal efficiency of the biofilters under different operating conditions. The raw water turbidity was highly variable in the range of 1.5-90 NTU. The higher turbidity was obtained during storm events. Table 5.2 shows the filtration velocities and the turbidity removal efficiency of the filters operated with various heights. The best turbidity removal efficiency was observed with GAC as a filter medium of up to 75%.



a) GAC biofilter, velocity = 0.12 m/hr, bed depth = 75 cm, column backwashed daily

b) GAC biofilter, velocity = 0.25 m/hr, bed depth = 40 cm, column backwashed daily



c) Anthracite biofilter, velocity 0.12 m/hr, bed depth 75 cm

d) Anthracite biofilter, velocity 0.25 m/hr, bed depth 40 cm

Figure 5. 2 Effect of filtration velocity on turbidity removal with the two filter media used (raw stormwater water turbidity = 1.5-90 NTU)

Table 5. 2 Summary on the turbidity removal efficiency

Media	**Velocity (m/h)**	**Media Height (cm)**	**Days of Operation**	**Average Turbidity Removal efficiency (%)**
GAC	0.25	40	40	75
GAC	0.12	75	60	68
Anthracite	0.25	40	40	60
Anthracite	0.12	75	60	50

Headloss development: Figure 5.3 shows the headloss (pressure drop) development profile of the biofilter as a function of time. The headloss in all cases was very low. It shows the head loss variation was 0.5–2.0cm and 0.5-4.7 cm for anthracite and GAC respectively. The headloss development is slightly higher for GAC implying that it becomes slightly more clogged due to more solid retention, adsorption and biological growth on the media as compared to that of anthracite. The filters were backwashed (at times shown in Figure 5.3) just to remove solid deposits in the pores of the filter and the excessive biological growth on the filter media. Biological activity was not disturbed by the backwash. The column was backwashed daily by having the water flow in the upwards direction. The water flow rate was sufficient enough to provide 10% expansion of the medium during the backwash. The backwash was performed for five minutes duration. As the filtration rate is low (which is similar to that of slow rate filter), backwashing is not practised in proto-type filtration systems. However, in laboratory-scale systems used in our experiments, we used backwash occasionally in order to maintain a constant flow rate.

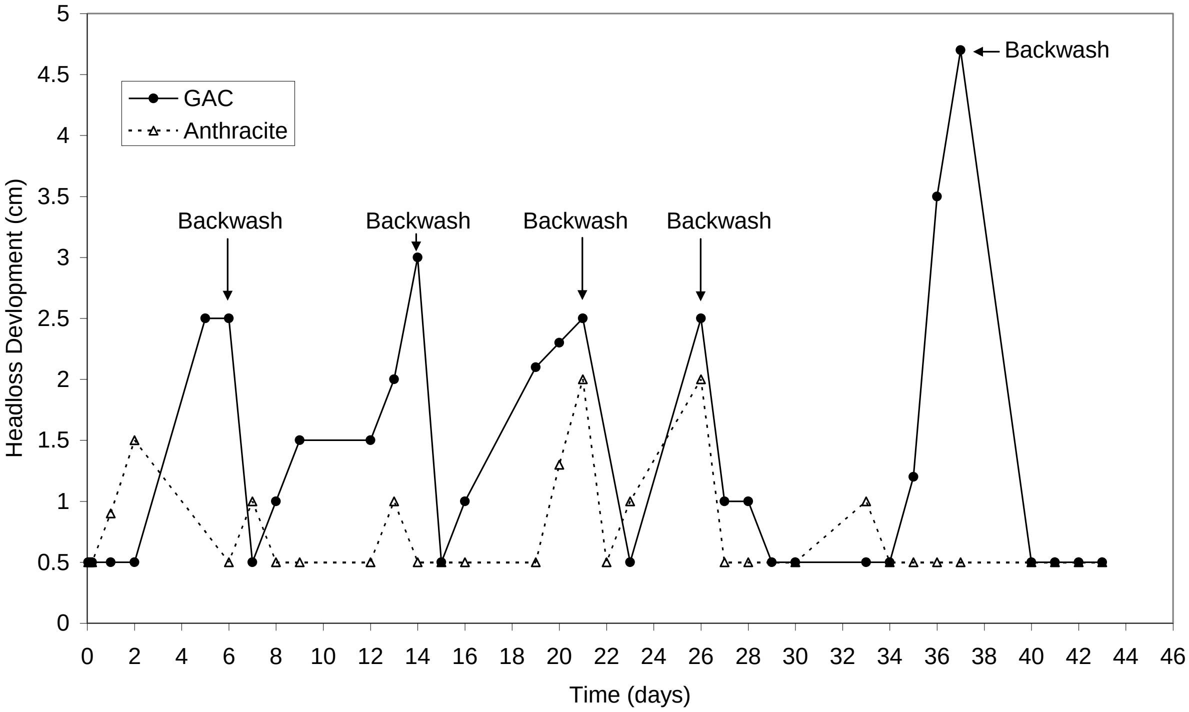


Figure 5. 3 Headloss development profile of GAC and anthracite biofilters

Dissolved Organic Carbon (DOC) removal efficiency: The temporal variation of dissolved organic carbon (DOC) concentration of raw influent stormwater and the filter effluents are presented in Figures 5.4 and 5.5. Also presented in these figures is the DOC removal efficiency. The average DOC removal efficiency by the two different filter media is presented in Tables 5.3 and 5.4. It can be seen that DOC removal was much higher, and almost 99%, for GAC compared to anthracite. In the initial stages the GAC filter works as an adsorbent and as a biological filter when microbes (biofilm) develop in the filter.

The DOC removal is both by adsorption and biological degradation in the case of GAC. It is difficult to differentiate between the removal by adsorption and by biological degradation. In the initial stages, the removal mechanism in the GAC filter is by adsorption, and as biological microbes develop it acts as a biofilter. At the intermediate stage both adsorption and biodegradation take place before biodegradation becomes the sole mechanism. In this study we worked with GAC and anthracite as media in order to represent high adsorption and low adsorption media conditions respectively. The adsorption capacity of anthracite is very much lower than GAC. This is reflected in the results of DOC removal which is virtually 100% for the GAC filter and only about 20% for the anthracite filter. The difference in the result can be explained in terms of the superior adsorption by GAC. The organic removal by bio-degradation does also occur as evidenced by the organic removal by the anthracite filter (after a few weeks of operation).

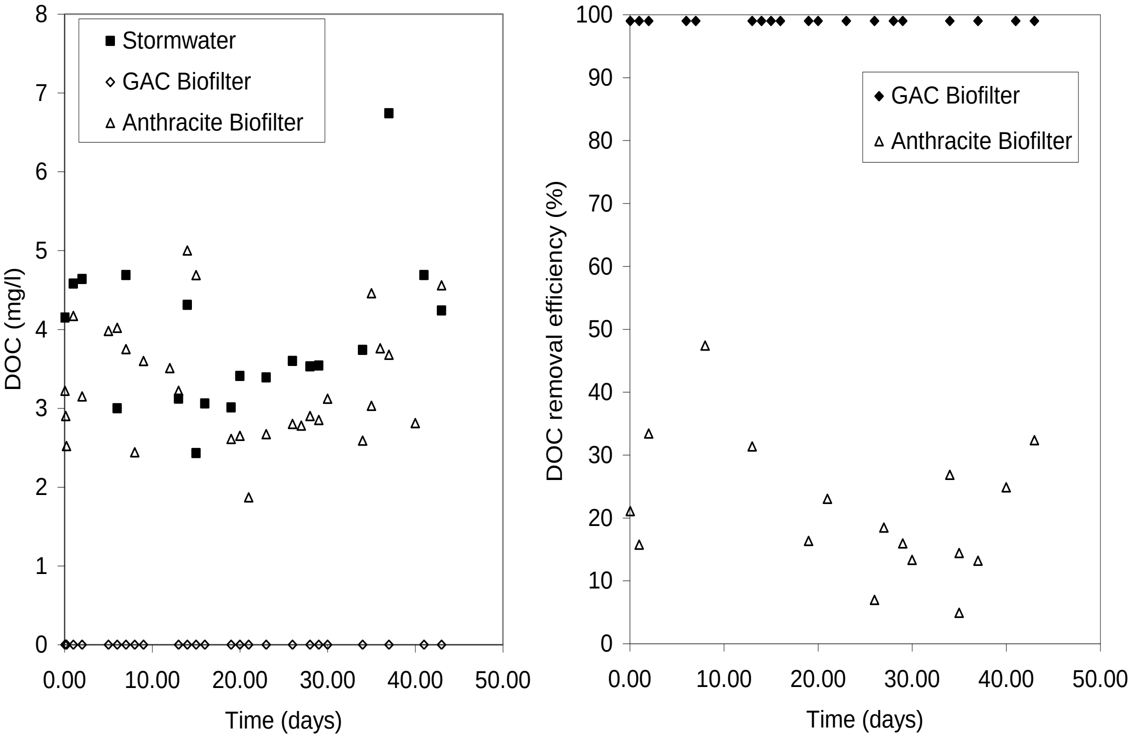
Table 5. 3 DOC removal efficiency (raw water DOC = 4.25-8.96 mg/L, empty bed contact time (EBCT) ~ 1.6h)

Media	**Velocity (m/h)**	**Media Height (cm)**	**Days of Operation**	**Average DOC Removal efficiency (%)**
GAC	0.25	40	50	99
Anthracite	0.25	40	50	21

Where EBCT = volume of water filtered/ filter volume

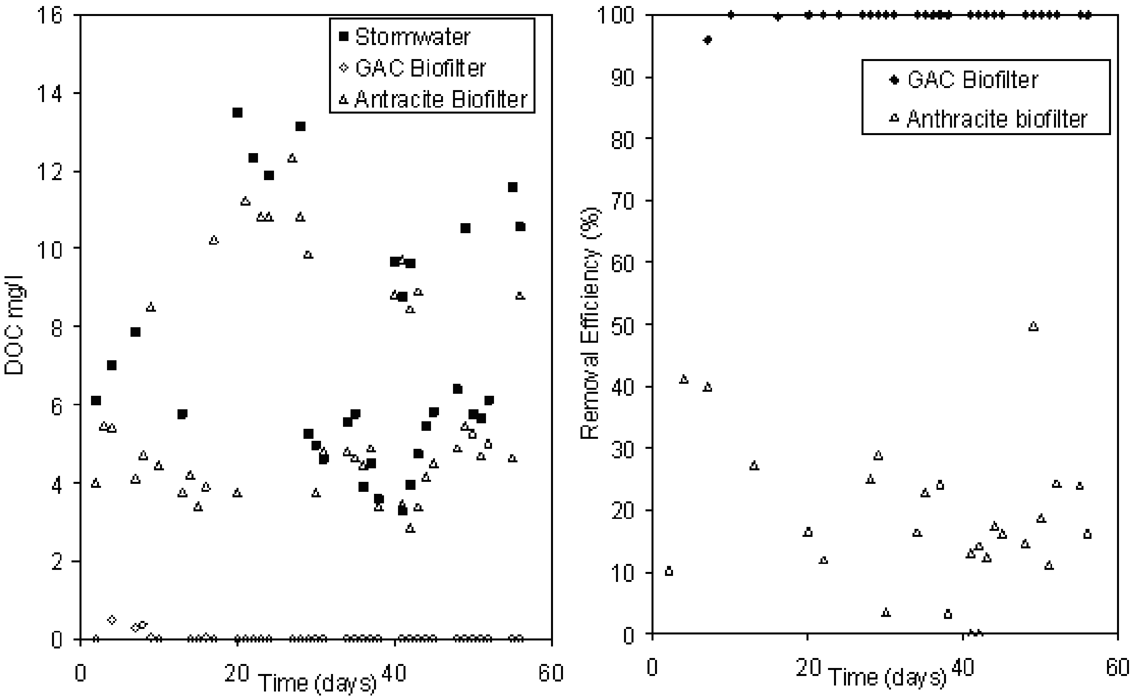
Table 5. 4 DOC removal efficiency (raw water DOC = 4.25-8.96 mg/L), EBCT ~ 6h for both media

Media	**Velocity (m/h)**	**Media Height (cm)**	**Days of Operation**	**Average DOC Removal efficiency (%)**
GAC	0.12	75	58	98
Anthracite	0.12	75	58	20



a) DOC values b) DOC removal efficiency

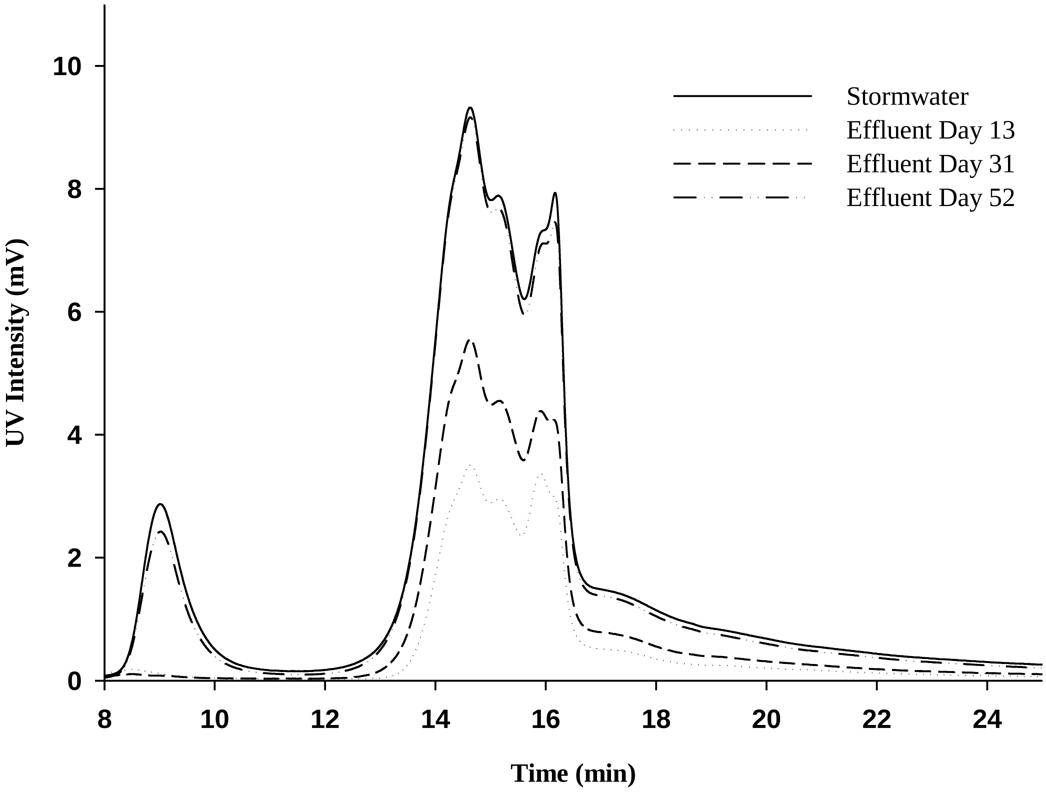
Figure 5. 4 Dissolved organic carbon removal (velocity = 0.25m/h, media height = 40cm, EBCT ~ 1.6h for both filters)



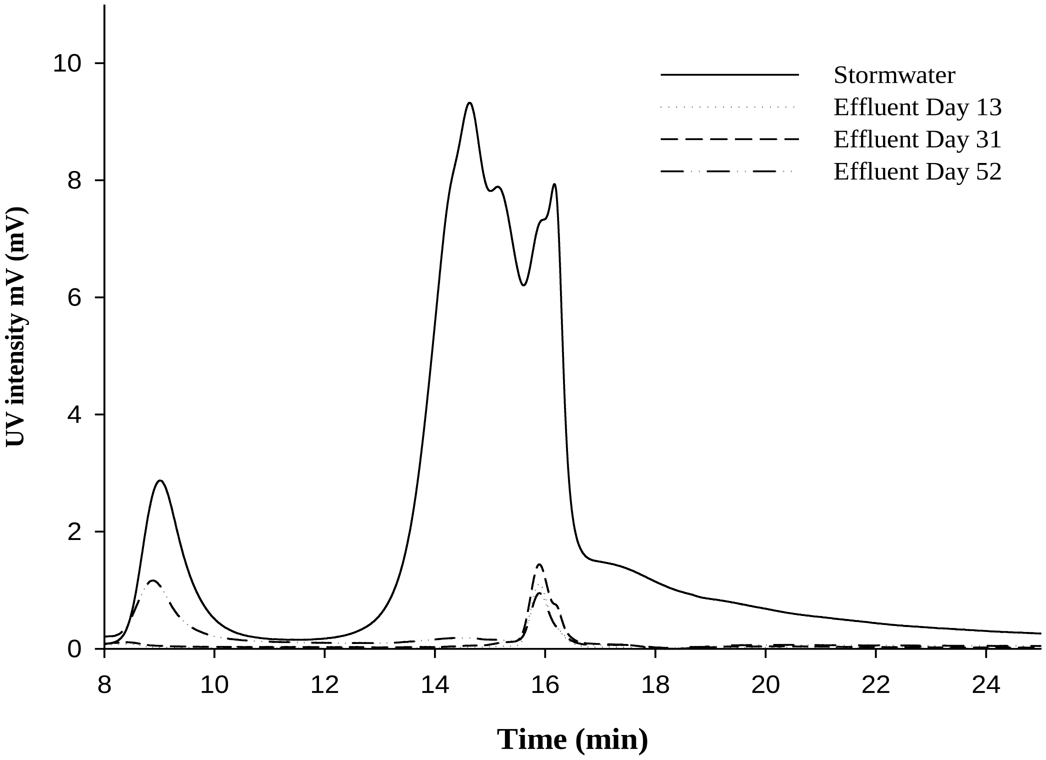
a) DOC values b) DOC removal efficiency

Figure 5. 5 Dissolved organic carbon removal (velocity = 0.12m/h, media height = 75cm, EBCT ~ 6h for both filters)

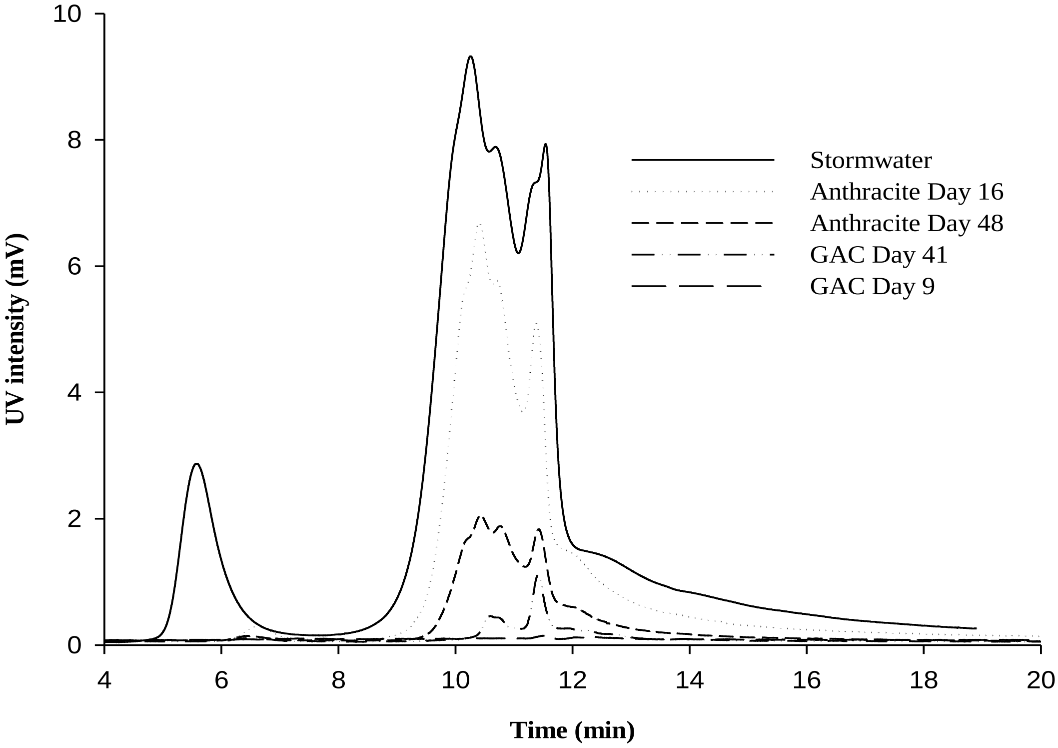
Molecular Weight Distribution (MWD) of organic compounds: In order to study the type of organics present in the stormwater, the molecular weight (MW) of organic matter was measured using the HPSEC. The results are presented in Figures 5.6 (a-c). It was found that all filters studied under different conditions were able to remove organics of large molecular weight sizes. The removal measured in terms of UV absorbance intensity was higher for the GAC filter. In this study, GAC and anthracite effectively removed the large MW compounds. Compared with the anthracite filter media, the GAC biofilter removed a much larger range of organic compounds present in the stormwater (Figure 5.6c). Figure 5.6c also shows the GAC biofilter removes organic matter earlier compared to anthracite.



a) MWD in anthracite biofilter, (velocity = 0.12 m/hr, media height = 75 cm)



b) MWD in GAC biofilter, (velocity = 0.12 m/hr, media height = 75 cm)



c) MWD in anthracite and GAC biofilter, (velocity = 0.25 m/hr, media height = 40 cm)

Figure 5. 6 (a-c) Molecular weight distributions of organic matters in stormwater before and after treatment

Nutrient removal efficiency: The removal efficiency for the total phosphorus (TP) and total nitrogen (TN) for the GAC and the anthracite filters with media height of 75 cm, are presented in Table 5.5. The TN and TP concentrations in the raw stormwater were relatively low and as such there was no attempt made to study the nutrient mechanism.

The concentration of TN in the raw stormwater was in the range of 5-9.5 mg/L and this compares with the upper end of the typical Australian range of concentration of 0.7-6 mg/L (Wong et al., 2000). The concentration of TP in the raw stormwater was in the range of 0.04- 0.35 mg/L and this compares with the lower to middle segment of the typical Australian range of concentration of 0.08 - 0.8 mg/L (Wong et al., 2000). Nevertheless the concentration of TN and TP were below the effluent discharge standard for wastewater effluent.

Based on this limited number of samples of raw stormwater analysed, the removal efficiency for phosphorus was up to 74% and that of nitrogen was up to 30%. However the nitrogen and phosphorus values were much lower than wastewater. The wide variation of TP removal (4-74%) may be due to the very low influent TP concentrations. A high (74%) and low (4%) removal was observed for the highest (0.35 mg/L) and lowest (0.03 mg/L) TP influent concentration.

Table 5. 5 Nutrient removal efficiency for GAC and Anthracite, media height = 75 cm respectively, velocity = 0.12m/h, total nitrogen (TN), total phosphorous (TP).

Total nitrogen (TN) mg/L before and after biofiltration					
Time (days)	Raw Stormwater mg/l	Effluent after GAC biofilter (mg/l)	Removal efficiency (GAC) %	Effluent after Anthracite biofiter (mg/l)	Removal efficiency Anthracite %
16	5	3.5	29	2.5	50
28	8.4	5.3	37	7.3	13
51	9.5	8.5	11	8.6	9
Total phosphorous (TP) mg/L before and after biofiltration					
Time (days)	Raw Stormwater mg/l	Effluent after GAC biofilter (mg/l)	Removal efficiency (GAC) %	Effluent after Anthracite biofilter (mg/l)	Removal efficiency Anthracite %
16	0.044	0.039	12	0.041	6
28	0.033	0.032	4	0.031	7
51	0.352	0.092	74	0.225	36

Heavy metal removal efficiency: Table 5.6 shows the removal efficiency of heavy metal for the GAC and anthracite filters with media heights of 40cm operated at a velocity of 0.25m/h. The heavy metals such as copper, iron, nickel, lead and zinc were present in stormwater in very small quantities (Table 5.1). Despite this, it is clear from Table 5.7 that heavy metals have been reduced in all filter operating conditions (Table 5.7). The GAC filter shows a higher removal efficiency than anthracite (Table 5.7).

Table 5. 6 Heavy metal average removal efficiency for GAC and anthracite (media height = 40 cm, velocity = 0.25m/h for both filters)

Heavy metal	**Average Influent Concentration mg/l**	**Removal efficiency Anthracite (%)**	**Removal efficiency GAC (%)**
Aluminium	0.11	47	52
Arsenic	0.002	43	39
Cadmium*	0.001	*	*
Chromium	0.002	17	30
Copper	0.02	0	74
Iron	0.66	71	88
Manganese	0.01	57	43
Nickel	0.04	81	95
Lead	0.006	91	98
Selenium	0.004	39	48
Zinc	0.04	67	97

* Cadmium concentration in stormwater was <0.001 and <0.0001 in the effluent.

Water hardness, pH, conductivity and colour removal efficiency: After filtration, the water hardness was almost the same as raw stormwater. Similarly the amount of bicarbonate also did not change. The bicarbonate and water hardness were in the range of 30-95 mg/L $CaCO_3$ equivalent, and 22-130 mg/L $CaCO_3$ equivalent respectively.

The raw water pH was an average of 7.0 ± 0.5. The raw water was considered as virtually neutral and in order to work with natural conditions and close to field conditions it was not buffered. The pH of the effluent was also around 7.0 ± 0.5 after filtration for all conditions and there was virtually no change in pH values. Previous studies with wastewater effluent showed that the pH did not vary and this may possibly be due to the initial neutral condition (Chaudhary et al., 2003).

The pH values were around 7.5 after filtration for all conditions, which implied that the filtered water was almost neutral. In terms of colour removal, the GAC filter was able to remove colour with up to 95% (from 19 to 1 PtCo), however the anthracite filter were able to remove only 18% (from 19 to 14 PtCo).

5.1.4 Summary of GAC and Anthracite media Biofilters

In this study, two different biofilters were tested for stormwater pollution control. The main conclusions were:

- The average turbidity removal efficiency of up to 75% and 60% was achieved using the GAC and anthracite media filter respectively.
- Headloss development was low for both anthracite and GAC filters.
- The highest DOC removal efficiency of up to 99% was achieved using the GAC media filter. However the anthracite filter showed removal efficiencies of up to 20%
- MWD showed almost similar trends to the DOC removal. Compared with anthracite filter media, the GAC biofilter removed a much larger range of organic compounds present in the stormwater. The GAC biofilter was found to remove organic matter earlier on when compared to anthracite.
- The colour removal was 95% using the GAC filter while the colour removal detected in the anthracite filter was small.
- In general the GAC filter shows higher heavy metal removal efficiency than anthracite and the removal of zinc, iron, lead and nickel were good. However the concentration of heavy metals in the raw stormwater sample was low.

5.2 Removal of diluted synthetic landfill leachate (SLL) by a GAC biofilter: Experiments and modelling

Landfill leachate is produced when rainwater infiltrates into the landfill and permeates through the decomposing waste within the landfill leaching out with it contaminants and pollutants. Untreated leachate if not properly managed can permeate through soil to ground water or mix with surface waters and contribute to the pollution of soil, ground water, and surface water. Therefore in this study, a synthetic landfill leachate (SLL) was used (TOC 50-65 mg/L) to represent the dilute leachate with ground water (during the passage of leachate to groundwater). The TOC of the landfill leachate is generally very high (in thousands of mg/L) depending upon the type and the age of the landfill. The composition of SLL used in this study is given in Table 3.2 (Chapter 3). Biofilter experiments with the diluted SLL were conducted at two different conditions. The experimental conditions are given in Table 5.7

Table 5. 7 Summary of the column experiments

Parameter	Experimental 1	Experimental 2
Filter media	GAC	GAC
Bed depth (cm)	30	35
Filtration rate (m/hr)	2	0.21
Average TOC of influent (mg/L)	65	50
Backwashing expansion	30%	30%
Backwashing duration and frequency	5 minutes every 24 hours	5 minutes every 24 hours

5.2.1 Mathematical Modelling

The purpose of the mathematical model was to simulate the organic removal efficiency of the GAC biofiltration system. It should be noted that this model developed for theoretical concepts was used to mainly explain the biofilter performance. In this simulation model, the performance can be described in two stages: adsorption during the initial stage and biodegradation in the latter stage. In practice, the prediction of the performance of a biofilter during the biological or steady phases is more important because the initial stage only lasts for a short duration of less than a day at the beginning of a run. Therefore the simulation of the adsorption processed was simplified.

A systematic representation of the mass balance in a biologically activated carbon system and the biofilm on the activated carbon is shown in Figure 5.7. The model is based on the fundamental mechanisms of transport of substrate in the bulk liquid, biofilm growth, transport and biodegradation within the biofilm, and adsorption on activated carbon. The following additional assumptions are made in relation to the modelling work.

1. The adsorbent particles are assumed to be spherical in shape and uniform in size

and the curvature effect of the adsorbent surface can be ignored. No biological reaction occurs inside the adsorbent particle.

2. The biofilm is thin relative to the radius of the adsorbent particle and can be modelled as a flat plate. The biofilm is homogeneous with respect to thickness, porosity, composition, and density. The specific surface area and bed porosity are constant with biofilm growth. Any increase in biofilm thickness is due to the growth of biofilm.
3. The biological activity is assumed to be substrate limiting and can be represented by the Monod equation.
4. The Glueckauf approximation may be used to describe intrapellet diffusion.

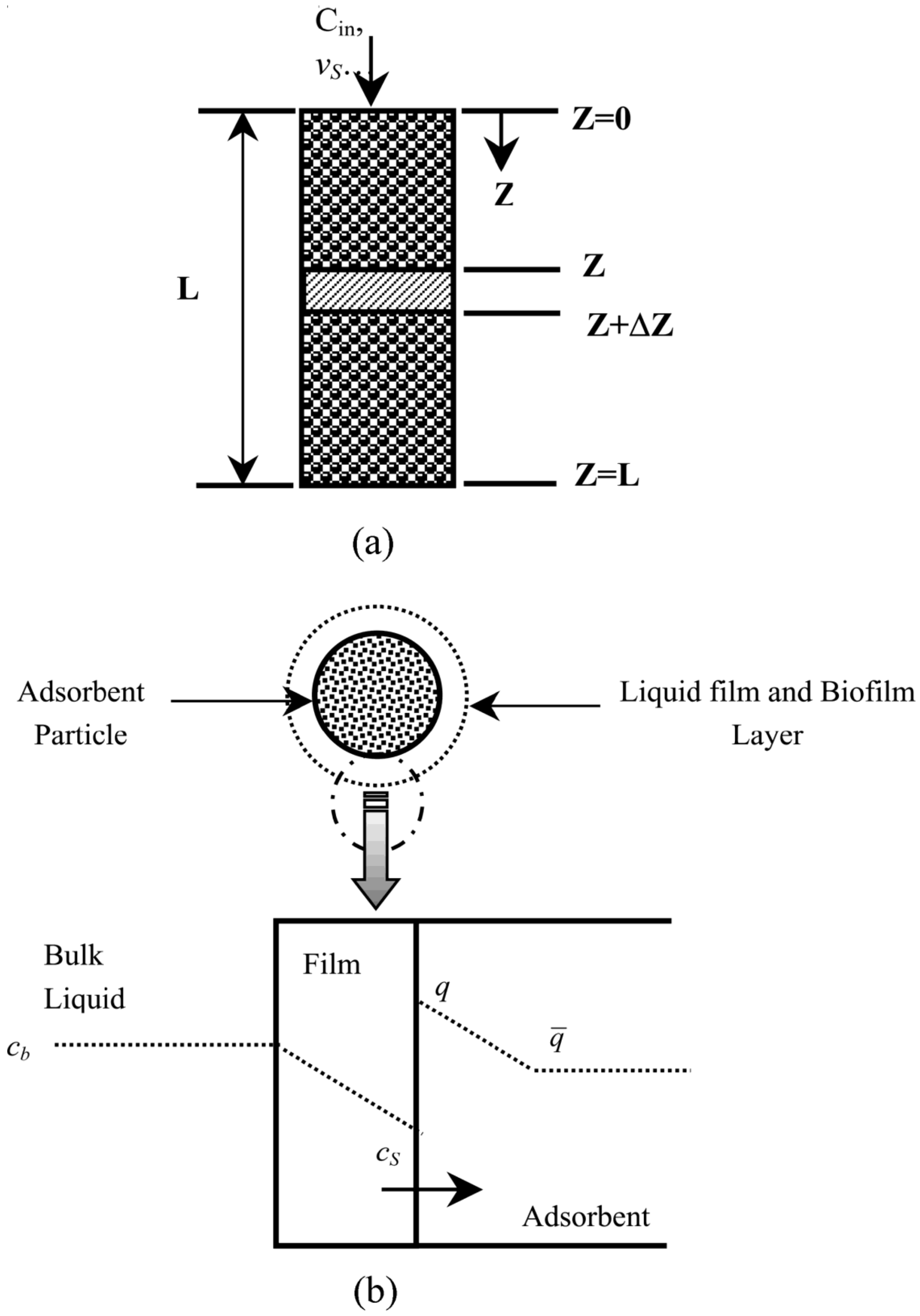


Figure 5. 7 Schematic representation of the mass balance in a bioactive GAC (b) and the biofilm on an adsorbent surface.

Substrate in the Bulk Liquid: The rates of removal of the substrate from the liquid phase by adsorption (γ_{ADS}) and biodegradation (γ_{BIO}) are given by:

$$\gamma_{BIO} = k_{max} \cdot \frac{C \cdot X_S}{K_S + C}, \qquad \gamma_{ADS} = (1 - \varepsilon_b) \cdot \frac{3N}{4\pi R_p^3} \tag{5.1}$$

Where N is the adsorbate uptake rate per pellet, ε_b is the bed porosity, R_P is the pellet radius, k_{max} is the maximum rate of substrate utilization, K_S is the Monod half velocity coefficient, X_S is the suspended cell concentration, and C is the liquid phase concentration (Shim et al., 2004).

The unsteady-state material balances on the substrate in the bulk liquid can be represented by the advection-diffusion equation with the inclusion of adsorption and reaction terms as follows:

$$\frac{\partial C}{\partial t} = D_{ax} \cdot \frac{\partial^2 C}{\partial z^2} - u \cdot \frac{\partial C}{\partial z} - \gamma_{BIO} - \gamma_{ads} \tag{5.2}$$

Where D_{ax} is the axial dispersion coefficient and u is the interstitial velocity. The initial and boundary conditions are:-

Initial condition, C = 0

Boundary condition at z=0 is $C=C_0$ and at z=L is $\frac{dC}{dz} = 0$

Biomass Suspended in the Bulk Liquid: Suspended biomass accumulates on the adsorbent due to deposition, growth, decay, and shear loss. The equation for suspended biomass in the bulk liquid is as follows:

$$\frac{\partial X_S}{\partial t} = \left(Y \cdot \frac{k_{max} \cdot C}{K_S + C} - K_d - \frac{\beta}{\theta \cdot \varepsilon_b} \right) \cdot X_S + \frac{1 - \varepsilon_b}{\varepsilon_b} \cdot a_f \cdot X_f \cdot \sigma \tag{5.3}$$

Where Y is the yield coefficient, K_d is the decay constant, β is the filtration efficiency, θ is the empty bed contact time, X_f is the cell density of biofilm, a_f is the specific surface area and σ is the biofilm shear loss coefficient.

The associated initial and boundary conditions are

Initial condition, $X_s = X_{so}$

Boundary condition at z=0 is $X_s = X_{so}$, and at z=L is $\frac{dX_s}{dz} = 0$. Z and L are defined in Figure 5.7.

