



**Design and experimental assessment of
stormwater constructed wetland systems**

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Abstract

This study focussed on the treatment of stormwater runoff using constructed wetlands (CWs): man-made systems engineered to replicate the treatment processes in natural wetlands. The main aims were to design and assess a novel configuration of CWs for stormwater treatment, while contributing to the further understanding of pollutant removal in CWs through the development of models to explain internal processes and predict performance. A vertical tidal-flow CW operational regime was applied to target enhanced nitrogen removal while maintaining high removal rates a range of high priority urban stormwater pollutants. Eight pilot-scale CW models were built to investigate the effect of key design and operational variables: substrate media, wetland surface area, and wetting and drying regimes.

The performance of the systems was considered successful when compared to results of similar pilot-scale CWs that operated without tidal flow. Results show that all eight models effectively reduced concentrations of solids and metals, with load reductions generally in excess of 90%. Nutrient removal – particularly nitrogen - was heavily affected by design and operation variables. Significantly, nitrogen removal in the systems outperformed similar pilot-scale CWs with alternative hydraulic operating conditions. Understanding of the internal CW treatment processes were backed up through statistical analysis and numerical modelling. These techniques highlighted important mechanisms such as the biological transformation of nitrogen and the importance of TSS removal to heavy metals reduction.

Overall, results show that the CW design has great potential for reduction of solids, metals and nutrients in stormwater. Further research at a field scale would better represent the performance of the systems in practice, and closer monitoring of dissolved oxygen and redox potential would enhance understanding of internal processes, particularly regarding nutrient behaviour. Results of this study can contribute to future CW research and design, through increased understanding of long-term pollutant removal in these types of system. In time, this may result in the wider application of CWs for stormwater treatment to make human water use more sustainable and better protect the environment.

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1. Introduction

1.1. Drivers of sustainable water management

In recent years there has been a growing global realisation that drastic changes are required in the way that water resources are managed. The Institution of Civil Engineers (ICE) reported in 2012 that “water scarcity is upon us”, and that water can no longer be considered a readily available resource to suit our desires in the UK (ICE, 2012). In the face of population increase and climate change, it is clear that human water use needs to adapt to become more sustainable. Freshwater resources must be sustained and safeguarded against pollution and we can no longer afford to waste potable water on non-potable uses in the manner that we have for so many years.

This issue has been identified and reflected in UK and European legislation. Concerning pollution, the European Union Water Framework Directive was published in 2000 after a poll of European countries revealed that 47% of respondents listed water pollution as a major concern in their country (European Commission, 2012). The Directive placed a large emphasis on dealing with diffuse pollution, which concerns runoff from roads and housing areas (Ellis et al., 2003). Article 1 of the Directive contains details of the ways in which urban surface drainage is to be targeted. Relevant objectives outlined include the banning of the direct discharge of urban runoff to groundwaters and the encouragement of sustainable water use.

The Flood and Water Management Act, passed in the UK in 2010, called for a change of approach in combating floods: to improve flood risk management rather than building flood defences (Butler et al., 2010). Drainage systems in new developments now must be approved by authorities after consultation with any bodies likely to be affected by the discharge. The developer no longer has an automatic right to send the drainage to the local sewer system, and it is now required that sustainable urban drainage systems (SUDS) be used to control surface drainage in new developments (Flood and Water Management Act, 2010).

“Future Water”, the UK government’s water strategy for England, placed a large focus on reducing the demand for water to 130 litres/person/day by 2030, or, as the report states “possibly even 120 litres per person per day depending on new technological developments and innovation” (DEFRA, 2008). The strategy points out the potential for rainwater harvesting in England and encourages the use of SUDS facilities to capture rainfall before it runs to water courses, thereby attenuating peak flows and preventing potential detriment to quality (Butler *et al.*, 2010).

Thus, a strong emphasis on sustainable water management has been developed through legislation in the UK, resulting in a need for stormwater treatment solutions that will help to improve effluent drainage quality and potentially produce re-usable water to ease the pressure on freshwater resources.

1.2. Constructed wetlands for stormwater treatment

Stormwater treatment and reuse can provide a sustainable water supply which boosts domestic supplies while protecting local watercourses from contaminants transported by stormwater runoff. One sustainable way of attenuating and treating stormwater is through the use of constructed wetlands (CWs). Natural wetlands can treat water through a variety of physical, chemical and biological processes, but there is such a large degree of variability in their functional components that it is extremely difficult to predict the quality of treated water that can be achieved (Brix, 1993). CWs are man-made systems specifically designed and engineered to replicate the natural pollutant treatment processes exhibited in natural wetlands, with the added benefit of increased control over the operational conditions (Vymazal and Kröpfelová, 2008). These aesthetically pleasing treatment systems have very low energy input requirements since the pumping of water is either not required at all or is only required in very small measure. CWs have been used to successfully treat many types of wastewater such as domestic wastewater, minewater discharge and industrial and agricultural effluents (Cooper, 2007; Gottschall *et al.*, 2007; Langergraber *et al.*, 2010; Soda *et al.*, 2012). CWs have also been successfully used for the treatment of stormwater runoff from roads, urban areas, and agricultural and industrial catchments (Vymazal, 2009; Idris *et al.*, 2012).

There are several types of CW configurations. Horizontal and Free-Water Surface CWs require relatively large areas of land for operation, as the water flows horizontally across the system. Vertical-flow (VF) CWs have smaller surface area requirements, as the water flows either downwards or upwards through the system. With the limited land space available in the UK, VF CW treatment systems are more suitable for implementation. VF CWs have been successfully used to treat stormwater (Li & Davis, 2009; Feng *et al.*, 2012), but traditionally have limited nitrate removal ability. This is due to high oxygen levels within the system, which inhibit denitrification processes. This means that total nitrogen removal is inhibited, and in some cases VF CWs leach nitrates (Bratieres *et al.*, 2008). To date, there has been no research carried out that directly addresses the limitations in nitrate removal by stormwater VF CWs. This study theorised that the application of a “tidal-flow” dosing regime to a VF CW would establish set periods of time in which the system is inundated with water, creating anoxic conditions in which denitrification processes could occur and thus increase nitrate removal.

The application of a tidal-flow CW for stormwater treatment is thus presented for the first time: designed to enhance nitrate removal, and therefore stronger total nitrogen removal. The performance of the CW in removing a range of stormwater priority pollutants (including solids, heavy metals and nutrients) is investigated to determine the overall effectiveness of the system.

1.3. Aims and objectives

The project has two main research aims, detailed below along with the relevant objectives:

Aim 1

To design and assess a vertical flow CW with tidal-flow operation for stormwater treatment.

Objectives:

1. To conduct a comprehensive literature review to identify the gaps in knowledge regarding CWs treating stormwater to date.

2. To design a CW system that addresses the findings and knowledge gaps identified in the literature review.
3. To determine the stormwater treatment efficiency of the system by assessing its general performance and comparing this to existing systems.
4. To determine the effect of the design and operational variables on the treatment efficiency of the system with a view to generating design and operational guidelines.
5. To carry out media characterisation and batch adsorption tests to determine the metal uptake capacity of media for use in the CWs and investigate influencing factors

Aim 2

To develop models to further the understanding and accurately predict the performance of the CW system and investigate the processes occurring within.

Objectives:

1. To conduct statistical analysis of the performance results of the system in order to develop predictive models.
2. To conduct mechanistic analysis of the performance results of the system with the aid of a numerical modelling software package to develop mechanistic understanding.

1.4. Outline of thesis

A literature review of constructed wetlands and their application for stormwater management and treatment in the UK is firstly given in chapter 2, but the research presented in this thesis has been carried out primarily through the design, construction and long-term operation of eight pilot-scale physical models in the School of Engineering, Cardiff University. Influent and effluent analysis was carried out over a period of 55 weeks to obtain a comprehensive dataset concerning the treatment performance of the CWs, and to determine the effect of the design and operation variables. Chapter 3 provides details of the experimental setup and procedure used to investigate the performance of pilot-scale tidal-flow CW systems.

Characterisation of the substrate media used in the CWs is presented in chapter 4, alongside the analysis of their metal adsorption characteristics. The adsorption characteristics were investigated to determine the extent to which metal reduction was attributable to adsorption in the systems. This was carried out by laboratory experiments, principally kinetic and equilibrium analysis. The performance results from the pilot-scale CW experiment are covered in chapter 5, examining the effect of the design variables and investigating the internal pollutant removal mechanisms.

Chapter 6 explores the application of HYDRUS 2D, a software package that simulates water, heat and solute transport through variably saturated media. HYDRUS was applied to enhance the understanding of the removal processes occurring in the CWs, and to aid making long-term performance predictions. Statistical analysis was carried out on the acquired data to increase understanding of internal CW processes and treatment mechanisms. This aspect of the work focused on the use of regression and principal component analysis. Regression models (simple and multiple) were then developed for performance prediction and comprehensive statistical analysis of the results from the pilot-scale CW systems is presented, along with the development of predictive performance models in chapter 7. Finally, the main conclusions of the project and recommendations for further work are presented in chapter 8.

2. Literature Review

2.1. Introduction

In recognition of the significant opportunity offered by CWs for stormwater management in the UK and the acute lack of guidelines and information regarding their application, this review aims to provide a concise appraisal of the state of the art of application of CWs for stormwater management in the UK, focusing on design, performance, retrofit issues, current guidelines, research and background knowledge, while drawing comparisons with the rest of the world. Firstly, constructed wetland (CW) technology is explored in its various forms and applications. This is followed by a novel review of the application of CWs for stormwater management in the UK, focusing on design, performance, retrofit issues, current guidelines, research and background knowledge, while drawing comparisons with the rest of the world. The use of vertical flow CWs for stormwater treatment is then investigated, highlighting the gaps in knowledge, research and practice that have influenced this project.

2.2. Constructed Wetlands

2.2.1. Introduction

The use of CWs for wastewater treatment, has grown in recent years due to their very effective removal of pollutants, low energy requirements, ease of maintenance and relatively cheap construction and operating costs. CWs have been successfully used to treat various types of wastewater including domestic wastewater, minewater discharge and industrial and agricultural effluents (Cooper, 2007; Gottschall *et al.*,

Part of this literature review has already been published as “Constructed wetlands for stormwater management in the UK: A concise review” – Lucas, R., Earl, E.R., Babatunde, A.O. and Bockelmann-Evans, B.N., 2015. *Civil Engineering and Environmental Systems*, 32(3), 251-268.

2007; Langergraber *et al.*, 2010; Soda *et al.*, 2012). They have also been used to treat stormwater runoff from roads, urban areas, and agricultural and industrial catchments (Vymazal, 2009; Idris *et al.*, 2012).

There are three main types of CW: free water surface; horizontal subsurface-flow and vertical subsurface-flow. These designs are described in the following sections. Additionally, the tidal-flow operation method of vertical subsurface-flow CWs is of high relevance to this project, so it is described in section 2.2.5.

2.2.2. Free water surface constructed wetlands

Free water surface (FWS) CWs are distinguished by an area of open water. Vegetation in a FWS CW can be emergent plants, submerged plants, free-floating plants or floating-leaved plants (Vymazal and Kröpfelová, 2008). Figure 2-1 shows an example of a FWS CW with emergent vegetation.

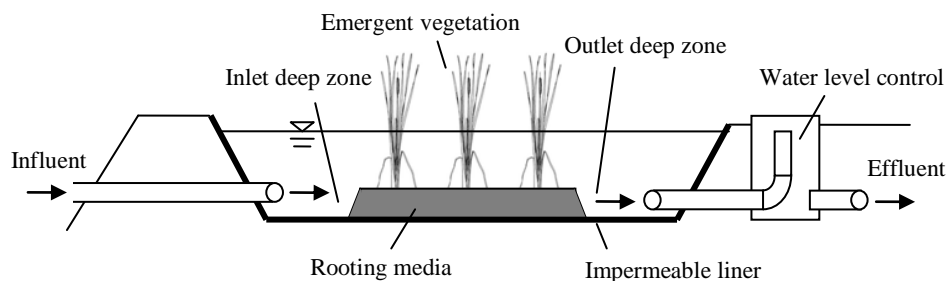


Figure 2-1 - Typical arrangement of a FWS CW (adapted from Kadlec and Wallace, 2009)

Where rooted macrophytes are incorporated, they grow in soil or an alternative media at the base of the CW. Water depths are usually shallow, and this, along with the presence of vegetation, helps to control the flow through the CW with the aim of creating plug-flow conditions (Reed *et al.*, 1998). Plug-flow conditions (in which the water velocity is constant across the cross-section of the CW perpendicular to the flow path) serve to maximise contact between the wastewater and the biological surfaces on which pollutant removal reactions take place.

FWS CWs are commonly used to treat less concentrated wastewaters, e.g. effluent from secondary or tertiary treatment, and are seldom used for primary treatment due to the danger of human exposure to pathogens (US EPA, 2000c). They are the most common type of CW utilised for stormwater treatment as they can cope well with the

stochastic nature of rainfall runoff. They are also commonly used for minewater, groundwater and leachate treatment (Kadlec and Wallace, 2009).

2.2.3. Horizontal subsurface-flow constructed wetlands

Subsurface-flow CWs differ from FWS CWs in that they do not feature a body of water on the surface: all flow moves through the porous substrate media. A typical horizontal subsurface-flow (HF) CW is shown in Figure 2-2.

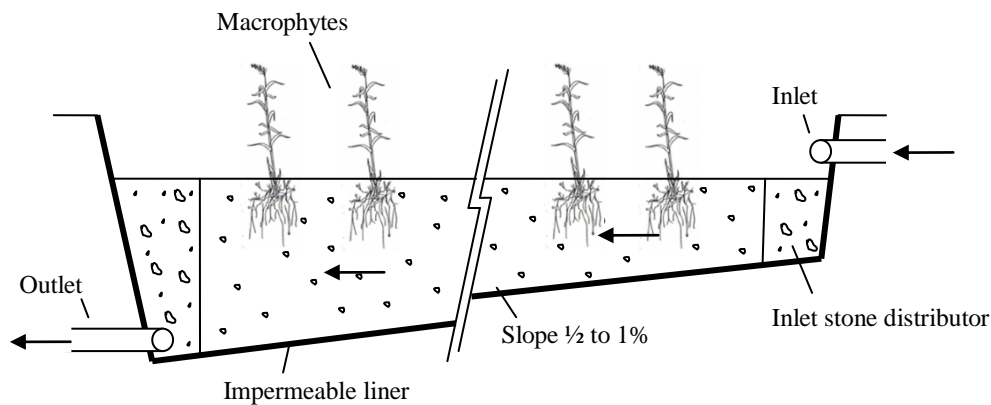


Figure 2-2 - Typical arrangement of a HF CW system (adapted from Cooper et al., 1996)

Often referred to as “reed beds”, HF CWs are typically constructed using gravel and/or soil as substrate media (Kadlec and Wallace, 2009). The bed of the CW is slightly inclined (gradient $\leq 1\%$) to encourage slow water flow from the inlet to the outlet (Ellis *et al.*, 2003). The wastewater is treated as it passes through various aerobic, anoxic and anaerobic zones (Cooper *et al.*, 1996). Since the system is constantly saturated, aerobic zones are confined to the roots of the macrophytes in the CW. Thus, oxygen transfer and therefore aerobic treatment processes (e.g., nitrification) are limited in HF CWs.

Since HF CWs contain their flow below the surface, they are suitable for treating primary effluent without posing the same level of threat to human health that a FWS CW would in that application (see Section 2.2.2). Therefore they are commonly used for this purpose. HF CWs are also more suitable for use in cold climates due to the

natural insulation provided by the media, hence preventing freezing and hydraulic failure (Kadlec and Wallace, 2009).

2.2.4. Vertical subsurface-flow constructed wetlands

Vertical subsurface-flow (VF) CWs receive influent wastewater in intermittent batches, thus they are not constantly saturated as in HF CWs. A typical VF CW is shown in Figure 2-3.

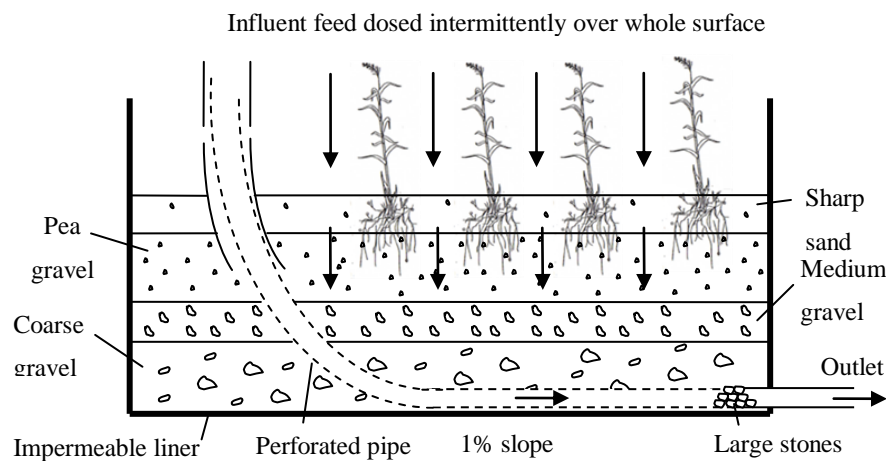


Figure 2-3 - Typical arrangement of a downflow VF CW system (adapted from Cooper et al., 1996)

VF CWs typically consist of layers of sand and gravel, with the wetland vegetation planted in the sand at the top of the system (Vymazal and Kröpfelová, 2008). In most VF CWs the influent wastewater is dosed at the top of the system, flooding the surface and then travelling down through the substrate media before it is collected at the bottom of the system from a gravel drainage layer. However, vertical up-flow systems also exist, where the wastewater enters the CW at the base of the media and is collected just below the surface. See Figure 2-4 for a depiction of how the water flows through an up-flow system.

The intermittent loading that takes place in a VF CW allows for excellent oxygen transfer. Between doses, the CW is drained and oxygen can then enter the system, providing aerobic treatment to the next batch of wastewater. Therefore, VF CWs are often favoured for their nitrification capabilities since nitrification is an oxidation process. The oxygen supplied by the rhizomes and roots of plants in VF CWs is negligible compared to that retained in the system between doses, and the main

reason for the inclusion of plants is to aid the hydraulic conductivity of the system. BOD₅ and COD removal efficiencies are high, but, because of the strong aerobic qualities found in VF CWs, denitrification is limited. TSS removal is high but not as high as in HF CWs, and clogging can become a problem in VF systems (Vymazal and Kröpfelová, 2008).

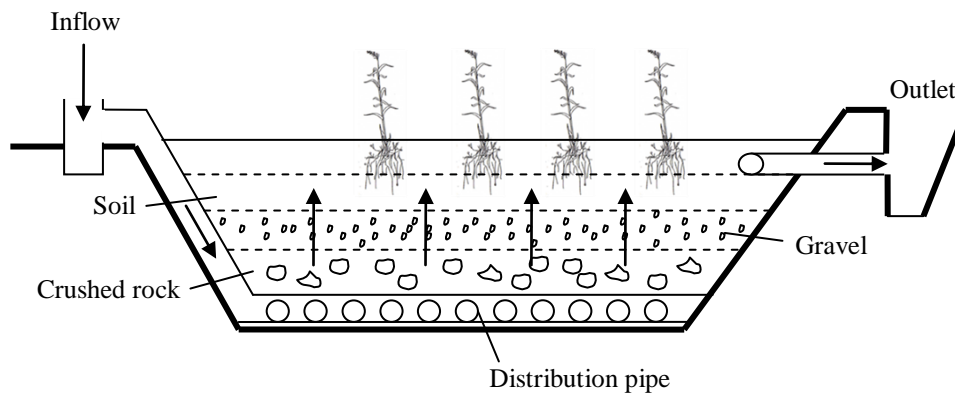


Figure 2-4 - Schematic representation of an upflow VF CW (adapted from Vymazal, 2001)

2.2.5. Tidal-flow vertical subsurface-flow constructed wetlands

Tidal flow CWs are VF systems with alternative hydraulic operating conditions. Instead of the influent wastewater simply percolating through the CW and leaving the system in one pass, each influent dose of water is held in the system and then released after a set period of time. As the CW is filled, influent NH₄-N is adsorbed to the media and influent organic matter is degraded by the CW biofilm (Kadlec and Wallace, 2009). Subsequently, as the water is drained from the CW, it acts as a “passive pump”, drawing air into the system (Sun et al., 2005). Atmospheric diffusion then causes oxidation of the biofilm, causing nitrification processes (NH₄-N converts to NO₂-N and then NO₃-N). As the CW is then refilled, the oxidised N is then released from the media, because oxidation has transformed the positive NH₄⁺ ion into negative NO₂⁻ and NO₃⁻ ions, which are repelled by the negative charge of the soil media. Influent organic matter provides a C supply for denitrification processes to occur in anoxic zones in the inner layer of the CW biofilm, where a high

oxygen diffusion resistance allows heterotrophic denitrifiers to survive (Hu *et al.*, 2014).

Since TVF CWs are capable of simultaneous nitrification and denitrification (Austin *et al.*, 2003, Hu *et al.*, 2014), they provide an advantage over traditional VF and HF systems, which can each only perform one of these processes effectively (nitrification in VF systems, denitrification in HF systems).

2.3. Constructed wetlands for stormwater management in the UK

2.3.1. Introduction

In the UK, CWs have been used for the treatment of various wastewaters, especially tertiary sewage treatment which accounts for 69% of the total number of UK systems (Constructed Wetland Association, 2008). However there is an acute lack of information regarding the use of CWs for stormwater management in the UK even though they have been implemented for the treatment of residential, highway and airport runoff (Cooper, 2007; Vymazal, 2009). In the very few cases for which details are available, design and operation information have been gleaned from general design guidance that is not specifically focussed on CWs for stormwater treatment (e.g., “the SUDS Manual”, Woods-Ballard *et al.*, 2007), and by transferring design knowledge from CW systems treating other types of wastewater. Furthermore, there are no UK stormwater CW design codes and no performance databases to aid in the deployment and assessment of these systems and these are important in order to instil confidence in designers and regulatory authorities when recommending CWs for stormwater management.

CWs can benefit the UK as they offer a unique opportunity for improving the resilience of the UK water infrastructure, particularly in response to climate change effects, water crisis (quality and quantity) and demographic changes. A recent report by the Institution of Civil Engineers (ICE) indicates that climate change is set to cause both increased rainfall intensity and decreased levels of summer precipitation (ICE, 2012), indicating that extended periods of flood and drought are likely to become commonplace in the future in the UK. Stormwater CWs can attenuate peak flow in times of flood and release the captured water slowly without diverting

harmful contaminants directly to local watercourses, while on the other hand recycling treated runoff decreases pressure on potable water supplies so that there is more water available in times of drought. Thus, stormwater CWs can be considered to offer a significant opportunity to improve stormwater management in the UK.

2.3.2. Background and state of the art for stormwater management using constructed wetlands in the UK

2.3.2.1. Development of stormwater management policy

CWs have been used in the UK for nearly thirty years, albeit mainly for the treatment of domestic, industrial and agricultural wastewater (Cooper *et al.*, 1996). However, the focus on urban stormwaters as a pollution problem in the UK is a relatively new one, and it is only through directives and policies established during the last 20 years that emphasis has shifted to the problem of urban runoff through the use of Sustainable Urban Drainage Systems (SUDS) (Dussaillant, 2012). This began in 1992 when the United Nations (UN) established AGENDA 21, a global plan for sustainable development, which concerns all areas in which humans affect the environment (United Nations, 2009). Since this plan was announced, water security and pollution have become more prominent features in European policies and recommendations (e.g., the European Union Water Framework Directive in 2000).

In the UK, the implementation of AGENDA 21 can be seen in the 1997 Environment Agency for England and Wales (EA) report “*Liaison with Local Planning Authorities*”, in which the Local AGENDA 21 development was laid out. The report promotes the use of sustainable drainage systems such as CWs to target contaminated surface water, calling for the use of “soft-engineered” SUDS systems (Ellis *et al.*, 2003). The NRA Thames region was one of the first in the country to focus on the control of surface water runoff as part of its local AGENDA 21 development, releasing a policy statement in 1998 entitled “*Surface Water Source Control*”. The statement laid out the plans to convert to the use of sustainable surface water storage, attenuation and treatment processes through soft-engineered facilities (Ellis *et al.*, 2003), thereby further promoting the use of CW systems.

The growing focus on sustainable water use became further evident in 2008 when the government unveiled their water strategy for England, named “Future water”. The strategy points out the potential for rainwater harvesting in England and encourages the use of SUDS facilities to capture rainfall before it runs to water courses, thereby preventing flooding and potential detriment to water quality (Butler *et al.*, 2010).

Perhaps the most direct initiative to promote sustainable stormwater management in the UK has come in the form of the Flood and Water Management Bill, which was presented before parliament in 2009. Amongst other significant improvements, the bill called for a change of approach in combating floods: to improve flood risk management rather than building flood defences (Butler *et al.*, 2010). The Flood and Water Management Act was subsequently passed in 2010. Drainage systems in new developments now must be approved by authorities after consultation with any bodies likely to be affected by the discharge, such as sewerage undertakers, the EA, highway authorities, British Waterways and any other relevant group. The developer no longer has an automatic right to send the drainage to the local sewer system, and it is now required that SUDS be used to control surface drainage in new developments (Flood and Water Management Act, 2010).

2.3.2.2. Stormwater management in the UK: state of the art

Going by the findings of the review on the development of stormwater management policy in the UK as presented in section 2.3.2.1., it is evident that there is an increasing emphasis on sustainable stormwater management in the UK and this provides a good opportunity for the use of CWs. According to the Constructed Wetland Association’s database, there are about 1021 CWs in the UK with only 67 of the systems used for treating stormwater. A breakdown of the 67 systems shows that 6 systems treat road runoff (all in England), 16 treat surface runoff (7 in England, 9 in Scotland), 5 treat storm sewage overflow in a separate storm bed (all in England) and 40 treat storm sewage overflow in combined systems which provide tertiary treatment (38 in England, 2 in Wales) (Constructed Wetland Association, 2008).

Figure 2-5 shows the general distribution of stormwater CWs across the UK. The majority of the systems are located in the English midlands, with several on either side of the Anglo-Welsh border and a small concentration in West Lothian, Scotland. There is a distinct lack of stormwater CWs in east and south-east England. The exact reason for this variation in geographical distribution is not clear, however the lower number of CWs in the south-east compared to the rest of UK might be due to its dense population concentration and lack of available land space as CWs are perceived to be land intensive - even though this is not necessarily true. Furthermore, the database indicates that there are no stormwater CWs in Northern Ireland, the northern regions of England and the majority of Wales and Scotland. There are well over 5.7 million fewer people in these locations compared to the midlands, east and south-east of England (Office for National Statistics, 2010), and hence they are more sparsely populated. Thus, CWs would be even more ideally suited to these areas. Furthermore, the passing of the Flood and Water Management Act and the growing focus on sustainable water use in the UK might accelerate the use of CWs for stormwater management in these areas.

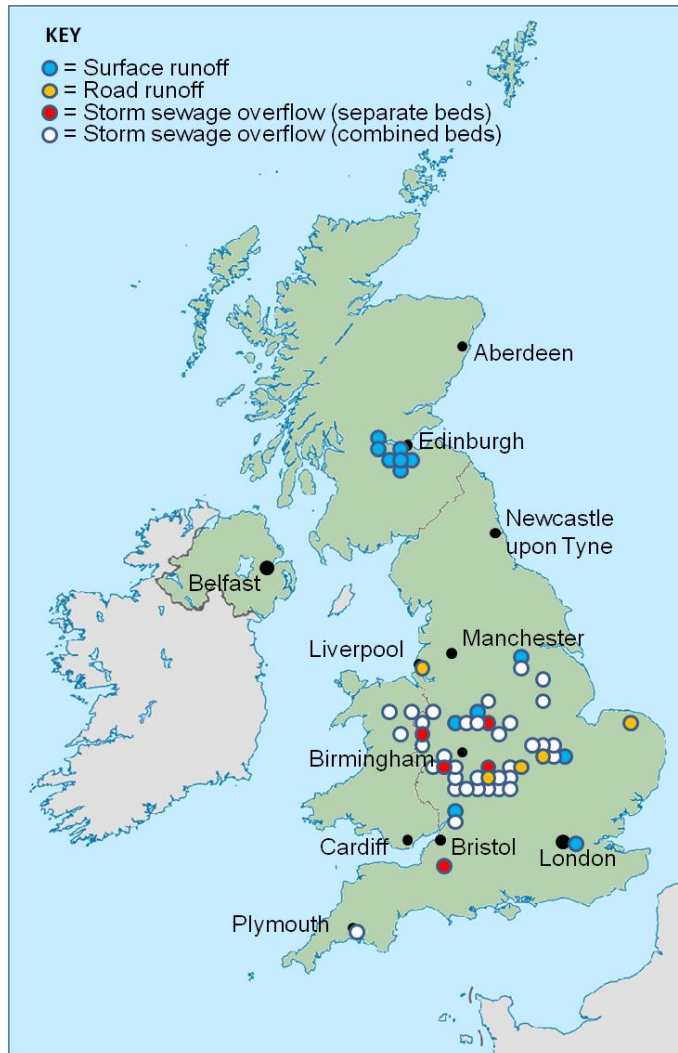


Figure 2-5 - Geographic distribution of CWs treating stormwater in the UK (developed from CWA database)

With the exception of two hybrid systems (treating surface runoff in Pumpherton and West Lothian, Scotland), all of the UK stormwater CWs are horizontal subsurface-flow systems. Subsurface-flow CWs are very efficient at removing suspended solids (SS), contributing to the reduction of other contaminants. Generally, horizontal subsurface-flow systems have been in use for much longer than vertical subsurface-flow systems. Guidelines published by the Water Research Council (WRc) in 1996 give comprehensive information on horizontal subsurface-flow system design but highlight that, at that time, there was “only a limited amount of information” regarding the design of vertical subsurface-flow systems (Cooper *et al.*, 1996). This might explain the predominance of horizontal-flow CWs, with

designers opting for the tried and tested system design.

The use of stormwater CW systems in the UK to date has been primarily for management of environmental flows (flood reduction and pollutant removal) and amenity value. This suggests that the application of CWs to treat water - particularly for non-potable uses - has not been explored fully. This is in sharp contrast to Australia where stormwater treated in CWs is often used for non-potable uses including toilet flushing, firefighting and irrigation (Hatt *et al.*, 2006).

2.3.2.3. Challenges to the implementation of CWs for stormwater treatment in the UK

A number of challenges to the implementation of CWs for stormwater management were identified. These include: (i) a lack of design codes and unified guidelines (discussed in section 2.3.4); (ii) the perception of excess land space required (discussed in section 2.3.5); (iii) ambiguity over drainage responsibilities and problems with developers. Although developers are willing to construct SUDS as part of new developments, they are likely to have purchased the land before they consult with the EA, and they will want to maximise the number of houses/buildings within the purchased area. Thus the developers are keen to avoid implementing SUDS measures that will reduce the potential number of houses they can build. In Scotland this issue is targeted by a cooperative system between developers, the Scottish Environment Protection Agency (SEPA) and water authorities which encourages the early consideration of SUDS in the development proposal (Shutes and Raggatt, 2010). Furthermore, developers have also expressed concerns on the lack of clear design guidelines; more so as there are no UK design codes for SUDS – particularly CWs. In addition, it is noted that there are so few experts available for consultation on construction that they have insufficient guidance to incorporate sustainable stormwater management systems into their developments (Ellis *et al.*, 2003). This problem has been addressed to an extent by the Construction Industry Research and Information Association (CIRIA) publication “The SUDS Manual” (Woods-Ballard *et al.*, 2007), which offers design methods for a range of SUDS. Despite this, the information provided for stormwater CWs in the manual is very limited.

In terms of highway drainage, there is unresolved confusion between the water companies and the highway authorities over the ownership of highway drains, and thus there is confusion over who takes responsibility for the discharge (Ellis *et al.*, 2003). In 2011 the Department for Environment, Food and Rural Affairs (DEFRA) attempted to allocate drainage responsibilities by defining a SUDS as “those parts of a drainage system that are not vested in a sewerage undertaker”. In response to this a survey of SUDS development groups was undertaken. The survey found that many felt that highways drainage is still not accounted for in this definition and thus the issue is still ongoing (DEFRA, 2012). These issues need to be addressed to ensure the successful application of CWs for stormwater management in the UK.

2.3.3. Priority pollutants

A combined list of stormwater “priority” pollutants in the UK and Europe and their removal efficiencies in stormwater CWs is presented in Table 2-1. This list is a combination of the results of research by Mitchell (2005, for UK priority pollutants) and Eriksson *et al.* (2007, for priority pollutants in European Countries), in which contaminants were designated as being priority pollutants based on the likelihood of their presence in stormwater, their effects on aquatic organisms in surface waters and their indirect effects on humans.

Table 2-1 shows that stormwater CWs have the capability to efficiently remove priority pollutants and achieve low effluent concentrations, thus improving runoff water quality. However, there were variations in removal efficiency and effluent pollutant concentrations, indicating that the pollutants have been more successfully removed in some CW systems than in others. For example, the highest BOD₅ effluent concentration level found was an extremely large value of 388 mg/l (Adeola *et al.*, 2009). BOD₅ concentrations in stormwater runoff are usually quite low, especially in urban and road runoff. The high BOD₅ concentration in this case was found at a CW in Heathrow Airport, London, during the winter when de-icing fluids are used. De-icing fluids contain propylene glycol, which causes high levels of BOD₅. The large quantities of de-icing fluids required at the airport during winter caused an overload of BOD₅ in the CW (Adeola *et al.*, 2009). Thus, while the CW may operate efficiently throughout the rest of the year, its inability to cope with the

BOD₅ overload has resulted in the high effluent concentration shown in Table 2-1. It should be noted that this is an exception and typical expected levels are 18 mg/l and below (e.g., Pontier *et al.*, 2001).

Due to the limitations of the desk study, performance data has not been included for the removal of several of the priority pollutants (mostly pollutants which are not prioritised in the UK). However, these pollutants can be removed by treatment processes exhibited in CWs, such as microbial degradation (for Di(2-ethylhexyl)phthalate and Pentachlorophenol (Nakamiya *et al.*, 2005; Rahman and Anuar, 2009)) and sorption (for herbicides, Di(2-ethylhexyl)phthalate, 2,4,4'-Trichlorobiphenyl and Pentachlorophenol (Nakamiya *et al.*, 2005; Gregoire *et al.*, 2009; Rahman and Anuar, 2009; Swires, 2009)). Platinum is removed by the same means as other heavy metals; sedimentation, filtration, adsorption and plant uptake (Walker and Hurl, 2002). The removal of oil and grease is usually carried out by separate units; the water flowing through these units to effectively remove oil and grease before entering the CW. Where oil or grease is an issue in a specific catchment, these units can be installed (as exhibited in Hares and Ward, 2004). Thus, CWs have the capability to effectively treat stormwater for most of the priority pollutants targeted in the UK.

2.3.4. Design and treatment performance

Formal design codes do not exist for the design of stormwater CWs in the UK, however recommendations for the design of stormwater CWs exist in the form of guidance manuals and technical reports. The most comprehensive of these is *Constructed Wetlands with Links to Sustainable Drainage Systems* (Ellis *et al.*, 2003). The authors reflect on the difficulties in wetland design and state that design

Table 2-1 - Combined list of stormwater priority pollutants in UK and Europe

Pollutant Group	Pollutant	UK Priority (Mitchell, 2005)	EU Priority (Eriksson et al., 2007)	Removal Efficiency (%)	Effluent Concentration (mg/l)	Refs
Basic Parameters	5-day Biochemical Oxygen Demand (BOD ₅)	✓	✓	24 - 76	0.6 – 388	1,2,
	Chemical Oxygen Demand (COD)	✓	✓	39 - 54	1 – 135	3,4,
	Suspended Solids (SS)	×	✓	18 - 94	2 – 172	5,6
	pH	×	✓	na	-	
	Phosphorus (P)	✓	✓	39 - 70	0.2 - 7.7	
	Nitrogen (N)	✓	✓	59 - 70	0 - 4.47	
	Kjehldal-Nitrogen (KN)	✓	×	58	0.74 - 2.18	
Metals	Cadmium (Cd)	✓	✓	10 – 99	<0.01	1,3,
	Chromium (Cr)	✓	✓	53 - 84	0.001	4,5,
	Copper (Cu)	✓	✓	32 - 97	BDL - 0.224	7,8,
	Iron (Fe)	✓	×	10	0.4 – 4.3	9,10
	Lead (Pb)	✓	✓	44 - 97	BDL – 1.2	
	Mercury (Hg)	✓	×	86*	-	
	Nickel (Ni)	✓	✓	22 - 77	BDL – 0.219	
	Platinum (Pt)	×	✓	-	-	
Zinc (Zn)	✓	✓	10 – 99	0.003 – 0.5		
PAH	Benzo[a]pyrene	×	✓	63	0.00001 – 0.00176	3
	Naphthalene	×	✓	71	0.00013 – 0.01701	
	Pyrene	×	✓	71	0.00013 – 0.01701	
Herbicides	Terbutylazine	×	✓	-	-	11,
	Pendimethalin	×	✓	58	<0.00001	12
	Phenmedipham	×	✓	-	-	
	Glyphosate	×	✓	77– 90	<0.00003 – 0.00057	
Misc.	Nonylphenol ethoxylates and degradation products	×	✓	-	-	13
	Di(2-ethylhexyl)phthalate	×	✓	-	-	
	2,4,4'-Trichlorobiphenyl (Polychlorinated biphenyl 28)	×	✓	-	-	
	Methyl <i>tert</i> -butyl ethyr	×	✓	16 - 93**	-	
	Pentachlorophenol (PCP)	×	✓	-	-	
	Oil and Grease	✓	×	47	Up to 13.6	

* Hg removal in a CW treating outfall discharge, to which stormwater contributes - Nelson et al., 2006.

** MTBE removal in a pilot-scale CW treating groundwater contaminated by gasoline – Chen et al., 2012

¹Scholes et al. (1999), ²Adeola et al. (2009), ³Terzakis et al. (2008), ⁴Birch et al. (2004), ⁵Kao et al. (2001), ⁶Pontier et al., (2001), ⁷Meiorin (1989), ⁸Shutes et al (2001), ⁹Shutes (2001),

¹⁰Bulk & Slak (2003), ¹¹Miller et al. (2002), ¹²Maillard et al. (2011), ¹³Schaad et al. (2008)

✓ = priority pollutant, × = not a priority pollutant, BDL = below detection limit (reported in reference as 0)

rules for CWs are usually developed from empirical methods. However, reports such as this endeavour to provide as much design guidance as possible, and in this section this advice is reviewed and compared to design recommendations provided in other parts of the world.

2.3.4.1. Sizing

Several methods are suggested for sizing stormwater CWs in the UK. Some general CW design approaches are employed and applied to stormwater CWs, such as kinetic design methods based on first order reaction rates. Here, the CW size and retention time required to effectively reduce specific pollutant concentrations are calculated in equations such as Equation 2.1, which has been taken from UK guidelines (Ellis *et al.*, 2003). This equation was developed empirically, assuming plug flow in the CW.

$$A_S = \left(\frac{-k}{Q}\right) \ln \left[\frac{(C_{out} - C^*)}{(C_{in} - C^*)} \right] \quad (2.1)$$

where: A_S = CW surface area (m²)

k = pollutant decay rate constant (m/day)

Q = inflow rate (m³/day)

C_{in} = inflow pollutant concentration (mg/l)

C_{out} = target outflow pollutant concentration (mg/l)

C^* = background pollutant concentration in CW (mg/l).

Values for k and C^* are dependent on the pollutant and the type of CW (e.g., sub-surface flow or surface flow), and recommended values are available in literature (e.g., Kadlec and Wallace, 2009). The k value used is often that representing BOD₅ reaction rates. BOD₅ decays in the CW very slowly, and thus using a BOD₅ k will result in conservative CW dimensions. This can lead to the oversizing of CWs, especially in the case of urban stormwater CWs, as the influent contains very low concentrations of BOD₅ compared to CWs treating other wastewater types, such as sewage. Stormwater CWs primarily target contaminants like SS and heavy metals.

Another issue with using a design approach such as this is the use of average flow rate and contaminant concentration values, as this does not accurately represent the stochastic nature of stormwater inflows and the variable incoming pollutant concentrations. Also, k values widely vary from one CW to another (Ellis *et al.*, 2003). Therefore, while this approach is useful as an initial estimate for the dimensions of a CW, it should not be relied upon for the sizing process.

Empirical stormwater CW design methods are popular due to the stochastic nature of storm events. One such example is to design the CW to a size capable of retaining water volumes that occur during a storm with a selected return period. UK recommendations state that an urban stormwater CW should be able to treat storms with a 10 year return period as a minimum (Ellis *et al.*, 2003), and in flood prone areas the EA recommend designing for a 1:200 year return period flood (Shutes *et al.*, 2005). Both UK and US guidelines cite the recommendation of Schueler (1992) that stormwater CWs should be able to retain 90% of all storm events producing runoff. The US EPA regards this target as “a reasonable and achievable goal” (US EPA, 2000a).

An alternative empirical approach offered in UK guidelines is to size a CW as a percentage of the size of the catchment area, using proven wetland to watershed area ratio (WWAR) values. UK guidelines recommend a wetland/watershed area ratio (WWAR) of 1–5% (Ellis *et al.*, 2003). US guidelines recommend a larger minimum WWAR of 2%, an indication of the greater land availability (US EPA, 2000a). Figure 2-6 is a plot of catchment area vs. CW surface area for a number of UK stormwater CWs for which information is available.

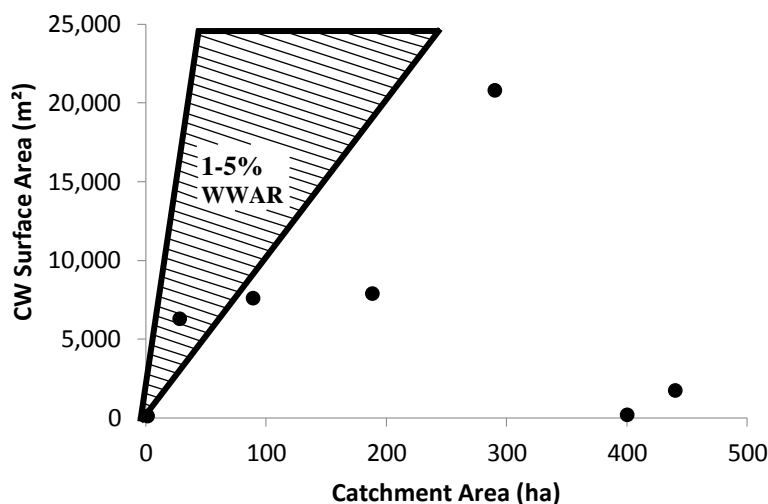


Figure 2-6 - Plot of CW surface area vs. catchment area drained for UK stormwater systems (plot based on data obtained from Ellis *et al.*, 2003; Adeola *et al.*, 2009)

Figure 2-6 shows that the majority of the CWs studied have a WWAR of below 1%. One CW has a WWAR comfortably within the recommended range of 1-5%. The average WWAR of these CWs is 0.71%. In contrast, a survey of US stormwater CWs found that the average WWAR was 4.26% (Ellis *et al.*, 2003). This is a relatively large WWAR and it may suggest the greater land availability in the USA.