Biofilm Diffusion and Biodegradation: Andrews and Tien, (1981) proposed a conceptual model of bio-film and its growth in which they assumed that the substrate diffuses through and is taken up by the biofilm. The diffusion of the substrate across the biofilm is accompanied by its biodegradation. The model equation for biofilm diffusion with Monod type is given by:

$$\frac{\partial S}{\partial t} = D_f \cdot \frac{\partial^2 S}{\partial x^2} - X_f \cdot \frac{k_{max} \cdot S}{K_S + S} \qquad 5.4$$

Where, D_f is the molecular diffusivity within biofilm and S is the concentration of substrate in the biofilm. However it is assumed that the amount adsorbed into the particles is small and can be ignored. Further it is assumed that no biological reaction occurs inside the adsorbent particle. The associated initial and boundary conditions are:

Initial condition, S=S*o*

Boundary condition at x=0 is S=0

at x=L_f is $D_f \cdot \frac{\partial S}{\partial x} = k_f.(C - S)$

Where k_f is the interphase mass-transfer coefficient from liquid to biofilm (Andrews et al., 1981).

Biofilm Growth and Decay: Since the concentration profiles are expressed over a film thickness and the biofilm thickness varies with time, a complete description of the biofilm requires the knowledge of the film thickness as a function of time. The biofilm accumulation in the GAC biofilter due to the biological activity, deposition, decay and shear loss at each time step may be written as follows:

$$\frac{dL_f}{dt} = \int_0^{L_f} \left(\frac{Y \cdot k_{max} \cdot S}{K_S + S} - b_{tot} \right) \cdot dr \qquad 5.5$$

Where, L_f is the biofilm thickness, and b_{tot} is the total biofilm loss coefficient.

The initial condition is

t=0, $L_f = L_{fo}$,

$$L_{fmax} = R_P \left[\frac{1}{(1 - e_{bo})^{1/3}} - 1 \right]$$

Support-phase Substrate Balance: The linear driving force approximation (LDFA) model was used to describe adsorption kinetics in this study:

$$\frac{\partial \bar{q}}{\partial t} = k_P \cdot (q_S - \bar{q}) \tag{5.6}$$

Where q is the adsorbed-phase concentration, $\bar{q}$ is average concentration of q, q_S is the value of q at the pellet surface, and k_P is the particle phase mass transfer coefficient.

Adsorption Isotherm: In this study, the Freundlich isotherm was used in the modelling of the biofiltration system. The isotherm parameters were determined using Freundlich isotherm model equation expressed by equation 5.7.

$$q = k_F C^{\frac{1}{n}} \tag{5.7}$$

Bed Porosity and Specific Surface Area: The growth of biofilm outside an adsorbent results in a change in the bed porosity and specific surface area. Alonso et al., (1997) and (1998) showed that the specific surface area could be calculated based on the consideration of the area and volume of biofilm lost in each contact point as compared with no contact point between solids. Then the specific area is given by:

$$a_f = \frac{3.(1-\varepsilon_{b0})}{2.R_p}.\left(1+\frac{L_f}{R_p}\right).\left[(2-P_n).\frac{L_f}{R_p}+2\right]$$

where, P_n is the number of characteristic packing spheres. Assuming L_f is small in relation to R_p then

$$a_f = \frac{3.(1-\varepsilon_{b0})}{R_p}$$

The bed porosity with biofilm, ε_b, is given by:

$$\varepsilon_b = 1-(1-\varepsilon_{b0}).\left[\left(1+\frac{L_f}{R_p}\right)^3 - \frac{P_n}{4}.\left(\frac{L_f}{R_p}\right)^2.\left(2.\frac{L_f}{R_p}+3\right)\right]$$

Assuming L_f is small in relation to R_p then

$$\varepsilon_b = \varepsilon_{bo}$$

Backwashing System: The daily backwash adopted in the experimental study to avoid the physical clogging of the biofilter was found not to have any significant effect on the organic removal efficiency of the filter. Further to this, several investigators have examined the bed expansion due to filter backwash (Ahmad et al., 1998; Lu et al., 1993), finding no major loss of biomass during backwash of the biofilter. Servais et al., (1994) backwashed the GAC biofilter with air scour and water routinely every 50-100 hours of a continuous run, but observed no significant difference in vertical biomass profiles before and after backwash. After backwashing, the bed length was assumed to be constant; and the specific surface area and bed porosity were calculated as follows [equations 5.8 and 5.9, respectively];

$$a_f = \frac{3.(1-\varepsilon_{b0})}{2.R_p}.\left(1+\frac{L_{f-bw}}{R_p}\right)^2.\left(1+\frac{L_f-L_{fo}}{R_{peff}}\right).\left[(1-P_n).\frac{L_f-L_{fo}}{R_{peff}}+2\right] \qquad 5.8$$

$$\varepsilon_b = 1-(1-\varepsilon_{b0}).\left[\left(1+\frac{L_f-L_{fo}}{R_{peff}}\right)^3-\frac{P_n}{4}.\left(1+\frac{L_f-L_{fo}}{R_{peff}}\right)^2.\left(2.\frac{L_f-L_{fo}}{R_{peff}}+3\right)\right] \qquad 5.9$$

5.2.2 Model validation with the experimental data

The model was checked with two sets of column data (the conditions of the biofilter column experiments are given in Table 5.7). The model parameters are summarised in Table 5.8. The experimental and model results are given in Figure 5.8. The drops in the model curve represent the backwash period.

Table 5. 8 Parameters used for model simulation of GAC biofilter

Physical and Biological Parameter	Exp 1	Exp
Diffusion coefficient, D_f (m^2/s)	$9.978x10^{-13}$	$4.339x10^{-13}$
Film mass transfer coefficient, K_f (m/s)	$9.86x10^{-6}$	$1.223x10^{-6}$
Solid mass transfer coefficent, k_s (1/s)	$9.68x10^{-6}$	$1.152x10^{-6}$
Biomass density, X_f (mg/L)	$8.53x10^{3}$	$2.532x10^{3}$
Yield coefficient, Y (mg/mg)	0.086	0.086
Decay coefficient, K_d (s^{-1})	$1.017x10^{-7}$	$6.157x10^{-7}$
Biofilm thickness, L_{f0} (m)	$1.0x10^{-6}$	$1.0x10^{-6}$
Suspended cell concentration, X_s (mg/L)	$1.0x10^{-08}$	$1.0x10^{-08}$
Shear Loss, σ (s^{-1})	$2.346x10^{-7}$	$6.596x10^{-7}$
Maximum rate of substrate utilization, K_{max} (s^{-1})	$1.605\ x10^{-4}$	$1.605\ x10^{-4}$
Monod half velocity coefficient, K_S (mg/L)	0.238	0.238
k value in Freundlich biofilter (eq 5.7)	0.084	
n value in Freundlich biofilter (eq 5.7)	1.726	

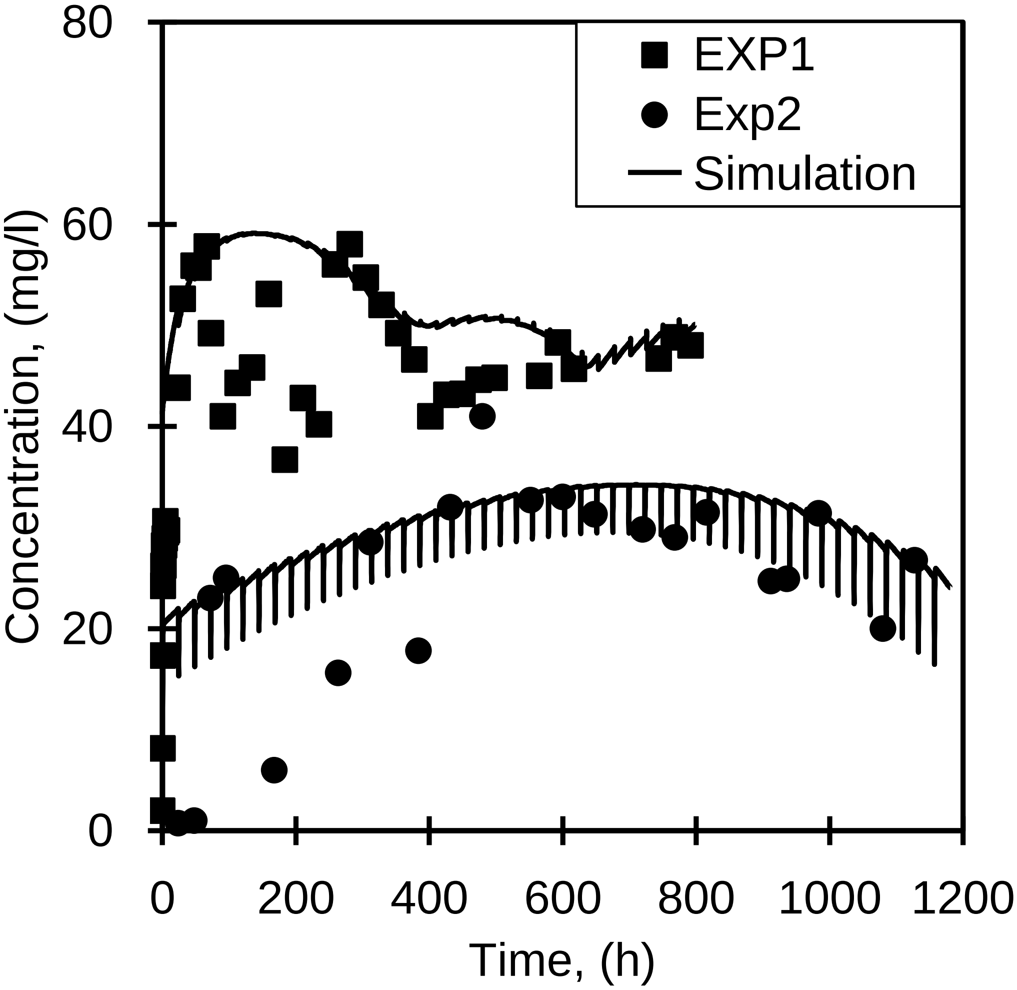


Figure 5. 8 Performance of GAC-packed biofilters with time for 60 days in SLL,

Also shown is the fit between experimental data and model simulation in the long term for variation in bed depth. (Experimental conditions are summarised in Table 5.7, model parameters are summarised in Table 5.8)

5.2.3 Summary

The GAC biofilter was found to remove a significant amount of organic matter from the diluted synthetic landfill leachate. The experiments were conducted at low (0.2 m/h) and high (2 m/h) flow velocity through the GAC filter to represent insitu and exsitu biofiltration. The results show that organic matter can be removed in a consistent manner for a long period of time. GAC bio-filtration led to a consistent TOC removal even after a long period of operation without the need to regenerate the activated carbon. Even after 30-50 days of continuous running, the organic removal efficiency from the GAC bio-filter was approximately 40% and 60% when high (2 m/hr) and (0.2 m/hr) low filtration velocities were used. It should be noted that the performance can be enhanced by using a larger filter depth which is the case in real situations.

5.3 Removal of stormwater pollutants using sand, GAC and Purolite filters in series

A few experiments were performed with sand, GAC and purolite filters in series to study the effect of simultaneous removal of solids, organics, heavy metals and nutrients.

5.3.1 Experimental methods

The stormwater collected from a stormwater channel at Carlton, in Kogarah, Sydney had the physical and chemical characteristics as shown Table 3.1. In this study, filtration experiments were conducted using three transparent acrylic filter columns in series (Figure 5.9).

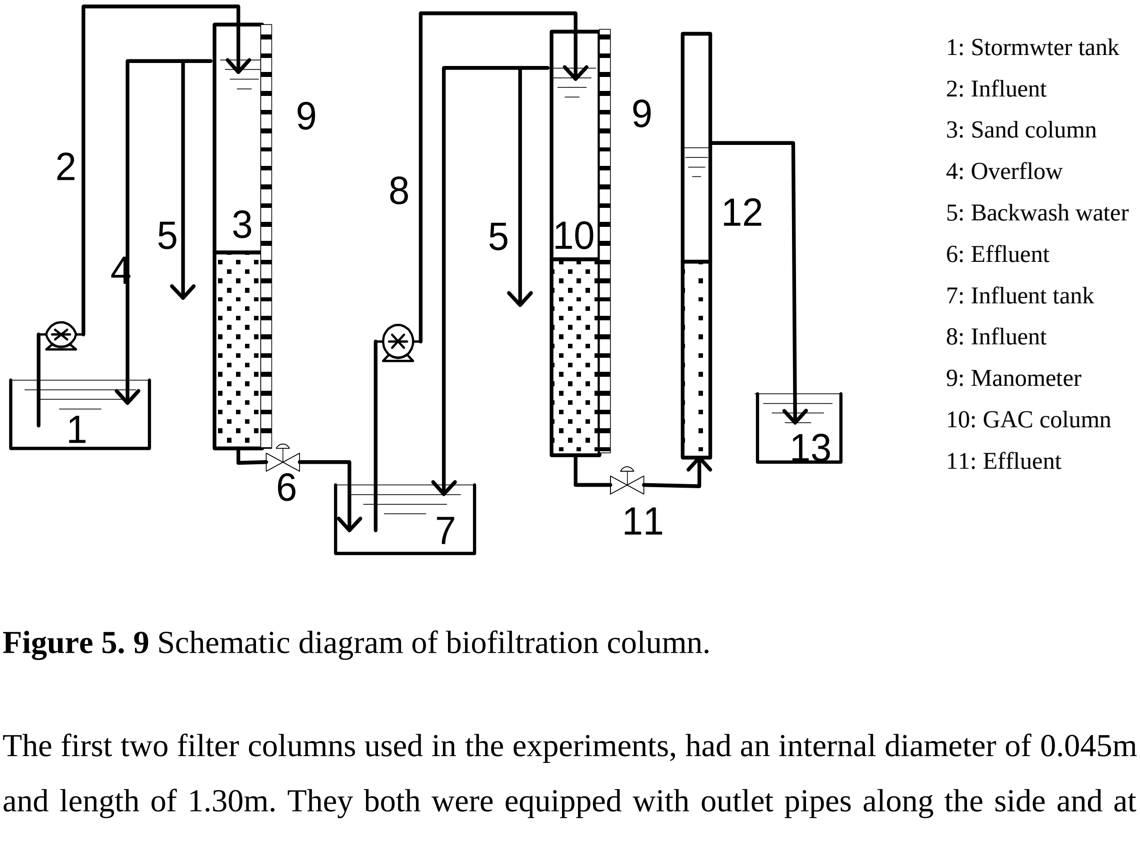


Figure 5. 9 Schematic diagram of biofiltration column.

The first two filter columns used in the experiments, had an internal diameter of 0.045m and length of 1.30m. They both were equipped with outlet pipes along the side and at the bottom of the columns. Prepared filter media of sand and (GAC) were packed in the columns up to a depth of 1m each. The sand and GAC filters were used mainly to remove solids and organics respectively. The columns were operated in down flow mode. Feed water was pumped from a feeding water tank to the top of the sand column passed through the filter bed, and then the effluent was fed to the GAC column as shown in figure 5.9. The filtrates were collected at the bottom of the columns for analysis on a velocity of 1m/h. The third filter column had an internal diameter of 0.02m and length of 0.50m. This filter was packed with Purolite in the columns up to a depth of 0.25m, and this column was operated in up flow mode. The effluent of the GAC column filter was pumped to the bottom of the Purolite column and then passed through the filter bed, at a velocity of 5m/h.

The properties of the sand and Purolite A-520E are shown in Tables 5.9 and 5.10. The properties of GAC are presented in Table 3.3 in chapter 3.

Table 5. 9 Properties of sand

Sand	
Specification	Estimated Value
Effective Size (mm)	0.55-0.65
Bulk Density (kg/m^3)	1500
Uniformity Coefficient	<1.5
Acid Solubility	<2%

Table 5. 10 Physical properties of Purolite A-520E

Purolite A-520E	
Polymer Matrix Structure	Macroporous Styrene-Divinyl benzene
Physical Form and Appearance	Opaque Cream Spherical Beads
Whole Bead Count	95% min.
Bulk Density (kg/m^3)	680
Screen Size Range:- U.S. Standard Screen	16- 50 mesh, wet
Particle Size Range	+1200 mm <5%, -300 mm <1%

5.3.2 Results and Discussion:

Turbidity removal: Figure 5.10 presents the variation of turbidity of the sand and GAC filters. Raw water turbidity was highly variable in the range of 3-70 NTU. Table 5.11 shows the turbidity removal efficiency of the filters operated with 1m heights and the filtration velocities of 1m/h. The best turbidity removal efficiency was observed using the sand filter medium of up to 70% followed by an additional 43% using the GAC filter medium.

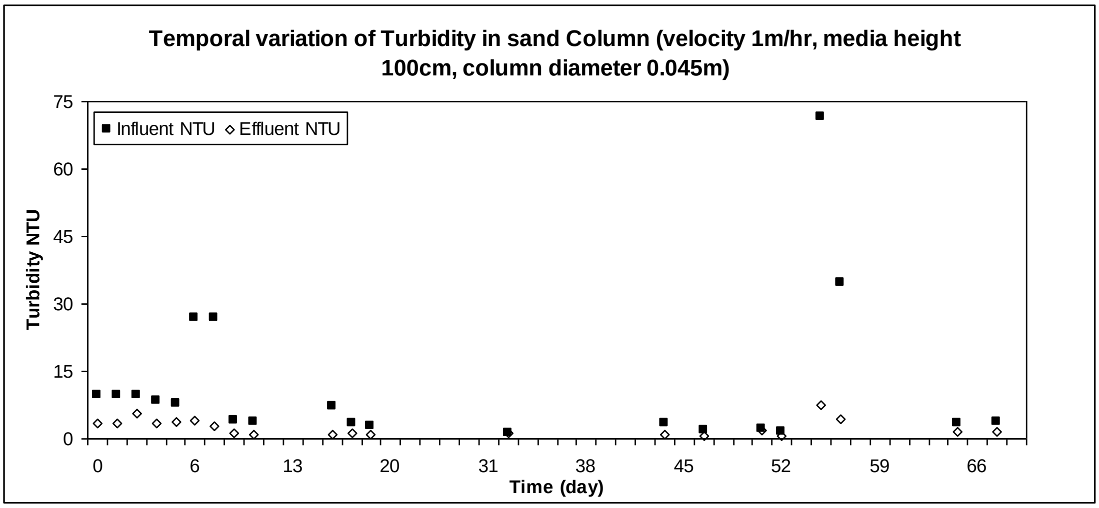


Figure 5.10a, Column backwashed three times only.

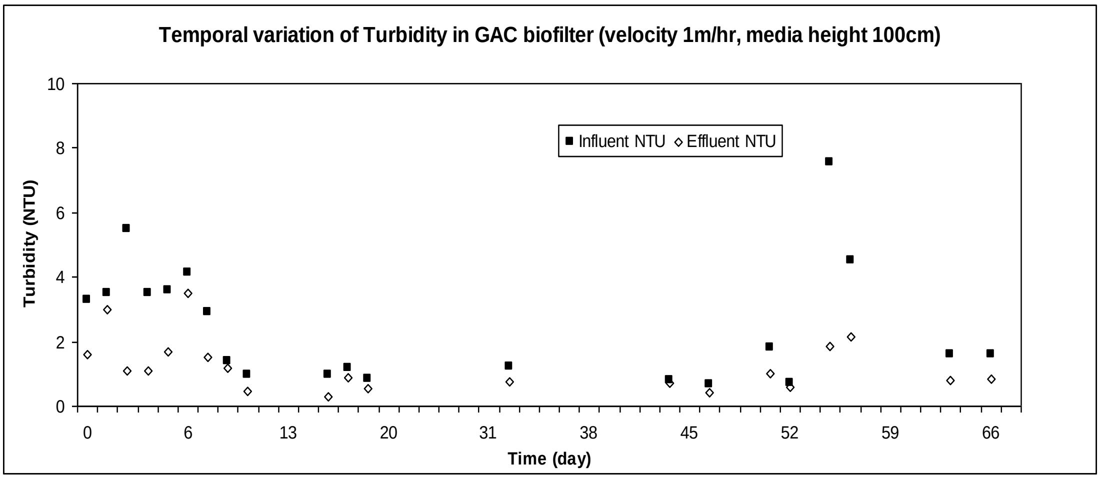


Figure 5.10b, Column backwashed three times only.

Figure 5. 10 (a and b) Effect of filter operating parameter on turbidity removal (raw water turbidity=3-70 NTU; v=velocity)

Table 5. 11 Turbidity removal efficiency

Media	**Velocity (m/h)**	**Media Height (m)**	**Days of Operation**	**Initial turbidity to the filter**	**Average Turbidity Removal efficiency (%)**
Sand	1	1	70	3 - 70	70
GAC	1	1	70	0.7 - 7.5	43

Headloss development: Figure 5.11 shows the headloss development profile of the biofilters as a function of time. The head loss variation was 4 to 13 cm and 6 to 100 cm for GAC & sand respectively. The sand filter had a higher headloss development due to the higher influent turbidity. It should be noted that filters were backwashed only three times during the 70 days of operation as indicated in figure 5.11.

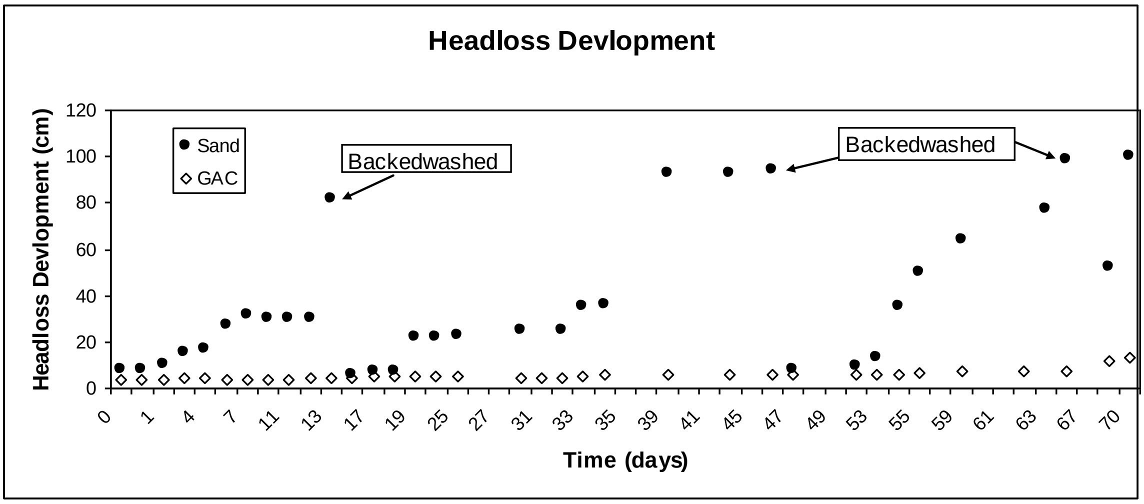


Figure 5. 11 Headloss development profile of GAC and sand biofilters

Total Organic Carbon (TOC) removal efficiency: The TOC removal efficiency by different media is presented in Tables 5.12. The highest TOC removal efficiency of almost 99% was achieved using the GAC media, GAC working as adsorbent and as boifilter.

Table 5. 12 TOC removal efficiency (raw water TOC 3.0-5.2 mg/L, empty bed contact time (EBCT) 1h)

Media	**Velocity (m/h)**	**Media Height (cm)**	**Days of Operation**	**Initial DOC**	**Average TOC Removal efficiency (%)**
Sand	1	100	70	3-4	6
GAC	1	100	70	3-4	99

Total organic carbon (TOC) variation of the stormwater and filtered effluent are presented in Figures 5.12 and 5.13. Also presented is the TOC removal efficiency in Figure 5.14. It can be seen that TOC removal was much higher (almost perfect) for the GAC filter compared with the sand filter.

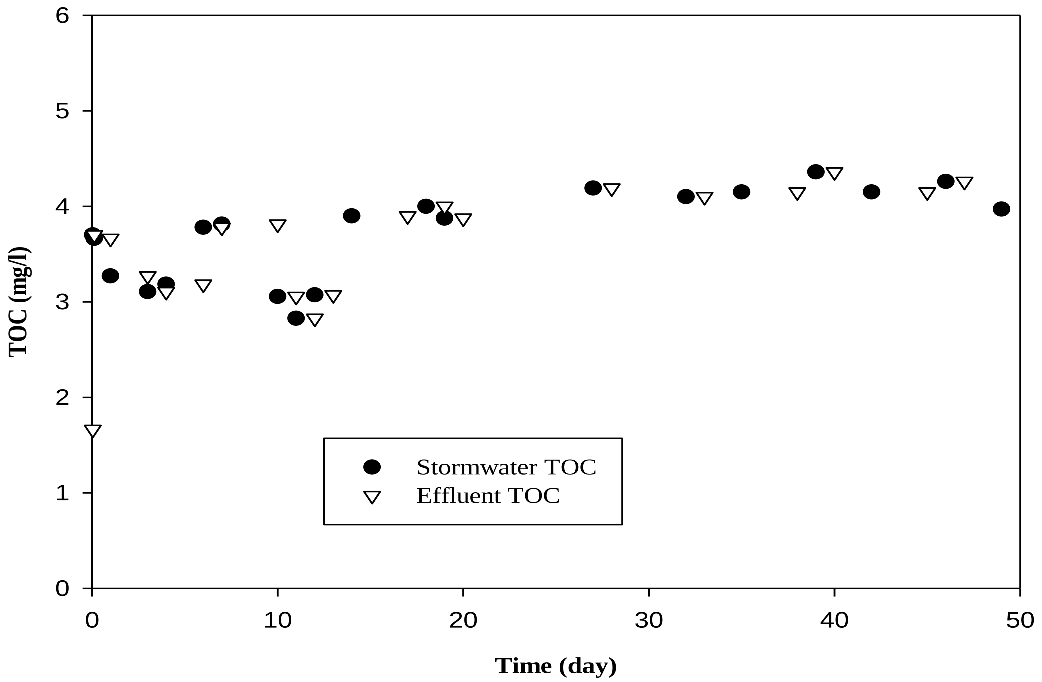


Figure 5. 12 Total organic carbon removal using sand filter media (velocity 1m/h, media height 100cm (EBCT) is 1h)

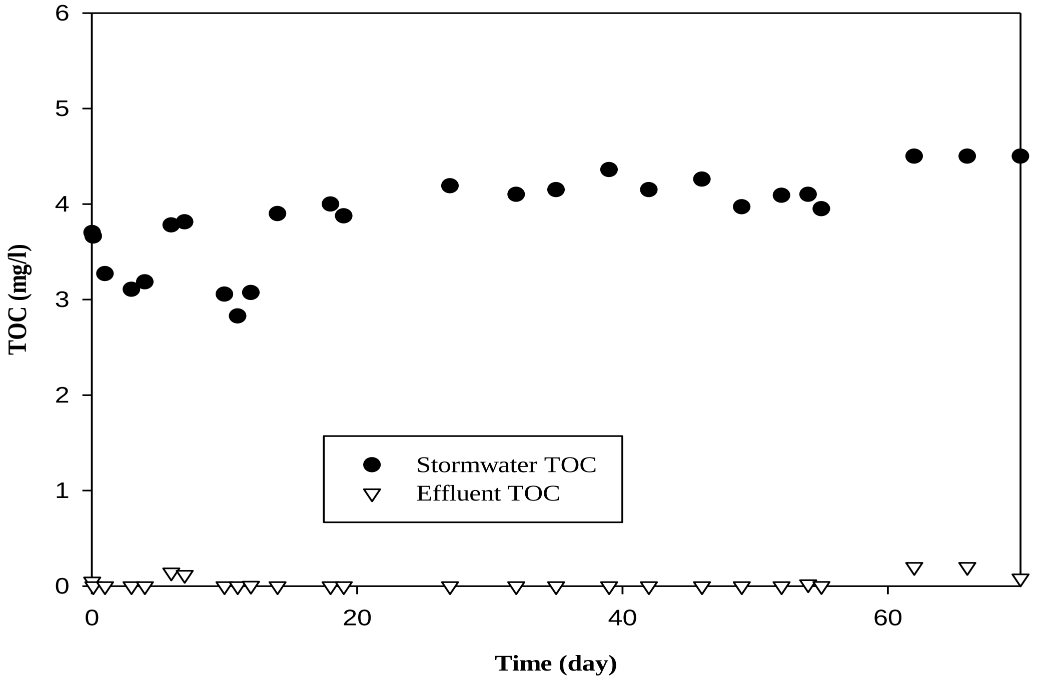


Figure 5. 13 Total organic carbon removal using GAC filter media (velocity 1m/h, media height 100cm (EBCT) is 1h)

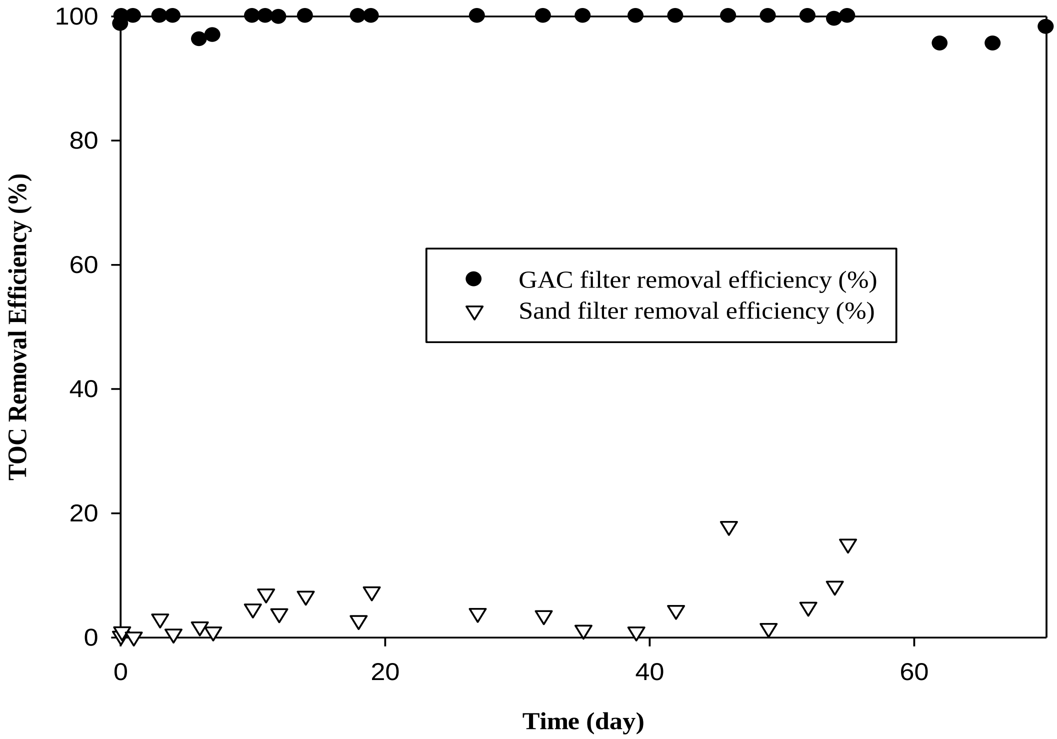


Figure 5. 14 TOC removal using GAC and sand filter media.

Nutrient removal efficiency: when using the Purolite A520E the removal efficiency of the nitrate (NO_3^{-N}) reached 89% within 6 hours, and then gradually decreased as shown in figure 5.15. Purolite A520E is a nitrate selective ionic exchange medium (Bae et al., 2002; Samatya et al., 2006a; Samatya et al., 2006b) However, as can be seen from Figure 5.15, the medium became exhausted within 48 hours and warranted frequent regeneration.

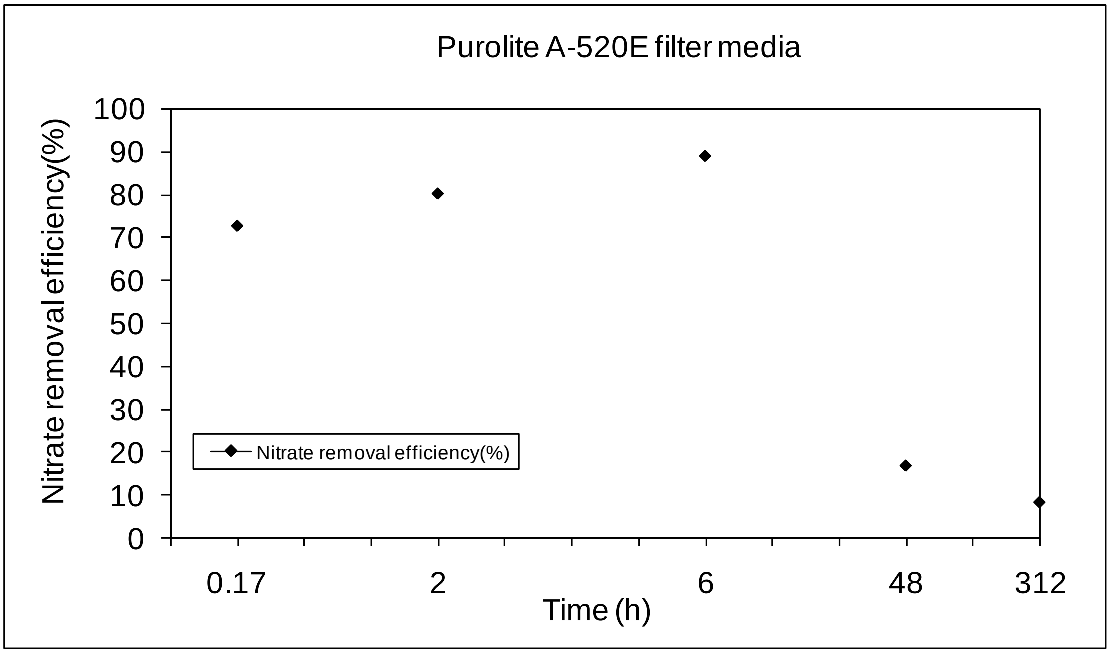


Figure 5. 15 Nutrient removal efficiency for Purolite A-520E, media height 24cm, velocity=5m/h.

5.3.3 Summary on the three stage filter

In this study, different filter systems that could be used for stormwater pollution control were tested. The main conclusions were:

- The highest TOC removal efficiency of up to 99% was achieved by the second stage GAC media filter and, the first stage sand filter achieved only 6% of the TOC removal.
- A major removal of turbidity of up to 70% was achieved by the sand media filter and, the second stage GAC filter resulted in an additional removal of 43%.
- Headloss variation was high for the sand filter as it encountered a high turbid stormwater.
- The use of the PuroliteA520E filter media was capable of removing up to 89% of nitrate within 6 hours, however no phosphate removal was achieved. Thus it is vital to have GAC and Purolite as a media in filtration systems along with sand to achieve organic and nutrient removal.

Chapter 6

6. Different media

6.1 Removal of Cd, Cu, Ni, Se, and Zn by a hydrous ferric oxide from polluted stormwater: intermittent runoff column kinetics

6.1.1 Introduction

Urban stormwater runoff consists of different types of heavy metals such as cadmium (Cd), copper (Cu), nickel (Ni), and zinc (Zn) and oxy anions such as selenate (SeO_4^{2-}) all of which are environmental contaminants of concern. These contaminants are derived from a variety of sources such as roof, road, building materials (Herngren and Goonetilleke 2006: Wahlin et al. 2006; Gobel et al. 2007) and are a leading cause of degradation of urban waterways due to their toxic and persistent nature. If stormwater is discharged directly into natural water bodies, these non-biodegradable contaminants can accumulate in the environment, causing both short-term (acute toxicity) and long-term (chronic toxicity) adverse effects on the environmental ecosystem. Some of these contaminants are essential nutrients (e.g. Cu, Zn, Se) to plants, animals and humans but at elevated concentrations they can be toxic. Others are not essential nutrients (e.g. Cd, Ni) but can be toxic to plants, animals and humans at high concentrations.