2.3.4.2. Hydraulic retention time

Retention time (i.e., the period of time that inflowing water is in the CW system before leaving as outflow) is an important parameter in CW treatment systems, since shorter hydraulic retention time (HRT) allows less time for wetland treatment processes to occur. The desirable HRT depends on which treatment processes are occurring in the wetland. For example, 3-5 hours is usually sufficient to allow for sedimentation of most coarse solids, but a HRT of more than 24 hours is recommended in the UK for the treatment of bacteria, degradable organics and toxic species found in finer solids fractions (Halcrow/UPRC, 2000). Reports by CIRIA (Martin *et al.*, 2000) and the Highways Agency (Department of Transport, Local Government and Regions, 2001) advise a 14 day retention period for UK systems during wet times of the year, but this long HRT is generally not required for urban

surface runoff, unless full nutrient reduction is required. In most UK urban runoff, nitrogen loads have an average of under 9kg/impervious hectare/annum; a concentration which does not require full reduction (Shutes *et al.*, 2005). The American guidelines (US EPA, 2000a, 2000c) do not give any specific recommendations regarding retention time, stating that this is dependent on the needs of the regulating body. However, they do say that a shallow marsh system with dense vegetation and near-flat gradient can hold shallow depths of water for “extended periods” of around 18 to 24 hours (US EPA, 2000a). The recommendation of this specific time range suggests that this HRT is regarded by the US EPA as a good standard for stormwater CWs, and matches the UK recommendations for the treatment of bacteria, degradable organics and toxic species.

Research conducted on vertical subsurface-flow CWs for combined sewer overflow (CSO) treatment in Germany claims that HRT should be restricted to a maximum of 48 hours, since extended inundation causes long periods of anaerobic conditions which hinder degradation processes (Uhl and Dittmer, 2005). It was also found that extended HRT can lead to clogging, due to the increased rate of biomass growth in the filter during the inundation period. This is likely to be more of a problem to CSO CWs than it is to solely stormwater CWs, due to the presence of sewage in CSO influent.

Factors which affect the HRT include the width to length ratio of the wetland, the presence of vegetation, the porosity of the substrate, the water depth and the bed slope (Ellis *et al.*, 2003). One way of increasing HRT is to increase wetland surface area. When dealing with urban stormwater, this is a problem. Due to the built-up nature of UK cities, there is a lack of open space in which CWs with large surface areas can be located. This issue is explored further in section 2.3.5. The use of a tidal-flow operation regime allows for control of the HRT. Thus, the retention time can be set to allow for maximum removal in a tidal-flow CW.

2.3.4.3. Media

The media chosen for a stormwater CW system is one of the most important selections in the design process. The material should ideally be locally and widely

available in order to encourage their implementation, and must be able to support vegetation. For subsurface-flow systems a hydraulic conductivity of 100-300 mm/hr is recommended in a temperate climate such as that of the UK, and the media should include some organic matter to increase water retention. The material should maintain a high permeability under compaction and should not be hydrophobic (FAWB, 2009a). Sand, gravel and loam are typical stormwater CW media choices (Hatt *et al.*, 2007a; Adeola *et al.*, 2009) and they are available UK-wide. USA recommendations simply state that topsoil or mulch should be used in order to support “vigorous” plant growth (New Jersey Department of Environmental Protection, 2004). In general, the American guidelines have a very prominent focus on the encouragement of biodiversity in stormwater CWs. This is not surprising since the systems are so large that there are opportunities to support large ecosystems. Alternative engineered media can be used in an attempt to increase removal efficiency for certain pollutants, but in terms of UK widespread implementation the use of locally available materials is a priority.

2.3.4.4. Constructed wetland plants

An important component of CW design is the choice of plants for the system. As well as biological processes, plants play a significant role in surface-flow systems as they reduce the flow velocity of the water in the wetland to aid sedimentation, which is particularly important since sedimentation is a major removal mechanism in wetland systems. Also, in subsurface-flow systems, plants help to maintain the hydraulic conductivity of the wetland, while heavy metal reduction is achieved by accumulation and storage in the rhizospheres of wetland plants (Kadlec and Wallace, 2009), thus they are instrumental in stormwater treatment. Two of the most commonly used plants in CWs, namely *Phragmites australis* (common reed) and *Typha latifolia* (reedmace), are readily available in the UK and indeed have been used in several UK stormwater wetlands (Ellis *et al.*, 2003). There are several species of plants that can be used in UK stormwater treatment systems, the most recommended being those that can grow quickly and constantly, spread well across the CW, absorb or convert pollutants, be easily harvested and look visually appealing (Ellis *et al.*, 2003). This is less specific than recommendations by the US EPA,

which refer to three species of macrophyte (*Sagittaria latifolia*, *Scirpus americanus* and *Scirpus validus*) that establish themselves quickly and spread well, thus encouraging biodiversity (US EPA, 2000a). This is another indication of the focus on biodiversity encouraged in US stormwater CWs, an initiative also encouraged in Italy for the design of CSO CWs (Meyer *et al.*, 2013).

2.3.4.5. Operation in cold climates

One concern over the use of CWs in the UK is their ability to operate in cold climates. The UK can be prone to cold temperatures, with extreme cases of less than -20°C in Scotland, England and Wales (Met Office, 2011). The main concerns of cold conditions are: ice formation, which in turn causes hydraulic issues; and the effect of low temperatures on microbiological treatment processes in the CW (Wittgren and Mæhlum, 1997). However, CWs have been shown to be fully operational and with negligible or no effect on performance in areas with more consistently cold climates or harsher winters than the UK, such as Norway (Giæver, 2003; Mæhlum and Jenssen, 2003) Minnesota (Kadlec *et al.*, 2003) and Switzerland (Züst and Schönborn, 2003). Subsurface flow CWs are more desirable than FWS systems because the water is below the ground surface and therefore experiences a degree of insulation (Werker *et al.*, 2002). Incorporating insulation into the design of the CW in the form of extruded polystyrene (XPS) is extremely effective in preventing freezing (Wittgren and Mæhlum, 1997), while other methods can be used such as straw insulation (Kadlec *et al.*, 2003) or even allowing the top of the water to freeze and lowering the water underneath the ice to create an air gap (Giæver, 2003). Thus, CWs can be operated in low UK temperatures, providing that those prone to freezing include insulation measures in their design.

2.3.4.6. Additional design features

“Constructed wetlands in UK surface drainage systems” contains further guidance on the design of CWs in the UK (Shutes *et al.*, 2005), emphasising the importance of factors such as designing CWs to exhibit uniform flow characteristics. Uniform flow implies that the CW is being run as efficiently as possible, with the whole of the system contributing to hydraulic and treatment processes. In Australia this is

promoted by recommending that stormwater CWs are designed with a length to width ratio greater than 3 to 1 (Wong *et al.*, 1999). Also encouraged is the incorporation of facilities to aid treatment in CWs, such as front-end sedimentation tanks (Shutes *et al.*, 2005), which can be extremely effective in reducing the SS load, thus reducing the risk of clogging and decreasing the concentrations of pollutants which attach the SS particles in the CW influent. This is common procedure in German CSO CWs (Meyer *et al.*, 2013) and in stormwater CWs in the USA, where the design guidelines include sediment forebays as a standard inclusion (US EPA, 2000a). In fact, the US EPA guidelines describe a very standard footprint for the design of stormwater CWs, specifically a shallow surface flow system with a sediment forebay at the inlet and a micropool at the exit. There is no mention of alternative subsurface-flow designs. This is an indication of the larger availability of land area in the USA in comparison to the UK. In the USA, the excessive land availability allows a reasonably standard general design for stormwater CWs to be recommended, which can be implemented in most places. The shortage of land availability in the UK means that CWs require more “tailoring” to their settings. This is discussed further in section 2.3.5. UK guidelines could benefit from the inclusion of additional features prominent in CSO CWs in other European countries. Reduced flow rate outlets are installed in the vertical subsurface-flow CSO CWs used in Italy, ensuring a long HRT and initial ponding on the media surface, which promotes good water distribution over the surface area so that the entire CW is being used efficiently. Meanwhile, in France, a saturated layer of water is standard design procedure to support vegetation during dry periods, and an aeration pipe is also installed to encourage aeration at these times (Meyer *et al.*, 2013). Studies conducted in Australia found that the incorporation of a saturated zone in pilot-scale vertical subsurface-flow CWs for stormwater runoff treatment had benefits to the removal of metals (Blecken *et al.*, 2009a) and nutrients (Zhang *et al.*, 2011). Information gathered from various systems in Germany found that influent arriving from CSO pipes directly on to the surface of a vertical subsurface-flow CW can cause erosive damage to plants and filter layers, and thus it is recommended that open inflow channels used as side weirs are used to reduce the inflow rate (Uhl and Dittmer, 2005). A reduced inflow rate would also benefit surface-flow CWs for the same

reasons, and additionally it would also reduce the amount of turbulence caused by inflowing water, thereby reducing the risk of particle re-suspension, which can have a negative effect on pollutant removal efficiency (see section 2.3.4.7).

2.3.4.7. Treatment performance

In order to review the capability of UK CWs to remove contaminants from stormwater runoff, data on the performance of stormwater CWs was collected and analysed to examine the range of removal efficiencies. The removal efficiencies for the most commonly reported contaminants in UK systems were then compared to removal efficiencies reported in systems from countries in continental Europe, Asia, Africa, North America and Australasia. The results are shown in Table 2-2.

Table 2-2 shows that most UK stormwater CWs can remove contaminants efficiently to levels comparable to other systems in the world. However, it is noted that phosphate removal is generally low (<50%), indicating limited phosphate absorbing capacity of the media used in the CW. Despite this, the data shows that the effluent phosphate concentrations corresponding to this removal efficiency were still well under the limits set for the respective sites (Revitt *et al.*, 1999). The range of removal efficiencies is quite wide for most pollutants, indicating a wide variation in the removal efficiencies of the systems. This highlights the importance of good system design and the need for reliable UK guidelines. Despite this, the performances obtained as shown in Table 2-2 are very close to - and in some cases better than - those obtained from CWs elsewhere. Negative removal efficiencies (shown as minus values) can be seen for both UK CWs and those from the rest of the world. This is often due to the re-mobilization of solid particles in CWs during heavy storms. In subsurface-flow CWs this may indicate that the system has become saturated or even blocked, causing ponding on the surface of the CW and effectively creating a surface-flow system, in which re-suspension of solids can occur. The re-suspension of particles increases the concentration of SS and other contaminants, such as heavy metals, which may be attached to the particles. This was found to be a consistent problem during the monitoring of stormwater CW sites in Brentwood and Dagenham (Scholes *et al.*, 1999). This problem can be tackled with a well-designed sediment forebay and appropriate measures to reduce flow velocity. Alternatively, a bed of

aggregates can be used to prevent sediment re-suspension (Nuttall *et al.*, 1997).

Table 2-3 shows the pollutant removal information for a selection of UK stormwater CWs for which performance information was available in published literature.

Table 2-2 – Performance and comparison of UK stormwater CWs

Pollutant	Removal efficiency (%)	
	UK Stormwater CWs	Rest of the World
Zn	-56 – 99	6 – 98
Pb	0 – 98	28 – 99
Cd	-89 – 99	0 – 99
Cu	-97 – 97	-15 – 94
Ni	34 – 85	-76 – 98
Cr	24 – 81	40 – 84
SS	-16 – 99	-98 – 91
BOD ₅	-63 – 99	-26 – 33
Faecal Coliforms (FC)	78 – 98	83 – 99
Nitrate	-21 – 66	-13 – 88
Phosphate	-18 – 48	17 – 51

Data from: Meiroin (1989), Revitt *et al.* (1999), Scholes *et al.* (1999), Carleton *et al.* (2001), Kao *et al.* (2001), Shutes (2001), Shutes *et al.* (2001), Bulc & Slak (2003), Ellis *et al.* (2003), Birch *et al.* (2004), Shutes *et al.* (2005), Terzakis *et al.* (2008)

Negative values represent negative removal efficiencies, normally due to re-suspension of particles in the CW

Table 2-3 - Pollutant removal efficiencies of a selection of UK stormwater CWs

Name	WWAR (%)	Pollutant Removal Efficiency (%)							Refs
		SS	Pb	Zn	Cu	Cd	BOD ₅	FC	
Anton Crescent	1	56	7	37	-	-	-	78	1
Great Notley Garden	0.42	-	89-97	10-99	94-97	10-99	-	-	1,2
Brentwood	0.005	-4-18	30-40	19-55	-15-39	-4-33	17-26	-	1, 3
Newbury Bypass	-	40-75	0-98	-56-76	-97-83	-89-99	-63-64	-	1, 4, 5
Hopwood Park 1	-	95-99	-	-	-	-	95-99	-	1
Hopwood Park 2	-	97	-	-	-	-	89	-	1
Dagenham	0.04	-16-35	37-69	31-71	23-66	48-72	-23-24	-	1, 6
Welsh Harp	-	97	-	-	-	-	-	85	1, 2
Heathrow surface flow	-	-	-	-	-	-	18	97	1
Heathrow subsurface flow	-	-	-	-	-	-	22	98	1

¹Ellis *et al.*, 2003; ²Shutes, 2001; ³Revitt *et al.*, 1999; ⁴Shutes *et al.*, 2001; ⁵Shutes *et al.*, 2005; ⁶Scholes *et al.*, 1999

Negative values represent negative removal efficiencies, normally due to re-suspension of particles in the CW

Table 2-3 shows varying degrees of pollutant removal efficiencies across the systems. The removal efficiencies obtained for the Brentwood system are relatively low and this is likely due to the small WWAR value of 0.005%. The CWs at Great Notley Garden and Dagenham both produce impressive removal efficiencies for several pollutants despite their small WWAR values (both values are below the recommended value of 1%). It should be noted that both of these CWs are in the south-east of the UK, which is relatively drier than the rest of the country. Therefore the reduced rainfall in this area may have allowed for efficient CW treatment performance despite the low WWAR values. The removal efficiencies at the Hopwood Park CWs are very high for both SS and BOD₅. Hopwood Park is a service station and is therefore unlikely to be a very large area. So it is probable that, with two CWs receiving runoff from the area, the WWAR value is relatively high, thus increasing treatment efficiency.

The information in Table 2-3 shows that CWs are capable of treating stormwater effectively in the UK; however there is a lack of consistency in their performances. This can be improved upon with the provision of unified and clear design guidance. Furthermore, due to the fact that land is at a premium in the UK, CWs for stormwater management tend to have WWAR values below the recommended minimum of 1% and this may affect the performance of the systems (although this warrants further investigation). Alternative design techniques that may be used to manage stormwater effectively in spite of the low land availability are discussed in section 2.3.5.

2.3.5. Implementation and retrofitting

Despite the increased use of CWs for stormwater treatment in the UK in recent years, there is a lack of performance data and monitoring results. This is probably due in part to the fact that CWs for stormwater management are likely to be implemented as part of a SUDS treatment train rather than as stand-alone treatment. Therefore direct performance monitoring of CW systems is generally not carried out; rather the treatment performance of the SUDS train as a whole will be determined.

In contrast, performance data is more widely available in countries like the USA, where there are far more CWs operating as stand-alone treatment systems (Moore and Hunt, 2012). As mentioned earlier in section 2.3.2.2, nearly all UK stormwater CWs are horizontal subsurface-flow systems. Horizontal flow systems are very land intensive, and it appears that vertical-flow systems (which generally have a smaller footprint) have been ignored as a design option. The CWA database lists 51 vertical down-flow CWs operating in the UK; 23 of which are used for tertiary treatment of sewage.

An alternative technique used to maximise treatment efficiency in areas of restricted land availability is effluent recycling. This method is used in the subsurface-flow CW at Heathrow Airport, London during winter periods when excess BOD₅ levels are caused by a significant increase in the use of anti-icing glycols. Longer retention times are required to reduce the BOD₅ levels and so the runoff is recycled back through the system to double the retention time (Adeola *et al.*, 2009).

Another method recommended in the UK to maximise HRT in CWs with low space availability is to increase the length of flow paths by introducing baffles (Woods-Ballard *et al.*, 2007). As water flows from the inlet to the outlet, it must flow down underneath the baffle and back up again, thus extending the flow path significantly and allowing more removal processes to occur.

Although SUDS implementation is being highly encouraged in new developments, most diffuse urban pollutants that discharge to surface waters originate from existing developments (Mitchell, 2005). Retro-fitting CWs is one way to utilise their treatment capabilities without having to find additional space to accommodate them. Retro-fitted CW systems are normally sited in existing structures such as a balancing pond or other flood attenuation systems. Indeed, the retro-fitting of SUDS in general is a practice that the UK should look to adopt if it is to effectively tackle urban stormwater pollution. The disadvantage of retro-fitting a CW is the lack of flexibility in sizing the system, since it must fit within the existing footprint. Therefore some sites may not be suitably sized to provide the surface area required for effective stormwater treatment, particularly since vegetation and substrate media has to be added to the existing area. It is also important to note that, since the retro-fitted

system will be built in place of an existing structure, there are many stakeholders to satisfy, such as local residents and their representatives, planning authorities, regulatory bodies and landowners (Ellis *et al.*, 2003).

Despite these issues, retro-fitting CWs is a technique that has already proven successful both in the UK (such as the former retention basin in Anton Crescent, Surrey, that has been converted into a CW treating runoff from a residential and light commercial catchment area (Ellis *et al.*, 2003)) and abroad (such as a retention basin in Slovenia which was converted into a CW that effectively removes solids and metals from highway runoff (Bulc and Slak, 2003)). The demonstrated success of these retro-fitted systems should encourage their further implementation in the UK.

2.4. Vertical-flow subsurface constructed wetlands for stormwater treatment

Based on the findings of section 2.3, the use of VF CWs should be a strong focus for further research. Firstly, it is important to investigate the use of VF systems for stormwater treatment.

Considerable research has been carried out in this field. Through various experimental investigations on pilot-scale systems, the research carried out has allowed for design optimisation in several areas, including plant choice, media depth, media choice and surface area sizing (Hatt *et al.*, 2007c; Bratieres *et al.*, 2008; Zhang *et al.*, 2011; Feng *et al.*, 2012). The literature shows high removal rates of heavy metals (Blecken *et al.*, 2009b; Feng *et al.*, 2012), TSS and phosphorus (Bratieres *et al.*, 2008). However, the research confirms that traditional VF CW operating conditions have limited N removal abilities due to their inability to denitrify. This is evident in Bratieres *et al.* (2008), where the systems leached nitrates and TN into the effluent, resulting in negative removal efficiencies. While nitrate concentrations increased, ammonia removal was consistently high, thus indicating the strong nitrification abilities of VF CWs. With nitrates not readily absorbent to soil due to their anionic form (Henderson *et al.*, 2007), denitrification is required to convert nitrates to N₂ gas. Unfortunately, traditional VF CW design does not allow for the

anoxic conditions required in which denitrification can occur (Kim et al., 2003; Davis et al., 2006; Vymazal and Kröpfelová, 2008).

Several modifications to the traditional VF CW design have been investigated, such as the introduction of a permanently saturated zone at the bottom of the CW (Zinger et al., 2007; Blecken et al., 2009a) to provide partial anaerobic conditions. An alternative technique explored by Scholz and Hedmark (2010) involves nearly constant saturation of the VF CW (parts of the CWs became unsaturated during release of effluent for 15 minute periods, 3 times per week, but the effluent water was then replaced with new influent water). This study found that plant uptake was the main removal mechanism for nitrogen removal. This is unsurprising, since the constantly saturated conditions mean that there is limited oxygen transfer in the system to cause nitrification. This places a heavy reliance on plants, which is controversial as some studies have claimed that macrophytes play very insignificant roles in pollutant removal (Mays and Edwards, 2001; Baldizón et al., 2002; Scholz and Xu, 2002). Furthermore, it has been determined that aerobic treatment processes occur mainly during the drained period in VF CWs (Hu et al., 2014); therefore constant saturation is not conducive to effective nitrification.

To date, there has been no investigation into the use of tidal flow CWs for stormwater treatment, in which influent stormwater is held in the CW for a set period of time to allow removal processes to occur, before being completely drained to allow re-entry of air into the system. The potential for improved TN removal is in the fixed retention time: during this time, anoxic conditions are developed in the CW which aid denitrification (Hu et al., 2014). Additionally, the fixed retention time allows for extended contact time for adsorption processes. The application of a tidal flow regime to a VF stormwater CW is the main focus of this thesis.

2.5. Summary

The literature review found that CWs have the potential to be invaluable for stormwater management in the UK, helping to protect local watercourses, attenuate flooding and allowing surface runoff to be re-used for non-potable purposes, thus reducing the strain on potable water supplies. The review has shown that CWs can

be used to treat stormwater for all of the priority pollutants concerning the UK, and existing UK CWs have shown their capability at effectively reducing contaminant concentrations from stormwater just as well as systems in the rest of the world. However, their widespread implementation is hindered by a lack of design codes and space restrictions in the UK. To address these issues, unified guidance needs to be developed based on further research into the use of CWs to treat urban stormwater, and system designs which are less land-intensive should be considered such as the use of VF CWs. However, the traditional VF CW design has limited nitrate removal capabilities, which affects the reduction of TN, a priority pollutant in stormwater. These findings were the main drivers behind this thesis: to develop a VF CW design that can effectively treat stormwater for nitrate removal and a range of priority pollutants and to understand the internal processes that contribute the reduction of these contaminants. In doing so, this study will contribute to the body of research devoted to understanding stormwater treatment through CWs and hopefully lead to the availability of improved guidance on their implementation in the UK.

3. Materials and Methods

3.1. Experimental set-up: pilot-scale constructed wetlands

Eight pilot-scale CWs were constructed using structured-wall high-density polyethylene (HDPE) pipes. Figure 3-1 shows a photograph of the setup at the School of Engineering, Cardiff University. The CWs were operated as vertical down-flow systems, and different operating conditions were applied depending on the variables that each individual unit was being used to investigate.



Figure 3-1 - Experimental set-up of the pilot-scale CW systems

The structured-wall HDPE pipes which housed the CWs were manufactured by Asset International Ltd. Each pipe had an internal diameter of 400 mm (minimum diameter available) and a height of 1000 mm. The pipes were sealed off at one end with HDPE plastic, thus providing the base of the CW. A main outlet tap was fitted on the base of the CW in the centre of this sealed end, An additional tap was fitted for overflow, but was not required. A typical pilot-scale CW unit, built from a single pipe length, can be seen in Figure 3-2.

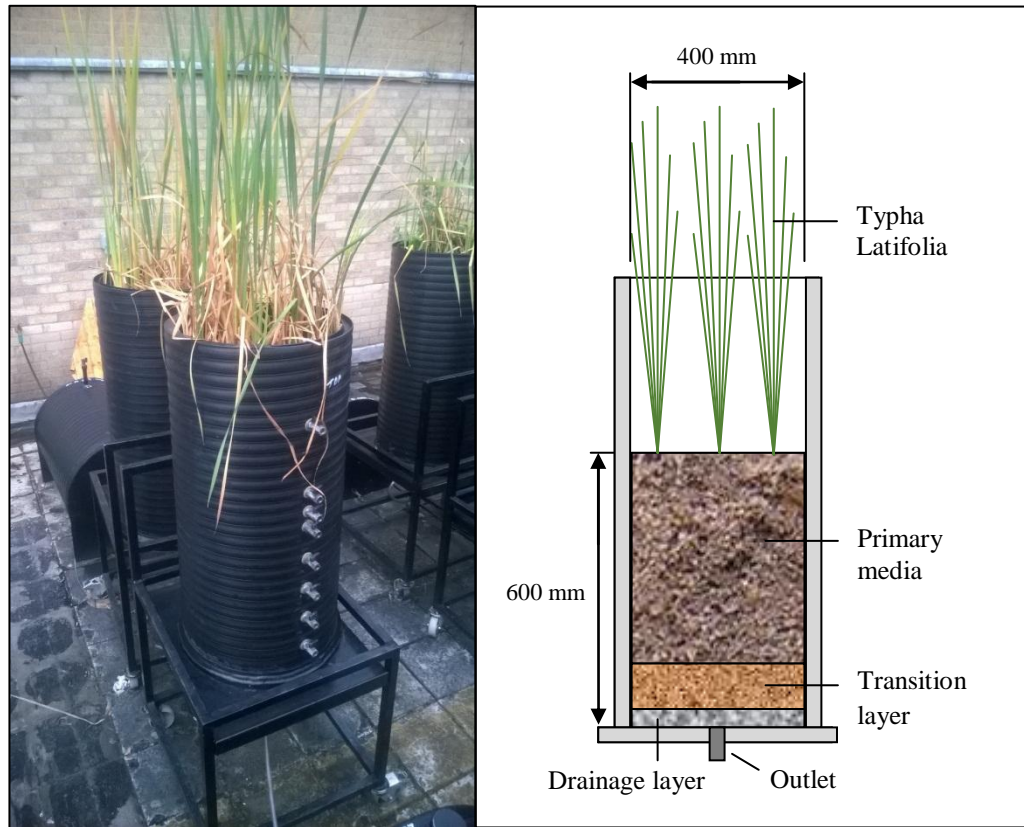


Figure 3-2 - Pilot scale CW housed in HDPE pipe

3.1.1. Media and plants

Sand and gravel are typical media used in vertical subsurface-flow stormwater CW systems. Similar stormwater treatment systems using sand-based CW media have shown good heavy metals removal (Hatt *et al.*, 2007a; Li and Davis, 2009), and heavy metals are one of the main pollutants of concern in stormwater runoff. Guidelines produced by the Facility for Advancing Water Biofiltration (FAWB) recommend the use of loamy sand in stormwater biofiltration treatment systems due to its high permeability under compaction, its organic matter content (which increases water holding capacity), its low nutrient content and its ability to support vegetation well (Blecken *et al.*, 2009a; FAWB, 2009a). Loamy sand was therefore selected as the main media in 6 out of the 8 CW units (units 1, 3, 4, 5, 6 and 7).

Gravel is cheap and readily available, and its use as CW media has been effective in suspended solids and heavy metal removal (Hatt *et al.*, 2007c). Unit 2 was therefore

constructed with a media arrangement where graded gravel is the predominant media in order to assess its performance.

Blast furnace slag (BFS) is an industrial by-product which has been shown to exhibit high adsorptive capacity for heavy metals and phosphorus (Grüneberg and Kern, 2001; Taylor, 2006; Korkusuz et al., 2007). Heavy metals and phosphorus are priority pollutants in stormwater treatment, and the utilisation of a by-product makes BFS a potentially valuable and sustainable material for use in CWs. Therefore, granulated BFS (diameter 4 – 12.5 mm) was selected as the main media in unit 8 (see Figure 3-3).



Figure 3-3 - Granulated BFS in CW unit 8

Each unit contained a drainage layer of fine gravel (6 mm diameter) and all systems (apart from unit 2, in which all layers are gravel) contained a transition layer consisting of sharp sand to ensure that none of the primary media is transported to the drainage layer. In unit 2, medium gravel (10 mm diameter) was placed as the transition layer and coarse gravel (20 mm diameter) made up the drainage layer.

Each CW unit was planted with *Typha latifolia* plants (density = 64 plants/m², see Figure 3-4). *Typha* has several benefits: it is found all over the world, is effective in

metals removal and it is renowned for its suitability for treating surface runoff (Ellis *et al.*, 2003).



Figure 3-4 - *Typha latifolia* prior to planting (left, centre) and immediately after planting in CW unit 2

Each CW consisted of a primary layer of substrate media (depth 450 mm), a transition layer (100 mm) and a drainage layer (50 mm). Table 3-1 details the operating conditions of all the pilot-scale units and shows the media configuration for all units. Figure 3-5 shows cross sections of the CWs in which the media composition can be viewed. The media of units 1,3,4,5,6 and 7 was loamy sand with a sand transition layer and gravel drainage layer. This media arrangement is recommended by the FAWB (2009a). The gravel layer structure of unit 2 is “typical” of a downflow vertical flow CW system as described in Cooper *et al.* (1996). The configuration of unit 8 is similar to that recommended by the FAWB, but with loamy sand replaced by BFS.

3.1.2. Sizing

3.1.2.1. Surface area

Under field conditions, the surface area of the CW would be determined by the size of the catchment that it is located in. The surface area is determined as a percentage of the size of the watershed area, and this is known as the wetland/watershed area ratio (WWAR). To clarify, a CW with a WWAR value of 5% would mean that the surface area of the CW is equal to 5% of the total catchment surface area. The design of CWs for stormwater treatment is so variable (due to the unpredictable nature of rainfall and the differing treatment requirements in different catchments) that there are no design codes specifying a WWAR value which should be used; instead the

value is usually taken from guidelines and recommendations. For example, Ellis et al. (2003) state that values of 1-5% are typical, and suggest using a WWAR of 2-3%. Ideally the WWAR value should be as small as possible to minimise land uptake without compromising treatment. This is especially important for retrofitting CW systems, which was identified in the literature review as a key process to increase the use of CW systems for stormwater treatment.

In this design the sizing method has effectively been reversed. The CW surface area is limited by the fact that the minimum available diameter of HDPE pipes (400 mm) was used for the pilot scale systems. Rather than starting with a watershed area and calculating the CW surface area, the CW area itself is known and the representative area of the catchment that can be treated by the system is determined. First, the surface area of the CW was determined based on a circular cross-sectional area. For all eight CWs, a diameter of 0.4 m gives a cross-sectional area of 0.126 m².

Three separate values of WWAR were used in the experiment to determine the performance of the system under different loading conditions. These values were 1.5%, 2.5% and 5%. 2.5% was the control WWAR, since it is within the 2-3% recommendation by Ellis et al (2003). This WWAR value was applied to units 1, 2, 3, 4, 6 and 8. Unit 5 had a 5% WWAR to investigate the extent to which pollutant removal is improved by increasing the representative surface area of a CW. Unit 7 had a 1.5% WWAR to determine if the CW system can exhibit efficient pollutant removal while only taking up a very small area of the catchment. Table 3-1 details the operating conditions of all the pilot-scale units, and shows which CW units were used to investigate WWAR value and the WWAR value for each unit. Any observed contrast in performance between the three different WWAR values should allow for an ideal WWAR value to be determined for this system design.

Representative catchment areas treated by the systems are calculated as follows:

$$\text{For a 1.5\% WWAR: } 0.126 \times \frac{100}{\text{WWAR}} = 0.126 \times \frac{100}{1.5} = \mathbf{8.4 \text{ m}^2}$$

$$\text{For a 2.5\% WWAR: } 0.126 \times \frac{100}{2.5} = \mathbf{5.04 \text{ m}^2}$$

$$\text{For a 5\% WWAR: } 0.126 \times \frac{100}{5} = \mathbf{2.52 \text{ m}^2}$$

3.1.2.2. Media depth

The pilot-scale CWs have a total media depth of 0.6 m, which reflects values found in literature and reports from other studies. The 0.6 m depth is 100 mm deeper than the depth determined by Feng *et al.* (2012), but with the inclusion of a recommended 150 mm deep transition/drainage layer, it was decided that an extra 100 mm of total depth would be beneficial to ensure that the primary media was able to provide plenty of surface area for adsorption and other pollutant removal processes. UK vertical-flow CWs have traditionally been constructed to a depth of 0.5–0.8 m (Cooper *et al.*, 1996). These typical depths are chosen to provide adequate hydraulic residence time (HRT) for traditional vertical-flow CWs to provide efficient treatment. Several studies of a similar pilot-scale set-up to this experiment use 0.8 m deep cells (Scholz, 2004; Blecken *et al.*, 2009a; Blecken *et al.*, 2010). Hatt *et al.* found that a gravel filter of depth 0.5 m was suitable for removing sediment and heavy metals (Hatt *et al.*, 2007c), and it has been recommended that 0.5 m is a sufficient depth for a stormwater infiltration treatment system (Feng *et al.*, 2012).

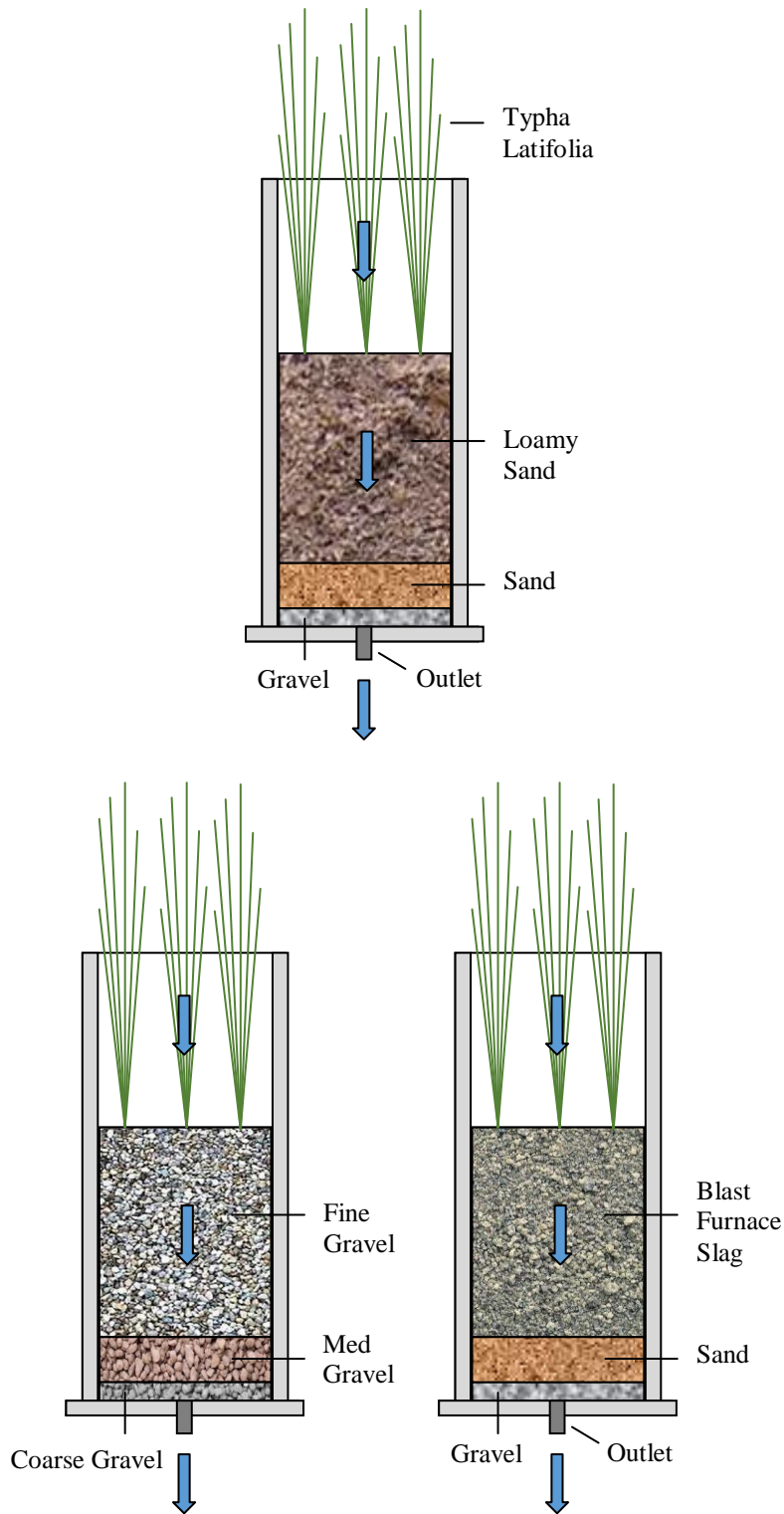


Figure 3-5 - Cross-section of loamy sand, gravel and BFS CW units

Table 3-1 - Variables matrix

		CW unit							
		1	2	3	4	5	6	7	8
WWAR (%)		2.5	2.5	2.5	2.5	5	2.5	1.5	2.5
Wetting/drying regime		Wet conditions	Wet conditions	Partially dry conditions	Wet conditions	Wet conditions	Extended dry conditions	Wet conditions	Wet conditions
Media composition (by depth)	0 – 450 mm	Loamy sand	Fine gravel	Loamy sand	Loamy sand	Loamy sand	Loamy sand	Loamy sand	Blast furnace slag
	450 – 550 mm	Sand	Med gravel	Sand	Sand	Sand	Sand	Sand	Sand
	550 – 600 mm	Fine gravel	Coarse gravel	Fine gravel	Fine gravel	Fine gravel	Fine gravel	Fine gravel	Fine gravel
Variable Investigated		(Control unit)	Media type	Wetting and drying regime	(Control duplicate)	WWAR (5%)	Wetting and drying regime	WWAR (1.5%)	Media type

*Fine gravel = 6 mm diameter; Med gravel = 10 mm diameter; Coarse gravel = 20 mm diameter

3.1.3. Semi-synthetic stormwater

Semi-synthetic stormwater was used in the experiment, rather than natural stormwater or fully synthetic stormwater. Natural stormwater was not available in the required quantities on site and it can also introduce a high degree of inconsistency in inflow concentrations and attributes, while 100% synthetic stormwater is less representative of real runoff. Semi-synthetic stormwater is a compromise which allows an ideal degree of control over inflow concentrations while simultaneously representing natural runoff better as it has been produced from stormwater sediment.

The semi-synthetic stormwater was produced by mixing real stormwater sediment with dechlorinated tap water, and adding laboratory-grade chemicals to achieve elevated pollutant concentrations where required. Stormwater sediment was collected from two locations: initially from a stormwater runoff pond in Nant y Briwnant, north Cardiff; then from gully pots in the car park of the School of Engineering, Cardiff University. The reason for the change of location after 3 months of operation was the unreliable access to the pond: at times of high rainfall the (normally subsurface) pond would flood and it was impossible to collect the sediments required.



Figure 3-6 - Stormwater pond at Nant y Briwnant, Cardiff: flooded conditions shown on right

The collected sediment was wet-sieved through a 1 mm sieve. This upper limit for the solids particle size is recommended by FAWB (2009) to replicate runoff that has not passed through a pre-treatment facility. The wet-sieving procedure produces slurry: a high concentration mixture of solids with water. The total suspended solids

(TSS_s) concentration of this slurry was then determined by standard methods (APHA *et al.*, 2012). A sample of the slurry was analysed in Cardiff University's CLEER (Characterisation Laboratories for Environmental Engineering Research) laboratory to determine the existing concentration of each of the contaminants listed in Table 3-2 (see section 3.1.7 for analysis procedures). Where pollutant concentrations were found to be lower than target inflow values, laboratory grade chemicals were added to the slurry to meet these targets (see section 3.1.4 for more detail). Equation 3.1 was used to determine the volume of slurry required for the desired total volume of semi-synthetic runoff.

$$V_S = \frac{TSS_T \times V_{ST}}{TSS_S} \quad (3.1)$$

where: V_S = volume of slurry (L)

TSS_T = target TSS concentration (mg/L)

V_{ST} = volume of semi-synthetic stormwater (L)

TSS_S = slurry TSS concentration (mg/L)

After V_S was determined, this volume was added to dechlorinated tap water (volume V_{ST}). The tap water was dechlorinated by the addition of sodium thiosulphate (0.1 g per 100 L of tap water, as recommended by FAWB, 2009). The mixture was then stirred continuously for 10 minutes to achieve uniform distribution of sediment in the water and adsorption of contaminants to the solids particles.

3.1.4. Pollutant concentrations

Inflow pollutant concentrations were representative of urban areas. The priority stormwater pollutants in UK and European urban areas were identified in the literature review (see Table 2-1).

The most up-to-date extensive study of urban stormwater pollutant concentrations worldwide is *Urban Stormwater Quality: A Statistical Overview*, by Duncan (1999). The report lists typical stormwater contaminants and their average concentrations in different types of catchment. The catchment type of interest to this experiment is "high urban" (highly urbanised catchments). The average concentration values from

Duncan (1999) were compared to those found in the literature review and adjusted where necessary.

Several pollutants have not been selected for the experiment due to the lack of data regarding their typical concentrations in urban stormwater. The selected contaminants are shown in Table 3-2, along with their target influent concentration values and the laboratory grade chemical that would be added to achieve the required concentration for each pollutant.

Table 3-2 - Target inflow contaminant concentrations and chemicals used to achieve them

Pollutant	Target concentration (mg/l)	Chemical added to produce semi-synthetic stormwater
TSS	180	-
TP	0.45	di-Potassium hydrogen phosphate (K ₂ HPO ₄) and di-Sodium hydrogen phosphate (Na ₂ HPO ₄)
PO ₄ -P	-	-
TN	3	Ammonium chloride (NH ₄ Cl)
NH ₄ -N	-	-
NO ₂ -N	-	-
NO ₃ -N	-	-
Pb	0.16	Lead nitrate (Pb(NO ₃) ₂)
Zn	0.35	Zinc sulphate heptahydrate (ZnSO ₄ .7H ₂ O)
Cu	0.07	Copper (II) chloride dihydrate (CuCl ₂ .2H ₂ O)
Cd	0.005	1000 mg/l standard solution
Cr	0.025	Chromium nitrate (Cr(NO ₃) ₃)
Ni	0.04	Nickel (II) chloride hexahydrate (NiCl ₂ .6H ₂ O)
Fe	2.9	Iron (II) Chloride tetrahydrate (FeCl ₂ .4H ₂ O)

3.1.5. Hydraulic loading

3.1.5.1. Average rainfall

In the case of stormwater treatment, the hydraulic loading volume (HLV) is based on rainfall patterns. Predictions for rainfall in a certain catchment are made based on past precipitation data from the area. The size of a catchment and the amount of precipitation are the two influential factors in determining the HLV.

Average annual rainfall (AAR) values were based on Met Office data from a range of stations located in urban areas across the UK from 1978 – 2011. This time range

was the widest available for the number of stations used, and it is a long enough period to provide reliable averages. The stations from which the data was obtained are listed below:

- Armagh, Northern Ireland
- Bradford, England
- Cambridge, England
- Cardiff, Wales
- Durham, England
- Heathrow (London) England
- Oxford, England
- Paisley, Scotland
- Sheffield, England

The distribution of these stations across the UK is shown in Figure 3-7. At least one station for each country in the UK provides rainfall data for an urban area, and the distribution is spread well across the map.