Treatment of urban stormwaters before entering the water bodies is regulated by legislation in different parts of the world. There is a broad range of treatment practices to remove pollutants from these waters. Among them, physical/chemical processes (sorption, filtration, ion-exchange, membrane systems etc.) are the most common. Sorption encourages researchers and water treatment operators to use easily available and low-cost materials as sorbents to treat contaminated water. Such materials include sand and sorbents prepared by coating sand, zeolite (Pitcher et al. 2004; Rangsivek and Jekel 2005; Pan et al. 2010) and natural materials such as iron, aluminium and manganese oxides (Trivedi and Axe 2000). Among the various naturally available cost effective sorbents, hydrous ferric oxide (HFO) is recognised as one of the most promising sorbent in the removal of heavy metals and oxy anions (Davies and Leckie 1978; Fukushi and Sverjensky 2007; Genc-Fuhrman et al. 2008) due to its surface complexation as well as surface precipitation with cations and anions (Farley et al. 1985; Dzombak and Morel 1986; Spadini et al. 2003). Most of the sorption studies on HFO have been limited to batch experiments and individual sorbents. A long term study of the simultaneous removal of several coexisted contaminant cations and anions on HFO in intermittent runoff conditions as occurring in natural field conditions between rainfall events has not been reported so far.

The objective of this work was to study the combined removal of coexisting heavy metals, Cd, Cu, Ni, and Zn and an oxy anion of Se in stormwater runoff and provide an overall assessment of the pollutant removal behaviour of HFO in a column experiment under intermittent elution condition simulating the natural runoff in the field situation between consequent rain events at the laboratory scale for a longer term.

6.1.2 Experimental

The experimental set up of this work was described earlier in chapter 3 Section 3.3.

6.1.3 Results and discussion

Sorption kinetics

The sorption of the contaminant ions in the column was different among the ions in all seven runs (Figure. 6.1). The C/C_0 values (C, ion concentration in the effluent; C_0, ion concentration in the influent) were below 1 for all the ions, except for Se at the 5th,6th and 7th runs where full breakthrough of the ion ($C/C_0 = 1$) was observed towards the end of these runs. This shows that the column has high affinity for the heavy metal cations and low affinity for the selenate anion. However, during the first one hour of the first run a large proportion of all the contaminant ions (including Se) were removed due to the presence of a high proportion of available sorption sites in HFO for these ions.

The order of decreasing removal efficiency in the 1st, 2nd and 3rd runs was Cu, Zn > Cd > Ni, Se and in the 5th, 6th and 7th runs it was Cu, Zn, Cd > Ni > Se (Table 6.1). Selanate ion sorption on iron oxides is considered to be low at neutral and alkaline pHs and high at acidic pHs (Fukushi and Sverjensky 2007; Rovira et al. 2008) due to a decrease in positive charges on the iron oxide surface and a decrease in the proportion of the strongly sorbing $HSeO_4^-$ species (increased proportion of the weakly sorbing SeO_4^- species) at neutral to alkaline pHs. This could be the reason for the low sorption of Se from the stormwater of close to neutral pH (pH 6.8) used in this study.

In contrast to selenium (Se) which is present in solution as an anion, the heavy metals tested in this study were present as cations and therefore their sorption is expected to increase with pH. At the pH of 6.8 of the stormwater these heavy metals are strongly sorbed to HFO because a significant proportion of these metals hydrolyse at this pH to produce metal hydroxide species (MOH^+, M = metal) which have much stronger sorption affinity to the oxide than the free divalent metal ions (M^{2+}) that are present at low pHs (Loganathan et al. 2011). The affinity of the heavy metals to iron oxides at pHs close to neutrality depends on the ease with which the metals hydrolyse in solution (first hydrolysis constant of the metal) (Forbes *et al.* 1976). Based on the respective first hydrolysis constants the metal affinity to iron oxides is expected to increase in the order Cd < Zn <Ni < Cu. However, Cornell and Schwertmann (2003) compared some published data of metal sorption to goethite and reported that the sorption capacity increases in the order Ni < Cd < Zn < Cu indicating that Ni sorption on iron oxides is the lowest. McKenzie (1980) also showed that Ni sorption on hematite and goethite was lower than that of Zn and Cu (Ni < Zn < Cu). The results of the current study conform to the orders of sorption capacity obtained in the above studies.

Another reason for the higher removal efficiency of Zn and Cu compared to the other ions is that the concentrations of Zn and Cu ions in the stormwater used in the study were much higher than the other ions (40 times for Zn and 12 times for Cu compared to other ions). Although the concentration of Zn in the stormwater was approximately 3 times higher than that of Cu, its removal efficiency is lower. This is probably due to the lower affinity of Zn to HFO than Cu (McBride 1989).

The removal efficiency of Zn and Cu, the ions which had the highest efficiency at the start, decreased with time. This is probably because with increased loading of the sorption sites with these ions, the ratio of the solid phase to solution phase concentration of these ions increased and this may have reduced the subsequent sorption of these ions to maintain mass action equilibrium. The reduced rate of sorption could also be due to increased unfavourable interactions between identical ions sorbed at high loadings.

The data suggests that contaminants removal could be more effective in intermittent runoffs than in continuous runoffs. In each continuous run the amount of ions removed decreased with time and reached a constant level at approximately 4-6 hrs. But stopping the runoff for 40 h and starting the next runoff after this period removed a large quantity of contaminants in the first few hours of the run (Figure. 6.1). This may be due to diffusion of the sorbed ions from the surface to the interior of the HFO structure during the 40 h of the no-elusion period and exposing the HFO surface sites made vacant for further sorption. Trivedi and Axe (2000) showed that sorption of metal ions on hydrous metal oxides is a two-step process: a rapid sorption of ions to the external surface of the oxides within a few hours followed by slow intraparticle diffusion along the micropore walls.

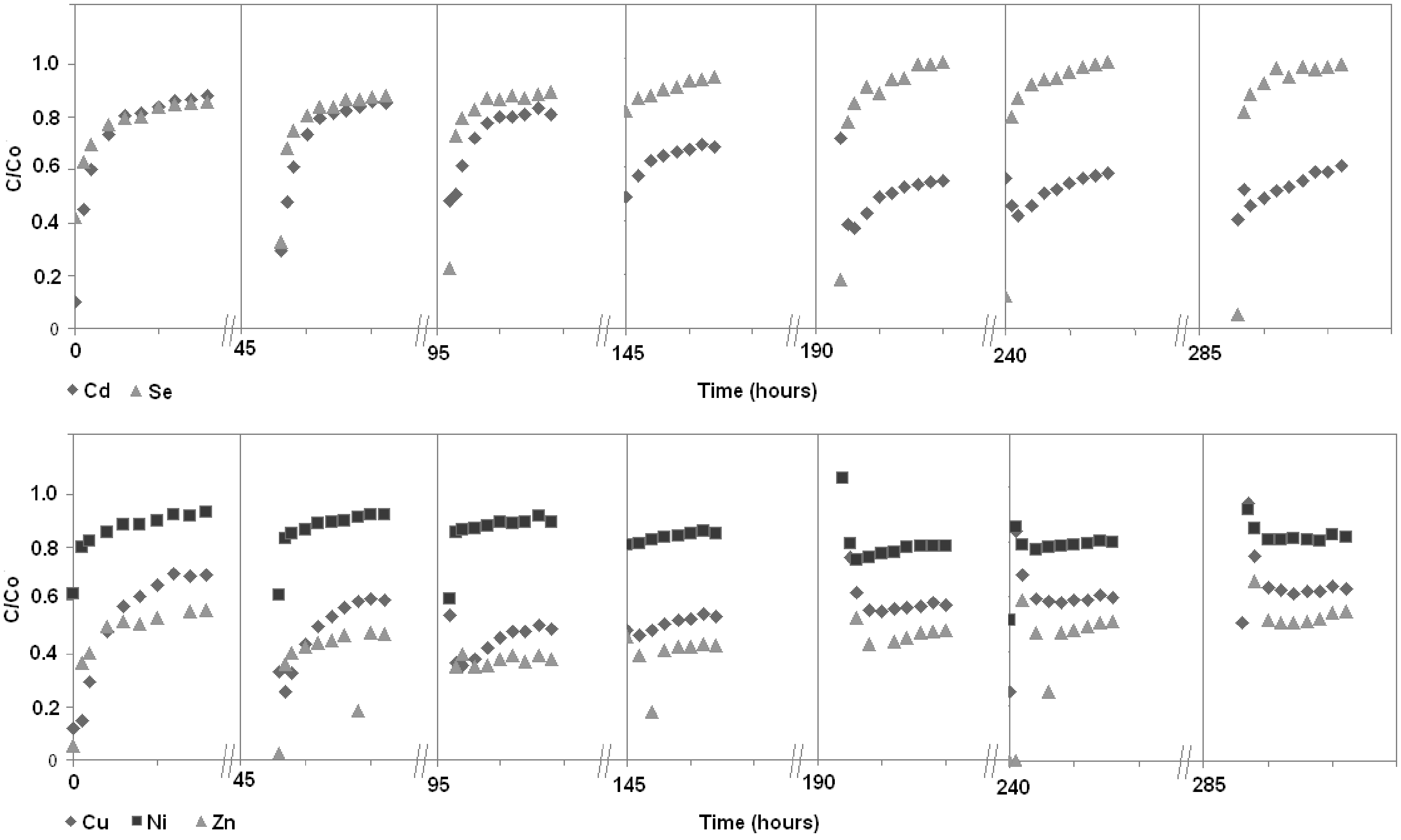


Figure 6. 1 Kinetics of sorption of contaminant ions in HFO column at different runs

Table 6. 1 Contaminant ions removal efficiency* of HFO in intermittent column runs

	Run 1	**Run 2**	**Run 3**	**Run 4**	**Run 5**	**Run 6**	**Run 7**
Cd	21	23	25	37	50	48	47
Cu	42	49	56	49	42	39	36
Ni	11	12	13	18	23	21	19
Se	20	18	17	12	8	8	8
Zn	45	54	63	59	55	49	44

*Removal efficiency = $\sum_{\text{time}=\ 0\ \text{to}\ 8\text{h}}$ (influent ion concentration – effluent ion concentration)/influent ion concentration.

Contaminant ions removal in distilled water wash

The cumulative amounts of contaminant ions removed from the column in distilled water wash after the 1st run were less than 2-5% of the respective amounts sorbed in this run for all ions except Ni where the percentage was 15% (Table 6.2). The ions removed in the wash were those in the pore solutions and those loosely held on the HFO surface. The results show that all ions are strongly sorbed in the column. Ni removal in the wash was the highest most likely because this ion was weakly sorbed to HFO.

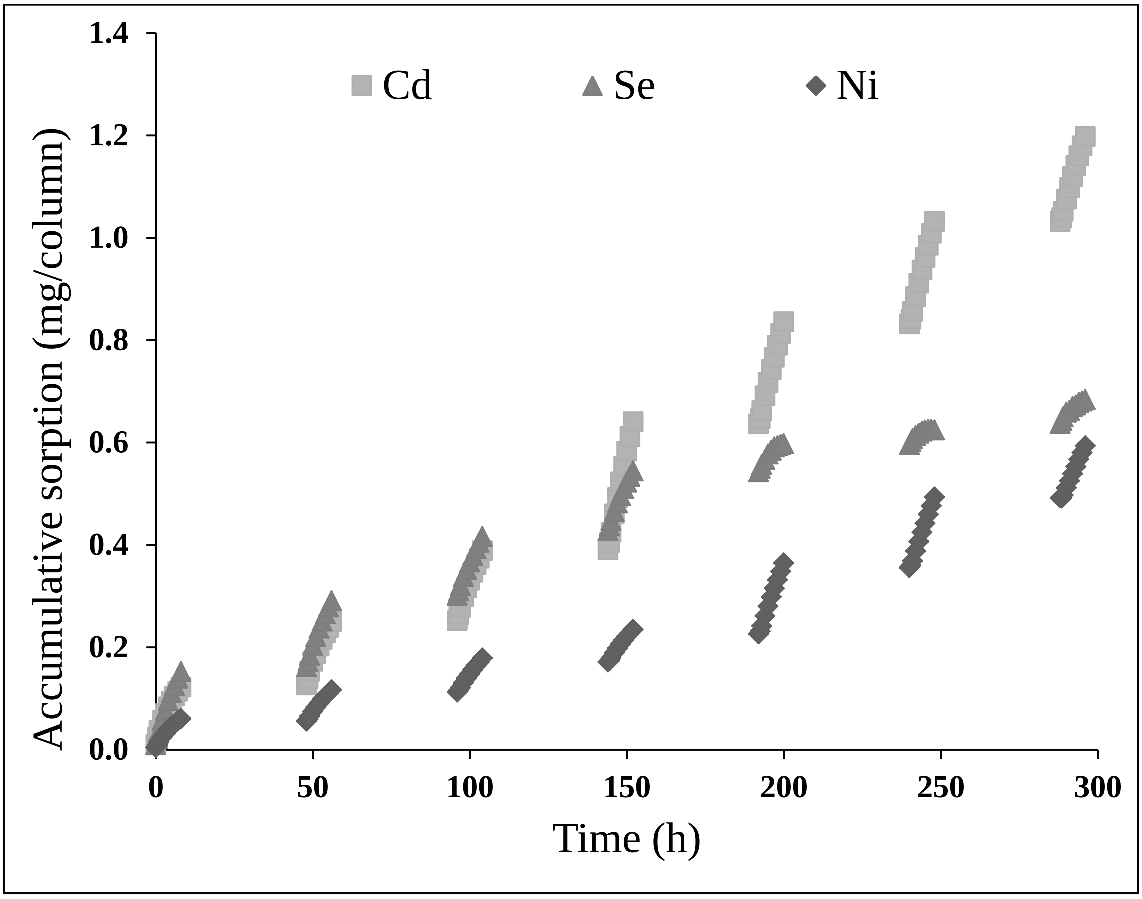
Table 6. 2 Cumulative amounts of contaminant ions removed from the column in distilled water wash after the 1st run and amount sorbed in the column after run 1.

Cumulative amounts (mg) eluted in distilled water wash after 1st run					
Time (min)	**Cd**	**Cu**	**Ni**	**Se**	**Zn**
10	0.0006	0.0071	0.0011	0.0003	0.0312
30	0.0024	0.0300	0.0047	0.0011	0.1356
60	0.0033	0.0398	0.0064	0.0014	0.1879
120	0.0046	0.0549	0.0090	0.0018	0.2697
Accumulated amounts sorbed (mg) in the column in 1st run					
	0.1223	1.449	0.0602	0.1526	10.74

Cumulative amounts of contaminants removed in column

The cumulative amounts (mg) of contaminant ions removed in the seven runs are shown in Figure 6.2. They were 62.22, 8.64, 1.20, 0.69 and 0.60, for Zn, Cu, Cd, Se and Ni, respectively. The relative amounts removed were generally in proportion to the concentration of the ions in the stormwater, except that the amount of Cd removed was twice the amounts of Ni and Se despite the concentration of these three ions in the stormwater being the same. This is probably because HFO has a higher affinity for Cd than the other two ions as discussed earlier in this paper. The cumulative sorption data also show that at the 7th run the sorption of Zn and Cu, the ions with the highest concentration in stormwater, has reached saturation showing that no significant amounts of these ions can be sorbed any more on the HFO. This is because the solution concentrations of these two ions have reached equilibrium with the sorbed ions and also there might have been unfavourable interactions between the closely spaced adjacent ions on the HFO surface.

The total amounts of contaminant metals (Cd, Cu, Ni, Zn) sorbed in the column was 72.66 mg indicating a sorption density of 72.66 mg in 8.7 g HFO or 8.3 mg/g HFO which is much lower than the maximum capacity of sorption of heavy metals on HFO (Sen et al., 2002). The remaining sorption sites on HFO would probably be used to remove Ni, Cd and Se in the subsequent runs as these ions had not reached the saturation point. The cumulative sorption curves for these three ions show signs of continued increase even after the 7th run (Figure. 6.2).



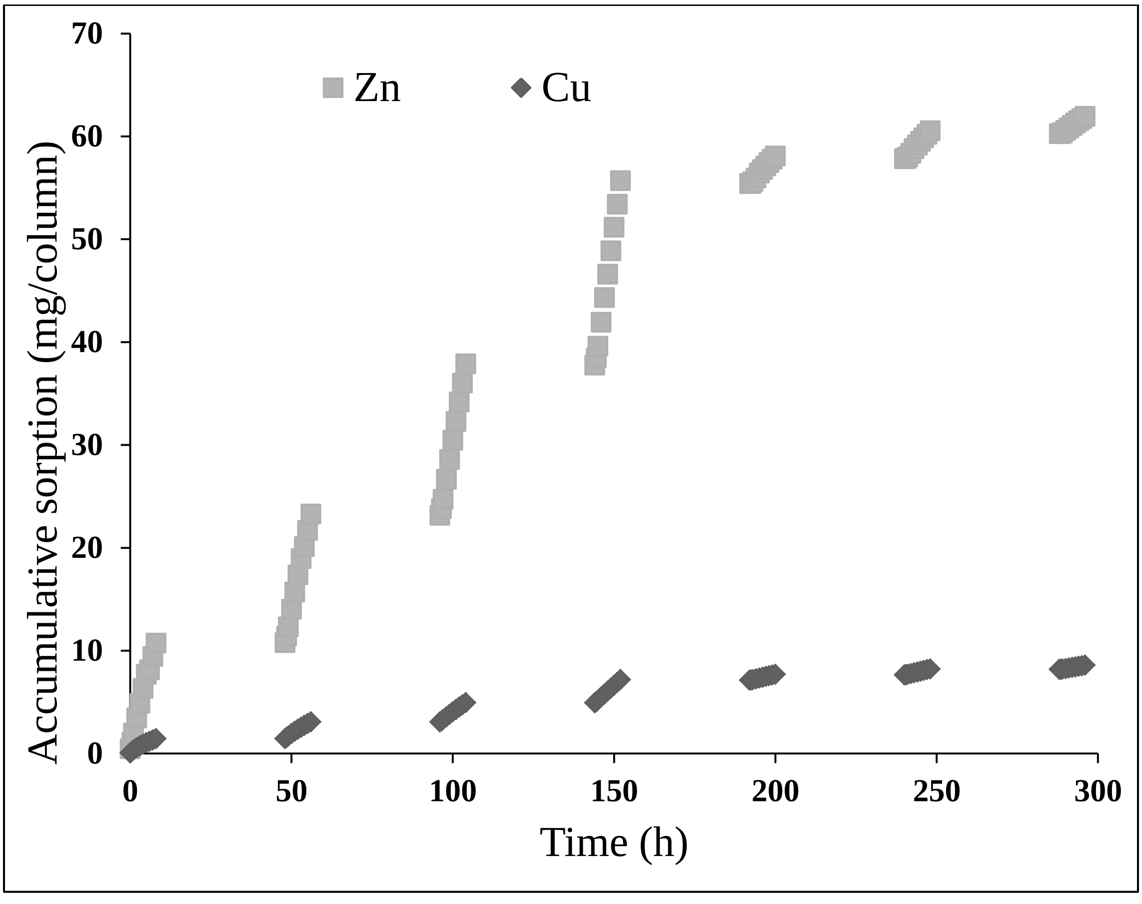


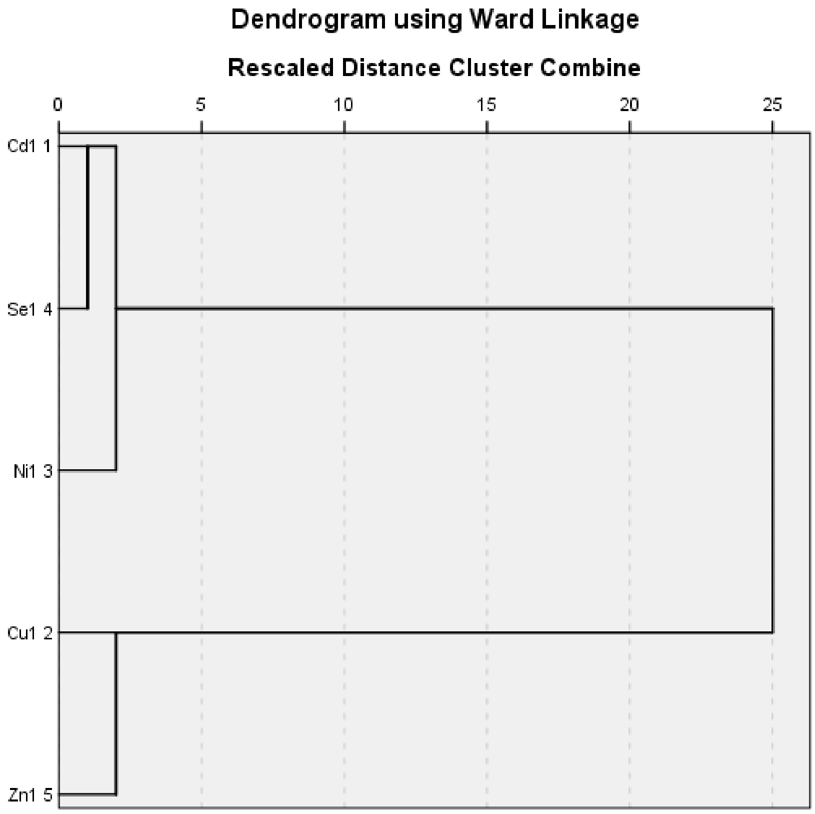
Figure 6. 2 Cumulative amounts of contaminant ions sorption with time

Cluster analysis

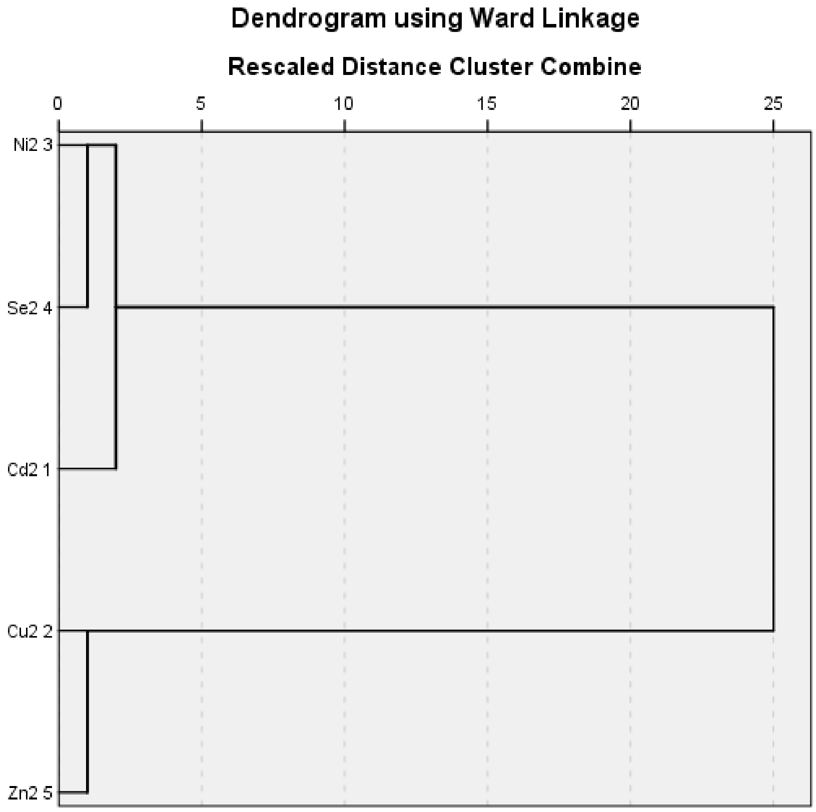
To differentiate the contaminant ion sorption behaviour quantitatively, cluster analysis was carried out for the 1st, 3rd, 5th and 7th runs. Cluster analysis is the grouping of a set of observations into subsets (called *clusters*) so that observations in the same cluster (subsets) are similar in some behaviour and closely related to one another than observations assigned to different clusters. In Cluster analysis, hierarchical clustering creates a hierarchy of clusters which may be represented in a tree structure called a dendogram. The distance between clusters is computed by Ward Linkage (to reduce sum of errors in a cluster) and Squared Euclidian distance (ordinary distance calculated by Pythagorean formula).

Figure 6.3 shows the dendogram obtained from cluster analysis for the individual runs. Similarities and dissimilarities in sorption can be seen in this figure. Among the contaminants, Cu and Zn formed one cluster whereas Cd, Se and Ni formed another cluster in runs 1 and 3. In runs 5 and 7, Cu, Cd and Zn formed one cluster whereas Ni and Se formed another cluster. As Cu and Zn have a higher affinity to HFO and present in higher concentrations compared with Ni, Cd and Se, possibly they form one cluster in run 1 and 3. However in run 5 and 7, as discussed earlier, with increased loading of the sorption sites with these metals the affinity of HFO for further sorption of these ions might have decreased, thus allowing the next metal of high sorption affinity (Cd) to be sorbed in higher quantities. This might have placed Cd along with Cu and Zn in one group in runs 5 and 7. These groupings are consistent with the changes in the order of contaminant affinity presented in the previous section.

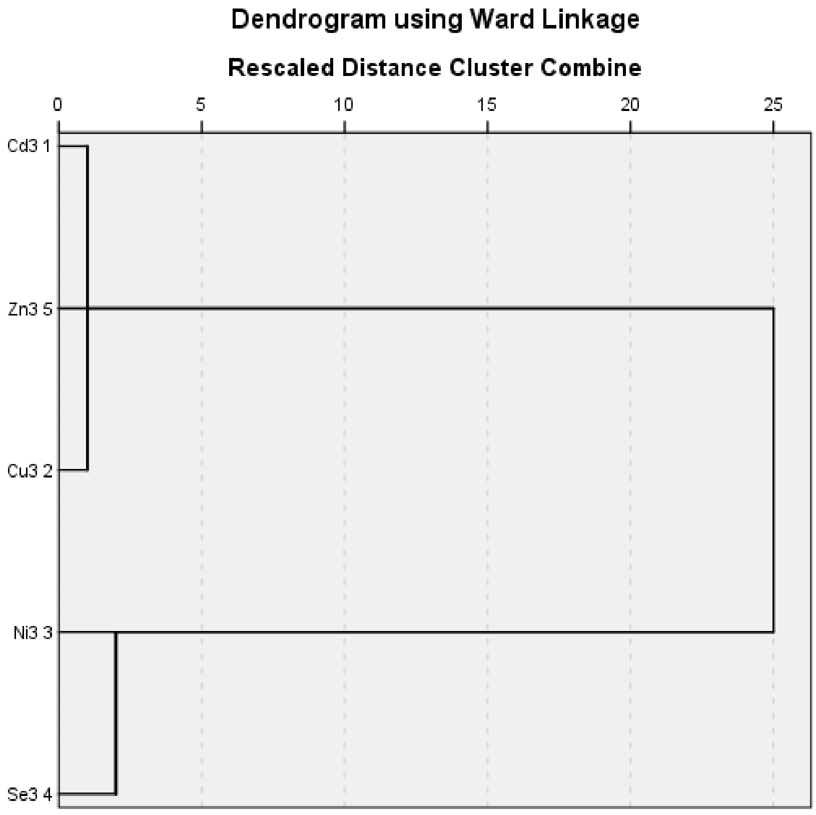
The result showed that the sorption of coexisted metals and oxyanions differ with time. Therefore a single kinetics measurement may not be applicable when working on natural intermittent runoff.


Dendrogram using Ward Linkage
Rescaled Distance Cluster Combine
0
5
10
15
20
25
Cd1 1
Se1 4
Ni1 3
Cu1 2
Zn1 5

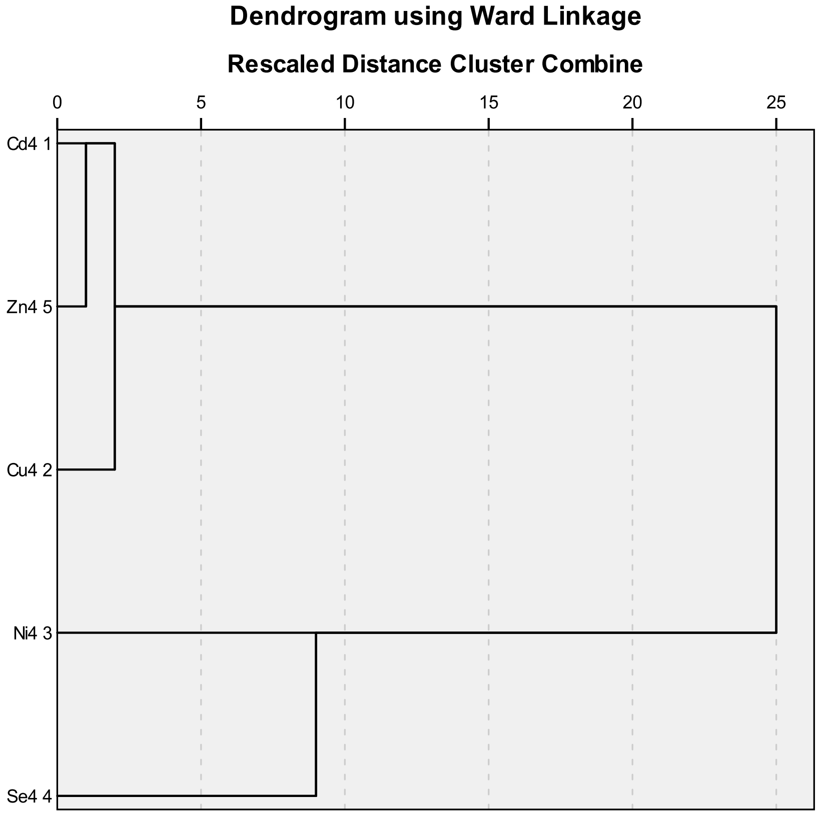
Run 1


Dendrogram using Ward Linkage
Rescaled Distance Cluster Combine
0
5
10
15
20
25
Ni2 3
Se2 4
Cd2 1
Cu2 2
Zn2 5

Run 3



Run 5



Run 7

Figure 6. 3 Cluster analysis presenting similarities and dissimilarities in sorption of contaminant ions in intermittent runs (Run1, Run 3, Run 5 and Run 7)

6.1.4 Summary

The column kinetics experiment showed that HFO is an effective sorbent in removing contaminant ions, especially Zn, Cd and Cu from stormwater over a long period. The intermittent conditions of runoff, each of 8 h duration followed by a 40 hr no-flow period could be more favorable for the removal process than the continuous removal process. The efficiency of removal for Cu and Zn was 42-63% for the first three runs and 36-59% for the last four runs. For Cd, Se and Ni the % efficiencies were 21-25, 17-20 and 11-13, respectively for the first three runs and 37-50, 8-12 and 18-23, respectively for the last four runs.

6.2 Removal of inorganic contaminants from simulated stormwater by three sorbents in columns under intermittent runoff condition

6.2.1 Introduction

Among the various naturally available cost effective sorbents, hydrous ferric oxide (HFO) is recognised as one of the most promising sorbents in the removal of heavy metals and oxy anions (Davies and Leckie, 1978; Fukushi and Sverjensky, 2007; Genc-Fuhrman et al., 2008) due to its ability for surface complexation as well as surface precipitation with cations and anions (Dzombak and Morel, 1986; Farley et al., 1985; Spadini et al., 2003). This sorbent was used to remove inorganic contaminants reported in section 6.1. Manganese oxides have also been considered the most important scavengers of heavy metals in aqueous solutions or wastewater due to their relatively high surface area, microporous structure, and presence of surface OH groups capable of reacting with heavy metals and, specifically sorbing anions (Han et al., 2006 a,b; Post, 1999; Trivedi and Axe, 2000; Young and Harvey, 1992). Lime and calcium carbonate have also been used to remediate ground water from heavy metals through the mechanism of “sweep precipitation” by coagulation, as a result of these materials increasing the pH. For example, Lee et al. (2007) reported that nearly 100% of Ni and Zn were removed by a column containing lime and suggested that the reason for this high removal efficiency was due to precipitation of these metals at high pH caused by the lime. Most of the sorption studies on metal oxides have been limited to batch experiments and individual sorbents. Long term studies of the simultaneous removal of several coexisted inorganic contaminant cations and anions from contaminated water by sorbents in intermittent runoff conditions as occurring in natural field conditions between consequent rainfalls are limited

The objective of this study was to compare the ability of three sorbents in the combined removal of coexisted heavy metals, Cd, Cu, Ni, and Zn and an oxy anion of Se in synthetic stormwater in a laboratory column experiment under intermittent elution conditions simulating the natural runoff in field situations.