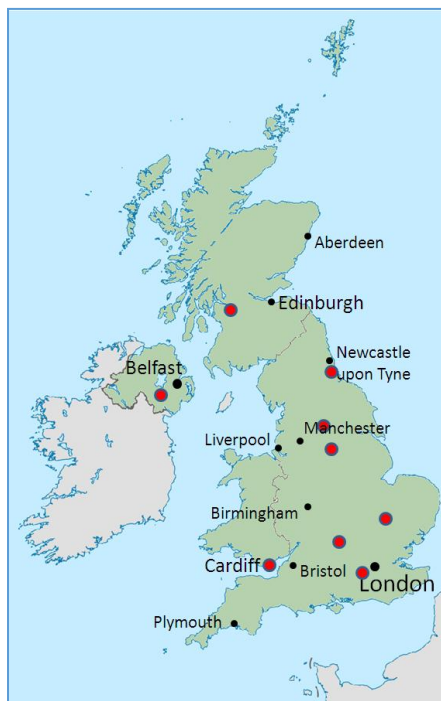


Figure 3-7 - Locations of weather stations (denoted by red markers) from which rainfall data was collected
Rainfall values (in mm) are provided for every month of every year at each station. These figures were totalled for each year in order to give an annual rainfall value, and then an AAR value was calculated for 1978 to 2011, inclusive. The AAR values

for each of the 9 stations were then averaged to give an AAR figure for UK urban areas (see Table 3-3).

The number of “rainy days” is counted as the number of days with >1 mm rainfall. The Met Office provides monthly and annual figures for the number of rainy days recorded in the following UK districts:

- North Scotland
- East Scotland
- West Scotland
- East and north-east England
- North-west England and north Wales
- Midlands
- East Anglia
- South Wales and south-west England
- South-east and central south England
- Northern Ireland

The AAR values recorded at each of the stations were matched up with their corresponding district figures for average number of rainy days experienced per year (1978-2011) in that area.

Table 3-3 - UK urban rainfall data, 1978-2011 (Met Office)

Station	Corresponding District	Average Annual Rainfall, 1978 – 2011 (inclusive) (mm)	Average annual number of days with >1 mm rain, 1978 – 2011 (inclusive)
Armagh	Northern Ireland	816	178
Bradford	NW England & N Wales	873	166
Cambridge	East Anglia	561	115
Cardiff	S Wales & SW England	1143	156
Durham	E & NE England	663	131
Heathrow, London	SE & Central S England	600	121
Oxford	Midlands	653	130
Paisley	West Scotland	1250	194
Sheffield	Midlands	833	130
	UK Average	821.33	146.78

The data is collated in Table 3-3, and gives an AAR value of **821 mm** for UK urban areas, along with a corresponding value of **147 rainy days**, from 1978 to 2011.

3.1.5.2. Runoff entering CW system

The average depth of rainfall for each event (an event = 1 rainy day) is calculated as below:

$$\text{Average rainfall per event} = \frac{\text{Average Annual Rainfall}}{\text{No of rainy days}} = \frac{821}{147} = 5.59 \text{ mm per event}$$

Representative sizing values were determined for 1.5%, 2.5%, and 5% WWARs in Section 3.1.2.1. An 80% impervious catchment is assumed, following guidance from the SUDS Manual (Woods-Ballard *et al.*, 2007). Thus, the influent dose volumes were determined as below:

For a 2.5% WWAR: $5.59 \text{ L/m}^2 \times 5.04 \text{ m}^2 \times 0.8 = 22.5 \text{ L per event}$

The influent dose volumes (per rainfall event) are summarised in Table 3-4.

The number of rain events per week is calculated as the number of rainy days divided by the number of weeks in a year, so:

$$147/52 = 2.83 = 3 \text{ events per week}$$

Therefore, the weekly influent volumes were calculated as follows:

For a 2.5% WWAR: $3 \times 22.5 \text{ L} = 67.5 \text{ L/week}$

The weekly influent volumes (per rainfall event) are summarised in Table 3-4.

Table 3-4 - Influent volumes for each WWAR value

WWAR value (%)	Catchment area (m ²)	Influent dose volume per event (L)	Weekly influent volume (L)
1.5	8.40	37.6	112.8
2.5	5.04	22.5	67.5
5	2.52	11.3	33.9

There were five separate inflow regimes, as detailed in Table 3-5.

The decision to keep regimes 1, 2 and 3 constant throughout the entirety of the experiment was based on investigation of the number of rainy days experienced per month in each of the districts given in the Met Office data. Data is shown in Table 3-6. Rainfall is distributed in each district relatively evenly throughout the year, and thus the inflow of regimes 1, 2 and 3 consist of the same dosage volume every week during the experiment.

Table 3-5 - Loading regimes (WC = wet conditions; PDC = partially dry conditions; EDC = extended dry conditions)

Loading regime	WWAR	Wetting/drying regime	Dosing patterns
1	2.5%	WC	3 x 22.5 L per week
2	5%	WC	3 x 11.3 L per week
3	1.5%	WC	3 x 37.6 L per week
4	2.5%	PDC	3 x 22.5 L for 1 week, followed by dry week, repeat cycle
5	2.5%	EDC	3 x 22.5 L for 1 week, followed by 4 weeks dry, 3 x 5 week cycles

3.1.5.3. Wetting and drying periods

Inflow regime 4 (see Table 3-5) consisted of intermittent wet (3 doses per week) and dry weeks (0 doses per week). The pattern was: 1 week wet; 1 week dry; 1 week wet; 1 week dry etc. The purpose of this arrangement was to replicate short-term dry weather spells and determine their effect on the performance of the CWs. This also gives some representation of the changeable weather in the UK, where rainfall patterns can be more stochastic in nature compared to other countries that experience annual monsoon seasons. This flow regime was named as “partially dry conditions”, or PDC.

Inflow regime 5 (see Table 3-5) consisted of an arrangement of both wet weeks and dry weeks. The purpose of this arrangement is to analyse the performance of the CW system when it experiences long periods of reduced rainfall/drought. This regime was named as “extended dry conditions”, or EDC. The ratio of wet weeks to dry weeks was based on the reduced rainfall experienced in East Anglia in spring 2011, a

three-month period that the Met Office recognises as particularly warm and dry. The region experienced only 2.1 days of rain > 1 mm in March 2011, followed by 1.8 days in April and 4 days in May. This is a total of 8 rainy days in 3 months. The wetting and drying regime was based on this statistic, and was calculated as follows:

1. The period March-May consists of 13 weeks, which, according to the established dosing regime of 3 doses per week, totals 39 wet days.
2. In the 2011 drought, there were only 8 wet days, which leaves a ratio of 8 wet days: 31 dry days.
3. $31/8 = 3.9 \approx 4$, therefore wet to dry ratio is taken as 1:4.
4. As this experiment is carried out in weeks, regime 3 had a single wet week followed by 4 dry weeks in one cycle.
5. There were 3 full cycles in each “dry season” to represent an extended period of drought. In between “dry seasons” the CW system received inflow regime 1.

Table 3-1 shows which CW units were used to investigate the effect of different dry periods and the wetting/drying regime of the units.

3.1.6. Systems operation

Influent doses were administered to the pilot-scale CWs 3 times per week, according to the inflow regimes described in Table 3-5. The semi-synthetic stormwater was transported from the mixing tank to the CWs in a 10 L bucket. To achieve uniform influent concentrations across the units, the stormwater was applied in a series of 3 passes (4 for unit 7, which had a larger inflow volume).

Each dose of stormwater was retained in the CWs for 24 hours. This value is recommended to allow sufficient time for treatment of bacteria, degradable organics and toxic species found in finer solids fractions (Halcrow/UPRC, 2000).

Exactly 24 hours after the inflow dosing, the water was released from the bottom of the CWs via the outlet tap.

3.1.7. Sampling and processing

Inflow sampling was conducted three times per week (once for each dose), while outflow sampling was limited to once per week due to analytical cost restraints. Weekly outflow sampling was sufficient to conduct a comprehensive analysis due to the extensive period of time over which the experiment was run. Inflow samples were taken from the feed tank immediately after the semi-synthetic stormwater had been mixed, prior to the dose. Outflow samples were taken from the outlet at the bottom of each CW unit, at the time of outflow release after the 24 hour retention period. For those units experiencing dry weeks, samples were only taken during wet weeks.

Table 3-6 - Average number of rainy days per month, 1978-2011 (Met Office)

District	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Min	Max	Max -Min
N Scotland	20.2	16.8	19.6	14.6	13.7	13.6	14.9	16.0	17.6	20.2	19.9	19.5	13.7	20.2	6.5
E Scotland	15.5	12.6	14.3	11.2	11.9	11.9	12.0	12.8	12.9	15.4	15.3	15.0	11.2	15.5	4.3
W Scotland	19.1	15.3	17.6	13.2	12.8	13.2	14.4	15.7	16.5	19.1	18.7	18.2	12.8	19.1	6.3
E & NE England	12.8	10.5	11.3	9.7	9.7	10.2	9.7	10.6	9.7	11.8	12.7	12.8	9.7	12.8	3.1
NW Eng & N Wales	16.2	12.5	14.6	11.7	11.7	11.9	11.8	13.5	12.9	16.2	16.5	16.5	11.7	16.5	4.8
Midlands	12.6	10.3	11.5	10.0	10.0	9.8	9.2	10.0	9.5	11.8	12.2	12.6	9.2	12.6	3.4
East Anglia	11.4	9.3	10.2	9.0	8.5	9.3	8.5	8.5	8.3	9.9	10.6	11.2	8.3	11.4	3.1
S Wales & SW Eng	16.1	12.6	13.9	11.2	11.0	10.2	10.6	11.4	11.5	15.4	15.7	16.1	10.2	16.1	5.9
SE & Cent S Eng	12.4	9.9	10.8	9.3	9.1	8.7	8.2	8.4	8.7	11.4	11.6	12.2	8.2	12.4	4.2
N Ireland	17.2	13.7	16.2	12.6	13.0	12.6	13.8	14.5	14.4	16.6	16.8	16.7	12.6	17.2	4.6

The parameters measured were total suspended solids (TSS), total nitrogen (TN), ammonium-nitrogen ($\text{NH}_4\text{-N}$), nitrite-nitrogen ($\text{NO}_2\text{-N}$), nitrate-nitrogen ($\text{NO}_3\text{-N}$), total phosphorus (TP), orthophosphate ($\text{PO}_4\text{-P}$), total Fe, Zn, Pb, Ni, Cd, Cr, Cu, pH, temperature and electrical conductivity (EC). For a seven week period during the experimental run, the dissolved metal concentrations were also determined. This additional analysis was not run over the entire period of the project due to time and budget restraints, so serves as a supporting analysis to the main experiment.

In-situ measurements were taken for pH, temperature and EC in both influent and effluent water, while all other pollutant concentrations were determined in the lab using the samples taken at the time of dosing (for influent) or release (for effluent). Samples were collected in 300 ml polyethylene bottles. For metal analysis, 40 mL volumes were acidified with nitric acid and stored at $<4^\circ\text{C}$, as recommended in standard methods (APHA *et al.*, 2012). TSS measurements were taken immediately after sample collection, so there were no further storage requirements.

Measurements for pH, temperature and EC were recorded using a HANNA HI 991301 probe. Heavy metal and TP concentrations were determined using an Optima 210 DV ICP OES (inductively coupled plasma optical emission spectrometer, Perkin Elmer). The ICP limits of detection are shown in Table 3-7. TN, $\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$, $\text{PO}_4\text{-P}$ and TSS concentrations were measured with a Hach Lange DR3900 benchtop spectrophotometer. The spectrophotometer limits of detection are shown in Table 3-8. TN, and $\text{PO}_4\text{-P}$ were measured using Hach Lange's cuvette tests, for which all required analytical reagents are provided, along with vessels for analysis. Digestion at 100°C was required for TN prior to testing, and this was achieved with the use of the Hach Lange LT-200 thermostat. $\text{NH}_4\text{-N}$ concentrations were determined using the "Nessler" method, which requires the addition of nessler liquid reagent prior to analysis. NO_2 and $\text{NO}_3\text{-N}$ were determined using powder pillow reagents (diazotization and cadmium reduction methods, respectively).

Table 3-7 - ICP-OES limits of detection

Parameter	Lower concentration detection limit (mg/L)
Fe	0.0055
Zn	0.0064
Pb	0.0195
Cd	0.0013
Ni	0.0051
Cr	0.0010
Cu	0.0013
TP	0.0445

Table 3-8 - Hach Lange DR3900 benchtop spectrophotometer limits of detection

Parameter	Lower concentration detection limit (mg/L)
TSS	5
TN	0.1000
NH ₄ -N	0.0212
NO ₂ -N	0.0020
NO ₃ -N	0.010
PO ₄ -P	0.05

4. Characterisation and Metal Adsorption Characteristics of Primary Media

4.1. Introduction

This chapter investigates the properties of the loamy sand and BFS used in the pilot-scale experiment. The elemental composition of the two types of media is determined and their suitability for adsorption of selected heavy metals that have been highlighted as priority pollutants in stormwater runoff (i.e. zinc (Zn), copper (Cu), lead (Pb), cadmium (Cd), chromium (Cr), nickel (Ni) and iron (Fe)) is investigated. Adsorption is a known cause of metal removal in CWs, but it is not possible to ascertain whether adsorption is taking place in a CW simply from measuring influent and effluent concentrations because metals can be removed in other ways such as sedimentation, precipitation and plant uptake. Thus, the primary substrate media materials of loamy sand and BFS were further scrutinised in order to determine their capacity for adsorption. The purposes of the experiments described in this chapter were:

- 1) To undertake physicochemical characterization of selected media for the removal of heavy metals in stormwater
- 2) To investigate the kinetics of heavy metal adsorption to loamy sand and BFS and the influencing factors
- 3) To determine the adsorption capacities of loamy sand and BFS for selected heavy metals.

Characterisation of media was carried out through elemental composition analysis, which provides valuable data regarding the constituents of both the loamy sand and BFS, and helps to understand some of the pollutant removal patterns discussed in chapter 5.

The batch adsorption technique - a commonly used, simple and reliable technique (Potgieter et al., 2006) - was implemented to generate data for kinetic models and

adsorption equilibrium isotherms. Adsorption isotherms describe the way in which pollutants interact with the adsorbent material. This is essential to understand the adsorption capacity of the adsorbent and for optimisation of adsorption mechanism pathways (Foo and Hameed, 2010). Kinetic models describe the rate of the adsorption reaction and provide an insight to the possible mechanism of adsorption (Gupta and Bhattacharyya, 2011).

4.2. Materials and methods

4.2.1. Characterisation of media

Samples of loamy sand media and BFS were taken from the pilot-scale CWs (at the beginning of the experiment) for use in the characterisation and batch adsorption experiments. Elemental composition of both materials was carried out with the use of an inductive coupled plasma-optical emission spectrophotometer (Perkin Elmer ICP-OES 2100 DV). Samples were air-dried for 2 weeks, and the BFS was subsequently ground to particle size <2 mm. 0.1 g samples of each material were inserted to vessels along with a digestion solution of concentrated hydrofluoric acid (HF). The final volume was 50 mL. The samples were then digested using low volume microwave digestion and then analysed for the concentrations of Al, Ca, Fe, Mg, Mn, Pb, Si and Zn using the ICP.

4.2.2. Synthetic metal solution

Stock metal solutions were prepared by dissolving laboratory grade chemicals in deionised water. Solutions were kept air-tight and stored, refrigerated, in the laboratory for no more than 2 weeks prior to use. Metal solutions for each experiment were prepared by diluting the appropriate stock solutions with deionised water to the desired concentrations.

4.2.3. Metal adsorption experiments

A series of batch adsorption experiments was carried out to determine the optimum adsorbent dosage, equilibrium time of adsorption, kinetic parameters and equilibrium adsorption parameters. These experiments are detailed in the following sections. All experiments were carried out in a laboratory with a constant temperature of 19°C.

4.2.3.1. Optimum dosage experiment

Three different masses of both adsorbents were investigated to determine the optimum dosage for the batch adsorption experiments. The mass values were 0.05 g, 0.1 g and 0.5 g. The adsorbents were added to 100 mL of each metal solution, contained in 200 mL bottles. The initial concentrations of the metal solutions were intended to be representative of the influent concentrations in the semi-synthetic stormwater used in the pilot-scale CWs. The initial adsorbate concentrations for the batch adsorption experiments are shown in Table 4-1.

The bottles were placed on a rotary shaker and shaken for a predetermined time of 48 hours. After 48 hours, the bottles were removed from the shaker and a 40 mL sample was taken from each mixture. Each sample was filtered using standard vacuum filtration, preserved with nitric acid and stored at a temperature of 4°C, as recommended in standard methods (APHA, 2012). The samples were then analysed for the metal of concern using an Optima 210 DV ICP OES (Perkin Elmer).

Table 4-1 - Initial adsorbate concentrations for all batch adsorption experiments

Metal	Initial adsorbate concentration in each test (mg/L)		
	Optimum dosage test	Equilibrium time test	Kinetic test
Fe	3.163	5.141	4.947
Zn	0.52	0.447	0.471
Pb	0.145	0.167	2.288
Ni	0.094	0.052	0.867(LS)/0.053(BFS)
Cd	0.275	0.273	0.261
Cr	0.084	0.083	0.998
Cu	0.073	0.107	0.119

4.2.3.2. Equilibrium time experiment

The second phase of the batch adsorption experiments was carried out to determine a general equilibrium time, in order to plan the sampling times and maximum time to be used in the equilibrium tests. The optimum dosage of each adsorbent for each metal was determined in the first phase of the experiments (see section 4.2.3.1), and

these masses were used for the equilibrium time phase. Again, the adsorbents were added to 100 mL of metal solution in 200 mL bottles (initial concentrations corresponding to Table 4-1) and placed on the rotary shaker.

10 mL samples were taken from each mixture at the following time steps: 1, 6, 24, 48 and 72 hours. Each sample was filtered, preserved, stored and analysed as described in section 4.2.3.1.

4.2.3.3. Kinetic testing

The third phase of the batch adsorption experiments was carried out to determine the rate of the adsorption reactions (i.e. to obtain data to fit into kinetic models). The optimum dosage of each adsorbent for each metal was determined in the first phase of the experiments (see section 4.2.3.1). This time, due to the increased number of samples required (due to additional sampling time steps), the adsorbents were added to 200 mL of metal solution in 200 mL bottles (initial concentrations corresponding to Table 4-1). Therefore, the adsorbent masses were doubled to ensure that the optimum dosage (in g/L) was maintained. Note that initial concentrations were increased significantly for Pb, Ni and Cr (for loamy sand), as the first tests conducted with the original lower concentrations of these metals did not produce detectable results. The samples were again placed on the rotary shaker.

10 mL samples were taken from each mixture at the following time steps: 5, 15, 30, 60, 120, 360 and 1440 minutes (the maximum time was determined from the second phase of the batch adsorption tests, see section 4.2.3.2). Each sample was filtered, preserved, stored and analysed as described in section 4.2.3.1.

4.2.3.4. Adsorption capacity

The fourth phase of the batch adsorption experiments was carried out to obtain data for input to adsorption isotherms. If an isotherm fits the data well, it allows adsorption capacity information to be determined. The optimum dosage of each adsorbent for each metal was determined in the first phase of the experiments (see section 4.2.3.1). For each adsorbent, five different adsorbate concentrations were produced (target concentrations were 1.0, 5.0, 10.0, 25.0 and 50.0 mg/l). The initial

concentrations for each metal are shown in Table 4-2. The adsorbents were added to 100 mL of each concentration of metal solution in 200 mL bottles and placed on the rotary shaker.

After 24 hours (maximum time determined in section 4.2.3.2), the bottles were removed from the shaker and a 40 mL sample was taken from each mixture. Each sample was filtered, preserved, stored and analysed as described in section 4.2.3.1.

Table 4-2 - Initial metal solution concentrations for adsorption capacity experiment

Adsorbent	Metal	Target concentration (mg/L)				
		1	5	10	25	50
Loamy sand	Fe	0.786	4.78	7.694	20.02	43.21
	Zn	1.053	7.294	11.84	36.54	49.19
	Pb	0.67	3.31	8.235	18.69	39.49
	Ni	0.946	4.621	10.23	23.57	47.62
	Cd	0.953	4.741	9.493	24.73	48.87
	Cr	1.032	4.766	9.905	23.41	45.91
	Cu	1.18	5.13	10.36	26.42	53.38
BFS	Fe	0.786	5.149	10.15	19.13	47.53
	Zn	2.337	7.676	14.03	36.5	53.32
	Pb	0.827	4.094	8.426	21.79	38.77
	Ni	1.019	5.209	10.18	23.37	47.92
	Cd	0.975	4.606	9.557	24.7	47.36
	Cr	1.009	4.744	9.9	22.15	47.09
	Cu	1.094	4.498	13.03	27.54	47.66

4.2.4. Kinetic models

The data from the tests described in section 4.2.3.3 was fitted to the pseudo-first-order and pseudo-second-order models in order to assess the kinetic characteristics of the metal adsorption. Their equations are described in the following sections.

4.2.4.1. Pseudo-first-order equation

The pseudo-first-order equation is given in Equation 4.1 (Ho and McKay, 1999).

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{4.1}$$

where: q_t = mass of adsorbate adsorbed per unit of adsorbent at time t (mg/g)

K_1 = pseudo-first-order rate constant (min^{-1})

Q_e = adsorption capacity at equilibrium (mg/g)

t = contact time (mins)

The equation can be written after integration and the application of initial conditions ($q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$) as in Equation 4.2.