6.2.2 Experimental

The experimental set up of this work was described earlier in chapter 3 Section 3.2. The three sorbents used in this study were hydrous ferric oxide (HFO), hydrous ferric oxide + calcium hydroxide ($CaOH_2$), and hydrous ferric oxide + calcium hydroxide + manganese oxide (MnO_2)

6.2.3 Results and discussion

6.2.3.1 Effect of flow rate on contaminants removal

The breakthrough curves (C/C_0vs time; C, ion concentration in the effluent; C_0, ion concentration in the influent) for all the contaminants at the flow rate of 0.75 m/h are presented in Figure 6.4. The breakthrough curves at the flow rate of 1.5 m/h had similar trends. The contaminants removal efficiencies of the sorbents in the three columns were calculated using the following equation.

$$\text{Removal efficiency} = Q \sum_{t=0.5}^{t=8} \left[C_o - \frac{C_{t-1} + C_t}{2} \right] \Delta t / C_o$$

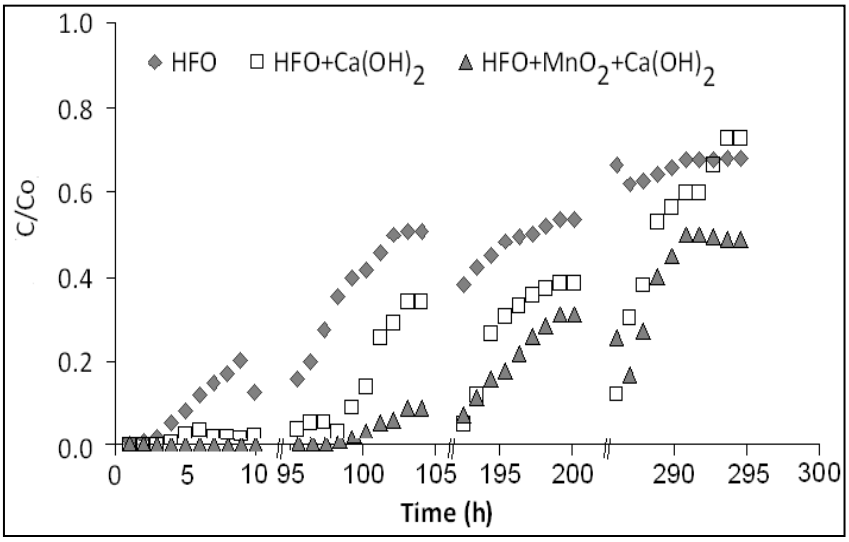
where Q = flowrate (L/h)

Co = influent concentration (mg/L)

C_t and C_{t-1} = effluent concentration (mg/L) at two consequent samplings

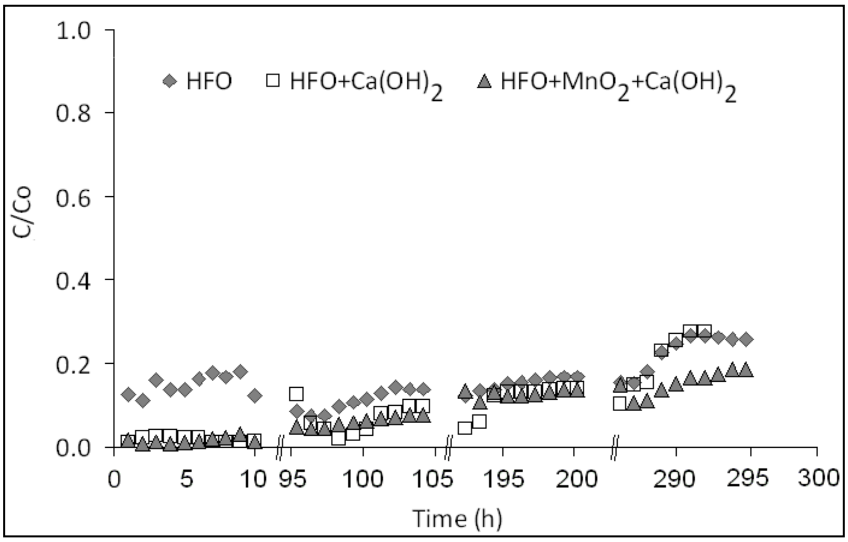
t = time at which removal efficiencies was calculated (h)

Δt = time interval between two consecutive samplings ($t_{(-1)}$ and t) (h)



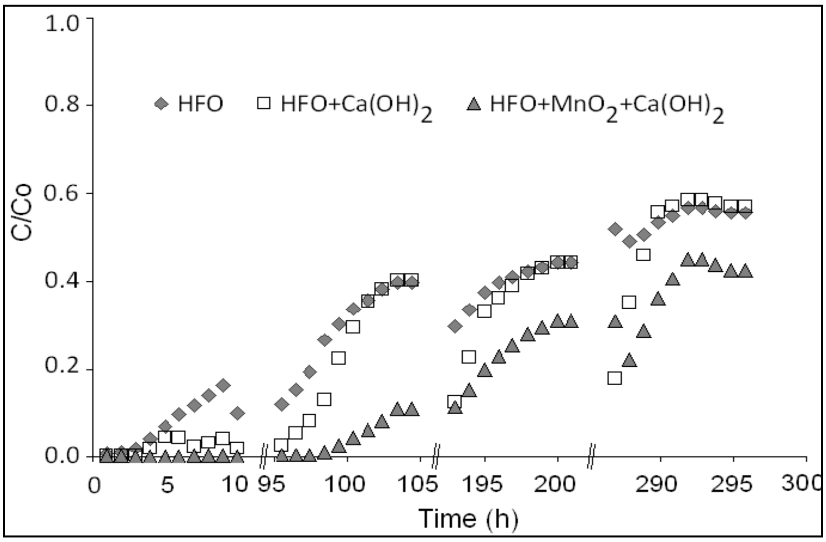
◆ HFO
□ HFO+Ca(OH)2
▲ HFO+MnO2+Ca(OH)2
C/Co
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
95
100
105
195
200
290
295
300
Time (h)

(a) Zn



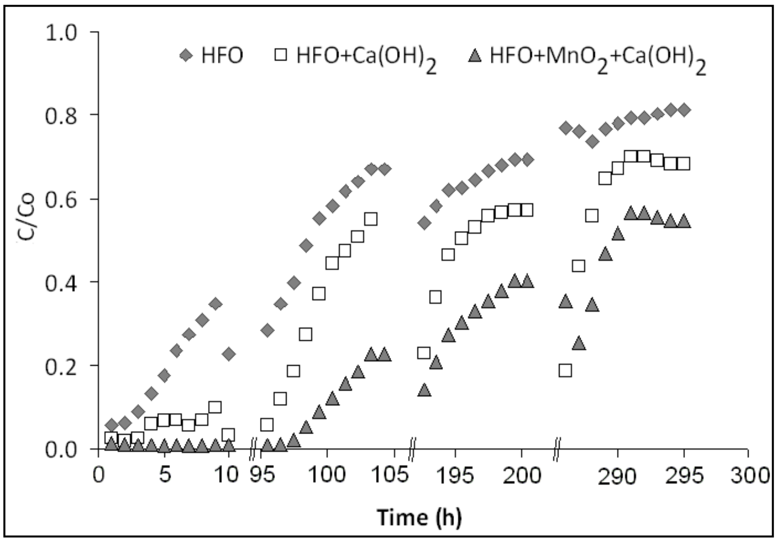
◆ HFO
□ HFO+Ca(OH)2
▲ HFO+MnO2+Ca(OH)2
C/Co
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
95
100
105
195
200
290
295
300
Time (h)

(b) Cu

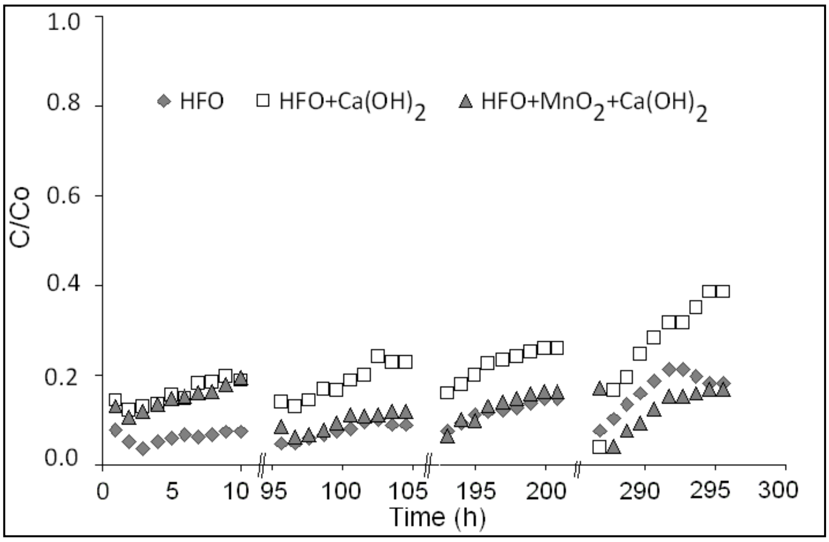


◆ HFO
□ HFO+Ca(OH)2
▲ HFO+MnO2+Ca(OH)2
C/Co
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
95
100
105
195
200
290
295
300
Time (h)

(C) Cd



(d) Ni



(e) Se

Figure 6. 4 (a-e) Breakthrough curves at 0.75m/h flowrate

The removal efficiencies were higher with the lower flow rate than with the higher flow rate in all columns (Figure. 6.5-6.9). The reason for this is that the retention time of the contaminants at the low flow rate was greater than the retention time at the high flow rate in the columns, and the supply speed of contaminant ions to column was lower resulting in higher removal efficiency. A similar outcome was obtained by Han et al. (2006b) in their study of Cu and Pb removal by manganese oxide coated zeolite. They used three flow rates (5.45, 7.69 and 10.0 ml/min) and concluded that the breakthrough time reaching saturation was increased significantly with a decrease of flow rate.

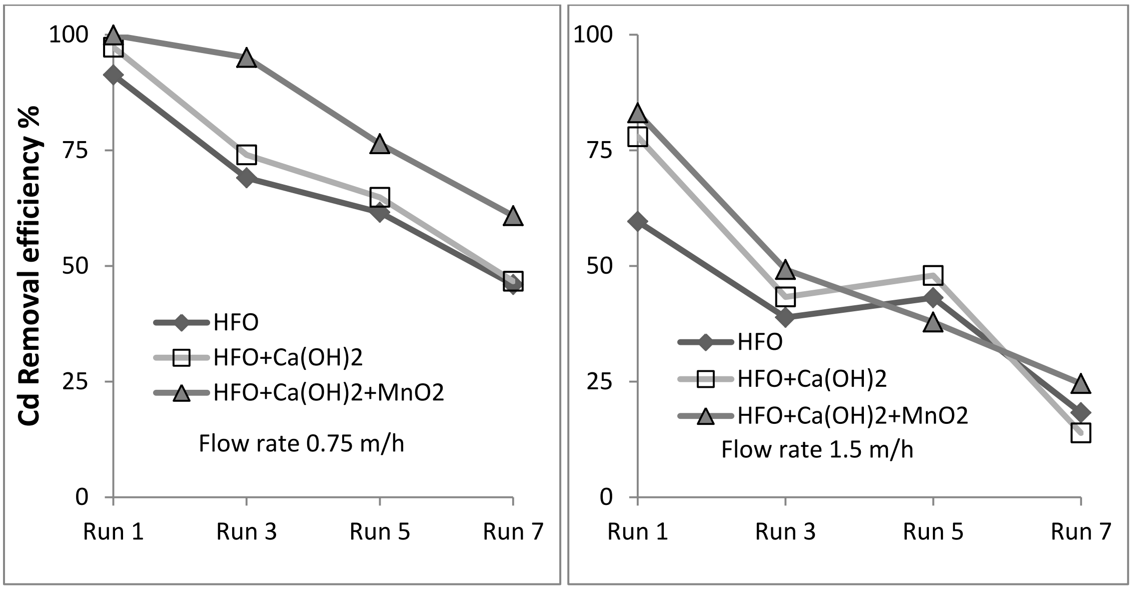


Figure 6. 5 Cd removal efficiency

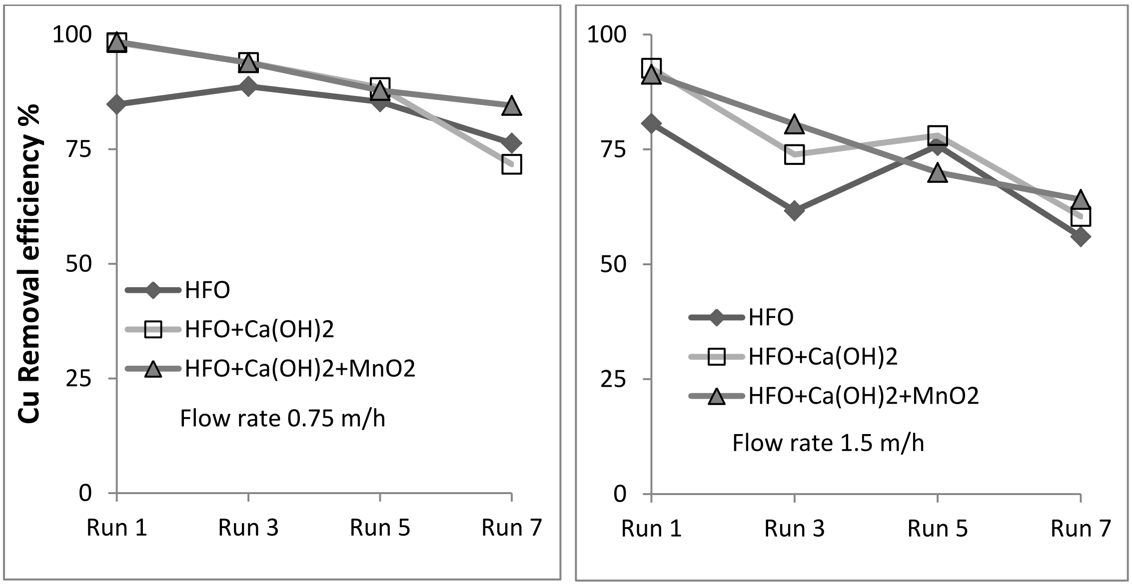


Figure 6. 6 Cu removal efficiency

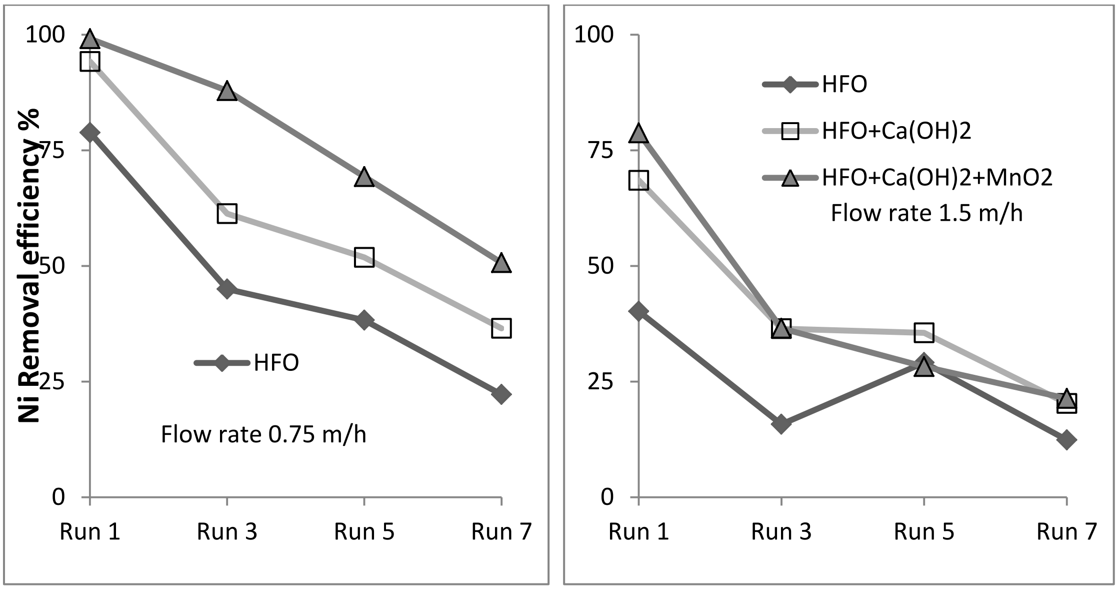


Figure 6. 7 Ni removal efficiency

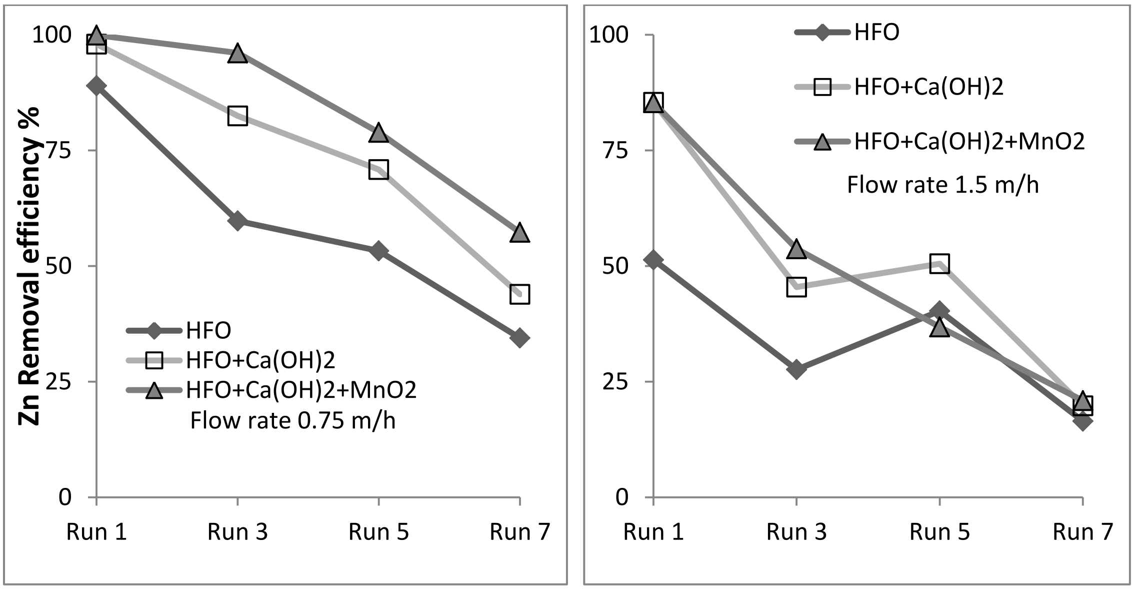


Figure 6. 8 Zn removal efficiency

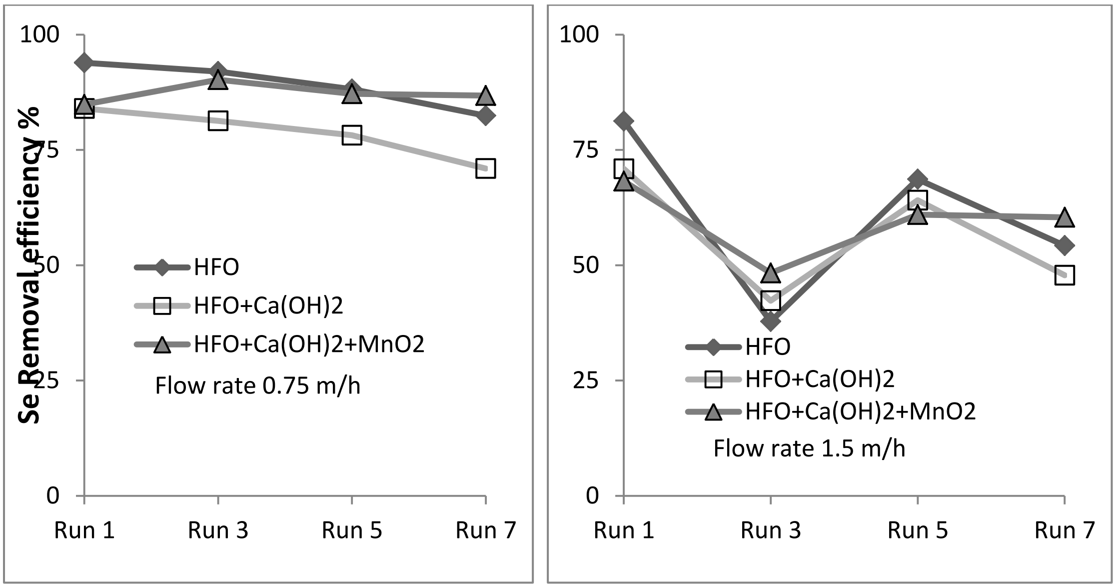


Figure 6. 9 Se removal efficiency

6.2.3.2 Effects of sorbents on contaminant removal

In Runs 1 and 3 the HFO columns with $Ca(OH)_2$ (with and without MnO_2) were able to remove more heavy metals (Cu, Zn, Ni and Cd) than the HFO only column, at both flow rates (Figure. 6.5-6.8) as a result of the increase of the pH caused by $Ca(OH)_2$ (Table 6.3). However an opposite effect was observed for Se at the low flow rate, especially when the HFO column was compared with the HFO + $Ca(OH)_2$ column (without MnO_2) (Figure. 6.9).

The negative charges on the sorbents increase with pH, therefore the heavy metals which occur as cations are sorbed in greater amounts at higher pHs. Because Selenium (Se) is present as anions (SeO_4^{2-}, SeO_3^{2-}), its sorption decreases when the pH is increased. Another reason for the decreased sorption of Se at high pH is due to the decrease in the proportion of the strongly sorbing $HSeO_4^-$ species and the increase in the proportion of the weakly sorbing SeO_4^- species at neutral to alkaline pHs (Fukushi and Sverjensky, 2007; Rovira et al., 2008).

Calcium hydroxide increased the pH to 9-10 in the first and third runs (Table 6.3) and at these high pHs it is possible that a high proportion of Cu, Zn, Cd and Ni might have precipitated. This could also be the reason for the high percentage of removal of these metals by the columns, which is consistent with the work of Lee et al. (2007) who also reported that nearly 100% of Ni and Zn were removed by a column containing lime. They suggested that the reason for this high removal efficiency was due to precipitation of these metals at high pH levels caused by the lime.

Table 6. 3 pH of effluents at the flow rate of 0.75 m/h

	Run 1	**Run 3**	**Run 5**	**Run 7**
HFO	7.3	7.2	6.9	6.9
HFO+$Ca(OH)_2$	10	9.1	7	6.9
HFO+$Ca(OH)_2$+MnO_2	9.8	9	7.1	7.1

In Runs 5 and 7 the difference in the removal efficiency for the majority of the contaminants between HFO and HFO+$Ca(OH)_2$ decreased (Figure. 6.5-6.9) because the pH in the effluents from the HFO+$Ca(OH)_2$ column declined to neutrality and reached that of the HFO column (Table 6.3). As the effect of the $Ca(OH)_2$ on heavy metals removal efficiency decreased due to the decreased pH, the effect of MnO_2 became important, especially at the low flow rate where the removal efficiency was greater than at the high flow rate as a result of the higher retention time of the metals on the sorbents (see section 6.2.3.1). The column with MnO_2 removed higher amounts of heavy metals and Se. This is because MnO_2 specifically sorbs oxyanions such as selenate and heavy metal cations (Balistrieri and Chao, 1990; Han et al., 2006 a,b). Overall the results showed that a mixture of HFO, $Ca(OH)_2$ and MnO_2 should be an efficient sorbent to remove heavy metal's cationic contaminants from polluted water. However for the oxy anion (Se) removal, the HFO+$Ca(OH)_2$+MnO_2 column had almost similar or less removal efficiency compared to the HFO only column, especially at the early stages of the treatment process where the effluent pHs were high. Two opposing factors contribute to the magnitude of the removal efficiency of Se by HFO+$Ca(OH)_2$+MnO_2. The higher pH caused by the $Ca(OH)_2$ tends to reduce the removal efficiency and the increase in sorption capacity for Se caused by the addition of MnO_2 tending to increase the removal efficiency of Se. The results indicate that unlike in the case of heavy metals the addition of $Ca(OH)_2$ to the HFO column would not be expected to remove additional Se.

6.2.3.3 Effect of time on contaminant removal

The removal efficiency of all contaminants decreased with time (Figure 6.5-6.9), and the C/C_o values increased with time for both flow rates (Figure 6.4, C/Co data shown only for the lower flow rate). This is due to a reduction of available sites for sorption and also repulsion of sorbed ions of the same species at neighbouring sorption sites. In the case of Ni, C/Co reached values close to 1 in Run 7 (Figure 6.4) as it has the lowest capacity for sorption on HFO (McBride, 1989). Cornell and Schwertmann (2003) also reported that the sorption capacity of Ni on iron oxides was the lowest compared to Cu, Zn and Cd.

At each run the increase of C/C_o with time was curvilinear but by allowing a 40 h no-flow period the subsequent run recommenced at a C/C_o value of approximately 0.05 (Figure 6.4). This shows that the intermittent conditions of runoff could be more favourable for the contaminant removal process than the continuous removal process. The reason for this is probably that some of the sorbed ions diffuse into the HFO during the no-flow dry period thereby the sorption sites which were earlier occupied by these ions became available for further sorption of ions. Trivedi and Axe (2000) showed that sorption of Cd and Zn by hydrous oxides of Fe and Mn continued to increase with time as a result of intraparticle diffusion of these heavy metal ions into the micropore walls of the oxides which started to occur within a few days of contact of Cd and Zn ions with these oxides.

6.2.3.4 Comparison of the removal efficiencies of contaminants

The efficiencies of Ni removal by all sorbents from Run 3 onwards were lower than the efficiencies of Cd and Se removal despite the concentrations of these three ions in the stormwater being the same (Figure 6.5-6.9). This shows that HFO has a lower affinity for Ni than the other two ions. At Runs 5 and 7, Se removal efficiency was higher than all the other ions except Cu. This is probably because at high loadings of heavy metal ions on the sorbents there were competitions for sorption as they were all heavy metallic cations with similar sorption mechanisms. But for Se which occurs in anionic forms there might have been less competition because of a different sorption mechanism for this ion and therefore Se was continued to be removed at high efficiency. Despite the Zn concentration in the stormwater being more than three times that of Cu concentration the removal efficiency of Zn was lower than that of the Cu in all sorbents. This is due to the higher sorption affinity of Cu compared to Zn in metal oxides and hydroxides (McBride, 1989). At the 7th run the sorption of Zn, the ion with the highest concentration in stormwater, was approaching saturation on the HFO column showing that no significant amounts of these ions would be sorbed any more on HFO (Figure 6.4). This is because the solution concentration of this ion has reached equilibrium with the sorbed ions. There may also have been unfavourable interactions between the closely spaced adjacent ions of the same species on the HFO surface at high sorption densities. The Cu ion which had the second highest concentration in the influent solution was far from reaching saturation on HFO because it is known to have the highest sorption capacity on HFO of all heavy metals tested (McBride, 1989;. Cornell and Schwertmann, 2003)

6.2.3.5 Contaminant ions removal in distilled water wash

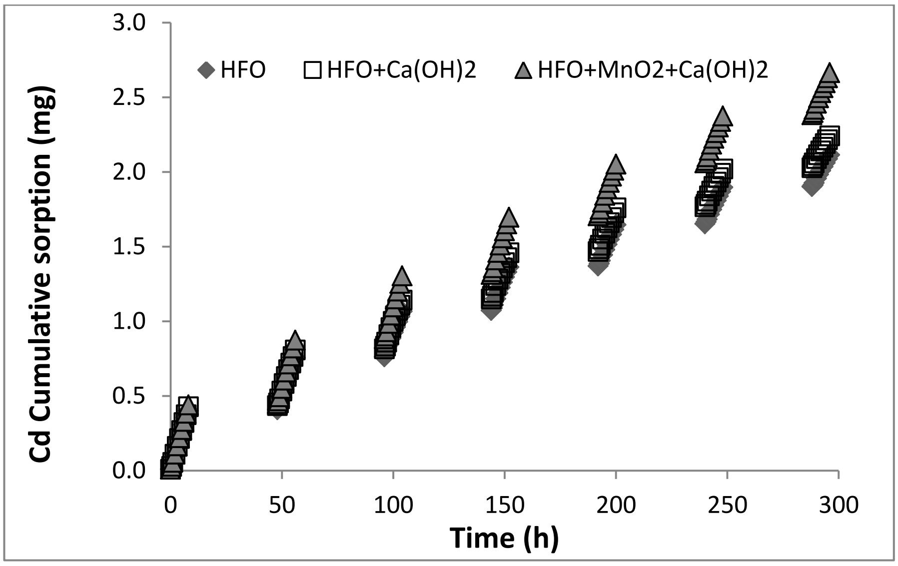
The cumulative amounts of contaminant ions removed from the columns in distilled water wash after the1st run were less than 2% of the respective amounts sorbed in this run for all ions except Se which rose to 7.5 and 10.6% when $Ca(OH)_2$ was added to the HFO column (Table 6.4). This shows that all the ions were strongly sorbed in the column except Se ions in the HFO columns with $Ca(OH)_2$. The small amounts of ions removed in the wash were probably those in the pore solutions and some of those loosely held on the HFO surface. Selenium removal in the wash was the highest because this ion was weakly sorbed at the high pHs caused by the addition of $Ca(OH)_2$. However the pHs declined to neutrality in the subsequent runs and this would be expected to reduce the distilled water removal efficiency of Se with the progress of time.

Table 6. 4 Cumulative amounts of contaminant ions removed from the column in the distilled water wash after the 1st run (A) as a percentage of cumulative amounts sorbed in the column in run 1 (B) for the flow rate of 0.75 m/h.

Column		Cd	Cu	Ni	Se	Zn
HFO	A (mg)	0.0025	0.0401	0.0065	0.0020	0.1449
	B (mg)	0.40	2.68	0.33	0.31	18.49
	A/B x 100	0.63	1.50	1.98	0.65	0.78
HFO+$Ca(OH)_2$	A (mg)	0.0013	0.0167	0.0023	0.0209	0.2864
	B (mg)	0.43	3.10	0.39	0.28	20.36
	A/B x 100	0.30	0.54	0.59	7.48	1.41
HFO+$Ca(OH)_2$+MnO_2	A (mg)	0.0002	0.0136	0.0009	0.0300	0.0086
	B (mg)	0.44	3.11	0.41	0.28	20.77
	A/B x 100	0.05	0.44	0.22	10.62	0.04

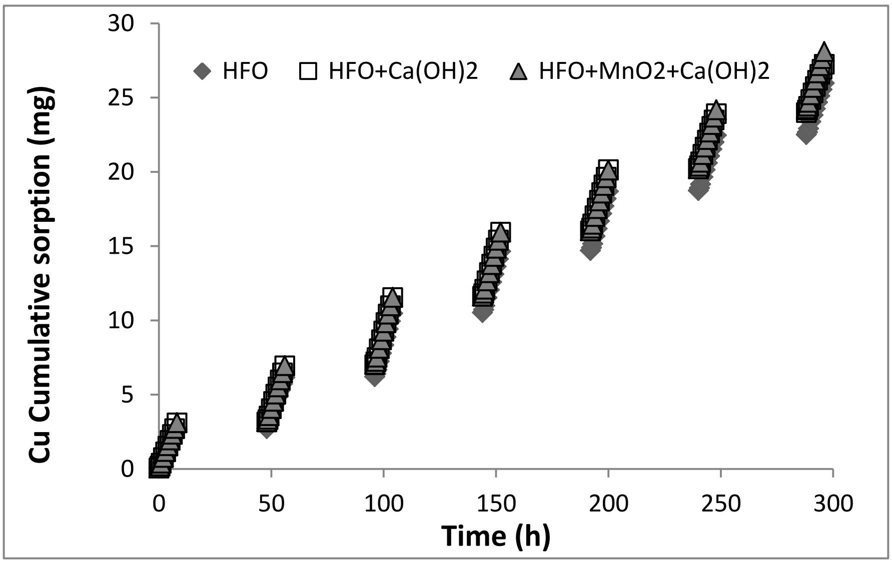
6.2.3.6 Cumulative amounts of contaminants removal in columns

The cumulative amounts (mg) of contaminant ions removed (sum total for all runs of the values obtained for the numerator in the equation in section 6.2.3.1) in the seven runs for each column at the flow rate of 0.75 m/h are shown in Figure 6.10 (a-e). The relative amounts of the contaminants removed were generally in proportion to their concentrations in the stormwater (Zn>Cu>Cd,Ni,Se). Between Cd, Ni, and Se which had the same influent concentration, Ni showed the lowest cumulative sorption on HFO for the reasons given in section 6.2.3.4 However the cumulative sorption of Ni increased with time and reached the maximum in Run 7 when $Ca(OH)_2$ and MnO_2 were added to HFO. The total amounts of contaminant metals, Cd, Cu, Niand Zn sorbed in the HFO column at the flow rate of 0.75 m/h were 0.02, 0.41, 0.02 and 1.30 mmol, respectively giving a total of 1.75 mmol heavy metals/HFO column. This indicates a heavy metals sorption density of 1.75 mmol in 8.7 g HFO or 0.2 mmol/g HFO. This value is higher than the maximum sorption capacity of 0.1 mmol/g granulated ferric hydroxide (GFH) reported for the simultaneous sorption of five heavy metals on GFH (Gene-Fuhrman et al. (2008). However, a maximum sorption capacity for Cu of 4 mmol/g HFO was reported by Sen et al. (2002). The difference in the sorption capacities obtained in the various studies is probably due to the difference in the characteristics of the HFO used in the studies as well as the experimental conditions at which the sorption studies were conducted (e.g. pH).



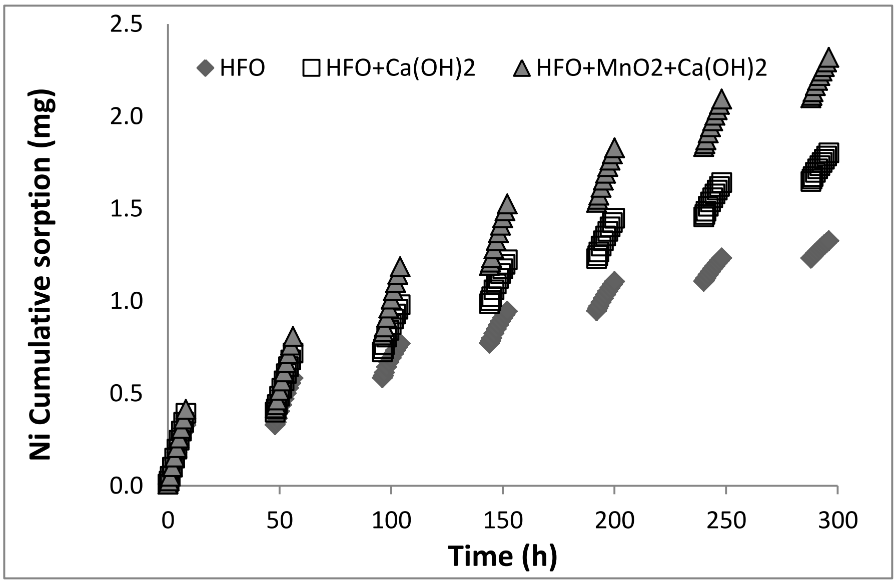
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Cd Cumulative sorption (mg)
HFO
HFO+Ca(OH)2
HFO+MnO2+Ca(OH)2
0
50
100
150
200
250
300
Time (h)

(a)



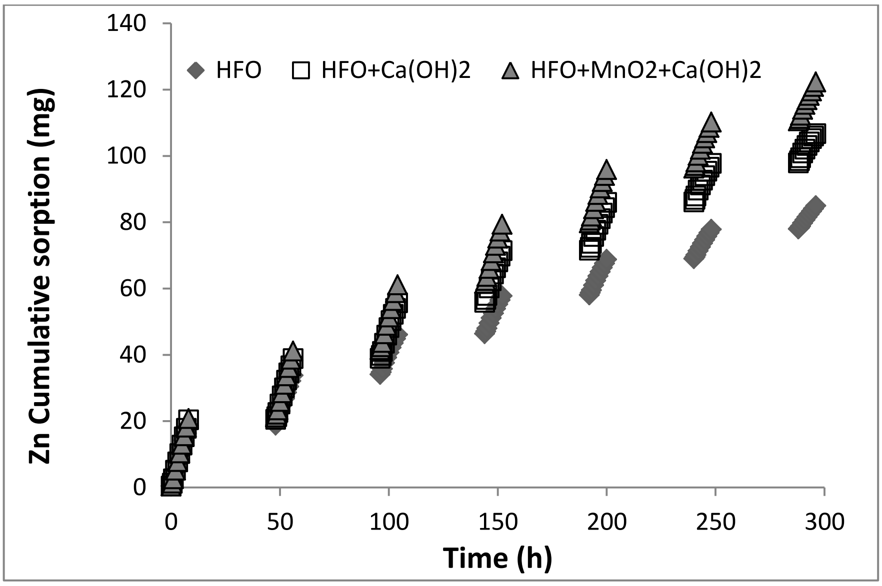
30
25
20
15
10
5
0
Cu Cumulative sorption (mg)
HFO
HFO+Ca(OH)2
HFO+MnO2+Ca(OH)2
0
50
100
150
200
250
300
Time (h)

(b)

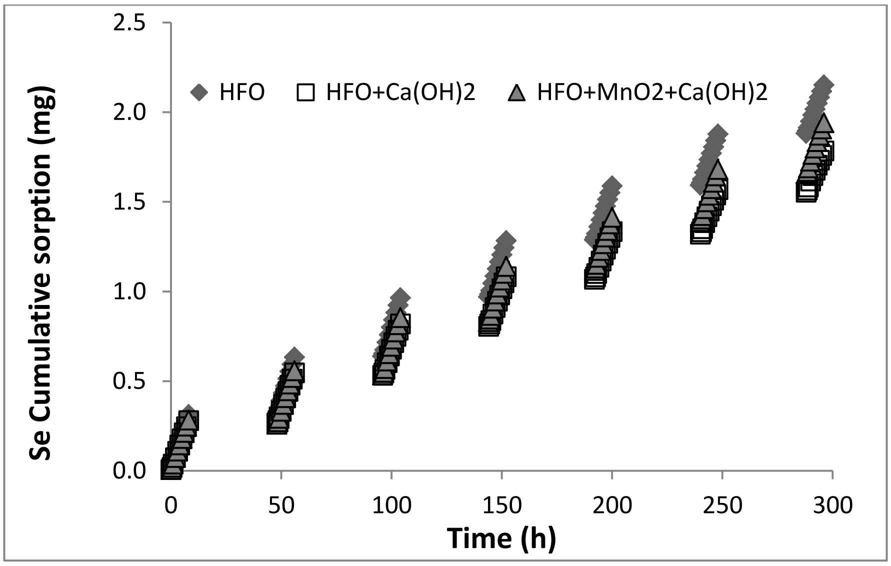


2.5
2.0
1.5
1.0
0.5
0.0
Ni Cumulative sorption (mg)
HFO
HFO+Ca(OH)2
HFO+MnO2+Ca(OH)2
0
50
100
150
200
250
300
Time (h)

(c)



(d)



(e)

Figure 6. 10 cumulative amounts (mg) of contaminant ions removed

6.2.4 Summary

The column kinetics experiment showed that the mixture of HFO, $Ca(OH)_2$ and $MnO_2$is an effective sorbent/filter media in removing both cationic (Cd, Cu, Ni, Zn) and oxy anionic (Se) contaminants from stormwater over a long period of time. This filter media has potential to be incorporated into a water treatment process (or treatment train) where other complimentary treatment systems are used to remove other contaminants of interest such as nutrients and organics to produce high quality effluent for reuse purposes. The intermittent conditions of runoff, each of 8 h duration followed by a 40 h no-flow period (wetting and drying condition) could be more favourable for the removal than a continuous removal process. Furthermore a lower flow rate of 0.75 m/h gave greater removal efficiency than a higher flow rate (1.5 m/h). The $Ca(OH)_2$ in the column produced a high pH at the initial runs that helped to remove more heavy metals but less Se. The presence of MnO_2 increased the removals of all contaminant ions.

Chapter 7

7. Heavy metals in road-deposited sediments; Analysis and treatment

7.1 Background

Urban road-deposited sediments (RDS) are potential pollution sources of stormwater runoff. They often contain elevated concentrations of heavy metals. Many of the heavy metals at elevated concentrations are both acutely and chronically toxic, with some being known carcinogens which can have wide-ranging adverse effects on humans and aquatic ecosystems (Scanlon 1991; Maher et al. 2008; Kadioglu et al. 2010). During rain, storms, and other street-washing events, the RDS and associated heavy metals are transported off-site and have the potential to end up in surface and subsurface water.

The mobility and transport of heavy metals and their bioavailability in the environment is a function of the chemical form of the metals. However, many studies evaluating the adverse effects of metals on the environment, measure only the total metal concentrations. To provide a more accurate measure of the potential mobility and bioavailability of the metals, a one step or sequential chemical extraction method should be utilised (Sutherland and Tolosa 2001; Birch and Scollen 2003; Robertson et al., 2003; Joshi et al., 2009). In the sequential extraction methods, reagents are used in a sequential order to extract different chemical forms of the metals. Each step in the sequential extraction is more destructive than the previous step and hence the metal fractions extracted are in decreasing order of mobility. Joshi et al., (2009) used 0.01 M HNO3 to extract 12 heavy metals in RDS from Singapore and found that Zn had the second highest concentration in the extract with Fe being the first therby, further supporting the notion of high Zn mobility in RDS.

In this chapter, only heavy metals are discussed. The concentrations of eight heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in RDS from nine sites along major motorways of Sydney, Australia; and, concurrently measurement of background concentrations in soils alongside these motorways were taken. The contamination of heavy metals in the RDS were then compared with those in the background soils using the enrichment factor (EF) and pollution index (PI); The possible sources of the metals were also identified using correlation and cluster analyses; The concentrations of the different chemical forms of the metals in RDS were also determined by a 3-step sequential extraction method.

7.2 Materials and methods

7.2.1 Study area

With a population of approximately 4.5 million, Sydney is Australia’s largest city. It is the State capital of New South Wales and is located on Australia's south-east coast, adjoining the Tasman Sea. Sydney has very high vehicular traffic density. The motorways chosen in this study for RDS sampling were M2, M5 and M7 which had an average annual daily traffic (AADT) of 93150 vehicles/day, 117800 vehicles/day and 119726 vehicles/day, respectively (Transurban sustainability report, 2009).

7.2.2 Sampling of RDS and soils

Nine RDS samples were collected along the city motorways (Figure 7.1) on asphalted pavements within the shoulder of the roads excluding the gutters within an area of approximately 2 m^2. The areas were carefully brushed using a clean plastic dustpan and were transferred into self-sealing polyethylene bags for transport to the laboratory for analysis. Duplicate soil samples (top 0.1 m depth) were also collected at distances of approximately 50-100 m away from the road shoulders of the RDS sampling sites in areas with no visible signs of contamination. These were also transported to the laboratory for analysis.

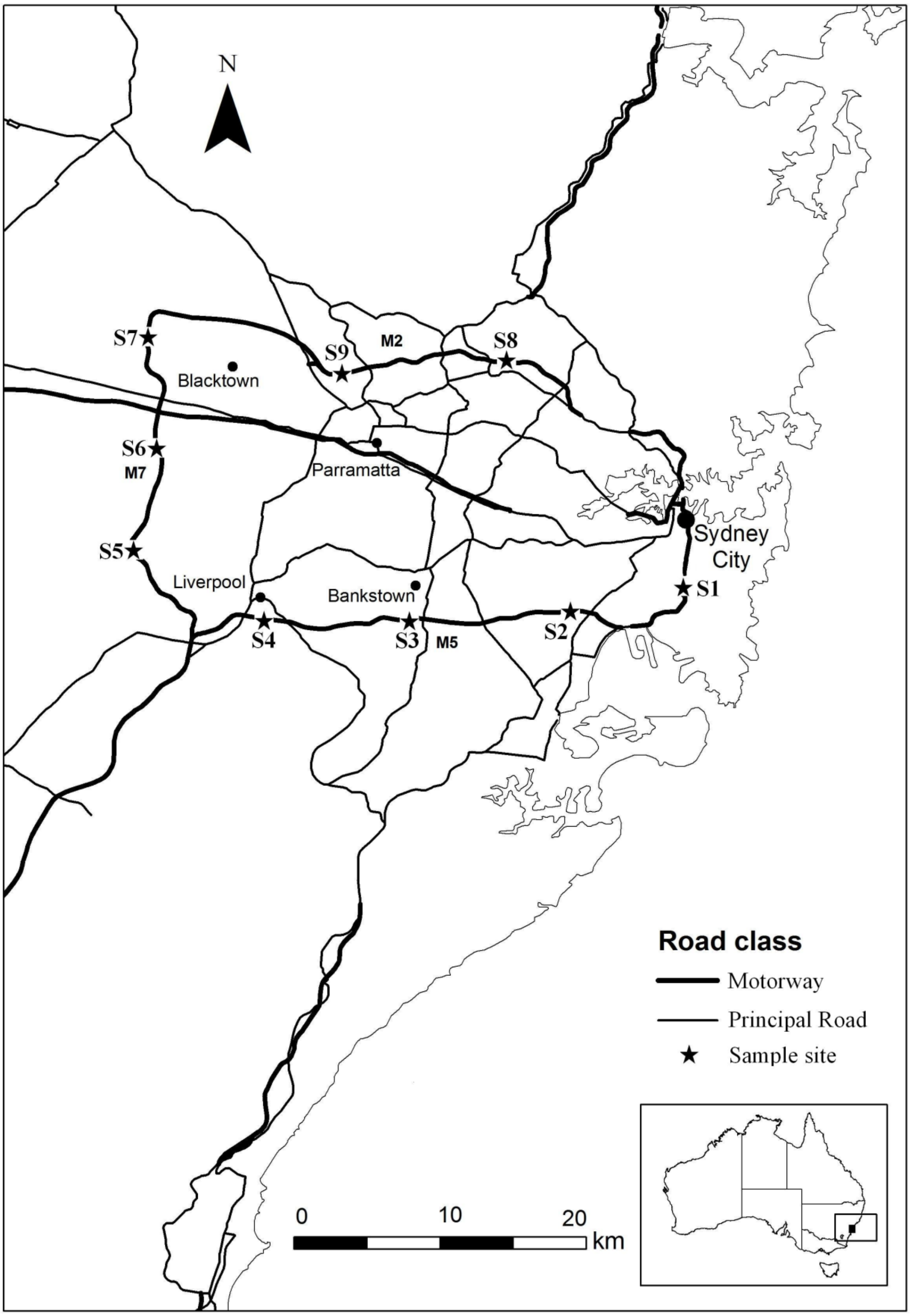


Figure 7. 1 RDS and soil sampling sites (S1 to S9 are the sampling sites; M2, M5 and M7 are the motorway roads).

7.2.3 Chemical analysis

The RDS and soil samples were dried in an oven at 100°C and passed through a stainless sieve with a 425 µm mesh. Total metal concentrations were determined using a microwave-assisted (CEM5000, CEM, U.S.A.), aqua regia digestion. Weighed portions (0.1 to 0.2 g) of the road-dust were digested in PFA-Teflon bombs in the presence of between 5 and 10 mL of concentrated nitric (70%) and hydrochloric (32%) acids in a one-to-three ratio. An internal pressure sensor was attached to the Teflon caps, which were mechanically tightened. The microwave digestion was operated at 100% maximum power for 30 min, during which the pressure in the vessels were maintained at > 500 kPa. It should be noted that no hydrofluoric acid was used and as such, trace quantities of silicate material remained undissolved. Aliquots of the samples were then diluted for analysis by ICP-MS.

Sequential extraction of the heavy metals was conducted according to the Standards, Measurements and Testing program of the European Union (Rauret et al., 1999; Sahuquillo et al., 1999). In this procedure exchangeable and water and weak-acid soluble metals were extracted first by acetic acid (0.1 M, pH 2.85), followed by extraction of reducible metal fraction by hydroxylamine hydrochloride (0.1 M, pH 2) and finally, extraction of oxidisable metal fraction by hydrogen peroxide (8.8 M)/ammonium acetate (1 M, pH 2). The metal concentrations of the extracts were similarly determined by ICP-MS.

ICP-MS analysis was performed using an Agilent 7700x ICP-MS (Agilent, U.S.A.) which was operating in helium cell mode. The instrument was used in helium cell mode to eliminate polyatomic interferences commonly associated with ^{52}Cr, ^{63}Cu, ^{58}Ni and ^{66}Zn. Data was collected using Agilent's Mass Hunter Software. System parameters were as follows: Sample Uptake Rate; 0.4 mL/min; Nebuliser; Micromist (Agilent); Spray Chamber: 2 °C; Sample Depth: 8 mm; Carrier Gas Flow: 1.01 L/min; Cell Gas Flow:5.0 mL/min (He); RF Power:1550 W; Dwell Time:0.1 s (Cr, Ni, Cu, Zn, Pb) and 1 s (Cd).

Extensive quality control measures were implemented to confirm the veracity of the data. Instrument tuning was performed at the start of each sample run using appropriate standards (Agilent Tuning Solution 1 µg/L). Initial calibration and frequent re-calibration ensured instrument drift was not observed. External calibration was performed using appropriate dilutions of a NIST-derived, high-purity multi-element standard (CertiPUR; Merck, Australia), which were made up daily. The isotopes of ^{52}Cr (verified at ^{53}Cr), ^{58}Ni (verified at ^{60}Ni), ^{63}Cu, ^{66}Zn, ^{111}Cd (verified at ^{114}Cd), ^{208}Pb (verified at $^{206/207}$Pb) were linear between 0.1 and 1000 µg/L across 7 points, with individual correlation coefficients between $R = 0.9974$ (^{208}Pb) and 1.0000 (^{66}Zn and ^{111}Cd). Excessive sample dilutions due to high element concentrations resulted in the matrix matching of standards having minimal impact on quantitative recovery. As such, a 2% HNO_3 matrix was used for all calibrations. This was confirmed by performing standard addition measurements on multiple samples.

In order to confirm the reliability of the digest method used for the heavy metals analysis, a certified standard reference material (NCSDC 73309) approved by the China National Analysis Center for Iron and Steel was analysed in parallel with the RDS and soil samples. The results of the measured values were compared with the certified values of reference standards, given in Table 7.1. Overall, the measured values were approximately equal to the certified values, suggesting that the chemical analysis and extraction methods used in the study are suitably accurate. The slight deviations in the values could be due to different methods used for obtaining the values for the certified samples as well as incomplete digestions associated with silicate sample matrices.

Table 7. 1 Comparison of measured metal concentrations obtained using microwave-assisted aqua-regia digestion and certified values on reference standard (NCSDC 73309)

	Certified value (mg/kg)	**Measured value (mg/kg)**	**Recovery (%)***
Fe	30700 ± 250	30828 ± 1978	100
Mn	2490 ± 0.2	2416± 164	97
Pb	636 ± 22	644 ± 45	101
Zn	373 ± 14	375 ± 29	101
Cu	79 ± 3	98± 0.1	124
Cr	40 ± 3	37 ± 3	91
Ni	14 ± 1.0	10 ± 4	73
Cd	2.3 ± 0.2	2 ± 0.1	82

*Recovery = Measured value/Certified value *100

7.2.4 Contamination assessment methods

Pollution Index (PI) and Enrichment Factor (EF) described in chapter 2 were used to determine the degree of heavy metal contamination in RDS from vehicles and roads.

For the determination of EF, Fe was chosen as the reference metal in this particular study, as it was also used by others (Gonzàlez -Macias et al., 2006; Lu et al., 2009; Tokalioğlu et al., 2003). The concentration of this metal in RDS was nearly the same as in the soils (low PI) and the only metal which had a high correlation between the concentrations in soils and RDS (see section 7.4) making it a satisfactory metal to be used as reference in the EF determination.

7.2.5 Statistical analysis

Correlation analysis was conducted between metals separately for RDS and soils to determine inter-metal relationships in RDS and soils (Chang et al., 2009). Similar analysis was also conducted for each of the metals between RDS and soils to determine intra-metal relationships (Chang et al., 2009). Pearson correlation coefficients were used to examine the degree of significance of the above relationships. A significant and positive correlation between metals often indicates that the metals are derived from the same sources (Chang et al., 2009; Faiz et al., 2009; Singh, 2011; Yongming et al., 2006)

Cluster analysis was performed to classify metals originating from different sources. This analysis, also known as data segmentation, groups observations into subsets (called clusters) so that observations in the same cluster (subsets) are more closely related to one another than observations assigned to different clusters. A hierarchical algorithm using Ward’s method (Aryal et al., 2011; Poulton, 1989) was used to establish clusters. The group of metals in a cluster is assumed to have originated from common sources (Wei et al., 2010; Yongming et al., 2006).

The correlation and cluster analyses were performed using Predictive Analysis Software (PASW) statistic version 18, previously called SPSS statistic.

7.3 Results and Discussion

7.3.1 Total metal concentrations

The total concentrations for each metal in RDS varied widely between sites (Figure 7.2 – 7.8). As expected, overall concentrations of Fe were substantially higher compared to the trace heavy metals measured, which decreased in the order, Mn > Zn > Cu > Cr > Pb > Ni > Cd (Table 7.2). A similar trend was observed with the background soils, where Fe > Mn > Zn ~ Ni > Cu ~ Pb > Cr > Cd. The order of metal concentrations measured in this study generally follows the order of abundance reported in previous RDS research (Kadioglu et al., 2010; Stone and Marsalek, 1996; Wei et al., 2009).

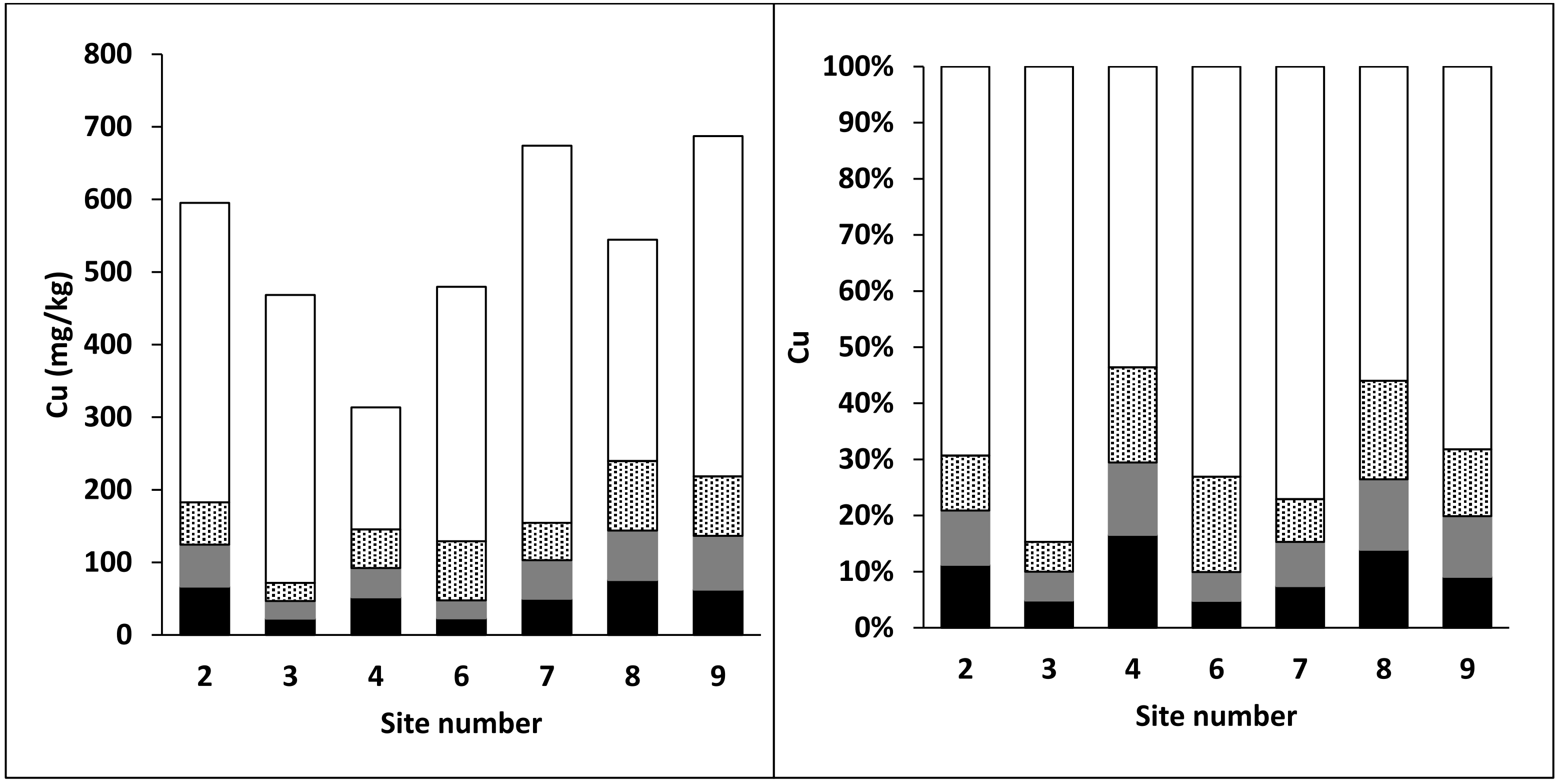


Figure 7. 2 Concentration distributions and percentages of Cu in different RDS chemical fractions

(■ Exchangeable + water and acid soluble, ▨ Reducible, ░ Oxidisable, □Residual)

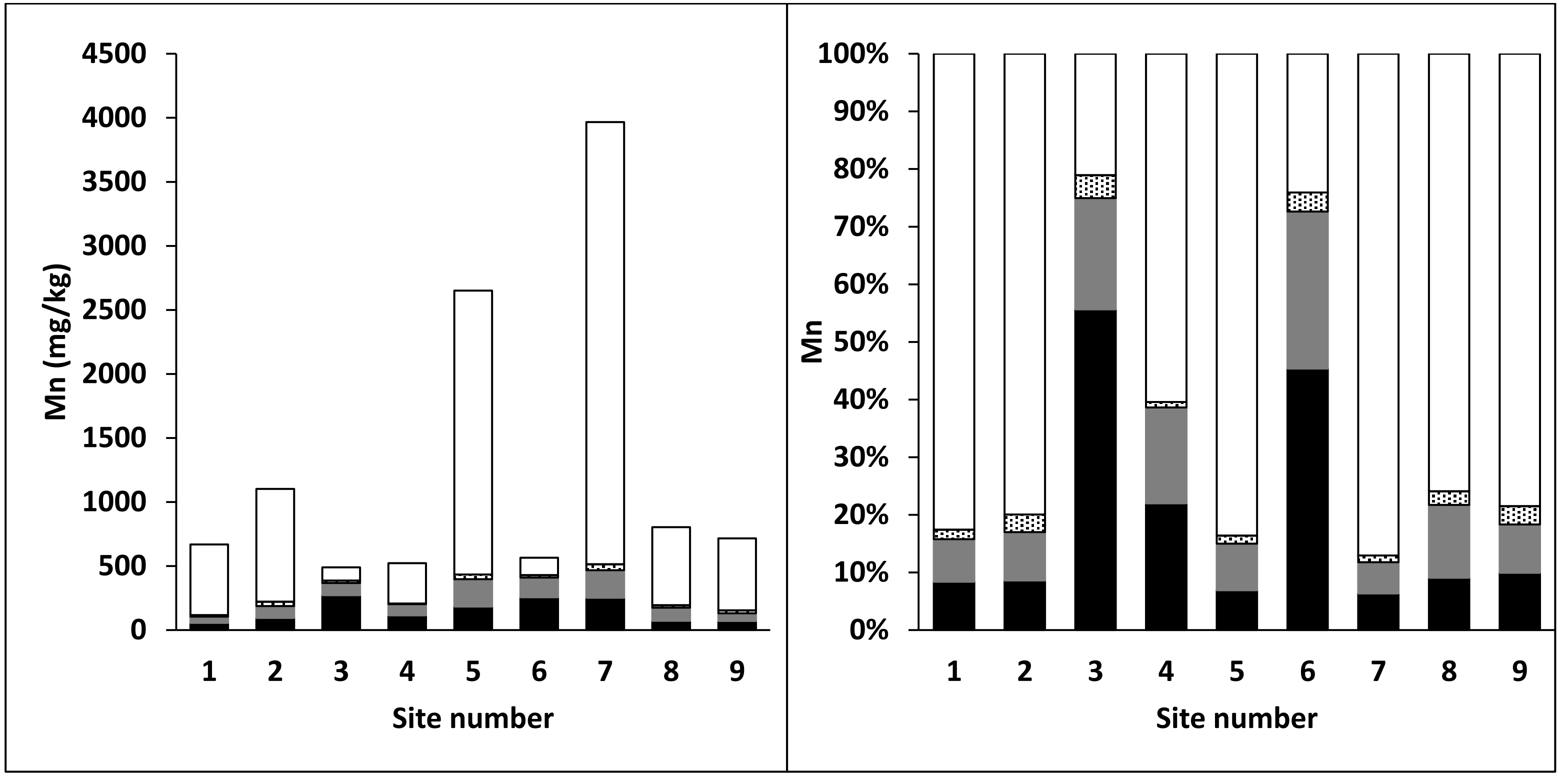


Figure 7. 3 Concentration distributions and percentages of Mn in different RDS chemical fractions.

(■ Exchangeable + water and acid soluble, ▩ Reducible, ░ Oxidisable, □Residual)

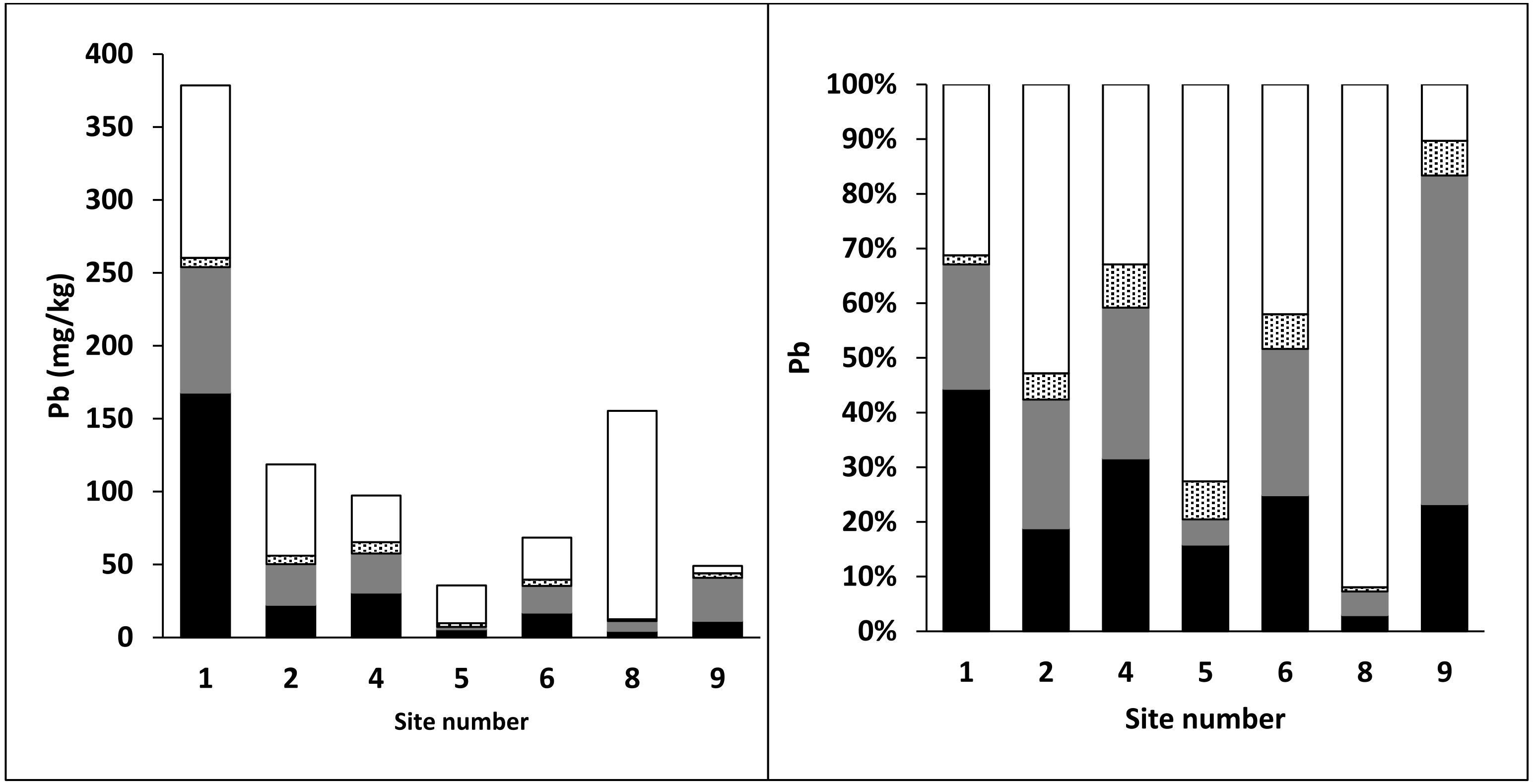


Figure 7. 4 Concentration distributions and percentages of Pb in different RDS chemical fractions

(■ Exchangeable + water and acid soluble, ▩ Reducible, ░ Oxidisable, □Residual)

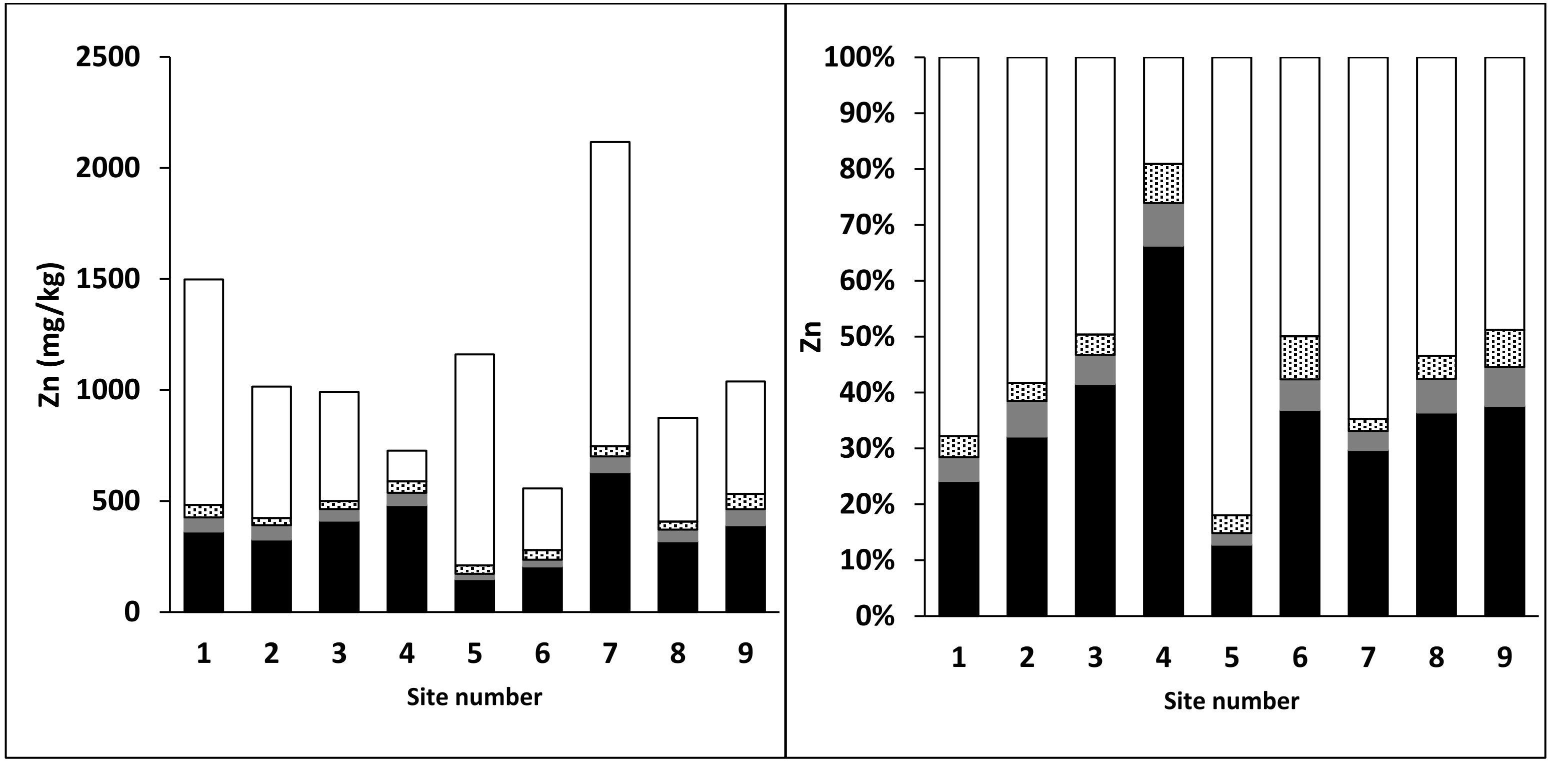


Figure 7. 5 Concentration distributions and percentages of Zn in different RDS chemical fractions

(■ Exchangeable + water and acid soluble, ▩ Reducible, ░ Oxidisable, □Residual)

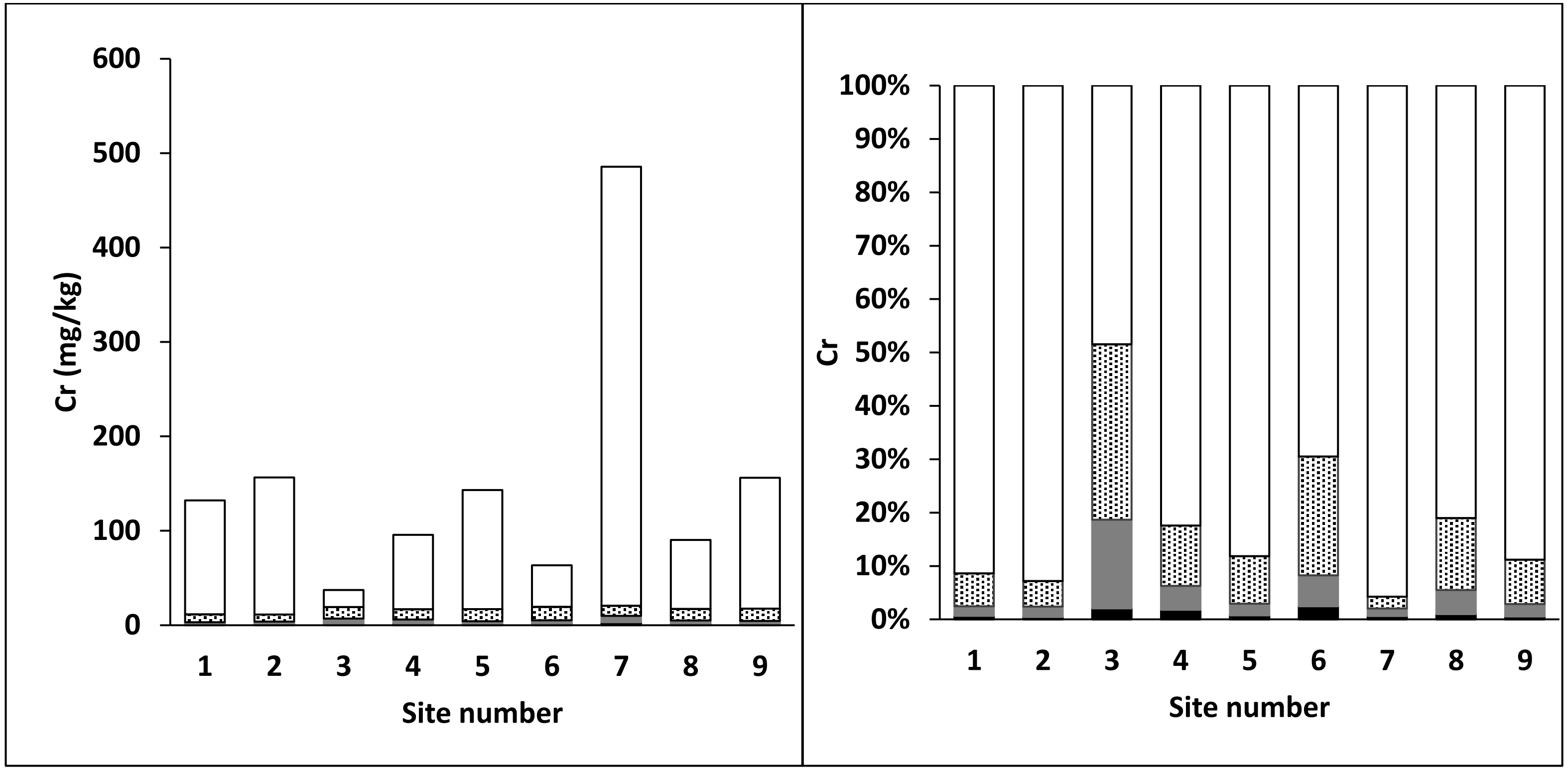


Figure 7. 6 Concentration distributions and percentages of Cr in different RDS chemical fractions

(■ Exchangeable + water and acid soluble, ▩ Reducible, ▨ Oxidisable, ☐Residual)