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (4.2)$$

The plot of $\log(q_e - q_t)$ versus t can then be used to provides values for K_1 and q_e . The gradient of the linear trendline is equal to $-K_1/2.303$ and the intercept of the $\log(q_e - q_t)$ axis is equal to $\log q_e$.

4.2.4.2. Pseudo-second-order equation

Kinetic data is also fitted to the pseudo-second-order equation, shown in Equation 4.3 (Vadivelan and Kumar, 2005). In the pseudo-second-order model the rate-controlling mechanism is chemisorption taking place at the adsorbent surface, where the removal of metal from a solution occurs through physicochemical interactions between the two phases (Robati, 2013).

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (4.3)$$

where: K_2 = pseudo-second-order constant (g/mg.min)

The equation can be written after integration and the application of initial conditions ($q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$) as in Equation 4.4.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (4.4)$$

If the pseudo-second-order model is suitable, the plot of t/q_t versus t produces a straight line from which K_2 and q_e can be determined. The gradient of the linear trendline is equal to $1/q_e$ and the intercept of the t/q_t axis is equal to $1/(K_2 q_e^2)$.

4.2.5. Adsorption isotherms

The theoretical adsorption capacities of the two adsorbents were calculated by fitting the experimental data obtained from the experiment described in section 4.2.3.4 with the Langmuir, Freundlich, Temkin and Harkins-Jura isotherms.

4.2.5.1. Langmuir isotherm

The Langmuir isotherm is one of the most commonly used adsorption isotherm equation (Liu, 2006). Use of the Langmuir model assumes that maximum adsorption occurs when a saturated monolayer of solute molecules on the adsorbent surface has been achieved (Sekar *et al.*, 2004). The isotherm is expressed as in Equation 4.5.

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (4.5)$$

where: q_e = mass of metal adsorbed per unit mass of adsorbent (mg/g)

C_e = equilibrium concentration of metal ions in solution (mg/L)

Q_0 = maximum adsorption capacity (mg/g)

b = Langmuir adsorption constant (L/mg)

The Langmuir adsorption constant (b) can be taken as a measure of the affinity of the metal for the adsorbent. Q_0 and b can be determined from a C_e/q_e versus C_e plot, using the linearised form of Equation 4.5, shown in Equation 4.6.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \quad (4.6)$$

Thus, the gradient of the linearised Langmuir isotherm plotted on a C_e/q_e versus C_e chart is equal to $1/Q_0$, and the intercept on the C_e/q_e axis is equal to $1/Q_0 b$.

4.2.5.2. Freundlich isotherm

The Freundlich adsorption isotherm is based on the relationship between the amount of metal that has been adsorbed per unit mass of the adsorbent and the remaining concentration of the metal in solution at equilibrium (Sekar *et al.*, 2004). The equation is shown in Equation 4.7.

$$q_e = K_f C_e^{1/n} \quad (4.7)$$

where: K_f = Freundlich constant (L/g)

$1/n$ = heterogeneity factor

The degree of non-linearity between metal solution concentration and adsorption is indicated by the value of n . If $n = 1$, adsorption is linear; if $n < 1$, the adsorption process is described as chemical; and if $n > 1$, the adsorption process is described as a favourable physical process. K_f and n can be determined from a $\log q_e$ versus $\log C_e$ plot, using the linearised form of Equation 4.7, shown in Equation 4.8.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4.8)$$

Thus, the gradient of the linearised Freundlich isotherm plotted on a $\log q_e$ versus $\log C_e$ chart is equal to $1/n$, and the intercept on the $\log q_e$ axis is equal to $\log K_f$.

4.2.5.3. Temkin isotherm

The Temkin isotherm assumes that the heat of sorption of all molecules in a single layer decreases linearly rather than logarithmically with coverage (Dada *et al.*, 2012). The isotherm is shown in Equation 4.9.

$$q_e = \frac{RT}{b_T} \ln (K_T C_e) \quad (4.9)$$

where: R = gas constant (8.31 J/mol K)

T = absolute temperature (K)

b_T = heat transfer (J/mol)

K_T = equilibrium binding constant (L/mg)

Equation 4.9 can also be expressed as in Equation 4.10.

$$q_e = B_1 \ln (K_T C_e) \quad (4.10)$$

where B_1 relates to the heat of adsorption and is equal to $(RT)/b$.

B_1 and K_T can be determined from a q_e versus $\ln C_e$ plot, using the linearised form of Equation 4.10, shown in Equation 4.11.

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (4.11)$$

Thus, the gradient of the linearised Temkin isotherm plotted on a q_e versus $\ln C_e$ chart is equal to B_1 , and the intercept on the q_e axis is equal to $B_1 \ln K_T$.

4.2.5.4. Harkins-Jura isotherm

The Harkins-Jura model regards the adsorbed layer as a two-dimensional liquid (Tóth, 2002). The model describes multilayer adsorption and the existence of heterogeneous pore distribution on the adsorbent surface (Ogbonna *et al.*, 2014). The isotherm is shown in Equation 4.12.

$$\frac{1}{q_e^2} = \left(\frac{B}{A}\right) - \left(\frac{1}{A}\right) \log C_e \quad (4.12)$$

where A and B are constants.

A and B can be determined from a $(1/q_e^2)$ versus $\log C_e$ plot. The gradient of the plot is equal to $(1/A)$, and the intercept on the $(1/q_e^2)$ axis is equal to (B/A) .

4.3. Results and Discussion

4.3.1. Elemental composition results

The results of the ICP analysis provided the concentration of each element in the HF acid. The values have been converted into masses and are presented in Table 4-3. The sample mass of the loamy sand used was 0.1053 g, and the mass of the BFS sample was 0.1011 g. Figure 4-1 presents each element mass as a percentage of the adsorbent sample mass.

Table 4-3 – Mass (mg) of elements in digested sample of adsorbate

Adsorbent material	Mg	Ca	Fe	Al	Pb	Mn	Zn	Si
Loamy sand	0.490	28.736	1.186	1.545	0.007	0.039	0.010	6.040
BFS	3.853	24.725	0.229	8.067	0.002	0.247	0.009	15.032

As the results show, the element with the largest presence in both materials is Ca, making up 27.3% of the loamy sand and 24.5% of the BFS. This is particularly significant with respect to chemical precipitation of $\text{PO}_4\text{-P}$ (see chapter 5). There is

also a significant presence of Si in both materials. The BFS contains approximately 8% Al, significantly greater than the 1.5% Al in the loamy sand. Similarly, the BFS contains an elevated percentage of Mg (3.8%) in comparison to the loamy sand (0.5%).

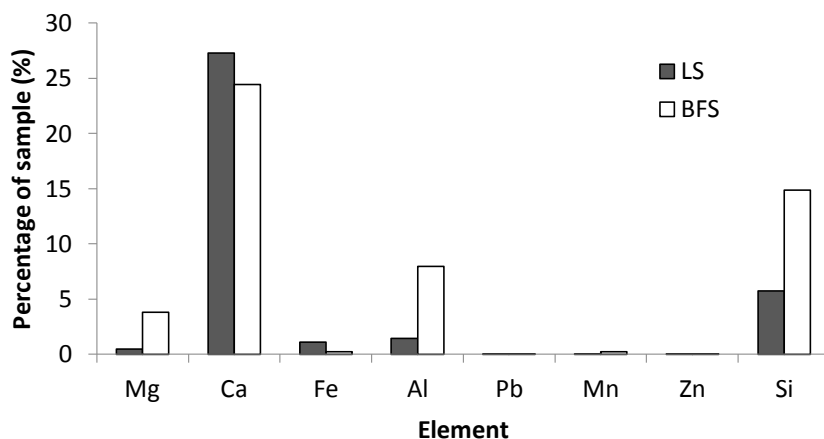


Figure 4-1 - Elements as percentage of adsorbent sample

4.3.2. Optimum dosage results

The results of the optimum dosage tests are shown in Figure 4-2. It was found that maximum removal of all metals was achieved at a loamy sand dosage of 0.05 g/L. At this dosage, final solution concentrations were below detection limits for all metals except Cr, of which 95% of the initial concentration was removed. Figure 4-2 shows that maximum removal of Fe, Pb, Cd, Cr and Cu was achieved at a BFS dosage of 0.5 g/L. Maximum removal of Zn and Ni was achieved at BFS dosages of 5 g/L and 1 g/L, respectively. The pH of the solutions is shown in Table 4-4.

Table 4-4 - pH values of metal solutions

Metal solution	Fe	Zn	Pb	Ni	Cd	Cr	Cu
pH	3.33	5.8	5.02	4.34	3.82	4.35	4.87

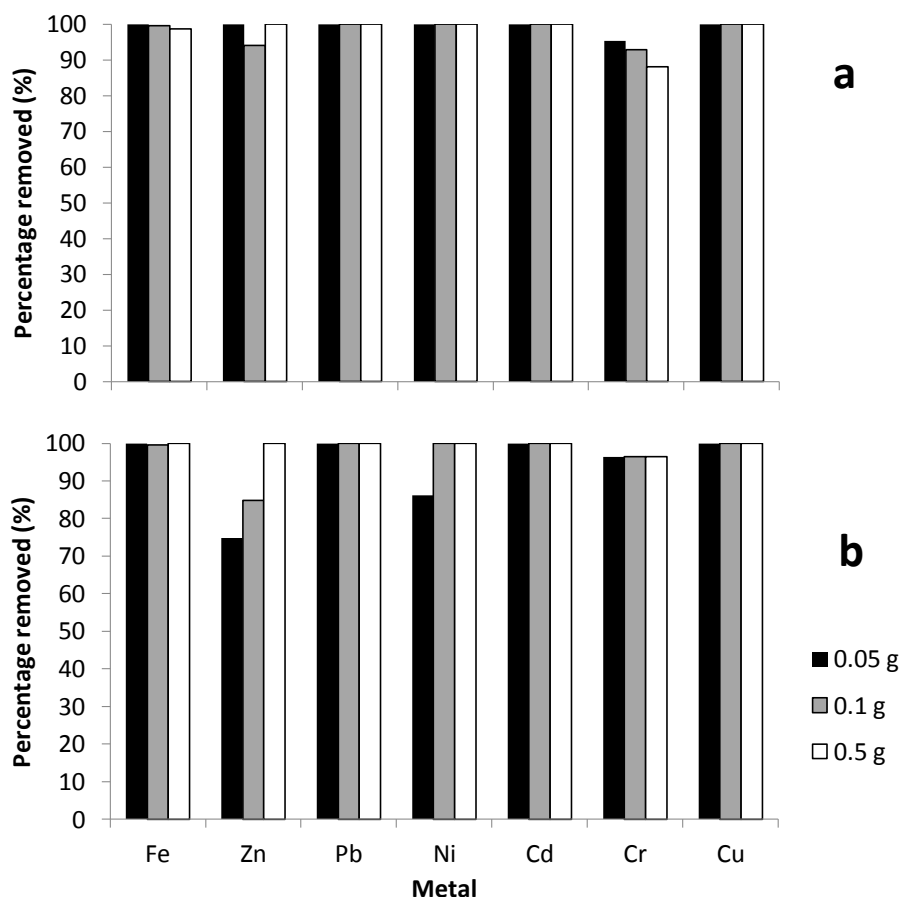


Figure 4-2 - Removal of metals per weight (expressed as percentage of initial concentration) in optimum dosage tests for (a) loamy sand and (b) BFS

4.3.3. Equilibrium time results

The results of the equilibrium time tests are shown in Figure 4-3. It was found that the majority of all metals were adsorbed to both the loamy sand and the BFS within 6 hours. To ensure sufficient time for any further adsorption, an equilibrium time of 24 hours was chosen for the kinetic and adsorption capacity tests.

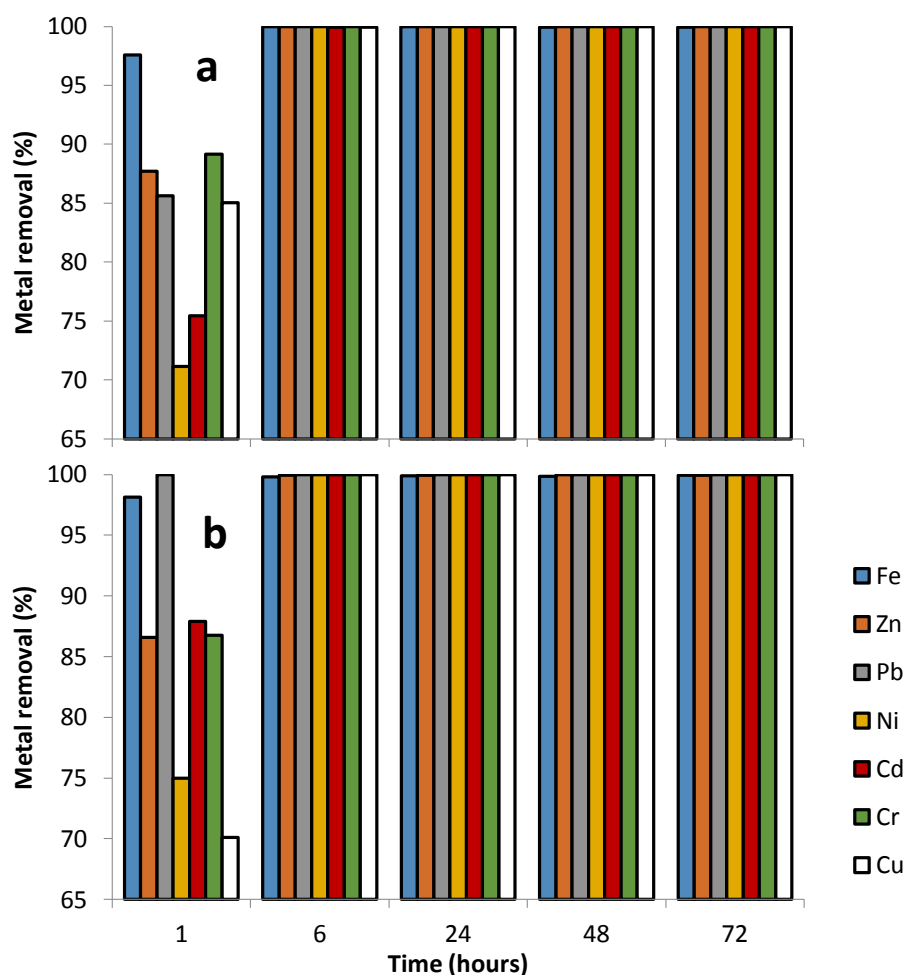


Figure 4-3 - Removal of metals at each sampling time step (expressed as percentage of initial concentration) in equilibrium time tests for (a) loamy sand and (b) BFS

4.3.4. Kinetic testing results

4.3.4.1. Loamy sand

The loamy sand results from the kinetic testing experiment are shown in Figure 4-4. The initial rate of reaction is rapid: the rate of removal of all metals is highest during the first 5 minutes of the experiment. The reaction then slows towards equilibrium for Pb, Cr, Fe, Zn and Cd. However, as Figure 4-4 shows, the experiment may have benefitted from a longer running time for the sake of Cu and Ni, which appear to have still been reacting after 24 hours. The high initial rate is attributable to the large

surface area of the loamy sand particles and availability of accessible macropores at the beginning of the test, while the rate decrease during the latter stages is due to adsorption sites becoming exhausted (Yu *et al.*, 2000; Babatunde and Zhao, 2010).

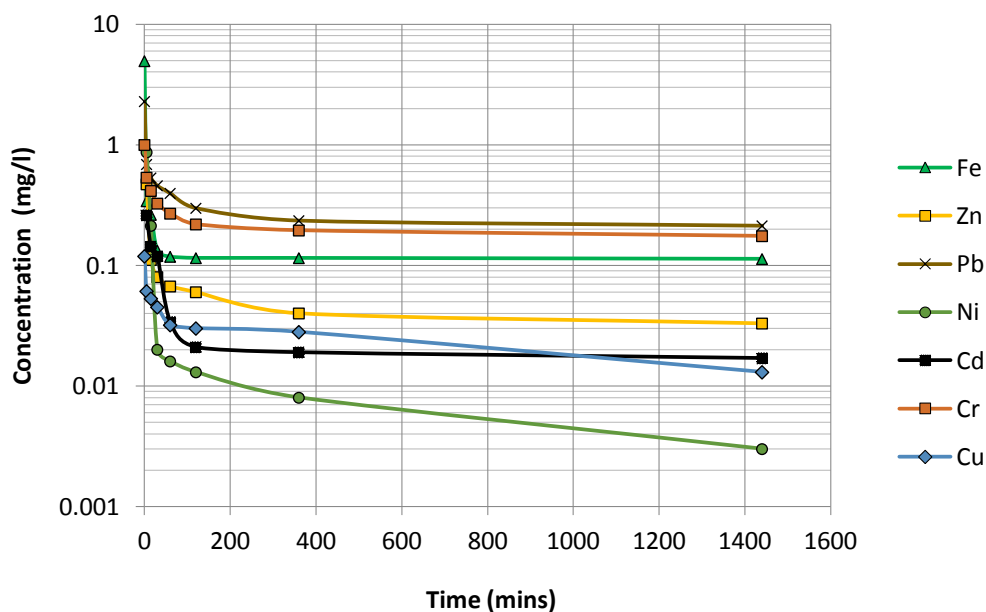


Figure 4-4 - Change in metal concentration over time for loamy sand samples

The loamy sand pseudo-first- and second-order models for all metals (based on the results found at time steps of 5, 15, 30, 60, 120 and 1440 mins) are shown in Figure 4-5 and Figure 4-6. From the slopes of the straight-line plots, the values of the rate constants of adsorption (K_1 and K_2) were determined. These are presented in Table 4-5 along with R^2 values to indicate the quality of the fit of the models to the data. Also presented in Table 4-5 are the q_e values calculated from the models for comparison to the experimental values as further indication of how well each rate model represents the adsorption of each metal to loamy sand.

Table 4-5 – Adsorption rate constants, R^2 and q_e values obtained from kinetic models for loamy sand

Metal	Pseudo-first-order			Pseudo-second-order			q_e (mg/g) experimental
	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/mg.min)	R^2	q_e (mg/g)	
Fe	0.0111	0.4928	0.091	0.6075	1	9.671	9.668
Zn	0.0085	0.9058	0.105	0.4979	1	0.883	0.882
Pb	0.0081	0.94	0.671	0.0712	1	4.158	4.150
Ni	0.0078	0.5446	0.072	0.6787	1	1.735	1.734
Cd	0.0099	0.5911	0.080	0.5210	1	0.493	0.492
Cr	0.0071	0.8146	0.413	0.1034	1	1.651	1.646
Cu	0.0028	0.5736	0.068	0.2930	0.9985	0.212	0.212

As the results presented in Table 4-5 show, the pseudo-second-order model was a far better fit to the data compared to the first-order model, with a near perfect fit for all metals. Predictably, an improved data fit produces more accurate q_e predictions, with the q_e values calculated from the second-order model proving to be extremely reliable when compared to the experimental values. The q_e values calculated from the first-order model are unreliable for all metals, even when the R^2 value is high (e.g., for Zn and Pb). Several other studies have also found the pseudo-second-order model to be the best representation of metal adsorption (Parab *et al.*, 2006; Nehrenheim, 2008; Demirbas *et al.*, 2009). This suggests that chemisorption controls the rate of adsorption of these metals to loamy sand and therefore the chemical reaction is the key mechanism in the process (Ho and McKay, 1999).