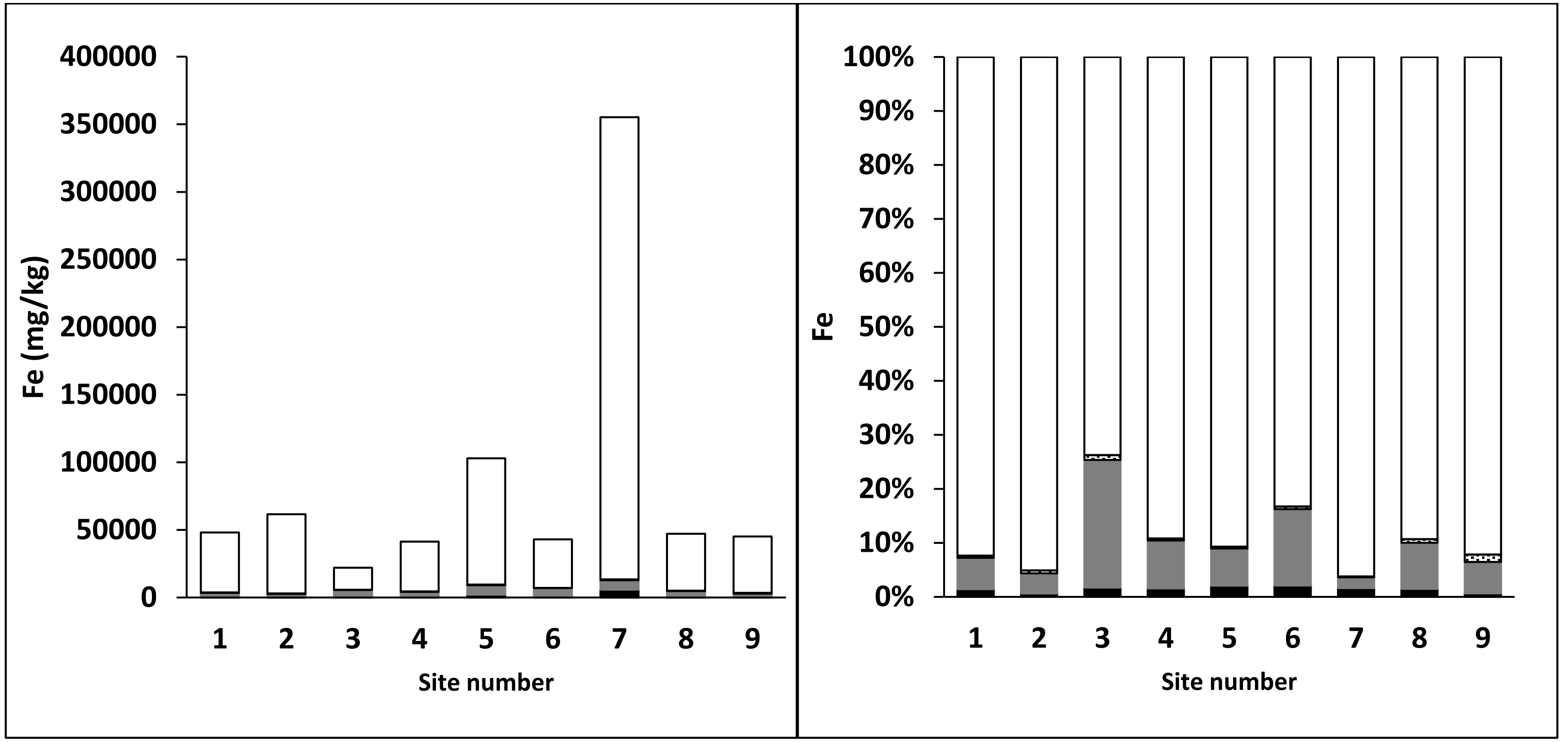


Figure 7. 7 Concentration distributions and percentages of Fe in different RDS chemical fractions

(■ Exchangeable + water and acid soluble, ▩ Reducible, ░ Oxidisable, □ Residual)

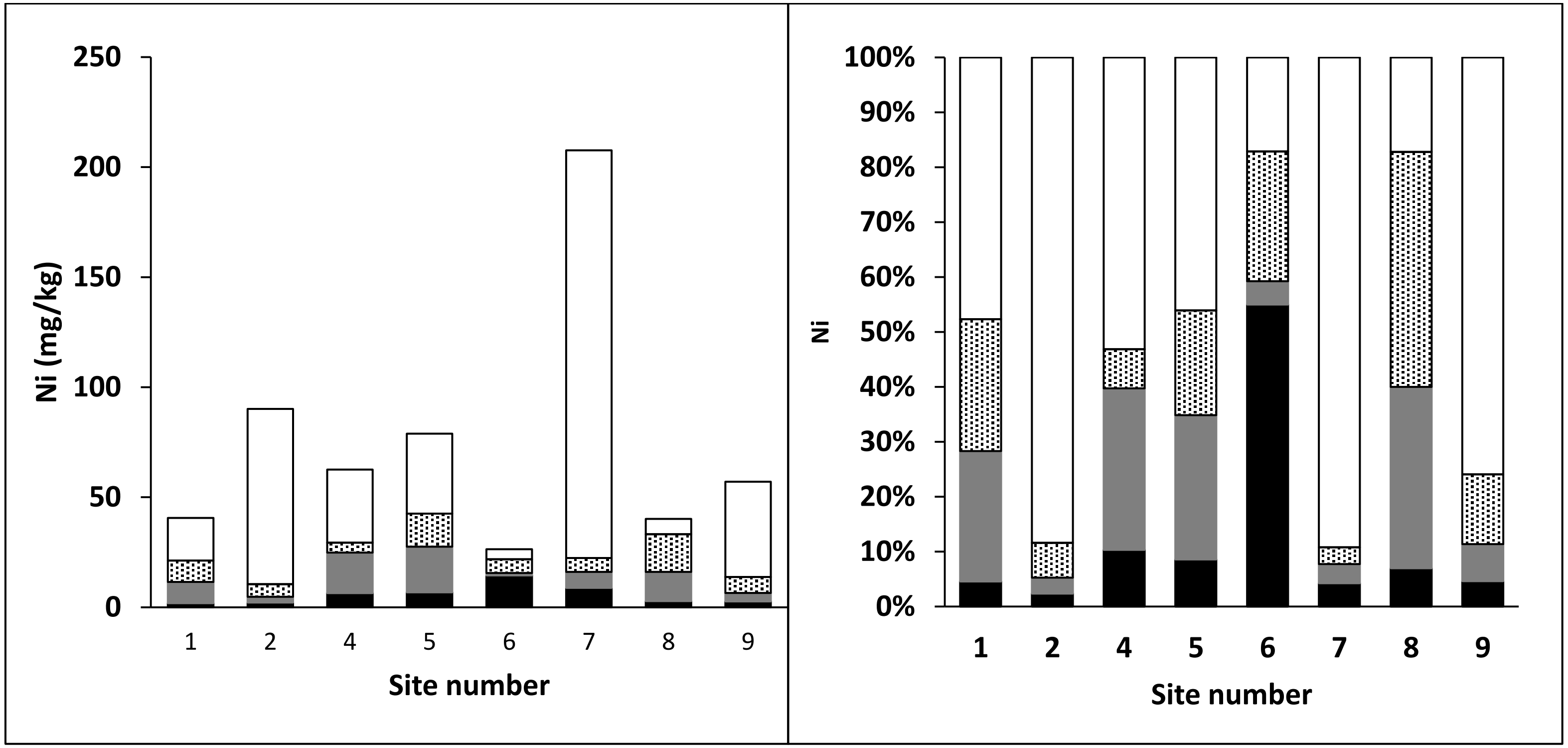


Figure 7. 8 Concentration distributions and percentages of Ni in different RDS chemical fractions

(■ Exchangeable + water and acid soluble, ▩Reducible, ░ Oxidisable, □Residual)

Table 7. 2 Heavy metal concentrations (mg/kg) in RDS and soils

Heavy metals	RDS range (mg/kg)	RDS mean (mg/kg)	Soil range (mg/kg)	Soil mean (mg/kg)
Fe	22036 - 355263	85201	6175 - 47210	31065
Mn	489 - 3966	1276	16 - 2460	750
Zn	557 - 2117	1109	71 - 238	152
Cu	314 - 730	544	6 - 225	69
Cr	49 - 486	152	10 - 79	35
Pb	36 - 379	119	24 - 198	64
Ni	20 - 208	69	27 - 242	147
Cd	0.24 - 1.72	0.73	0.01 - 0.49	0.18

7.3.2 Metal enrichment in RDS

The mean PI values for Cu, Zn, Cr, Cd, Pb, Fe, Mn and Ni were, 8.1, 7.3, 3.4, 3.1, 2.3, 2.0, 1.7, and 0.7, respectively. The corresponding median PI values were 7.4, 6.9, 3.5, 3.0, 2.0, 1.9, 2.0, and 0.4 (Figure 7.9). The mean EF values for Cu, Zn, Cr, Cd, Mn, Pb and Ni were 6.1, 3.8, 1.9, 1.8, 1.6, 1.1, and 0.2. The corresponding median EF values were 5.2, 3.4, 2.0, 1.6, 1.1, 0.6, and 0.2 (Figure 7.10). Both the PI and EF values indicate that Cu and Zn have moderate to high enrichment in the RDS compared with Pb and Ni, which have minimal or no enrichment. These results are similar to those of Lu et al. (2009) reported for the street dusts of Baoji, NW China who measured EFs of 6 (Zn), 3.5 (Cu), 1.2 (Ni) and 0.85 (Mn).The exception to this was Pb, which had an EF of 9.0. RDS from Islamabad expressways (Pakistan), also displayed the highest PI for Cu followed by Pb and Zn, whereas Cd and Ni had the lowest pollution index (Faiz et al., 2009). Previous research would suggest that the high enrichment values for Cu and Zn were the likely result of brake linings and tyre wear, respectively (Kadioglu et al., 2010; McKenzie et al., 2009; Taylor, 2007). The low enrichment values for other metals, especially Ni, Mn, Fe and Pb suggest that these metals are primarily derived from natural sources. The low to moderate enrichment values of Cr and Cd could be partly attributed to vehicle activity and road surface wear (Ewen et al., 2009; Taylor, 2007). Unlike certain other studies (Greece where leaded gasoline was still used, Christoforidis and Stamatis, 2009; Pakistan, leaded gasoline phased out only three years prior to sampling, Faiz et al. 2009; China, Lu et al., 2009; India, Singh, 2011), Pb was not found to be enriched in RDS, likely due to the restricted use of leaded gasoline since the 1990s in Australia.

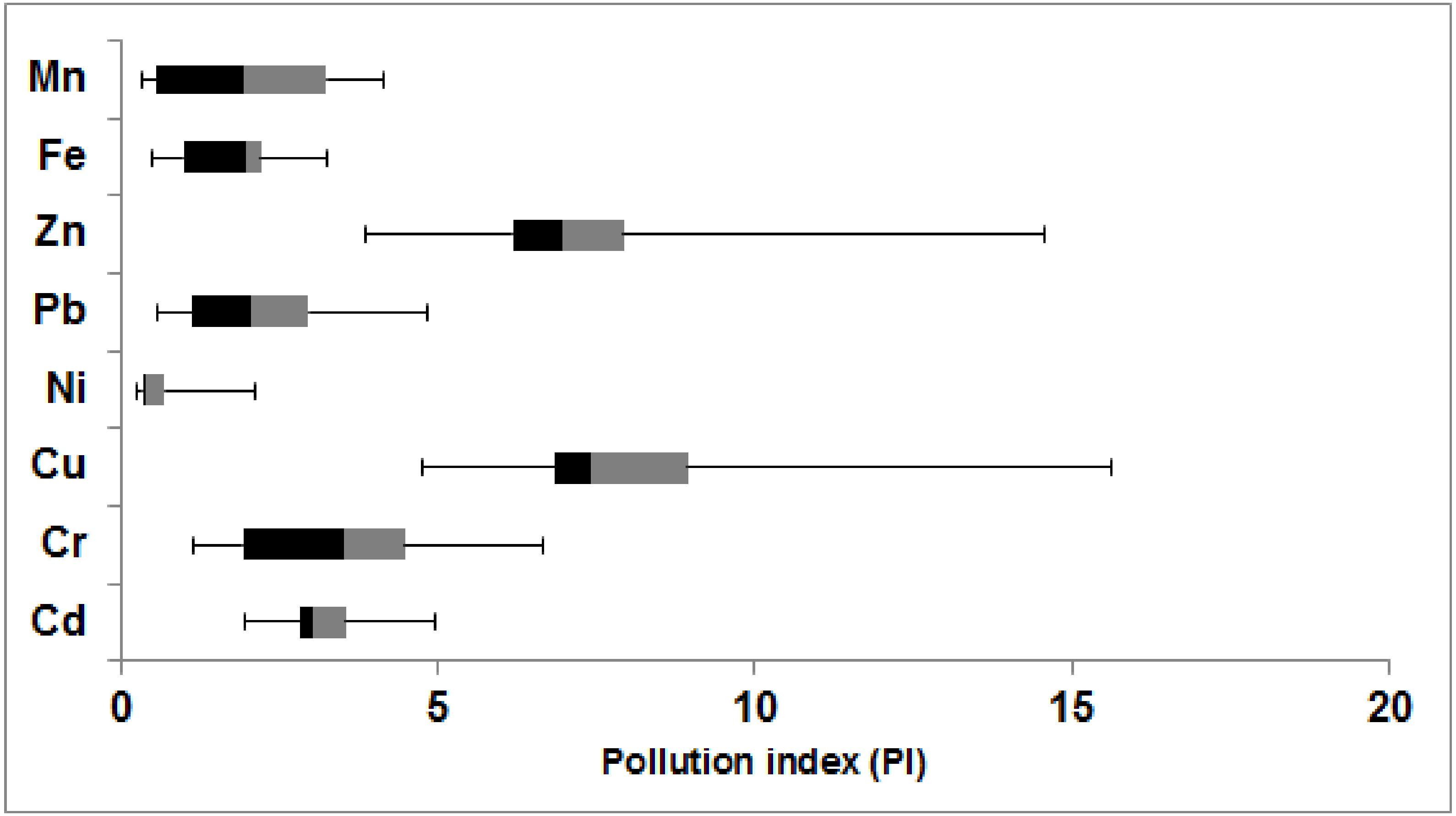


Figure 7. 9 Boxplot of pollution index for metals in RDS

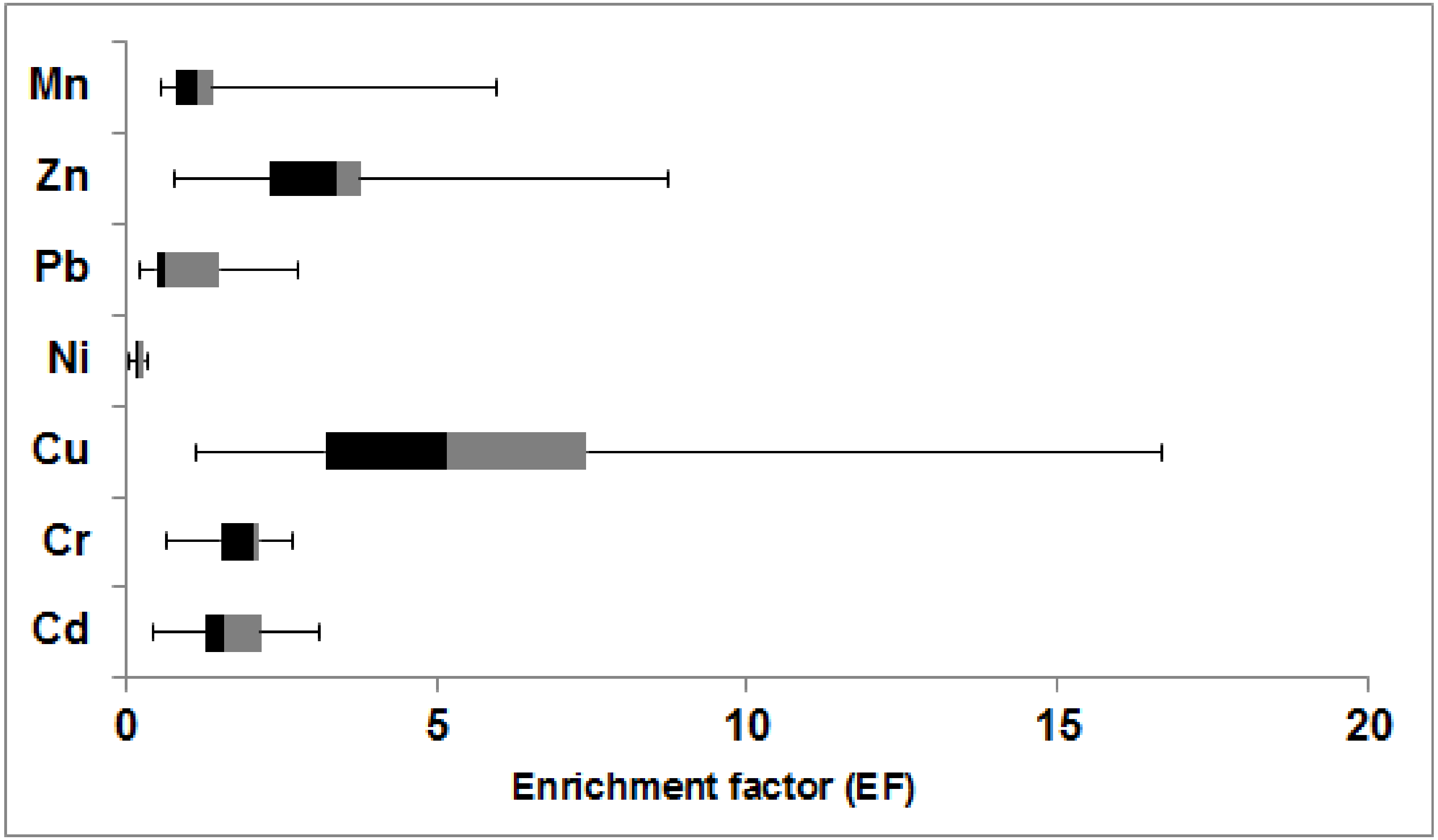


Figure 7. 10 Boxplot of enrichment factors for metals in RDS

7.3.3 Correlation analysis

Correlation analysis of each metal between RDS and neighbouring soils showed a significant relationship only for Fe (r = 0.767, $p < 0.01$). This shows that, aside from Fe, the concentration distributions in RDS were different from those in soils, supporting the validity of using Fe as the reference metal for the enrichment analysis. The correlation coefficients between each metal in RDS and in soils are presented in Table 7.3. The data from the background soils show a strong, positive correlation between Fe, Cr, Ni and Mn, suggesting that these metals may have originated from a common source or sources. As these soil samples were located a substantial distance away from the roads, the possible contributing sources are industry and lithology. With no major industry or mining activity within approximately 20 km of the sampling sites, it is likely that the source of these metals was from natural deposition. Among the other metals, significant correlations were observed between Cu and Zn and between Cd and Pb indicating a common source or sources for the two metals in each pair (Table 7.3).

Table 7. 3 Inter – metal correlation for RDS and soil samples.

Metal	**Fe**	**Mn**	**Zn**	**Cu**	**Cr**	**Pb**	**Ni**	**Cd**
RDS								
Fe	**1.000**							
Mn	**0.926*****	**1.000**						
Zn	**0.837****	**0.779****	**1.000**					
Cu	**0.311**	**0.169**	**0.604**	**1.000**				
Cr	**0.971*****	**0.874*****	**0.878*****	**0.463**	**1.000**			
Pb	**0.016**	**-0.103**	**0.383**	**0.553**	**0.095**	**1.000**		
Ni	**0.954*****	**0.897*****	**0.794****	**0.291**	**0.970*****	**-0.014**	**1.000**	
Cd	**0.750***	**0.625**	**0.872*****	**0.537**	**0.793****	**0.648***	**0.735***	**1.000**
Soil								
Fe	**1.000**							
Mn	**0.782****	**1.000**						
Zn	**0.502**	**0.496**	**1.000**					
Cu	**0.404**	**0.129**	**0.740***	**1.000**				
Cr	**0.837****	**0.934*****	**0.703***	**0.340**	**1.000**			
Pb	**-0.138**	**0.149**	**0.655***	**0.290**	**0.193**	**1.000**		
Ni	**0.994*****	**0.838****	**0.545**	**0.415**	**0.833****	**-0.073**	**1.000**	
Cd	**-0.087**	**-0.209**	**0.597**	**0.522**	**-0.068**	**0.761****	**-0.087**	**1.000**

***Significant at *P*<0.05; ** significant at *P*< 0.01; ***significant at *P*< 0.001**

As observed in the soils data, the same four metals, Fe, Cr, Ni and Mn were significantly correlated with each other in the RDS (Table 7.3). However, each of these metals were also correlated with Zn and Cd but not with Pb or Cu. Metal enrichment data (PI and EF values) showed that Fe, Cr, Ni and Mn concentrations in RDS were not much higher than those in soils. Therefore, considering both enrichment and correlation analysis, it appears that these metals are probably derived mainly from natural sources. Significant correlations of Zn and Cd with these metals in RDS but not in soils, suggests that Fe, Cr, Ni and Mn may also have had a minor part of their origin coming from vehicle activity.

7.3.4 Cluster analysis

Three main groups were identified in the dendrogram obtained for background soils in the cluster analysis (Figure 7.11): (1) Ni, Fe, Cr, and Mn; (2) Cd and Pb; and (3) Cu and Zn. Cluster analysis of the RDS samples also produced three clusters. The metals in the first cluster are the same for both soils and RDS, which indicates that the source of these metals is probably the same for both RDS and soils. This is consistent with the metal enrichment data which showed that these four metals had low PI and EF. This data suggests that these metals are likely to be derived from natural sources. As opposed to the group 1 cluster data, the metals in the second (Zn and Cd) and third (Cu and Pb) groups in RDS samples were different from those in the respective groups in soils (Cd and Pb in group 2 and Cu and Zn in group 3). Again, the data are in agreement with the correlation results for RDS metals, which showed that Zn was significantly correlated with Cd, and Cu with Pb (Table 3). These differences between soils and RDS samples may indicate that vehicle activity had some influence on the metals in groups 2 and 3. The association of Zn and Cd may suggest that tyre wear was probably the common source as both of these metals are constituents of tyres (Charlesworth et al., 2003; Thorpe and Harrison, 2008). The association of Cu and Pb may be due to their origin from a common source such as brake linings (Thorpe and Harrison, 2008). Cluster 1 (Cr, Fe, Ni and Mn) and cluster 2 (Zn and Cd) of RDS are joined together at a higher level (longer linkage distance) implying a less defined, yet common source. This is in agreement with the correlation data for RDS (Table 3) which showed that Zn and Cd were significantly correlated with Cr, Fe, Ni, and Mn.

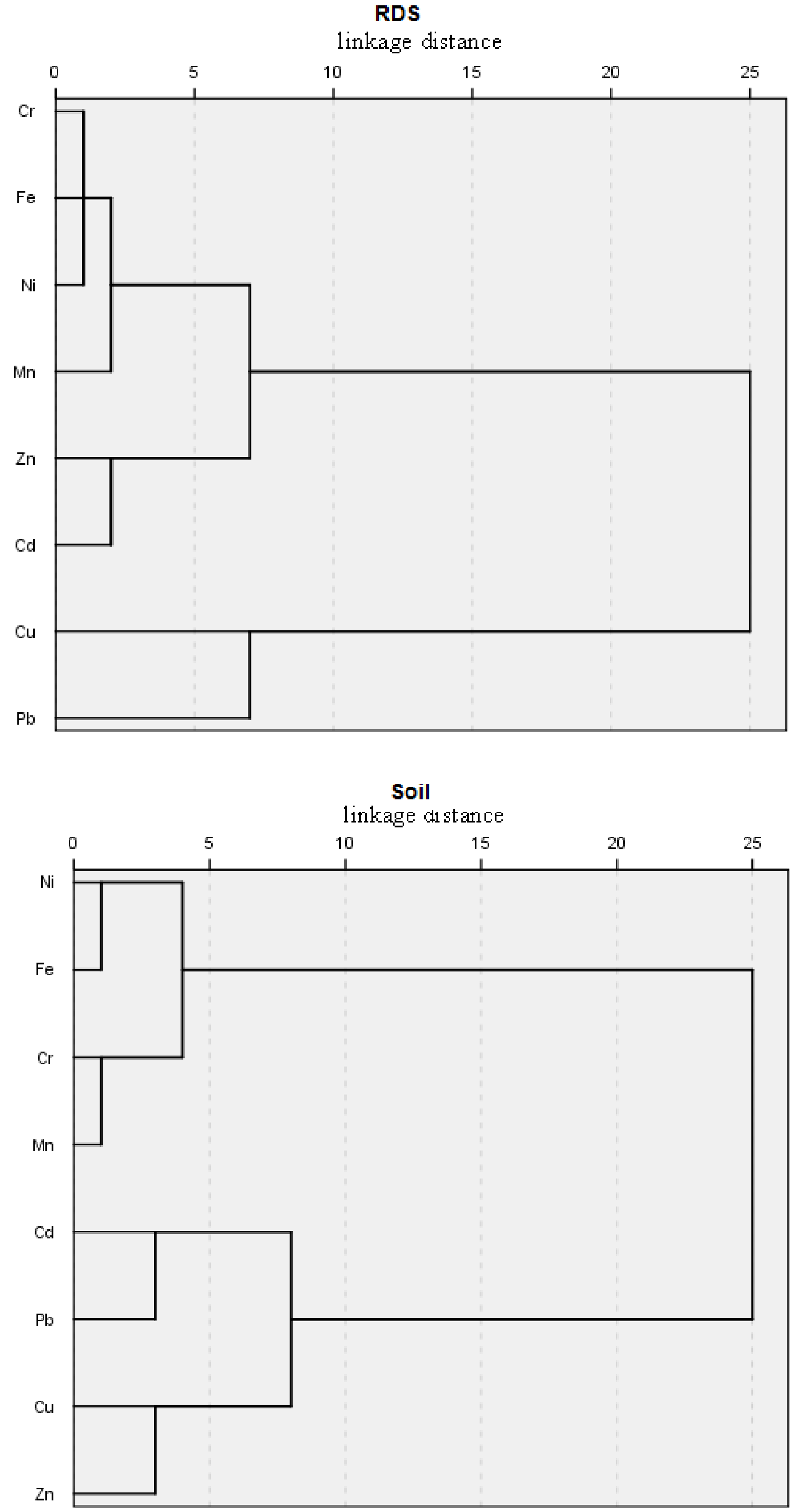


Figure 7. 11 Hierarchical dendrograms for 8 metals in RDS and soil obtained by Ward's hierarchical clustering method.

7.3.5 Metal fractionation

Fractionation profiles show that a major proportion of metals are associated with the residual fraction at all sites (50-85% Cu, 20- 85% Mn, 10- 90% Pb, 20- 80% Zn, 50-85% Cr, 75- 95% Fe, 20- 90% Ni) (Figure 7.2- 7.8). This indicates that the metals mainly exist in the immobile phase of RDS which is not readily bioavailable and therefore they do not provide an elevated environmental risk. The high percentage of residual fraction most likely reflects the geological characteristics of the samples (Stone and Marsalik, 1996). On average, Fe and Cr had the highest percentage of residual fraction. Many others have also reported high percentages of metals in the residual fraction of RDS. For example, Kumar et al. (2010) found 60-90% of Cu, Zn, Pb and Cd were contained in the residual fraction of RDS in Tokyo, Japan; and Singh (2011) reported 40-80% of Fe, Mn, Cu, Ni, Pb, Zn, Cr, and Co in the residual fraction of RDS from the North Eastern States of India.

Of all the metals, Zn had the highest percentage within the exchangeable fraction (15-65%), which suggests that it is likely to be the most mobile of all metals in RDS for release into the stormwater runoff from the roads. A high percentage of exchangeable Zn has also been observed by many others (Hamilton et al., 1984; Robertson et al., 2003). However, Kumar et al. (2010) observed that both Zn and Cd contained higher percentages in the exchangeable fraction when compared to Cu, Pb, and Ni. Certain studies have shown that Cd had a higher exchangeable fraction over Zn, Cu, Pb and Ni (Duong and Lee, 2009; Stone and Marsalik, 1996). It is expected that the metals recently deposited from anthropogenic sources (as evidenced by high EF values) would be more likely to occur in the exchangeable fraction when compared to a less mobile phase. For example, Tokalioğlu et al. (2003) found that Cd, which had an EF of 57 compared to EFs < 10 for Cu, Ni, Pb, Cr, Co, Mn and Zn, had the highest exchangeable fraction of all metals. Our results showed that both Zn and Cu had a high EF. However, this translated into a high exchangeable fraction for Zn alone, with a significant fraction of Cu associated with the organic fraction.

Copper was the only metal to be measured appreciably in the organic fraction (5-25%) (Figure 7.2).Similar studies have also reported that among all metals measured, Cu was most frequently associated with organic matter (Kumar et al., 2010; Robertson et al., 2003; Singh, 2011; Stone and Marsalik, 1996). The close association of Cu with organic matter is due to its strong tendency to form organic complexes and adsorb to organic colloids (Loganathan et al., 2011). Despite the fact that Cu appears potentially less bioavailable, its persistence in RDS suggests it may be vulnerable to remobilisation as a consequence of either bacterial breakdown of organic matter due to high levels of bacterial activity in stormwater runoff, or to changes in pH and redox conditions such as the oxidising environment that is encountered during sediment transport at the initial stages of a storm (Robertson et al., 2003).

Intermediate between the residual and the exchangeable fractions, there are the other two fractions, oxidisable and reducible, which are less mobile than the exchangeable fraction. However the heavy metals in these fractions can be released into the environment with changes in redox potential, pH and temperature of the water and sediments during RDS transport during runoff.

7.4 Summary

Across Sydney’s motorways, at sites away from major industry and mining areas, RDS significantly enriched only Cu and Zn, likely due to a contribution from traffic related activities such as brake linings and tyre wear, respectively. Enrichment data as well as correlation and cluster analyses suggested that Fe, Mn, Cr and Ni had a primarily lithogenic origin. Cadmium was significantly correlated with Zn and Pb with Cu, suggesting possible common origins for each of these pairs of metals. Metal fractionation data showed that a large percentage of all metals across most sites were in the residual fraction. Iron and Cr had the highest residual fraction further implying their lithogenic origin. Of all the metals, Zn had the highest exchangeable fraction that is readily-mobile. This suggests that Zn is likely to be the most mobile of all metals in RDS and may be released in appreciable amounts into the stormwater runoff from the roads. Copper was the only metal present appreciably in the organic fraction. Thus, it is necessary to remove these heavy metals before it enters to storage from the stormwater runoff. Furthermore, this study concentrated only on the heavy metals. It is equally important to measure the organic in particular, the poly aromatic hydrocarbon in the RDS.

7.5 Adsorptive removal of zinc dissolved from road-deposited sediments by a hydrous ferric oxide

7.5.1 Background

Remediation measures that have been used to reduce the heavy metals load in RDS include the direct removal through street sweeping, water flushing or the use of chemical suppressants (Taylor 2007; Loganathan et al., 2012b). Indirect measures which intercept the contaminants in transit, including vegetation strips, filtration systems such as permeable pavements, buffer strips and grass swales (Aryal et al. 2010), sedimentation ponds (Taylor 2007) and soil infiltration (Murakami et al., 2008) have not always been entirely successful. Removal of heavy metals by adsorption processes have been reported to be a reliable and efficient alternative (Aguado et al., 2009; Zhou and Haynes 2011). However, the majority of studies reported on adsorptive removal of heavy metals from stormwater have used model synthetic waters (Liu et al. 2005; Genc-Fuhrman et al. 2008; Wu and Zhou 2009) or stormwater spiked with heavy metals (Aryal et al. 2011). This section presents a study on the adsorptive removal of Zn, the metal found to have the highest total concentration and most enriched in RDS, using a hydrous ferric oxide.

7.5.2 Materials and methods

7.5.2.1 Methods

Sampling of RDS : The RDS samples were collected along major motorway number M7 (average annual daily traffic density of 119,726 vehicles day-1 (Transurban sustainability report 2009)) in Sydney, the largest city in Australia, on the asphalted pavement within the shoulder of the road excluding the gutters over an area of approximately 2 m2. Details of the sampling regime were discussed in section 7.2.2.

Acid and water solubility of metals in RDS: During transport of the RDS in stormwater, much of the coarser size fraction remains on the road surface or settles down in sediment storage areas (sewer inlets, gully pots, sediment traps), whereas the finer size fraction continues to be suspended in water and transported for longer periods and therefore has the potential to end-up in natural water bodies. Furthermore, a high proportion of the metals are generally found in the finer size fraction due to the associated increase in surface area (Varrica et al., 2003). Therefore, the finer size fraction of the RDS was selected for further experiments relating to metal dissolution. Samples of 10 g of < 75 µm size RDS fraction were agitated with 250 mL of either deionised water or 0.01 M HNO3 (Analar grade) for 24 h in a flat shaker at a speed of 120 rpm at 25 ± 2oC. At the end of this period the suspensions were centrifuged for 20 min at 3500 rpm and the supernatant solutions were analysed for heavy metals using ICP-MS, as described in section 7.2.3.

7.5.2.2 Methods for Zinc adsorption on hydrous ferric oxide

The 0.01 M HNO3 extracts of the < 75 µm RDS samples were diluted to four times their original volume before the pH was adjusted to 6.8 to simulate the pH generally found in natural stormwater (Aryal et al. 2011). The diluted solution was subsequently used for the following Zn adsorption study. The dilution was found to be necessary in order to obtain a sufficiently large volume of solution for the adsorption study using different doses of adsorbent. However the dilution reduced the Zn concentration used for the study.

A hydrous ferric oxide (HFO) (30-80 mesh) with the chemical formula of FeOOH obtained from Sigma Aldrich (USA) was used as the adsorbent. X-ray diffraction analysis (Appendix A) indicated that the HFO was amorphous with the presence of some nano-size iron oxides as reported for other HFO materials (Davies and Leckie 1978; Trivedi and Axe 2000). Adsorption experiments were conducted in a set of glass flasks with 150 mL of diluted acid extracts and varying HFO doses (15, 30, 75, and 150 mg flask-1) combined at room temperature (25 ± 2°C). The suspensions were agitated in a flat shaker at a shaking speed of 120 rpm for 24 h. Aliquots from samples were taken at different periods of time (5, 25, 30, 60, 120, 360, and 1440 min) and analysed for Zn concentrations in the solution phase by ICP-MS after centrifuging the suspension for 20 min at 3500 rpm. The amount of Zn adsorption, q_t (mg g^{-1}), at time t (min) was calculated by Equation 7.1,

$$q_t = (C_o - C_t)\ V/M \qquad 7.1$$

Where C_o= initial concentration of Zn (mg L-1); C_t = concentration of Zn at time t (mg L^{-1}); V = volume of the solution (L) and M = mass of adsorbent used (g).

The data for Zn adsorption at different periods of time was fitted to pseudo-first order and pseudo-second order kinetic models (Ho and McKay 1998; Aryal et al. 2011). The linearised form of the pseudo-first order equation is given by Equation 7.2.

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad 7.2$$

Where q_e is the amount of Zn adsorbed at equilibrium (mg g^{-1}), and k_1 is the pseudo-first order rate constant (min^{-1}). The linearised form of the pseudo-second order equation is given by Equation 7.3.

$$t/q_t = 1/(k_2\, q_e^2) + (1/q_e)\, t \qquad 7.3$$

Where k_2 is the pseudo-second order rate constant (g mg^{-1} min^{-1}).

The kinetic data showed that Zn adsorption reached pseudo-equilibrium in approximately 24 h. Therefore, the data at 24 h were modelled using Langmuir and Freundlich equilibrium adsorption isotherms (Prasad et al. 2000; Nur et al. 2012). The linearised form of the Langmuir adsorption equation is given by Equation 7.4.

$$c_e/q_e = 1/(q_{max}\, K_L) + c_e/q_{max} \qquad 7.4$$

Where c_e is the equilibrium concentration of Zn (mg L-1), q_{max} is the maximum adsorption capacity of Zn on HFO (mg g^{-1}), and KL is a Langmuir adsorption constant. The linearised form of the Freundlich adsorption equation is given by Equation 7.5.

$$\ln q_e = \ln K_F + 1/n\, (\ln c_e) \qquad 7.5$$

Where K_F (L g^{-1}) and n are Freundlich adsorption constants.

7.5.3 Results and Discussion

7.5.3.1 Zn mobility studies

Total and soluble concentrations of metals: The total and acid soluble metal concentrations in the RDS generally followed the order Zn, Mn > Cu > Cr, Pb, Ni > Cd

(Table 7.4). This order agrees with the total metal concentrations in RDS from 8 other sites in Sydney reported in section 7.3.1. The similarity of the order for the total and acid soluble metal concentrations shows that the acid soluble metal concentration is strongly related to the total metal concentration. This was found to be true for all metals except in the case of Zn and Mn where the total Zn concentration was higher than that of Mn but acid solubility was in the reverse order. As expected the water soluble metal concentrations were much lower than the acid soluble concentrations.

The high concentrations of total and acid soluble Zn (Table 7.4) and the large proportion of Zn generally associated with the mobile soluble + exchangeable fraction (Section 7.3.1) show that, among the metals tested, Zn was most likely to be transported by stormwater to the natural water bodies.

Table 7. 4 Total, acid soluble, and water soluble metal concentrations in < 75 µm particles of RDS

Metal	Total metal (mg kg^{-1})	0.01 M HNO_3 soluble metal (mg kg^{-1})	Water soluble metal (µg kg^{-1})
Zn	727	9.30	805
Mn	522	23.03	63
Cu	314	1.10	1377
Pb	97	0.077	0.8
Cr	96	0.057	760
Ni	63	0.261	46
Cd	0.6	0.014	81

The high concentration of total and acid soluble Zn (Table 7.4) and the large proportion of Zn association with the mobile soluble + exchangeable fraction (see section 7.3.5) show that, among the metals tested, Zn had the highest potential to move with the stormwater to end up in natural water bodies.

7.5.3.2 Zinc adsorption study

The adsorption data was analysed only for Zn because the removal efficiency of this metal is more important than the other metals due to its high mobility potential among the metals in RDS as reported in the previous sections. Removal efficiency of Zn by HFO as a function of time for varying doses of HFO is presented in Figure 7.13. The results showed that for all HFO doses the adsorption of Zn was rapid during the initial period of 100 min and thereafter it increased more slowly to reach an approximate equilibrium state in about 24 h. The percentage of Zn removal increased with the dose of HFO. At 24 h, the removal percentages were approximately 70, 85, 90, and 95% for the HFO doses of 0.1, 0.2, 0.5, and 1 g L^{-1}, respectively (Figure 7.12). The increase in removal with HFO dose can be attributed to the increase in surface area of HFO providing increasing number of adsorption sites for Zn. However, the amount of Zn adsorbed per g of HFO decreased from 0.063 to 0.012 mg g^{-1} for the 0.1g L^{-1} and 1g L^{-1} HFO doses, respectively. This is because, as the HFO dose increased, the equilibrium concentration of Zn decreased, resulting in lower adsorption capacity per unit weight of adsorbent in accordance with the law of mass action.

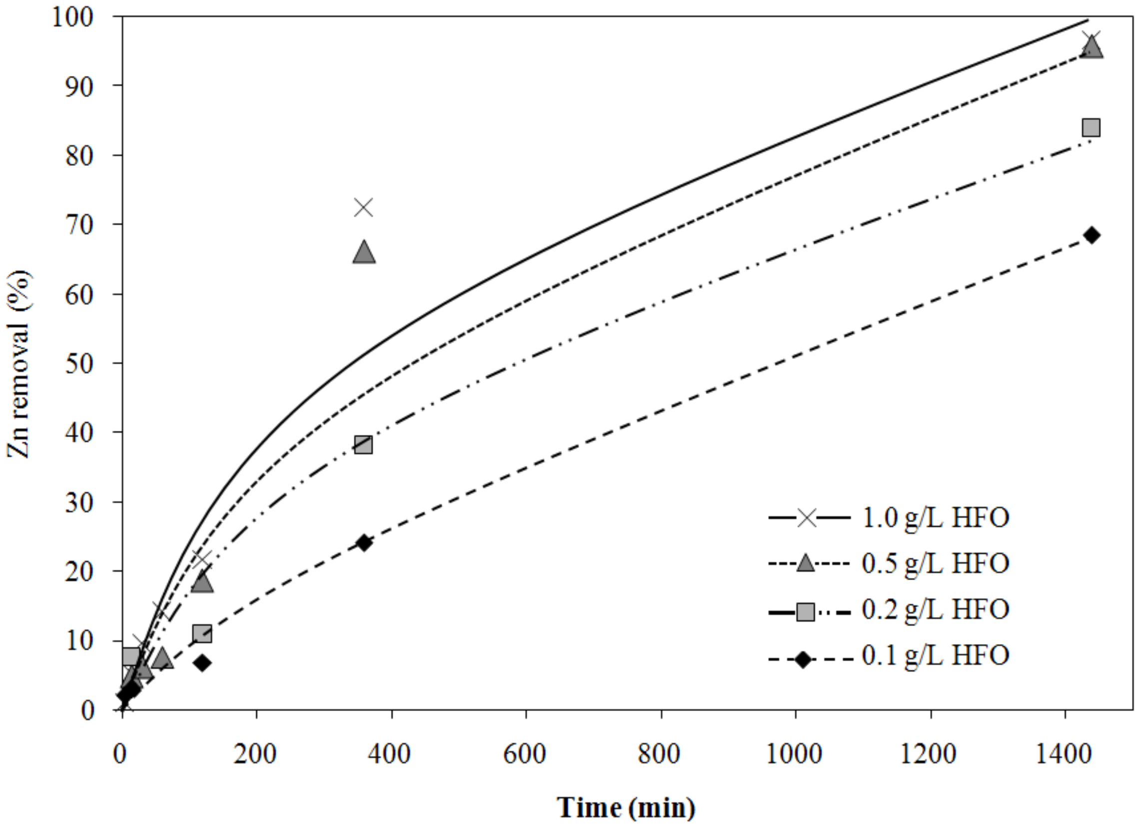


Figure 7. 12 Percentage of Zn removed by HFO from a diluted mild acid extract of RDS containing 0.093 mg Zn L^{-1}.

The adsorption kinetic data fitted well to both the pseudo-first order (R2 = 0.997) and pseudo-second order (R2 = 0.919) models with the fit being better for the former model (Figure 7.13). Furthermore, the quantity of Zn adsorbed at equilibrium (q_e) determined from the pseudo-first order model (0.014 mg g^{-1}) was approximately equal to the experimental value (0.013 mg g^{-1}), whereas the value determined from the pseudo-second order model (0.019 mg g^{-1}) was higher than the experimental value (Table 7.5). Aryal et al. (2011) also found that the pseudo-first order model fitted their data on the adsorption of Zn, Cu, Ni, Cd, and Se by the same HFO used in this study better than the pseudo-second order model. Ho and McKay (1998) reported over 250 studies in the literature on the kinetics of pollutant adsorption on various adsorbents following a pseudo-first order model, but when they reanalysed data from selected studies, the data fitted better to the pseudo-second order model. More recently, Plazinski et al., (2009) explained that in many cases the kinetic data would fit better to the pseudo-second order model because this model has the ability for ‘smoothing’ the experimental data. The reason for the pseudo-first order model fitting the adsorption data of Zn better in this study and of several heavy metals in the study of Aryal et al. (2011) could be a result of the very low concentrations of metals used in the respective studies. Plazinski et al., (2009) explained that, at low concentrations of adsorbate the rate of adsorption is independent of the adsorbed amount present on the adsorbent surface at a given time and thus the data followed pseudo-first order kinetics.

Table 7. 5 Kinetic and equilibrium models parameters for the adsorption of Zn on HFO

Kinetic models

		q_e	Pseudo first order			Pseudo second order		
HFO	C_o	experimental	q_e	k_1	R^2	q_e	k_2	R^2
g L^{-1}	mg L^{-1}	mg g^{-1}	mg g^{-1}	min^{-1}		mg g^{-1}	g mg^{-1} min^{-1}	
1	0.093	0.0135	0.014	0.0033	0.997***	0.019	0.109	0.919***

Equilibrium models

Langmuir		Freundlich	
q_{max} (mg g^{-1})	0.22	K_F (L g^{-1})	1.55
K_L	26	n	1.28
R^2	0.686	R^2	0.940*

*, significant ($p < 0.05$); ***, significant ($p < 0.001$)

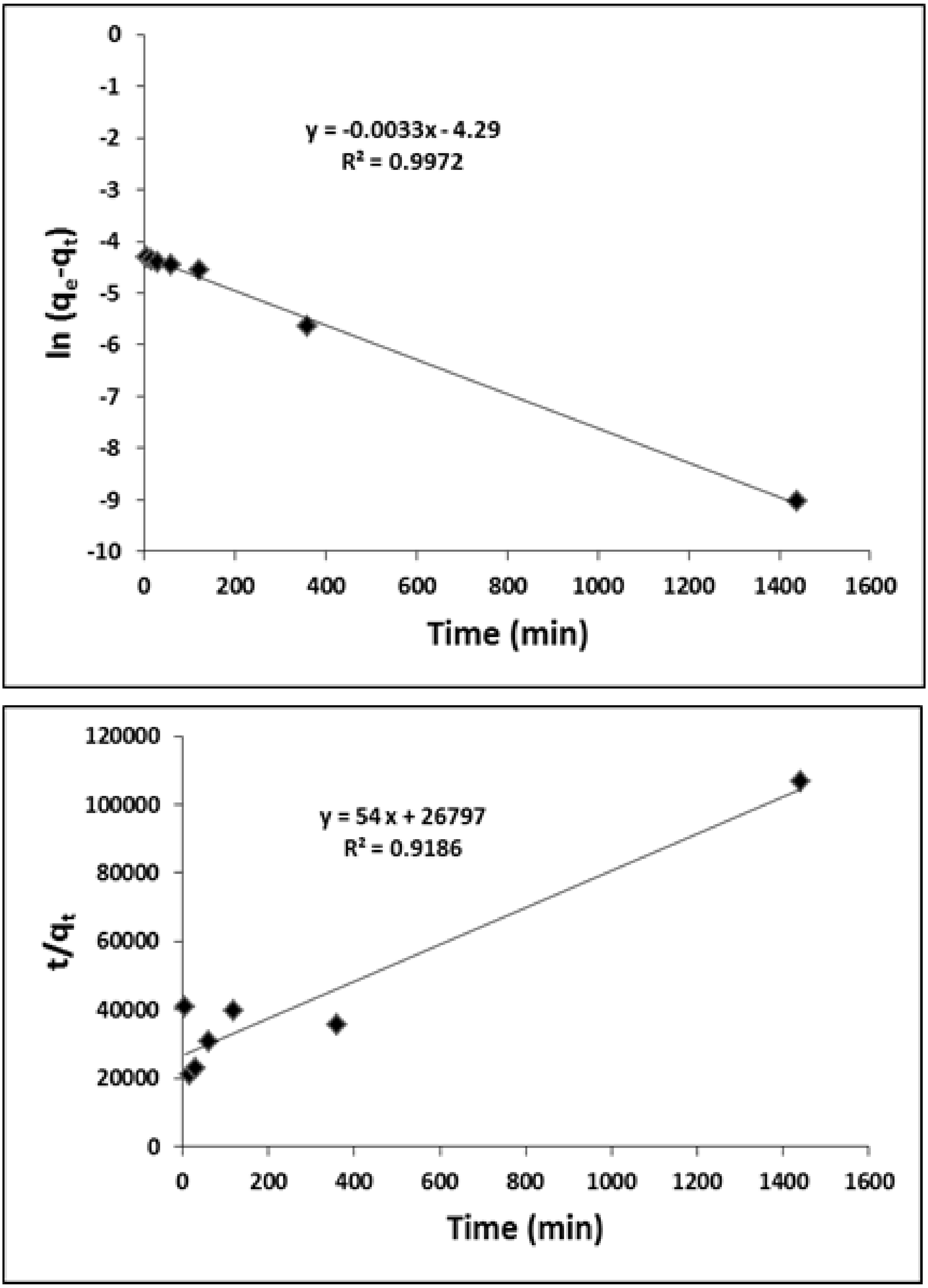


Figure 7. 13 Kinetics of Zn adsorption on HFO. (a) Pseudo-first order model plot; (b) Pseudo-second order model plot.

The equilibrium adsorption study was conducted with a small number of samples due to the availability of only a limited volume of acid extract of the RDS having appreciable Zn concentration. Within this small set of adsorption data the Freundlich model was found to be satisfactory for describing the equilibrium adsorption relationship (R2 = 0.940, number of samples 4) (Table 7.5, Figure 7.14). The relationship obtained by the Langmuir adsorption model was not significant (R2 = 0.686). The Freundlich adsorption model describes adsorption on exponentially distributed heterogeneous surface sites and their energies, whereas the Langmuir adsorption model describes adsorption on homogeneous surfaces having surface sites of similar adsorption energies (Faust and Aly 1989). The satisfactory fit of the data to the Freundlich model suggests that Zn was adsorbed on heterogeneous sites on the HFO. The value of the Freundlich constant ‘n’, which estimates the adsorption intensity of Zn on the HFO surface, was higher than 1, indicating favourable adsorption (Table 7.6). As HFO has a zero point of charge around neutral pH (Streat et al. 2008) and the solution used for the adsorption study also had near neutral pH, the main mechanism of adsorption of Zn is unlikely to be electrostatic attraction (outer-sphere complexation) but rather occurring by ligand exchange (inner-sphere complexation) (Lee and Anderson, 2005; Loganathan et al., 2012).

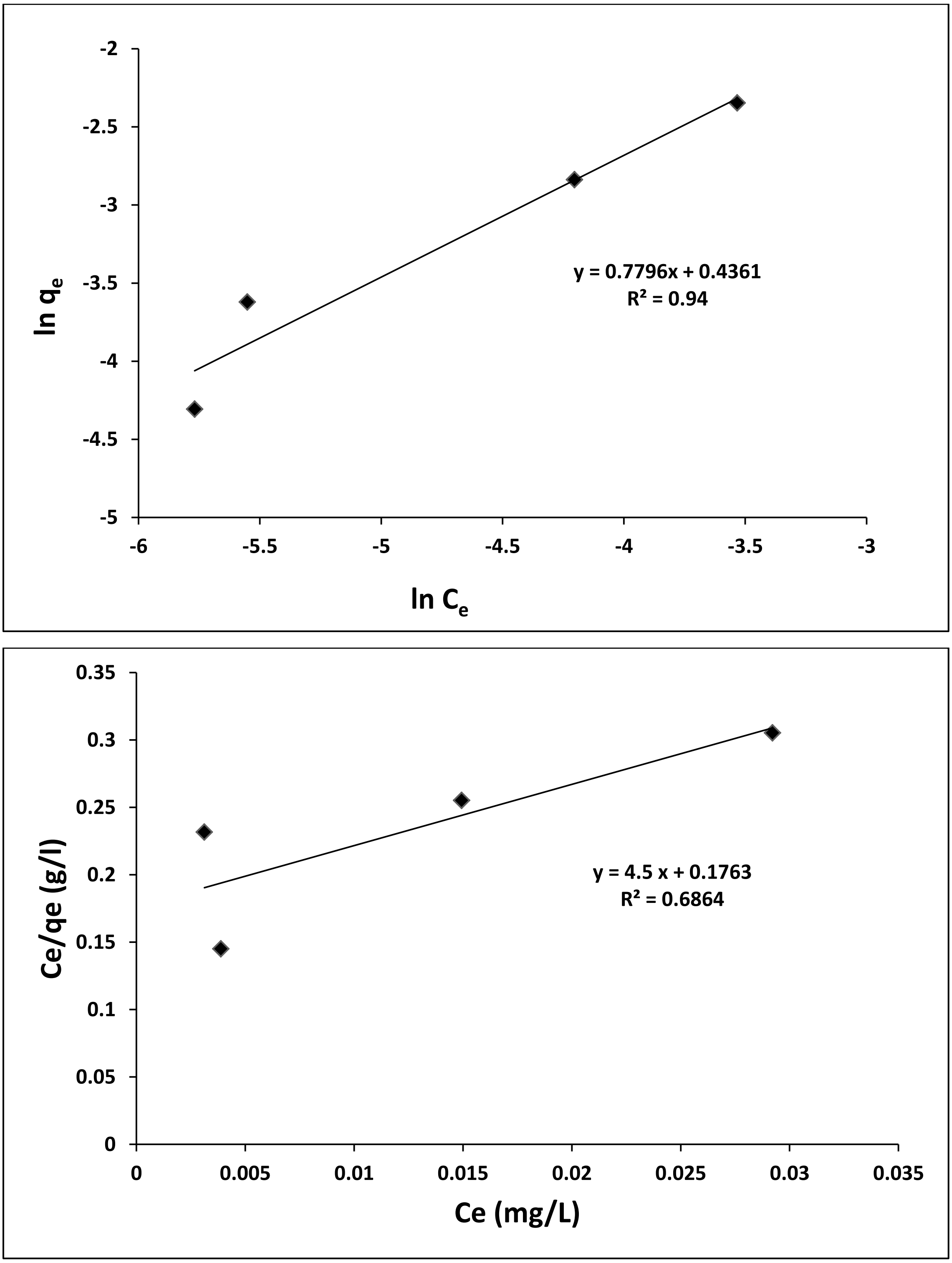


Figure 7. 14 Equilibrium Zn adsorption on HFO. (a) Freundlich isotherm model plot; (b) Langmuir isotherm model plot.

7.5.4 Summary

Among the seven heavy metals tested in this study, Zn was found to be the metal having the highest total and acid-soluble concentrations as well as the highest soluble + exchangeable fraction concentration in RDS from a motorway site in Sydney, Australia, experiencing high vehicle traffic density. Zinc along with Cu, was enriched in the RDS as a result of vehicle activity. In a batch equilibrium study, 1 g HFO L^{-1} was able to remove approximately 95% of Zn in 24 h from a model stormwater containing 0.093 mg Zn L^{-1} obtained from a diluted and pH adjusted (pH 6.8) mild acid extract of the RDS. The equilibrium adsorption data fitted well to the Freundlich adsorption model. The kinetic adsorption data fitted well to both the pseudo-first and second order models, with the fit being better for the pseudo-first order model. The study suggests that hydrous ferric oxide can be used to effectively remove Zn and possibly other heavy metals from contaminated stormwater.

Chapter 8

8. Conclusions

8.1 Conclusions

It is important to explore sustainable measures of improving urban stormwater quality to meet water quality objectives for harvesting and/or discharge to surface waters. Some of the common contaminants that contaminate urban stormwater are suspended solids, poly aromatic hydrocarbon (PAHs), heavy metals and biodegradable organic (BOD). Onsite remediation is a confined system designed such that all treatment processes take place within the system, and adequate treatment occurs prior to the release of stormwater to the surrounding environment or to the conventional drainage system. This is done by restricting or limiting water and pollutant movement to a certain area.

GAC and anthracite media biofilters

In this study, GAC and anthracite media biofilters were tested for stormwater pollution control. The main conclusions were:

- The average turbidity removal efficiency of up to 75% and 60% was achieved using the GAC and anthracite media filters, respectively.
- Headloss development was low for both anthracite and GAC filters.
- The highest DOC removal efficiency of up to 99% was achieved using the GAC media filter. However the anthracite filter showed removal efficiencies of only up to 20%.
- Molecular weight distribution of organic compounds showed an almost similar trend to the DOC removal. Compared with anthracite filter media, the GAC biofilter removed a much larger range of organic compounds present in the stormwater. The GAC biofilter was found to remove organic matter earlier as compared with anthracite.
- The colour removal was 95% using the GAC filter while the colour removal detected in the anthracite filter was small.
- In general the GAC filter showed a higher heavy metal removal efficiency than anthracite and the removals of zinc, iron, lead and nickel were good. However the concentration of heavy metals in the raw stormwater sample was low.

In another study, the GAC biofilter (filter depth 30 cm and 35 cm) was found to remove a significant amount of organic matter from the diluted synthetic landfill leachate. The experiments were conducted at high (2 m/h) and low (0.2 m/h) flow velocity through the GAC filter to represent insitu and exsitu biofiltration. The results showed that organic matter can be removed in a consistent manner for a long period of time. GAC bio-filtration led to a consistent TOC removal even after a long period of operation without the need to regenerate the activated carbon. Even after 30-50 days of continuous running, the organic removal efficiency from the GAC bio-filter was approximately 40% and 60% when high (2 m/hr) and (0.2 m/hr) low filtration velocities were used, respectively. It should be noted that the performance can be enhanced by using a larger filter depth which is the case in real situations.

The three stage filter system

In this study, three different filter systems that could be used for stormwater pollution control were tested. The main conclusions were:

- The highest TOC removal efficiency of up to 99% was achieved by the second stage GAC media filter. The first stage sand filter achieved only 6% of the TOC removal.
- A major removal of turbidity of up to 70% was achieved by the sand media filter and, the second stage GAC filter resulted in an additional removal of 43%.
- Headloss variation was high for the sand filter as it encountered by high turbid stormwater.
- The use of the PuroliteA520E filter media as the third stage filter was capable of removing up to 89% of nitrate within 6 hours, however no phosphate removal was achieved. Thus it is vital to have GAC and Purolite as a media in a filtration system along with sand to achieve organic and nutrient removal.

Heavy metals removal using hydrous ferric oxide

The column kinetics experiment showed that HFO is an effective sorbent in removing contaminant ions, especially Zn, Cd and Cu, from stormwater over a long period. The intermittent conditions of runoff, each of 8 h duration followed by a 40 hr no-flow period could be more favorable for the removal process than the continuous removal process. The efficiency of removal for Cu and Zn was 42-63% for the first three runs and 36-59% for the last four runs. For Cd, Se and Ni the % efficiencies were 21-25, 17-20 and 11-13, respectively for the first three runs and 37-50, 8-12 and 18-23, respectively for the last four runs.

Heavy metals removal using a mixture of hydrous ferric oxide, calcium hydroxide and manganese oxide

The column kinetics experiment showed that a mixture of HFO, $Ca(OH)_2$ and MnO_2 is an effective sorbent/filter media in removing both cationic (Cd, Cu, Ni, Zn) and oxy anionic (Se) contaminants from stormwater over a long period of time. This filter media has potential to be incorporated into a water treatment process (or treatment train) where other complimentary treatment systems are used to remove other contaminants of interest such as nutrients and organics to produce high quality effluent for reuse purposes. The intermittent conditions of runoff, each of 8 h duration followed by a 40 h no-flow period (wetting and drying conditions) could be more favourable for the removal process than a continuous removal process. Furthermore a lower flow rate of 0.75 m/h gave greater removal efficiency than a higher flow rate (1.5 m/h). The $Ca(OH)_2$ in the column produced a high pH at the initial runs that helped to remove more heavy metals but less Se. The presence of MnO_2 increased the removals of all contaminant ions.

Urban road-deposited sediments

Across Sydney's motorways, at sites away from major industries and mining areas, RDS significantly enriched only Cu and Zn, likely due to a contribution from traffic related activities such as brake linings and tyre wear, respectively. Enrichment data as well as correlation and cluster analyses suggested that Fe, Mn, Cr and Ni had a primarily lithogenic origin. Cadmium was significantly correlated with Zn, and Pb with Cu, suggesting possible common origins for each of these pairs of metals. Metal fractionation data showed that a large percentage of all metals across most sites were in the residual fraction. Iron and Cr had the highest residual fraction further implying their lithogenic origin. Of all the metals, Zn had the highest exchangeable fraction that is readily-mobile. This suggests that Zn is likely to be the most mobile of all metals in RDS and may be released in appreciable amounts into the stormwater runoff from the roads. Copper was the only metal present appreciably in the organic fraction. Thus, it is necessary to remove these heavy metals before it enters to storage from the stormwater runoff. Furthermore, this study concentrated only on the heavy metals. It is equally important to measure the organics, in particular, the polyaromatic hydrocarbon in the RDS.

References

Abdel-Samad H, Watson P R. An XPS study of the adsorption of lead on goethite (a-FeOOH). Applied Surface Science 1998; 136(4): 46-54.

Abollino O, Giacomino A, Malandrino M. and Mentasti E. Interaction of metal ions with montmorillonite and vermiculite. Applied Clay Science 2008; 38(3–4): 227–36.

Aguado J, Arsuaga J M, Arencibia A, Lindo M, Gascón V. Aqueous heavy metals removal by adsorption on amine-functionalized mesoporous silica. Journal of Hazardous Materials 2009; 163: 213–21.

Ahmad R, Amirtharajah A. Detachment of Particles during Biofilter Backwashing. Journal of the American Water Works Association 1998; 90: 74-85.

Allen S J, 1996. ‘Types of Adsorbent Materials’ in Use of Adsorbents for the Removal of Pollutants from Wastewaters, ed. G. McKay, CRC Press, Florida, United States of America, pp. 59 – 97.

Allison R, Pezzaniti D. ‘Gross Pollutant and Sediment Traps’ in Australian Runoff Quality – A Guide to Water Sensitive Urban Design, ed. T.H.F. Wong, Engineers Australia, Australia, 2005, pp. 1–16

Alonso C, Suidan M T, Sorial G A, Smith F L, Biswas P, Smith P J, Brenner R C.. Gas treatment in trickle-bed biofilters: biomass, how much is enough? Biotechnology and Bioengineering 1997; 54: 583-94.

Alonso C, Suidan M T, Kim B R, Kim B J. Dynamic Mathematical Model for the Biodegradation of VOCs in a Biofilter: Biomass Accumulation Study. Environmental Science and Technology 1998; 32: 3118- 23.

Ambe S. Adsorption Kinetics of Antimony (V) Ions onto a-Fe203 Surfaces from an Aqueous Solution. Langmuir 1987; 3:489-93.

Anderson J. Potential for water recycling in Australia—expanding our horizons. Desalination 1996; 106 (1-3)106:151–56.

Andrews G F, Tien C. Bacterial Film Growth in Adsorbent Surfaces, American Institute of Chemical Engineers 1991; 27 (5): 396- 403.

ANZECC (2000a).Australian and New Zealand guidelines for fresh and marine water quality. Volume 1: The guidelines. Canberra, Australia, Australian and New Zealand Environment and Conservation Council, Agriculture and Resource

Management Council of Australia and New Zealand.

ANZECC (2000b).Australian and New Zealand guidelines for fresh and marine water quality. Volume 2: Aquatic Ecosystems. Canberra, Australia, Australian and New Zealand Environment and Conservation Council, Agriculture and Resource Management Council of Australia and New Zealand.

Argue J R , Pezzaniti D, 2005. Infiltration systems. In: Wong, T.H.F. (Ed.), Australian Runoff Quality: A Guide To Water Sensitive Urban Design. Engineers Australia, Sydney.

Aribike D S, Olafadehan O A. Modeling of Fixed Bed Adsorption of Phenols on Granular Activated Carbon. Theoretical Foundations of Chemical Engineering 2008; 42 (3):257–63

Aryal R, Vigneswaran S, Kandasamy J, Naidu N. Urban stormwater quality and treatment. Korean Journal of Chemical Engineering 2010; 27(5): 1343-59.

Aryal R, Vigneswaran S, Loganathan P, Kandasamy J, Mohammed T. Hydrous iron oxide for removal of inorganic contaminants in simulated stormwater: A batch sorption kinetics study. Korean Journal Chemical Engineering 2011; 28:1706-12.

Asami M, Aizawai T, Morioka T, Nishijma W, Tabata A, Magara Y. Bromate removal during transition from new granular activated carbon (GAC) to biological activated carbon (BAC) Water Research 1999; 33 (12):2797-804.

Australian Bureau of Statistics.3222.0 – Population Projections, Australia, 2006-2101. Released 2008. http://www.abs.gov.au/Ausstats/abs@.nsf/mf/3222.0

Australian Drinking Water Guidelines (2004), National Water Quality Management Strategy, Endorsed by NHMRC 10 – 11 April 2003. ISBN Print: 186496118X,

ISBN Online: 1864961244.

Bae B, Jung Y, Han W, Shin H. Improve brine recycling during nitrate removal using ion exchange. Water Research 2002; 36(13): 3330- 40.

Baek S O, Field R A, Goldstone M E, Kirk P W, Lester J N, And Perry R. A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior. Water, Air, and Soil Pollution 1991; 60: 279-300.

Balistrieri L S, Chao T T. Adsorption of selenium by amorphous iron oxyhydroxide and manganese dioxide. Geochimica et Cosmochimica Acta 1990; 54: 739-51.

Barraud S, Gautier A, Bardin J P, Riou V. The impact of intentional stormwater infiltration on soil and groundwater. Water Science and Technology 1999; 39(2): 185– 92.

Beecham S. Water Sensitive Urban Design: A Technological Assessment, Journal of the Stormwater Industry Association, Waterfall, 2003 Vol. 17.

Begum S, Rasul M G, Brown R J. A comparative review of stormwater treatment and reuse techniques with a new approach: Green Gully. WSEAS Transactions on environment and development 2008; 4(11): 1002-13.

Bilotta G S, Brazier R E. Understanding the influence of suspended solids on water quality and aquatic biota. Water Research 2008; 42:2849 – 61.

Bingham D, Boucher W, Boucher P. Urban runoff pollution prevention and control planning Handbook 1993 EPA/625/R93/004 September 1993 pp(1-173).

Birch G F, Scollen A. Heavy metals in road dust, gully pots and parkland soils in a highly urbanised sub-catchment of Port Jackson, Australia. Australian Journal Soil Research 2003; 41:1329-42

Blecken G T, Zinger Y, Deletić A, Fletcher T D, Viklander M. Influence of intermittent wetting and drying conditions on heavy metal removal by stormwater biofilters. Water Research 2009a; 43: 4590-98.

Blecken G T, Zinger Y, Deleti´c A, Fletcher T D, Viklander M. Impact of a submerged zone and a carbon source on heavy metal removal in stormwater biofilters. Ecological Engineering 2009b; 35 (5): 769–78.

Borchardt D, Sperling F. Urban stormwater discharges: ecological effects on receiving waters and consequences for technical measures. Water Science and Technology 1997; 36 (8-9):173–8.

Brinkmann W L F. Urban stormwater pollutants: sources and loadings. Geology Journal 1985; 11: 277-83.

Brown P A, Gill S A, Allen S J. Metal removal from wastewater using peat. Water Research 2000; 34 (16) :3907-16.

Castleton H F, Stovin V, Beck S B M, Davison J B. Green roofs; building energy savings and the potential for retrofit. Energy and Buildings 2010; 42:1582–91.

Cimino G, Cappello R M, Caristi C, Toscazo G. Characterisation of carbons from olive cake by sorption of wastewater pollutants. Chemosphere 2005; 61: 947–55.

Chang S, Wang K, Chang H, Ni W, Wu B, Wong R, Lee H, Comparison of source identification of metals in road-dust and soil. Soil Sediment Contaminant 2009; 18: 669-683.

Characklis W G, Marshall K C. "Microbial fouling," In Biofilms. Wiley, New York 1990 pp. 523 – 584.

Charlesworth S, Everett M, McCarthy R, Ordonez A, de Miguel E. A comparative study of heavy metal concentration and distribution in deposited street dusts in a large and a small urban area: Birmingham and Coventry, West Midlands, UK. Environmental International 2003; 29:563-73.

Chaudhary D S, Vigneswaran S, Jegatheesan V, Ngo H H, Moon H, Shim W G, Kim S H. Granulated activated carbon (GAC) adsorption in tertiary wastewater treatment: experiments and models, Journal Water Science and Technology 2003; 47(1):113-20.

Chaudhary D S, Vigneswaran S, Ngo H H, Shim W G, Moon H, Biofilter in water and wastewater treatment. Korean Journal Chemical Engineering 2007; 20 (6):1054-65.

Cherkauer D S and Zager J P. Groundwater interaction with a kettle-hole lake: relation of observations to digital simulations. Journal of Hydrology 1989; 109: 167-84.

Chiew F H S, Mudgway L B, and McMahon T A. 1997 ‘‘Urban stormwater pollution.’’ Cooperative Research Centre for Catchment Hydrology, Industry Rep., Melbourne, Australia.

Chouyyok W, Wiacek R J, Pattamakomsan K, Sangvanich T, Grudzien R M, Fryxell G E. Phosphate Removal by Anion Binding on Functionalized Nanoporous Sorbents Environment Science Technology 2010; 44:3073–78.

Christoforidis A, Stamatis N. Heavy metal contamination in street dust and roadside soil along the major national road in Kavala’s region, Greece. Geoderma 2009; 151: 257-63.

Clark S, Pitt R, Easton J, Mirov O, Parmer K and Field R. 1997, Pollutant Removal Capacity of Stormwater Filtration Media – Breakthrough Tests, 70th Annual Water Environment Federation Conference and Exposition, Chicago, United States of America United States of America

Clark, S. and Pitt, R., 1999, Stormwater Treatment At Critical Areas – Evaluation of Filtration Media, US Environmental Protection Agency EPA/600/R-00/010, Ohio, United States of America.

Cornell R M and Schwertmann U. The iron oxides: structure, properties, reactions, occurrences and uses, (2003). 2nd Edition, Weinheim Wiley – VCH, 664 pages.

Coombes P, Kuczera G, Kalma J D, Argue J R. An evaluation of the benefits of source control measures at the regional scale. Urban Water 2002; 4:307–20.

Cooper C M and Lipe W M. Water quality and agriculture: Mississippi experiences. Journal of Soil and Water Conservation 1992; 47 (3): 220-23.

Craig Windram, Drought in Australia- The lessons we can learn for tackling climate change. Think Carbon website for Craig Windram 22 Jun 2009

http://thinkcarbon.wordpress.com/2009/06/22/drought-in-australia-%E2%80%93-the-lessons-we-can-learn-for-tackling-climate-change/

CSIRO 1999, Urban stormwater: Best Practice Environmental Management Guidelines, CSIRO Publishing, Collingwood Australia.

Dahlenburg J. An Overview of Resources Available to Facilitate the Planning, Design and Uptake of Water Sensitive Urban Design (WSUD), Stormwater Industry Association 2005 Regional Conference, Port Macquarie, NSW SUSTAINABLE STORMWATER: You Are Responsible - Justify Your Decisions. 20-21 April 2005.

Dallmer L. SQIRTS – an on-site stormwater treatment and reuse approach to sustainable water management in Sydney. Water Science Technology 2002; 46 (6–7):151–58.

Davis B S, Birch G F. Spatial distribution of bulk atmospheric deposition of heavy metals in metropolitan Sydney, Australia. Water Air Soil Pollution 2011; 214:147-62.

Davies J A, and Leckie J O. Surface ionization and complexation at the oxide/water interface. II. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. Journal of Colloid and Interface Science 1978; 67(1):90-107.

DEC. (2006) Managing Urban Stormwater-Harvesting and Reuse, NSW Department of Environment and Conservation, Vol 1 and 2, ISBN 1741378753. April 2006, NSW Government, Sydney, Australia DEC 2006/137.

Dechesne M, Barraud S, Bardin J. Indicators for hydraulic and pollution retention assessment of stormwater infiltration basins. Journal of Environmental Management 2004; 71: 371–80.

Della Rocca C, Belgiorno V and Meric S. Overview of in- situ applicable nitrate removal processes. Desalination 2007; 204 (1-3):46-62.

Department of the Army, USA, Technical Manual TM 5-813-8, Water Desalination 1986.

Dierkes C, Benze W, Wells J. 2002, Sustainable Urban Drainage and Pollutant Source Control by Infiltration, 6th Regional Conference on Urban Stormwater, Stormwater Industry Association, Orange, Australia

Drapper D, Tomlinson R., Williams P. Pollutant concentration in road runoff: Southeast Queensland case study. J. Environmental Engineering 2000; 126:313–20.

Dunphy A. PhD thesis 2007, The Development of Confined Water Sensitive Urban Design (WSUD) Stormwater Filtration/Infiltration Systems for Australian Conditions. University of Technology Sydney, Australia.

Duong T T T, Lee B. Determining contamination level of heavy metals in road dust from busy traffic areas with different characteristics. Journal Environmental Management 2011; 92:554-62.

Dzombak D A and Morell F M M. Sorption of cadmium on hydrous ferric oxide at high sorbate/sorbent ratios: equilibrium, kinetics, and modeling. Journal of Colloid and Interface Science 1986; 112(2):588-98.

Eaton A, Clesceri L, Rice E, Greenberg A, (2005) Standard Methods for the Examination of Water & Wastewater. 21st ed. 2005, Published jointly by: American Public Health Association, American Water Works Association, Water Environment Federation

Edwards M, Hidmi L, and Gladwell D, Phosphate inhibition of soluble copper corrosion by-product release. Corrosion Science 2002; 44 (5): 1057–71.

Ellis J B, Revitt D M. Incidence of heavy metals in street surface sediments: solubility and grain size studies. Water Air Soil Pollution 1982; 17: 87–100.

Emilsson T. Vegetation development on extensive vegetated green roofs: Influence of substrate composition, establishment method and species mix. Ecological Engineering 2008; 33: 265–77.