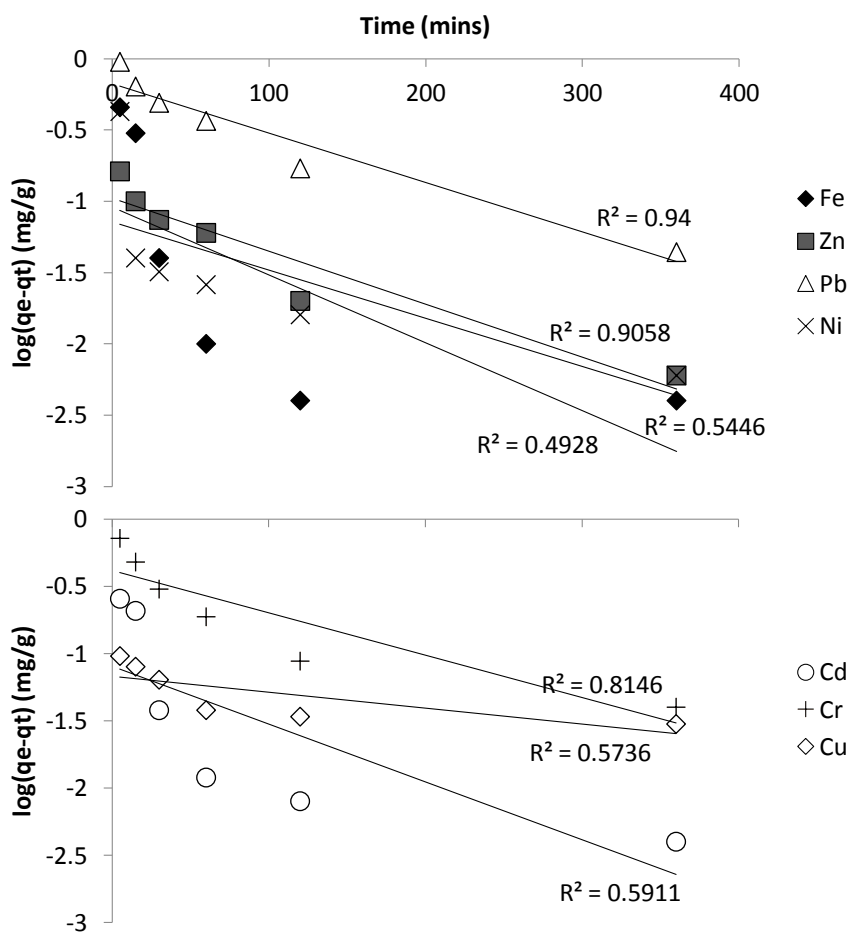


Figure 4-5 - Pseudo-first-order model for all metals (loamy sand)

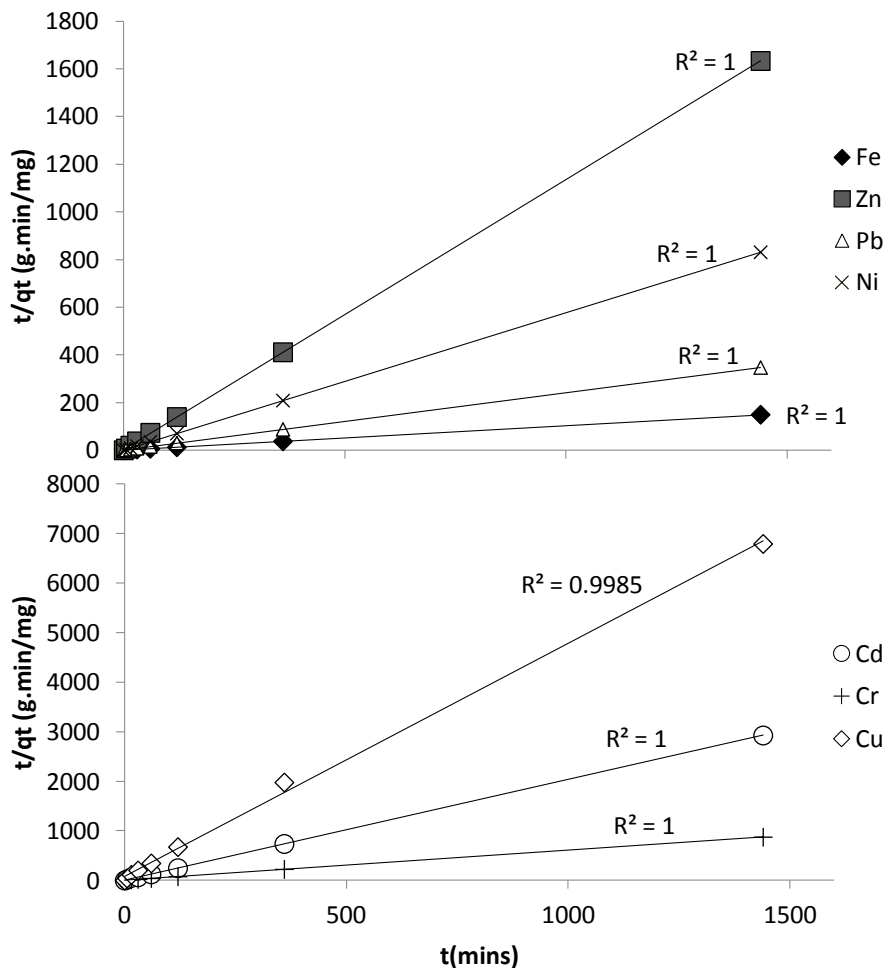


Figure 4-6 - Pseudo-second-order model for all metals (loamy sand)

4.3.4.2. Blast furnace slag

The BFS results from the kinetic testing experiment are shown in Figure 4-7. The initial rate of reaction is rapid: the rate of removal of all metals is highest during the first 5 minutes of the experiment. The reaction then slows towards equilibrium for Fe, Pb, Cr, Cu and Ni. However, as Figure 4-7 shows, the experiment may have benefitted from a longer running time for the sake of Zn and Cd, which appear to have still been reacting after 24 hours.

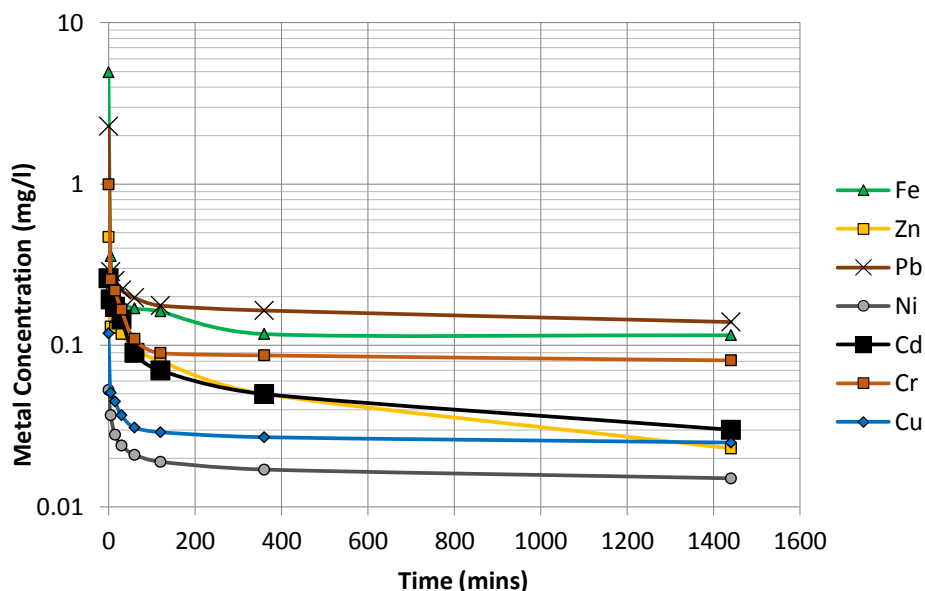


Figure 4-7 - Change in metal concentration over time for BFS samples

The BFS pseudo-first- and -second-order models for all metals (based on the results found at time steps of 5, 15, 30, 60, 120 and 1440 mins) are shown in Figure 4-8 and Figure 4-9. From the slopes of the straight-line plots, the values of the rate constants of adsorption (K_1 and K_2) were determined. These are presented in Table 4-6 along with R^2 values to indicate the quality of the fit of the models to the data. Also presented in Table 4-6 are the q_e values calculated from the models for comparison to the experimental values as further indication of how well each rate model represents the adsorption of each metal to BFS.

Table 4-6 - Adsorption rate constants, R^2 and q_e values obtained from kinetic models for BFS

Metal	Pseudo-first-order			Pseudo-second-order			q_e (mg/g) experimental
	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/mg.min)	R^2	q_e (mg/g)	
Fe	0.0117	0.9418	0.278	0.1941	1	9.662	9.662
Zn	0.0039	0.9657	0.021	1.0166	0.9998	0.090	0.090
Pb	0.0044	0.7603	0.198	0.1387	1	4.299	4.296
Ni	0.0055	0.7814	0.012	2.2209	0.9999	0.038	0.038
Cd	0.0055	0.8370	0.246	0.0831	0.9997	0.469	0.462
Cr	0.0090	0.7069	0.185	0.2471	1	1.837	1.834
Cu	0.0064	0.7626	0.031	1.1329	1	0.188	0.188

As the results presented in Table 4-6 show, the pseudo-second-order model was a much better fit to the data compared to the first-order model, with a near perfect fit for all metals. Predictably, an improved data fit produces more accurate q_e predictions, with the q_e values calculated from the second-order model proving to be extremely reliable when compared to the experimental values. The q_e values calculated from the first-order model are unreliable for all metals, even when the R^2 value is high (e.g., for Fe and Zn). Several other studies have also found the pseudo-second-order model to be the best representation of metal adsorption (Parab *et al.*, 2006; Nehrenheim, 2008; Demirbas *et al.*, 2009). This suggests that chemisorption controls the rate of adsorption of these metals to BFS and therefore the chemical reaction is the key mechanism in the process (Ho and McKay, 1999).

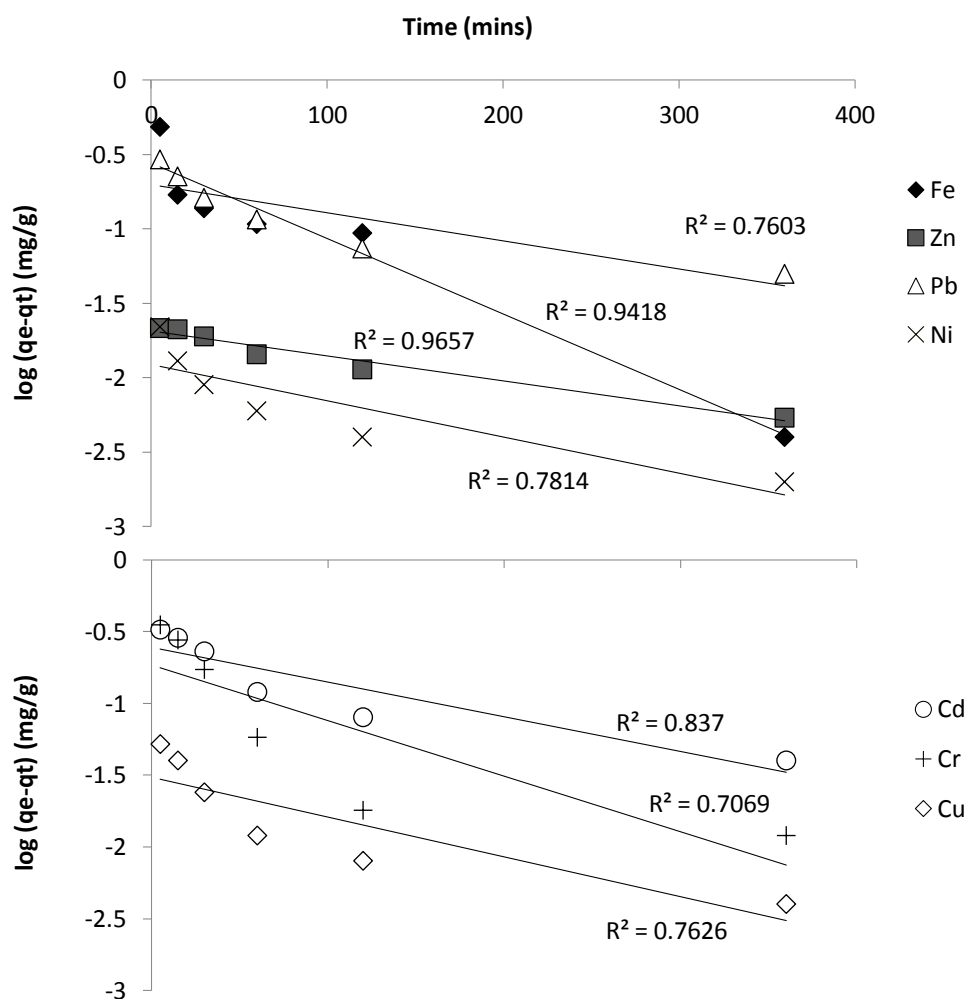


Figure 4-8 - Pseudo-first-order model for all metals (BFS)

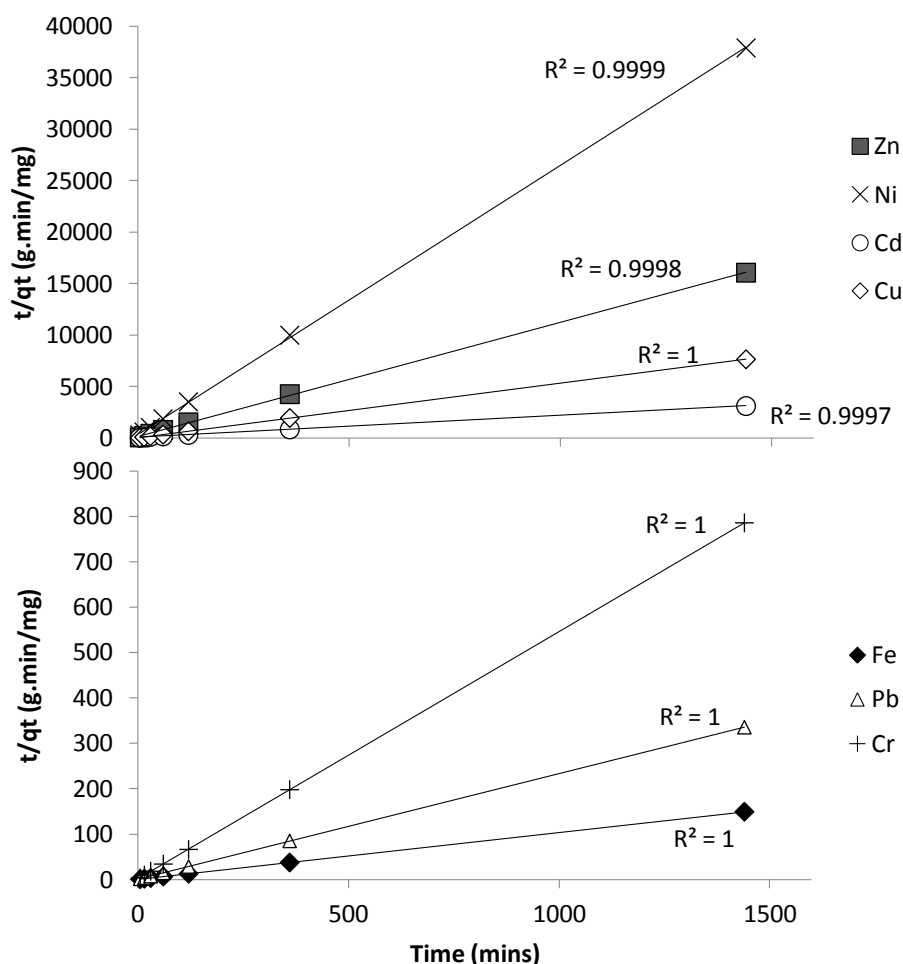


Figure 4-9 - Pseudo-second-order model for all metals (BFS)

4.3.5. Adsorption capacity results

4.3.5.1. Loamy sand

The linearised Langmuir, Freundlich, Temkin and Harkins-Jura adsorption isotherms for the loamy sand experiment are shown in figures 4-10, 4-11, 4-12 and 4-13, respectively. The R^2 (correlation) value of the trendlines denotes how well the isotherm fits the data obtained from the experiment, and thus gives an indication of its suitability to represent the adsorption capacity of the loamy sand for the metal in question. The Langmuir plots were used to determine Q_0 , b and R^2 values, given in Table 4-7. The Freundlich plots were used to determine K_f , n and R^2 values, also given in Table 4-7. The Temkin plots were used to determine B_T , K_T and R^2 values,

also given in Table 4-7. The Harkins-Jura plots were used to determine *A* and *B*, also given in Table 4-8.

Table 4-7 - Results of all four tested adsorption isotherms for loamy sand

	Langmuir			Freundlich		
Metal	Q_0 (mg/g)	b (L/mg)	R^2	K_f (L/g)	n	R^2
Fe	60.976	4.5556	0.9994	31.5200	2.6532	0.6025
Zn	10.7875	0.2114	0.9777	2.8041	2.9291	0.9868
Pb	34.8430	11.0385	0.9999	21.4882	2.7218	0.7822
Ni	9.6339	0.0666	0.5993	1.7147	3.1230	0.8651
Cd	-4.1600	-0.0095	0.0714	2.8714	2.9274	0.1709
Cr	5.4201	-0.5062	0.9516	5.0153	7.3910	0.7422
Cu	10.0400	0.2214	0.9855	2.3708	2.5974	0.9504
	Temkin			Harkins-Jura		
Metal	B_1	K_T (L/mg)	R^2	A	B	R^2
Fe	7.5801	239.1532	0.8624	14.0845	0.2761	0.2453
Zn	1.5517	8.8868	0.9344	6.2972	1.4049	0.8597
Pb	4.2561	511.6472	0.7809	8.3056	0.2143	0.4894
Ni	1.1492	4.4560	0.5702	4.1929	1.6059	0.9838
Cd	0.6961	1.1864	0.3220	0.2061	4.0161	0.0237
Cr	0.5971	2.6756	0.5245	18.9394	1.5284	0.9168
Cu	1.6461	5.0698	0.9870	4.7847	1.3531	0.7314

As shown by the high R^2 values in Table 4-7, the Langmuir isotherm was found to give the best representation of Fe, Zn, Pb, and Cr adsorption. Ni was best represented by the Harkins-Jura isotherm, having an R^2 value of 0.98. The Freundlich isotherm gave the best representation of Zn, at $R^2 = 0.99$. Cu was best represented by the Temkin isotherm, at $R^2 = 0.99$. None of the isotherms were suitable for representation of Cd.

The high Q_0 value of 61 mg/g, obtained from the Langmuir isotherm, shows Fe adsorbs well to loamy sand. This value significantly outperforms Q_0 values associated with alternative adsorbent materials found in literature (e.g., Karthikeyan *et al.*, 2005; Nieto *et al.*, 2010; Rose and Rajam, 2012). The relatively large value of $b = 4.6$ L/mg also implies that loamy sand has an affinity for Fe. The loamy sand

also had a good capacity for Pb, with $Q_0 = 34.8$ mg/g and $b = 11$ L/mg. This significantly outperforms several studies with alternative adsorbent materials (e.g., Ricordel *et al.*, 2001; Sekar *et al.*, 2004; Jeyakumar and Chandrasekaran, 2014). The Cu adsorption capacity of 10 mg/g is also significantly higher than Q_0 values reported in other studies using alternative adsorbents (e.g., Artola *et al.*, 2000; Yu *et al.*, 2000, Demirbas *et al.*, 2005). The Cr Q_0 value was generally lower than values reported in literature (e.g., Dantas *et al.*, 2001; Kobya *et al.*, 2004; Parab *et al.*, 2006). Of the metals that are best represented by the Langmuir isotherm, it can be said that the adsorption capacities rank in the order $Fe > Pb > Cu > Cr$.

Since the Zn adsorption process is well represented by the Freundlich isotherm, it can be said that it is a physical process as $n > 1$. An n value of between 1 and 10 indicates effective adsorption (Tryball, 1980), thus it can be said that the loamy sand was an effective adsorbent for Zn. The K_F constant is indicative of the adsorption capacity of the adsorbent (Demirbas *et al.*, 2009) and the Zn K_F value of 2.8 L/g exceeds those found in similar studies investigating alternative adsorbents (e.g., Ricordel *et al.*, 2001; Vinod *et al.*, 2012) with the exception of carbon-based adsorbents, which appear to outperform the rest of the field (e.g., Ramos *et al.*, 2002; Lu and Chiu, 2006).

The Temkin modelling of Cu adsorption to loamy sand gives a positive value for B_1 , which means that $b_T > 0$. This indicates an exothermic process (Patrulea *et al.*, 2013). Since Ni is best described by the Harkins-Jura isotherm, it may be said that multilayer adsorption is occurring in the reaction between Ni and the loamy sand.