Eriksson E, Baun A. Selected stormwater priority pollutants - a European perspective. Science of The Total Environment 2007; 383(1-3):41-51.

Environmental Protection Agency. 1992. Managing Non-point Source Pollution: Final Report to Congress on Section 319 of the Clean Water Act. United States Environmental Protection Agency #EPA-506/9-90. Washington, DC: USEPA

Office of Water.

Environmental Protection Agency. 1993. Guidance Specifying Management Measures for Sources of Nonpoint Source Pollution in Coastal Waters. United States Environmental Protection Agency #840-B-92-002. Washington, DC: USEPA Office of Water.

Evangelisti & Associates in association with Tony Wong and Alan Tingay & Associates (1998) A Manual for Managing Urban Stormwater Quality in Western Australia. Prepared for Water and Rivers Commission.

Ewen C, Anagnostopoulou MA, Ward NI. Monitoring of heavy metal levels in roadside dusts of Thessaloniki, Greece in relation to motor vehicle traffic density and flow. Environmental Monitoring Assessment 2009; 157: 483-98.

Faiz Y, Tufail M, Javed M , Chaudhry M, Siddique N. Road dust pollution of Cd, Cu, Ni, Pb and Zn along Islamabad Expressway, Pakistan. Microchemical Journal 2009; 92:186–92.

Farley K J, Dzombak D A, Morel F M M. A surface precipitation model for the sorption of cations on metal oxides. Journal of Colloid and Interface Science 1985; 106: 226-42.

Faust S D, Aly O M (1989) Adsorption Process for Water Treatment. Butterworths, Boston.

Forbes E A, Posner A M and Quirk J P The specific adsorption of divalent Cd, Co, Cu, Pb, and Zn on goethite. Journal of Soil Science 1976; 27:154-66.

Fukushi K, and Sverjensky D A. A surface complexation model for sufate and selenate on iron oxides consistent with spectroscopic and theoretical molecular evidence. Geochimica et Cosmochimica Acta 2007; 71: 1-24.

Genc-Fuhrman H, Wu P, Zhou Y and Ledin A. Removal of As, Cd, Cr, Cu, Ni and Zn from polluted water using an iron based sorbent. Desalination 2008; 226:357-70.

Gobel P, Dierkes C. and Coldewey W C. Storm water runoff concentration matrix for urban areas. Journal of Contaminant Hydrology 2007; 91:26–42.

Gonzàlez-Macias C, Schifter I, Lluch-cota DB, Mendez-Rodriguez L, Hernàndez-Vazquez S. Distribution, enrichment and accumulation of heavy metals in coastal sediments of Salina Cruz Bay, Mexico. Environmental Monitoring Assessment 2006; 118: 211-30.

Gerritse R G, Barber C and Adeney J A. The impact of residential urban areas on groundwater quality: Swan Coastal Plain, Western Australia. CSIRO (1990) Water Resources Series No 3, Canberra, ACT, Australia.

Green Roofs for Healthy Cities Award of Excellence 2006, http://www.hydrotechusa.com/ballard_index.html

Greenway M. Stormwater Treatment Trains in Subtropical Australia Wetland and Pond Systems: How Effective are they in Improving Water Quality and Enhancing Ecosystem Biodiversity? 2005, 10th International Conference on Urban Drainage, Copenhagen, Denmark

Hamilton RS, Revitt DM, Warren RS. Level and physicochemical association of Cd, Cu, Pb and Zn in road sediments. Science Total Environment 1984; 33:59-74.

Han R, Zou W, Zhang Z, Shi J, Yang J. Removal of copper(II) and lead(II) from aqueous solution by manganese oxide coated sand I. Characterization and kinetic study. Journal of Hazardous Materials (2006a); B137: 384–95.

Han R, Zou W, Li H, Li Y, Sh J. Copper(II) and lead(II) removal from aqueous solution in fixed bed columns by manganese oxide coated zeolite. Characterization and kinetic study. Journal of Hazardous Materials (2006b); B137: 934–42.

Hatt B E, Deletic A, Fletcher T D, Integrated treatment and recycling of stormwater: a review of Australian practice. Journal of Environmental Management 2006; 79: 102–13.

Haubner S, Reese A, Brown T, Claytor R, Debo T. Georgia Stormwater Management Manual Volume 2 (Technical Handbook) First Edition, Atlanta Regional Commission, August 2001.

Herngren L, Goonetilleke A. and Ayoko G A. Analysis of heavy metals in road-deposited sediments. Analytica Chimica Acta 2006; 571:270–78.

Ho Y S, McKay G. A comparison of chemisorption kinetic models applied to pollutant removal on various sorbants. Trans Institute Chemical Engineering 1998 Part B 76: 332–340.

Hoang T T L, Vigneswaran S, Ngo H H, Kandasamy J, and Chaudhary D, Performance Evaluation and Mathematical Modelling of Granular Activated Carbon (GAC) Biofiltration in Wastewater Treatment, Korean Journal of Chemical Engineering 2008; 25(2):03-16.

Hofmann A, Pelletier M, Michot L, Strander A, Schurtenberger P, Kretzschmar. Characterization of the pores in hydrous ferric oxide aggregates formed by freezing and thawing Journal of Colloid and Interface Science 2004; 271:163–73.

Hrapovic L. (2001). Biodegradation of organic contaminants under diffusive transport through clayey soil. London.Ont, The University of Western Ontario. Ph.D. thesis.

Huber, S. A. Evidence for membrane fouling by specific TOC constituents. Desalination 1998; 119(1-3):229-34.

Ioannidou O, Zabaniotou A. Agricultural residues as precursors for activated carbon production. Renewable and Sustainable Energy Reviews 2007; 11(9): 1966-2005.

James Melonas, A Citizen’s Guide to Stormwater Management in Maryland, August 2004

Jim C Y, Tsang S W. Ecological energetics of tropical intensive green roof Energy and Buildings 2011; 43: 2696–704.

Jorgensen T C, Weatherley L R. Ammonia removal from wastewater by ion exchange in the presence of organic contaminants, Water Research 2003; 37:1723-8.

Joshi UM, Vijayaraghavan K, Balasubramanian R. Elemental composition of urban dusts and their dissolution characteristics in various aqueous media. Chemosphere 2009; 77: 526-33.

Kadioglu YK, Üstündag Z, Solak A, Karabiyikoglu G. Sources of environmental pollution in Ankara (Turkey): Geochemistry and traffic effects-PEDXRF applications. Spectroscopy Letters 2010; 43:247-57.

King K W, Balogh J C, Harmel R D. Nutrient flux in storm water runoff and base flow from managed turf. Environmental Pollution 2007; 150: 321-28.

Kookana R S, Naidu R, and Tiller K G. Sorption non-equilibrium during cadmium transport through soils. Australian Journal of Soil Research 1994; 32:635–51.

Kumar M, Furumai H, Kurisu F, Kasuga I. Evaluating the mobile heavy metal pool in soakaway sediment, road dust and soil through sequential extraction and isotope exchange. Water Science Technology 2010; 62:920-28.

Latimer J S, Hoffman E J, Hoffman G, Fasching J L, Quinn J G. Sources of petroleum hydrocarbons in urban runoff. Water Air and Soil Pollution 1990; 52: 1-21.

Lee M, Paik I S, Kim I, Kang H, Lee S. Remediation of heavy metal contaminated ground water originated from abandoned mine using lime and calcium carbonate. Journal of Hazardous Materials 2007; 144: 208–14.

Lee S, Anderson P R. EXAFS study of Zn sorption mechanisms on hydrous ferric oxide over extended reaction time. Journal of Colloid and Interface Science 2005; 286 (1): 82–9.

Lenntech Water Treatment Solution: http://www.lenntech.com/mineral-water/composition.htm#ixzz0f0U5pluf

Liu D, Sansalone J J, Cartledge F K. Comparison of sorptive filter media for treatment of metals in runoff. Journal Environmental Engineering ASCE 2005; 131 (8): 1178–86.

Loganathan P. Vigneswaran S, Kandasamy J, Naidu R. Cadmium sorption and desorption in soils – a review. Critical Reviews in Environmental Science Technology 2011 (in press) DOI: 10.1080/10643389.2010.520234.

Loganathan P, Vigneswaran S, Kandasamy J, Naidu R. Cadmium sorption and desorption in soils: A review. Critical Reviews in Environmental Science and Technology 2012a; 42: 489-533.

Loganathan P, Vigneswaran S, Kandasamy J. Road-deposited sediment pollutants: a critical review of their characteristics, source apportionment and management. Critical Reviews in Environmental Science and Technology 2012b (in press).

Loska K, Wiechuła D. Application of principal component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik Reservoir. Chemosphere 2003; 51: 723–33.

Lu P, Huck P M. Evaluation of Methods for Measuring Biomass and Biofilm Thickness in Biological Drinking Water Treatment. AWWA, Water Quality Technology Conference (WQTC). 1993, Miami, Florida.

Lu X, Wanga L, Lei K, Huganga J, Zhaia Y. Contamination assessment of copper, lead, zinc, manganese and nickel in street dust of Baoji, NW China. Journal Hazard Material 2009; 161:1058–62.

Lynam D R, Pfeifer G D. Human health effects of highway-related pollutants, in: Hamilton RS, Harrison RM. (Eds), Highway Pollution, Studies in Environmental Science 44. 1991. Elsevier, Amsterdam, pp 259-80.

Martin B D, Parsons S A and Jefferson B. Removal of phosphate from municipal wastewaters using a polymeric anion exchanger bound with hydrated ferric oxide nanoparticles, water science and Technology 2009; 60 (10):2637-45.

McBride M B. Reactions controlling heavy metal solubility in soils. Advances in Soil Science 1989; 10:1–56.

McKay G. Use of adsorbents for the removal of pollutants from wastewaters, CRC Press Inc., Florida, USA, 1996.

McKenzie E R, Money J E, Green P G, Young T M. Metals associated with stormwater-relevant brake and tyre samples. Science Total Environment 2009; 407:5855-60.

McKenzie R M. The adsorption of lead and other heavy metals on oxides of manganese and iron. Australian Journal of Soil Research 1980; 18:61-73.

Mitchell V G, Mein R G, McMahon T A. The Reuse Potential of Urban Stormwater and Wastewater 1999 (No. 99/14). Cooperative Research Centre for Catchment Hydrology, Melbourne.

Mitchell V G, Mein R G, McMahon T A. Utilising stormwater and wastewater resources in urban areas. Australian Journal of Water Resources 2002; 6 (1): 31–43.

Mouritz M J. PhD Thesis 1996, Sustainable Urban Water Systems: Policy and Professional Praxis, ISTP, Murdoch University, Australia.

Nanda S, Sarangi P K, Abraham J. Microbial biofiltration technology for odour abatement, International Research Journal of Microbiology 2011; 2(11):415-22.

Ng AH-M, Chang H C, Zhang K, Ge L, and Rizos C. Land Subsidence Monitoring in Australia and China using Satellite Interferometry. International Association of Geodesy Symposia 2008; 133(4):743-50.

Ngabe B, Bidleman F T, Scott G I. Polycyclic aromatic hydrocarbons in storm runoff from urban and coastal South Carolina. Science Total Environment 2000; 255: 1–9.

Nogaro G, Mermillod-Blondin F, Montuelle B, Boisson J, Lafont M, Volat B, Gibert J. Do tubificid worms influence organic matter processing and fate of pollutants in stormwater sediments deposited at the surface of infiltration systems. Chemosphere 2007; 70:315–28.

Novotny V, 1995. Nonpoint Pollution and Urban Stormwater Management, first ed. Technomic Publishing Company, Inc., PA.

Novotny V, Witte J W. Ascertaining aquatic ecological risks of urban stormwater discharges. Water Research 1997; 31 (10):2573–85.

Nur T, Johir MAP, Loganathan P, Vigneswaran S, Kandasamy J. Effectiveness of purolite A500PS and A520E ion exchange resins on the removal of nitrate and phosphate from synthetic water. Desalination Water Treat 2012 (in press).

Pan B J, Qiu H, Pan B C, Nie G Z, Xiao L L, Lv L, Zhang W M, Zhang Q X and Zheng S R. Highly efficient removal of heavy metals by polymer-supported nanosized hydrated Fe(III) oxides: Behaviour and XPS study. Water Research 2010; 44(3): 815-824.

Pathirana S, Connell D W, Vowles P D. Distribution of aromatic hydrocarbons (PAHs) in an urban roadway system. Ecotoxicology and Environmental Safety 1994; 28:256-69.

Pitcher S K, Slade R C T and Ward N I. Heavy metal removal from motorway stormwater using zeolites. Science of the Total Environment 2004; 334:161-66.

Pitt R, Clark S, Field R. Groundwater contamination potential from stormwater infiltration practices. Urban Water 1999; 1: 217– 36.

Plazinski W, Rudzinski W, Plazinska A (2009) Theoretical models of sorption kinetics including a surface reaction mechanism: A review. Advances in Colloid and Interface Science 2009; 152 (1-2): 2-13.

Post J E. Manganese oxide minerals: Crystal structures and economic and environmental significance. Department of Mineral Sciences, Smithsonian Institution, Washington, DC 20560-0119. PNAS March 30, 1999 vol. 96 (7) 3447-54.

Poulton DJ. Statistical zonation of sediment samples using ratio matching and cluster analysis. Environmental Monitoring Assessment 1989; 13:379-404.

Prasad M, Saxena S, Amritphale SS, Chandra N. Kinetics and isotherms for aqueous lead adsorption by natural minerals. Industrial and Engineering Chemical Research 2000; 39: 3034–37.

Prasad A S, Bao B, Beck F W J, Sarkar F H. Zinc activates NF-κB in HUT-78 cells. Journal of Laboratory and Clinical Medicine 2001; 138(4): 250–6.

Primo O, Rivero M J, Urtiaga A M, Ortiz I. Nitrate removal from electro-oxidized landfill leachate by ion exchange. Journal of Hazardous Materials 2009; 164: 389–93.

Purolite 2010, http://purolite.com/default.aspx?RelID=606288&ProductID=223

Rangsivek R, and Jekel M R. Removal of dissolved metals by zero-valent iron (ZVI):

Kinetics, equilibria, processes and implications for stormwater runoff treatment. Water Research 2005; 39: 4153-63.

Rauret G, Lopez-Sanchez JF, Sahuquillo A, Rubio R, Davidson C, Ure A, Quevauviller P. Improvement of the BCR three step sequential extraction procedure prior to the certification of the new sediment and soil reference materials. Journal Environmental Monitoring 1999; 1:57-61.

Robertson DJ, Taylor KG, Hoon SR. Geochemical and mineral magnetic characterization of urban sediment particulates, Manchester, UK. Applied Geochemistry 2003; 18:269-82.

Rodgers M, Mulqueen J, Healy M G. Surface clogging in an intermittent stratified sand filter. Soil Science Society of America Journal 2004; 68:1827–32.

Rovira M, Giménez J, Martínez M, Martínez-Lladó X, de Pablo J, Marti V and Duro L. Sorption of selenium (IV) and selenium (VI) onto natural iron oxides: Goethite and hematite. Journal of Hazardous Materials 2008; 150: 279-84.

Sahuquillo A, Lopez-Sanchez JF, Rubio R, Rauret G, Thomas RP, Davidson CM, Ure AM. Use of a certified reference material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure. Analytica Chimica Acta1999; 382:317-27.

Samatya S, Kabay N, Yuksel U, Arda M, Yuksel M. Removal of nitrate from aqueous solution by nitrate selective ion exchange resins. Reactive & Functional Polymers 2006a; 66 (11):1206–14.

Samatya S, Yuksel U, Arda M, Investigation of selectivity and kinetic behavior of strong-base ion exchange resin Purolite A 520E for nitrate removal from aqueous solution. Separation Science and Technology 2006b; 41 (13) :2973–88.

Sansalone J J, Koran J M, Smithson, J A, Buchberger S G. Physical characteristics of Urban Roadway solids transported during rain events. Journal of Environmental Engineering 1998; 124 (5): 427-40.

Sansalone J J. Adsorption Infiltration of Metals in Urban Drainage – Media Characteristics. The Science of the Total Environment 1999; 235 (1 – 3): 179 – 88.

Sartor J D, and Boyd G B. 1972. ‘‘Water pollution aspects of street surface contaminants.’’ Rep. No. EPA-R2-72-081, United States Environmental Protection Agency, Washington, D.C.

Schnelle J, Jänsch T, Wolf K, Gebefügi I, Kettrup A. Particle size dependent concentrations of polycyclic aromatic hydrocarbons (PAH) in the outdoor air. Chemosphere 1995; 31 (4): 3119–27.

Schueler T. 1987. Controlling Urban Runoff: A practical Manual for Planning and Designing Urban BMPs. Metropolitan Washington council of Governments, Washington D.C.

Schueler T R, Kumble P A and Herafy M A, 1992, A Current Assessment of Urban Best Management Practices, Water Resources Publications (prepared for the USEPA), United States of America.

Scanlon PF. Effects of highway pollutants upon terrestrial ecosystems, in: Hamilton RS, Harrison RM. (Eds), Highway Pollution, Studies in Environmental Science 44. 1991. Elsevier, Amsterdam, pp 281-338.

Sen T K, Mahajan S P and Khilar K C. Adsorption of Cu^{2+} and Ni^{2+} on iron oxide and kaolin and its importance on Ni^{2+} transport in porous media. Colloids and Surfaces A: Physicochemical. Engineering Aspects 2002; 211 (1): 91-102.

Servais P, Billen G, Bouillot P. Biological colonization of granular activated carbon filters in drinking-water treatment. Journal of Environmental Engineering 1994; 120(4): 888-99.

Shaheen D G, 1975 Environment Protection Agency Report No. R2-72-081. U.S. Government Printing Office, Washington D.C.

Sheikholeslami R. (2007). Study of the interactive effects of inorganic and biological fouling in RO desalination units Phase - a, MEDRC Series of R & D Reports. MEDRC Project: 00-AS-001, The Middle East Desalination Research Center Muscat, Sultanate of Oman.

Shim W G, Chaudhary D, Vigneswaran S, Ngo H H, Lee J W, and Moon H. Mathematical Modeling of Granular Activated Carbon (GAC) Biofiltration System, Korean Journal Chemical Engineering 2004; 21 (1): 212-20.

Singh AK. Elemental chemistry and geochemical partitioning of heavy metals in road dust from Dhanbad and Bokaro regions, India. Environmental Earth Sciences 2011; 62:1447-59.

Singh G, Johir M A H, Kandasamy J, Vigneswaran S, Kus B, Naidu R. Stormwater Management Harvesting and Reuse, Encyclopedia of Sustainability Science and Technology, Physics and Astronomy, Springer 2012 (in press).

Spadini L, Schindler P W, Charlet L, Manceau A and Ragnarsdottir K V. Hydrous ferric oxide: evaluation of Cd-HFO surface complexation models combining Cdk EXAFS data, potentiometric titration results, and surface site structures identified from mineralogical knowledge. Journal of Colloid and Interface Science 2003; 266: 1-18.

Srivastava VC, Mall I D, Mishra I N. Treatment of Pulp and Paper Mill Wastewaters with Poly Aluminium Chloride and Bagasse Fly Ash, Colloids and Surfaces A: Physiochemical and Engineering Aspects. 2005; 260 (1 – 3): 17 – 28.

Stone M, Marsalek J. Trace metal composition and speciation in street sediment: Sault Ste. Marie, Canada. Water Air Soil Pollution 1996; 87:149-69.

Streat M, Hellgardt K, Newton NLR. Hydrous ferric oxide as an adsorbent in water treatment: Part 3: Batch and mini-column adsorption of arsenic, phosphorus, fluorine and cadmium ions. Process Safety and Environmental Protection 2008; 86: 21–30.

Sustainable Tools for Environmental Performance Strategy (STEPS), Water sensitive urban design element Moreland city council http://www.sustainablesteps.com.au/doc.html

Taylor K. Urban environments, in: Perry C, Taylor K. (Eds), Environmental Sedimentology. 2007 Blackwell Publishing Ltd, Oxford, UK, pp 190-222.

Tessier A, Campbell PGC, Bisson M. Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry 1979; 51:844-51.

Thomas J F, Gomboso J, Oliver J E, Ritchie V A, 1997. Wastewater re-use stormwater management and the national water reform agenda ((CSIRO Land and Water Research Position Paper; 1). No. Research Position Paper 1). CSIRO Land and Water, Canberra, ACT.

Thorpe A, Harrison RM. Sources and properties of non-exhaust particulate matter from road traffic: A review. Science Total Environment 2008; 400:270-82.

Tien C. Adsorption Calculations and Modeling, Butterworth-Heinemann series in chemical engineering: Boston, 1994.

Tokalioğlu S, Kartal S, Birol G. Application of a three-stage sequential extraction procedure for the determination of extractable metal contents in highway soils. Turkey Journal Chemistry 2003; 27:333-46.

Toledo E A, Gushikem Y, Castro S G C. Antimony (III) Oxide Film on a Cellulose

Fiber Surface: Preparation and Characterization of the Composite Journal of Colloid and Interface Science 2000; 225:455–459.

Trombulak SC, Frissell CA. Review of ecological effects of roads on terrestrial and aquatic communities. Conservation Biology 2000; 14:18-30.

Transport SA 2002, Protecting waterways, Prepared by the Environment Operations Unit, SOGC and the Stormwater Services Section with the assistance of the Urban Water Resources Centre of the University of South Australia.

Transurban Sustainability Report, 2009. http://www.transurban.com/sr09/sustainability+report+2009.pdf

Trivedi P. and Axe L. Modeling Cd and Zn Sorption to Hydrous Metal Oxides. Environmental Science and Technology 2000; 34: 2215-23.

Trivedi P, Axe L, and Tyson T A. An Analysis of Zinc Sorption to Amorphous versus Crystalline Iron Oxides Using XAS. Journal of Colloid and Interface Science 2001; 244 (2):230–38.

United Nations. United Nations expert group meeting on population distribution, urbanization, internal migration and development, Population Division, Department of Economic and Social Affairs, United Nations Secretariat New York, 21-23 January 2008.

Urfer D, Huck M, Booth S D J, Coffey B M. Biological filtration for BOM and particle removal: a critical review. Journal American Water Works Association 1997; 89 (12):83–98.

Varrica D, Dongarra G, Sabatino G, Monna F. Inorganic geochemistry of roadway dust from the metropolitan area of Palermo, Italy. Environmental Geology 2003; 44(2): 222-30.

Villarreala E L, Dixon A. Analysis of a rainwater collection system for domestic water supply in Ringdansen, Norrko¨ping, Sweden. Building and Environment 2005; 40: 1174–84.

Vinod K G, Imran A. Utilisation of bagasse fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater. Separation and Purification Technology 2000; 18: 131–40.

von Uexküll O, Skerfving S, Doyle R, Braungart M. Antimony in brake pads-a carcinogenic component? Journal Cleaner Production 2005; 13: 19-31.

Wahlin P, Berkowicz R and Palmgren F. Characterisation of traffic-generated particulate matter in Copenhagen. Atmospheric Environment 2006; 40: 2151–59.

Walsh C J, Leonard A W, Ladson A R, Fletcher T D. Urban Stormwater and the Ecology of Streams, Cooperative Research Centre for Freshwater Ecology and Cooperative Research Centre for Catchment Hydrology 2004, Canberra, Australia

Water Sensitive Urban Design Elements, Sustainable Tool for Environmental Performance Strategy (STEPS), Moreland City Council.

http://www.sustainablesteps.com.au/pdf/Water%20Sensitive%20Urban%20Design%20Elements.pdf

Weaver D M. Managing nutrient losses from rural point sources and urban environments. Fertilizer Research 1993; 36: 165-70.

Weckwerth G. Verification of traffic emitted aerosol components in the ambient air of Cologne (Germany). Atmospheric Environment 2001; 35:5525-36.

Wei B, Li X, Mu S. Spatial distribution and contamination assessment of heavy metals in urban road dusts from Urumqi, NW China. Microchemical Journal 2009; 93:147-52.

Wei B, Jiang F, Li X, Mu S. Contamination levels assessment of potential toxic metals in road dust deposited in different types of urban environment. Environment Earth Sciences 2010; 61:1187-96.

Westerlund KG. ‘Metal emissions from Stockholm traffic – wear of brake linings’, Reports from SLB-analys No 3, (2001), The Stockholm Environment and Health Protection Administration, Stockholm.

World Health Organisation and Food Agriculture Organisation of the United Nation, Vitamin and mineral requirements in human nutrition, 2nd edition 2004.

Wong T H F. An Overview of Water Sensitive Urban Design Practices in Australia 2006 Water Practice & Technology Vol 1 No 1 © IWA Publishing 2006 doi: 10.2166/WPT.2006018.

Wong T H F, Breen P F. 2002. Recent advances in Australian practice on the use of constructed wetlands for stormwater treatment. In: Proceedings of the 9th international Conference on Urban Drainage, Portland, Oregon, USA, 9–13.

Wu P, Zhou Y. Simultaneous removal of coexistent heavy metals from simulated urban stormwater using four sorbents: A porous iron sorbent and its mixtures with zeolite and crystal gravel. Journal Hazardous Material 2009; 168: 674–80.

Xie B, Liang S B, Tang Y, Mi W X, Xu Y. Petrochemical wastewater odour treatment by biofiltration. Bioresource Technology 2009; 100:2204–9.

Yongming H, Peixuan D, Junji C, Posmentier ES. Multivariate analysis of heavy metal contamination in urban dust of Xi’an, Central China. Science Total Environment 2006; 355:176-86.

Young L B, Harvey H. The relative importance of manganese and iron oxides and organic matter in the sorption of trace metals by surficial lake sediments. Geochimica et Cosmochimica Acta 1992; 56: 1175–86.

Zhou Y, Haynes RJ. Sorption of heavy metals by inorganic and organic components of solid wastes: Significance to use of wastes as low-cost adsorbents and immobilising agents. Critical Reviews in Environmental Science and Technology 2011; 40: 909-77.

Appendix A

XRD Test Report

Yu Wang
Analytical Centre, University of New South Wales
G65, Chemical Science Building
Phone: 61-2-9385 4669
Email: yu.wang@unsw.edu.au

Samples

Samples named with sample L and sample 2.

Measurement Conditions:

Operator	MPD
Raw Data Origin	XRD measurement (*.XRDML)
Scan Axis	Gonio
Start Position [?Th.]	10.0341
End Position [?Th.]	94.9761
Step Size [?Th.]	0.0260
Scan Step Time [s]	147.0657
Scan Type	Continuous
PSD Mode	Scanning
PSD Length [?Th.]	3.35
Offset [?Th.]	0.0000
Generator Settings	40 mA, 45 kV
Goniometer Radius [mm]	240.00
Spinning	Yes

XRD Results

Table 1 Result for Sample L

Phases	Iron Oxide	Other phase
Chemical formula	Fe2O3	
ICDD No	056-1302	Amorphous
Color in Diagram	Red	
Confident score	16	

Note:

1. Detectable limit for XRD is 0.5%wt;
2. The scale of Confident score is 0-100, for major phase it should be above 60;
3. Quantitative analysis limit is <4%wt;
4. XRD only provides structure information of the samples; Accuracy of elemental information is subject to status of substitution or vacancy. XRF analysis is recommended.

Comment:

Sample L seems an amorphous with some nano-size Fe2O3.

Table 2 Result for Sample 2

Phases	Mn O2, manganese(IV) oxide	Mn O2	Si O2, Quartz
Chemical formular	Mn O2	Mn O2	SiO2
ICDD No	04-005-4881	04-007-2142	01-089-8940
Color in Diagram	Red	Blue	Green
Confident score	66	45	22

Note:

1. Detectable limit for XRD is 0.5%wt;
2. The scale of Confident score is 0-100, for major phase it should be above 60;
3. Quantitative analysis limit is <4%wt;
4. XRD only provides structure information of the samples; Accuracy of elemental information is subject to status of substitution or vacancy. XRF analysis is recommended.

Comment:

Sample 2 contains two types of MnO2, the major phase is 04-05-4881

(Tetragonal Space group: P42/mnm; Space group number:136

a (Å): 4.3880

b (Å): 4.3880

c (Å): 2.8650

Alpha (°): 90.0000

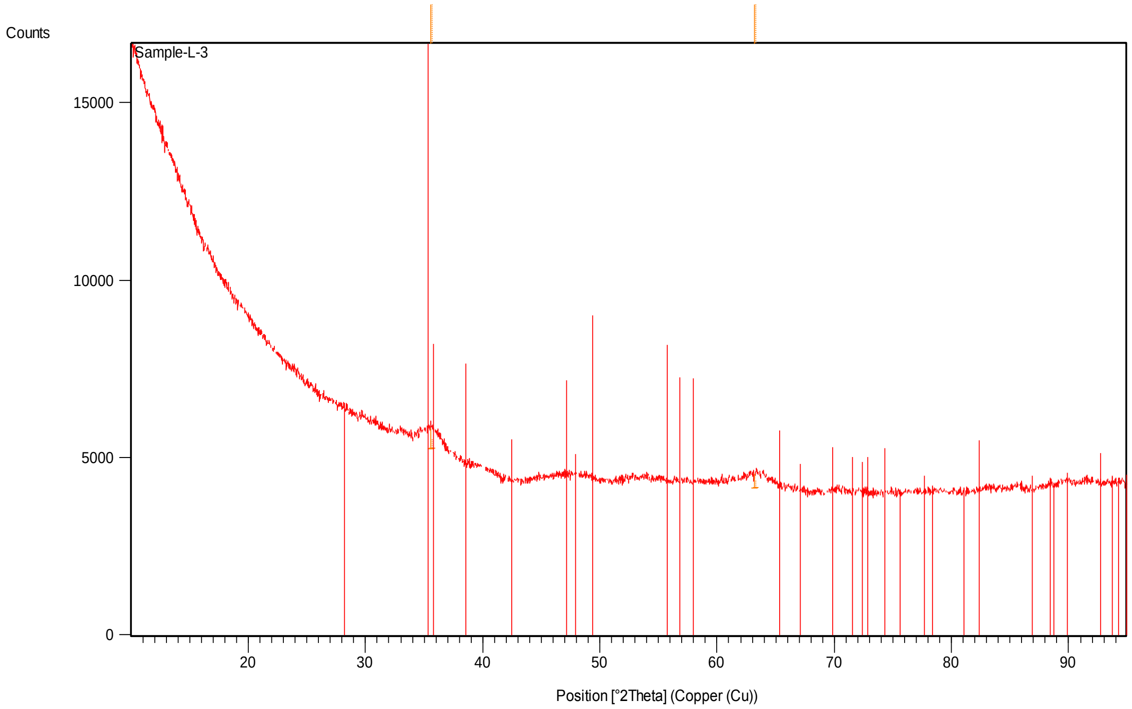
Beta (°): 90.0000

Gamma (°): 90.0000

The quartz is minor phase identified by single peak. It is possible that presence was carbon.

Main Graphics, Analyze View:

1. Sample L



Sample L

Peak List:

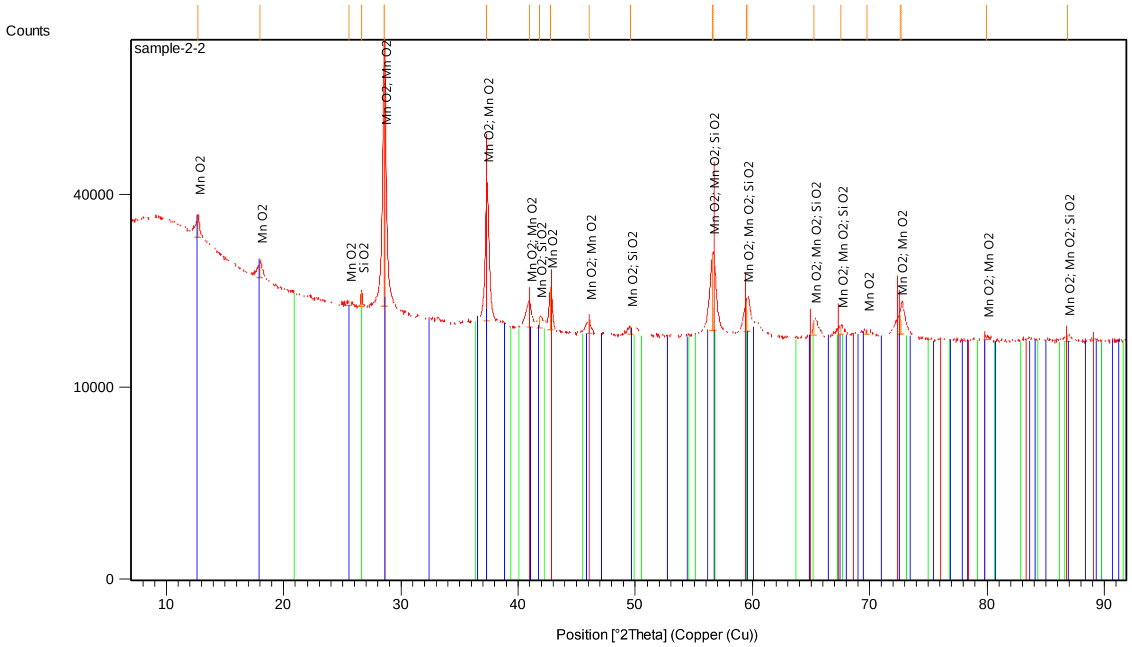
Pos. [2Th.]	Height [cts]	FWHM [2Th.]	d-spacing [Å	Rel. Int. [%]
35.5920	589.32	2.4690	2.52037	100.00
35.6834	294.66	2.4690	2.52037	50.00
63.2020	411.12	3.5731	1.47003	69.76
63.3772	205.56	3.5731	1.47003	34.88

Pattern List:

Visible	Ref. Code	Score	Compound Name	Displacement [2θTh.]	Scale Factor	Chemical Formula
*	00-056-1302	16	Iron Oxide	0.246	0.863	Fe_2O_3

Appendix B

2. Sample 2



Peak List: (Bookmark 3)

Pos. [2Th.]	Height [cts]	FWHM [2Th.]	d-spacing [Å]	Rel. Int. [%]
12.6535	4669.85	0.6809	6.99011	8.14
12.6851	0.00	0.6809	6.99011	0.00
17.9561	2684.20	0.4635	4.93605	4.68
18.0010	1557.18	0.4635	4.93605	2.71
25.5931	697.21	0.4093	3.48068	1.22
26.6482	2357.87	0.1023	3.34522	4.11
28.5653	57377.01	0.2594	3.12234	100.00
28.6378	40163.91	0.2594	3.12234	70.00
37.3303	24661.87	0.2303	2.40890	42.98
40.9667	3757.71	0.3582	2.20309	6.55
41.8650	1536.67	0.3070	2.15787	2.68
42.7784	6185.50	0.1791	2.11388	10.78
46.0510	1916.00	0.3582	1.97100	3.34

49.5965	1166.79	0.7164	1.83808	2.03
56.5900	12235.78	0.5080	1.62506	21.33
56.7433	3237.13	0.5080	1.62506	5.64
59.4987	4242.92	0.5112	1.55237	7.39
59.6615	2970.04	0.5112	1.55237	5.18
65.2088	1864.26	0.2047	1.43075	3.25
67.5497	1182.36	0.3582	1.38675	2.06
69.7278	513.54	0.8187	1.34867	0.90
72.5732	2793.85	0.8071	1.30157	4.87
72.7824	1955.70	0.8071	1.30157	3.41
79.9937	407.51	0.6140	1.19944	0.71
86.8347	860.19	0.4992	1.12075	1.50

Pattern List: (Bookmark 4)

Visible	Ref. Code	Score	Compound Name	Displacement [2Th.]	Scale Factor	Chemical Formula
*	04-005-4881	66	Mn O2, manganese(IV) oxide	-0.136	0.877	Mn O2
*	04-007-2142	45	Mn O2	-0.181	0.313	Mn O2
*	01-089-8940	22	Si O2, Quartz	0.264	0.049	Si O2