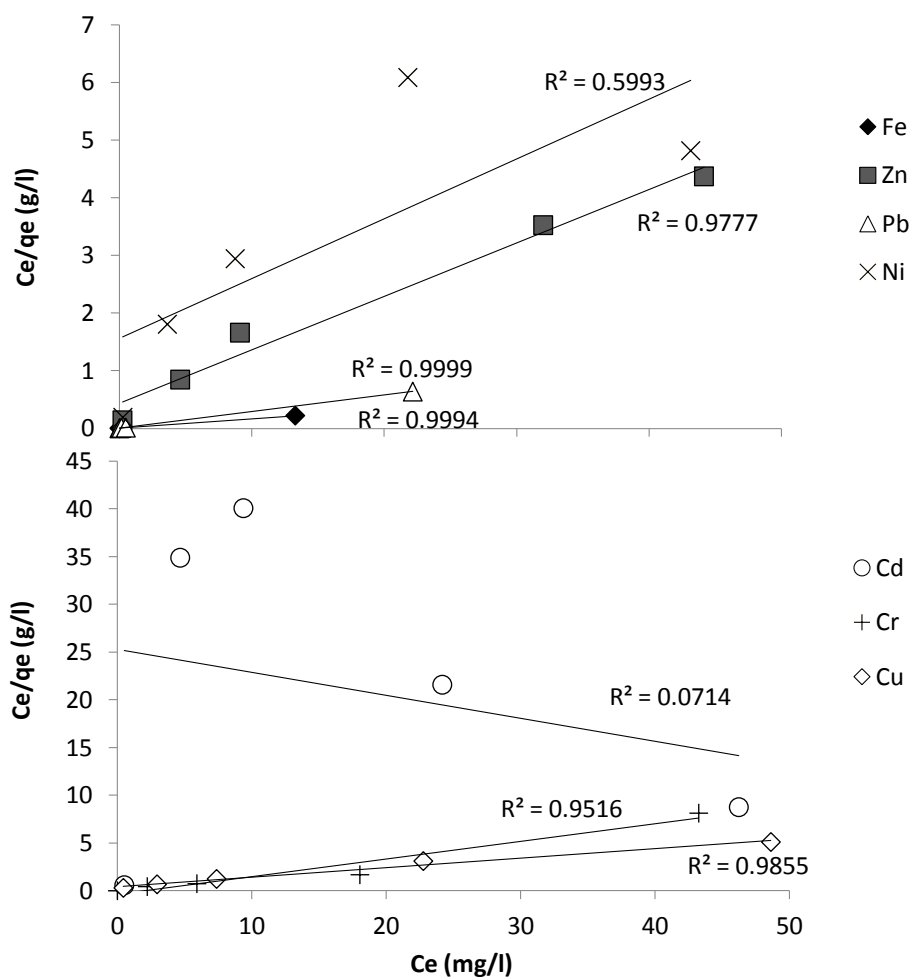


Figure 4-10 - Linearised Langmuir isotherm plots for all metals (loamy sand)

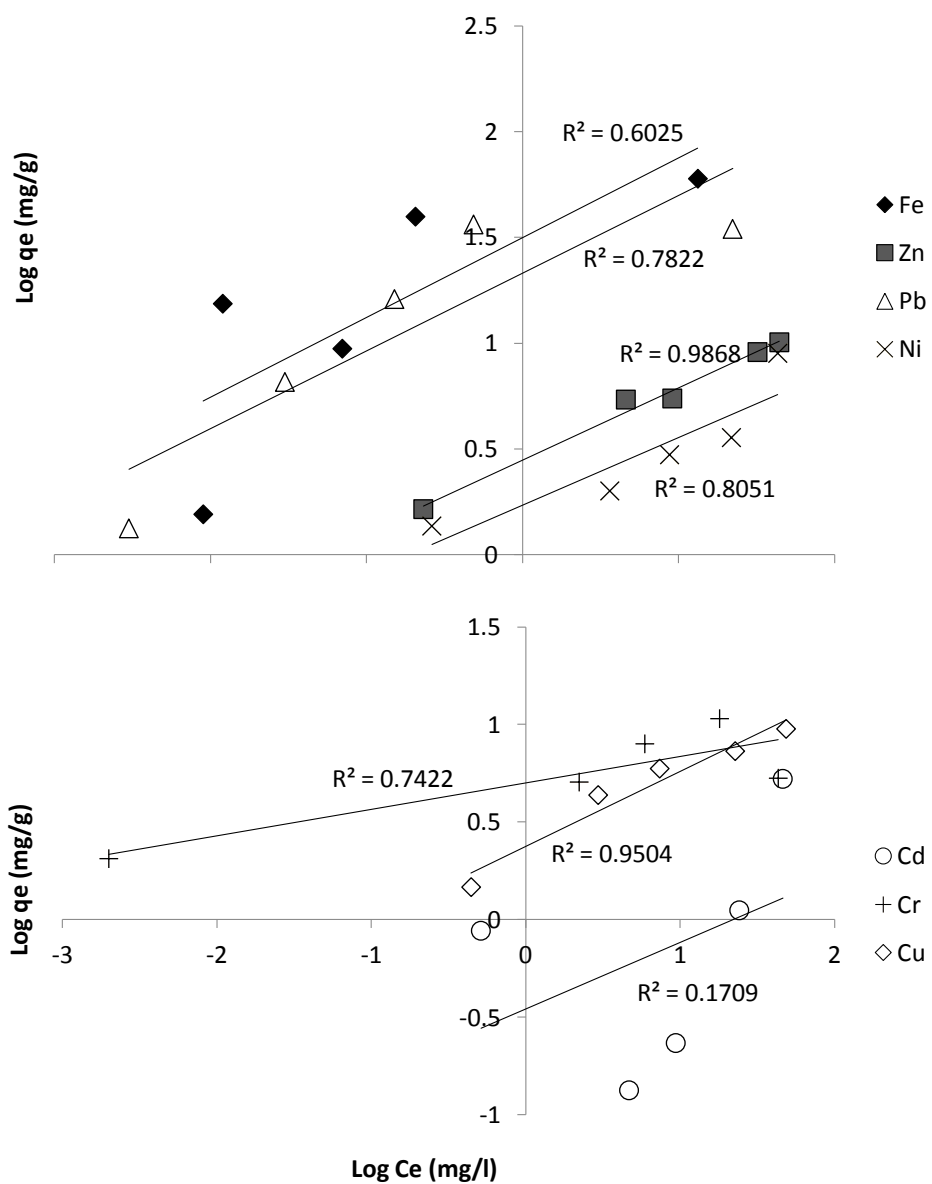


Figure 4-11 - Linearised Freundlich isotherm plots for all metals (loamy sand)

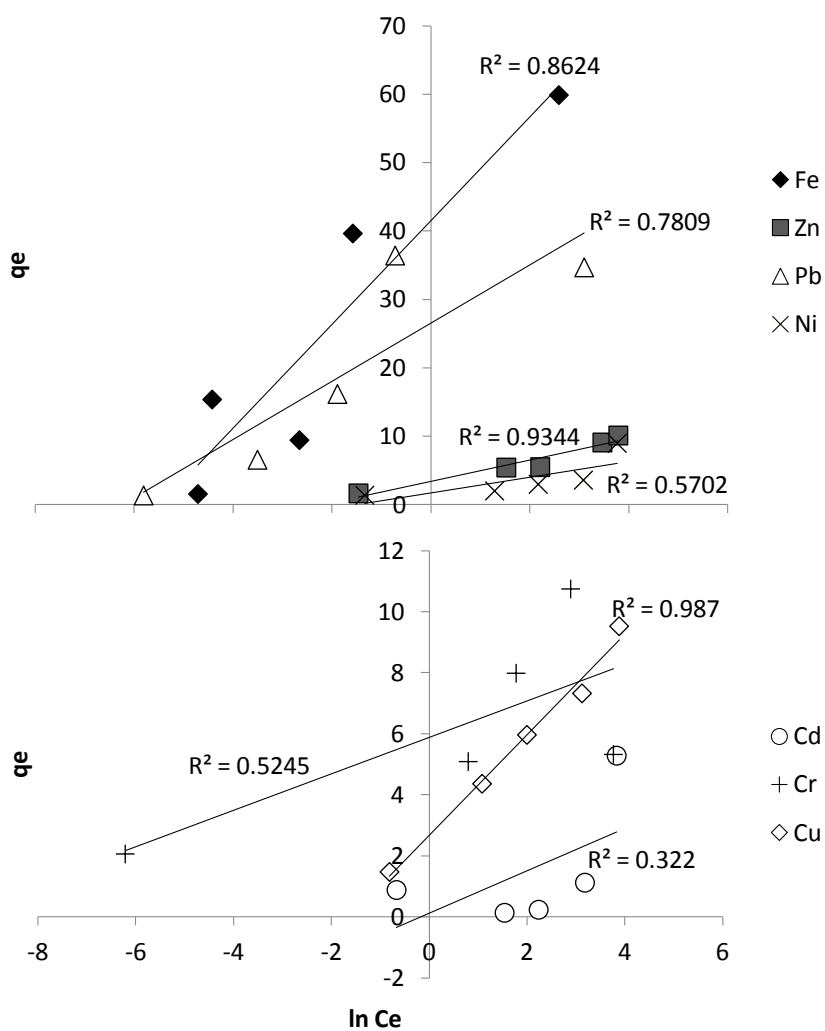


Figure 4-12 - Linearised Temkin isotherm plots for all metals (loamy sand)

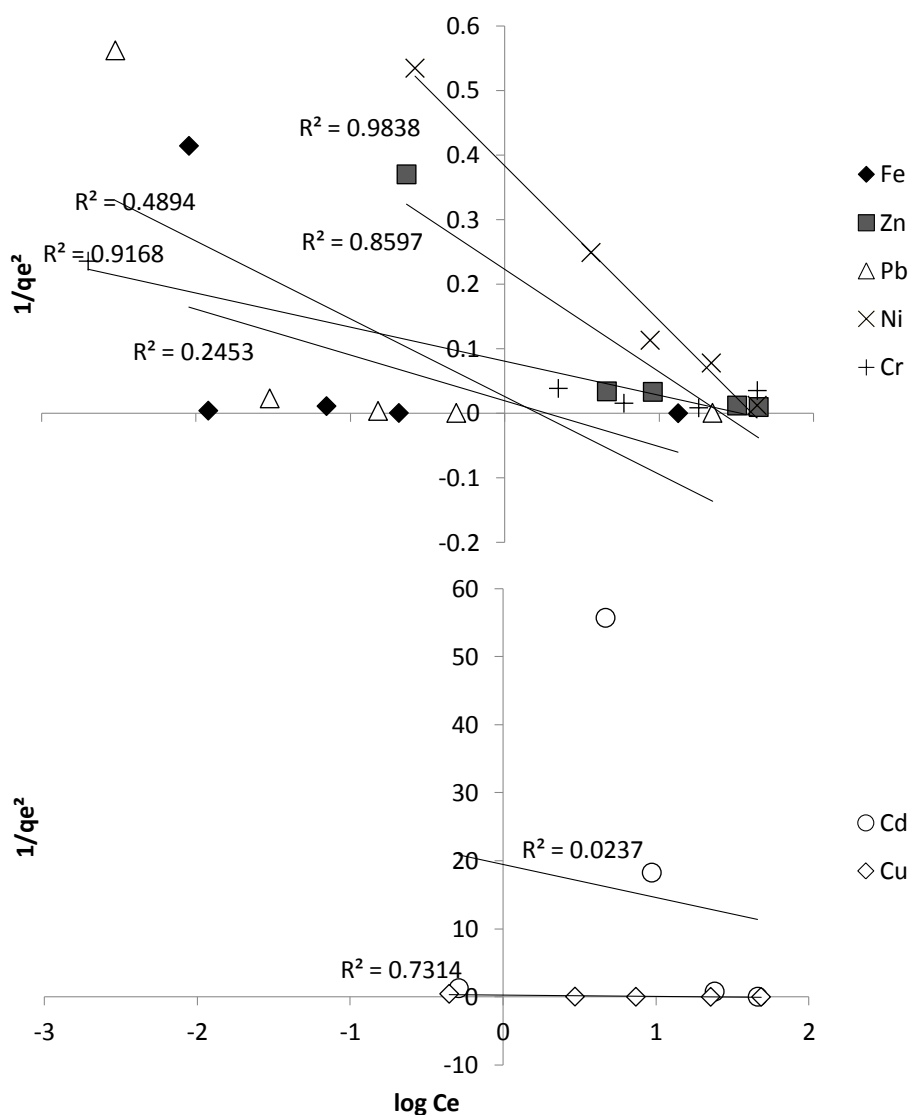


Figure 4-13 - Harkins-Jura isotherm plots for all metals (loamy sand)

4.3.5.2. Blast furnace slag

The linearised Langmuir and Freundlich adsorption isotherms for the BFS experiment are shown in figures 4-14, 4-15, 4-16 and 4-17. The R^2 (correlation) value of the trendlines denotes how well the isotherm fits the data obtained from the experiment, and thus gives an indication of its suitability to represent the adsorption capacity of the BFS for the metal in question. The Langmuir plots were used to determine Q_0 , b and R^2 values, given in Table 4-8. The Freundlich plots were used to determine K_f , n and R^2 values, also given in Table 4-8. The Temkin plots were used

to determine B_I , K_T and R^2 values, also given in Table 4-8. The Harkins-Jura plots were used to determine A and B , also given in Table 4-8.

Table 4-8 - Results of all four tested adsorption isotherms for BFS

	Langmuir			Freundlich		
Metal	Q_0 (mg/g)	b (l/mg)	R^2	K_f (L/g)	n	R^2
Fe	67.1141	1.5684	0.9989	26.0256	1.9592	0.8917
Zn	2.1533	0.2913	0.6984	1.1880	7.0771	0.3570
Pb	55.8659	2.9344	0.9935	26.8164	2.8563	0.6828
Ni	2.8653	0.0821	0.9408	0.2787	1.6790	0.0537
Cd	-15.9744	-0.0063	0.0131	0.2154	1.1776	0.7190
Cr	9.1266	0.0487	0.4525	1.8655	4.6318	0.4883
Cu	11.9761	0.6827	0.9428	4.5709	3.3434	0.7374
	Temkin			Harkins-Jura		
Metal	B_I	K_T (L/mg)	R^2	A	B	R^2
Fe	8.8927	59.2172	0.9034	8.2372	0.2290	0.5868
Zn	0.1585	17309.15	0.2166	0.9553	1.6475	0.6699
Pb	6.5784	265.8192	0.9576	18.7617	0.6473	0.2131
Ni	0.5171	1.4728	0.8986	0.0856	1.3204	0.7541
Cd	1.7484	0.6377	0.6799	0.1338	1.5176	0.6949
Cr	0.7883	11.5497	0.4292	8.0257	2.5024	0.45
Cu	2.1352	21.5413	0.4431	11.4286	1.3086	0.8495

As the results in Table 4-8 show, the adsorption of Fe, Pb, Ni, Zn and Cu were best represented by the Langmuir isotherm. Cd was best represented by the Freundlich isotherm ($R^2 = 0.72$), whereas none of the isotherms adequately represented Cr adsorption.

The BFS's adsorption capacity for Fe and Pb was found to be high, at 67.1 mg/g and 55.9 mg/g respectively. These values significantly exceed those found in other studies using alternative adsorbent materials for both Fe (e.g., Nieto *et al.*, 2010; Rose and Rajam, 2012; Karthikeyan *et al.*, 2013) and Pb adsorption (e.g., Ricordel *et al.*, 2001; Sekar *et al.*, 2004; Jeyakumar and Chandrasekaran, 2014). Compared to loamy sand, the lower b values show that BFS has a lower affinity for these two metals. The Cu adsorption capacity of 12 mg/g is also significantly higher than Q_0

values reported in other studies using alternative adsorbents (e.g., Artola *et al.*, 2000; Yu *et al.*, 2000; Demirbas *et al.*, 2005). The Ni Q_0 value of 2.9 mg/g is generally lower than those found in other studies (e.g., van Hullebusch *et al.*, 2005; Vijayaraghavan *et al.*, 2005; Parab *et al.*, 2006), while the value for Zn (2.2 mg/g) was comparable with literature values (e.g., Demirbas *et al.*, 2005; Jordao *et al.*, 2009; Choi, 2012). Of the metals that are best represented by the Langmuir isotherm, it can be said that the adsorption capacities rank in the order Fe > Pb > Cu > Ni > Zn.

The K_F value of 0.2 L/g for Cd was generally exceeded by those values reported in the literature for alternative adsorbents (e.g., Ricordel *et al.*, 2001; Mathialagan and Viraraghavan, 2002; Pandhare *et al.*, 2013). Its corresponding n value is 1.67, which suggests that effective adsorption took place (since $1 > n > 10$).

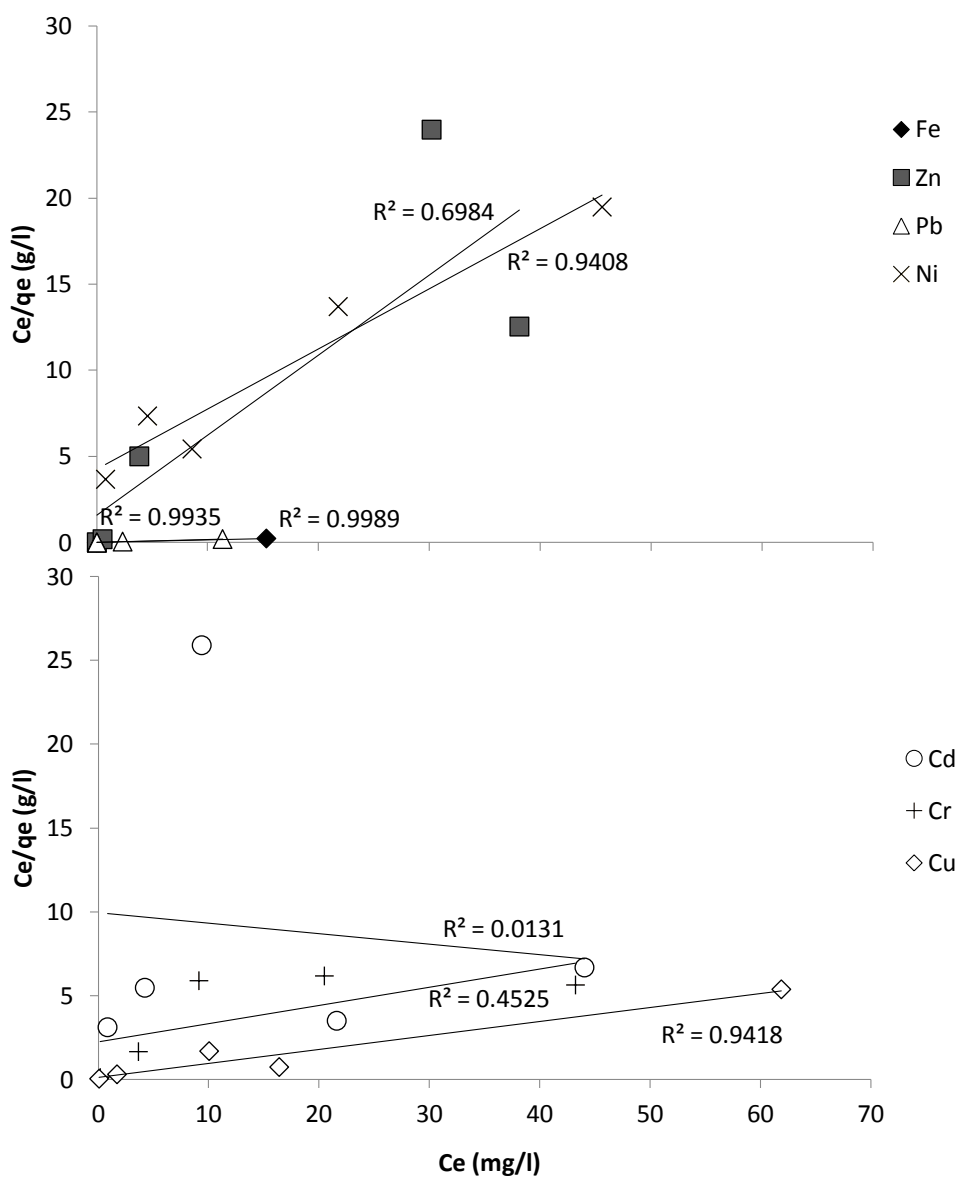


Figure 4-14 - Linearised Langmuir isotherm plots for all metals (BFS)

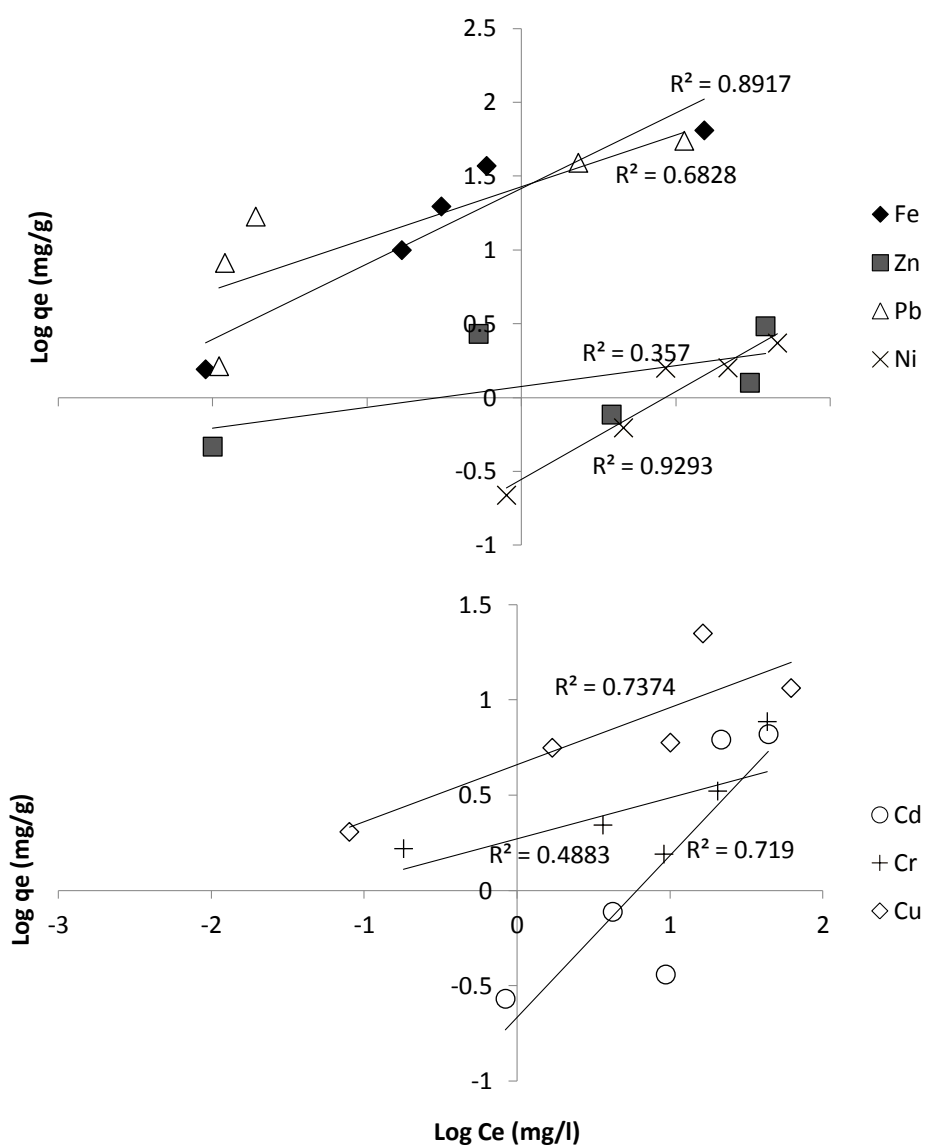


Figure 4-15 - Linearised Freundlich isotherm plots for all metals (BFS)

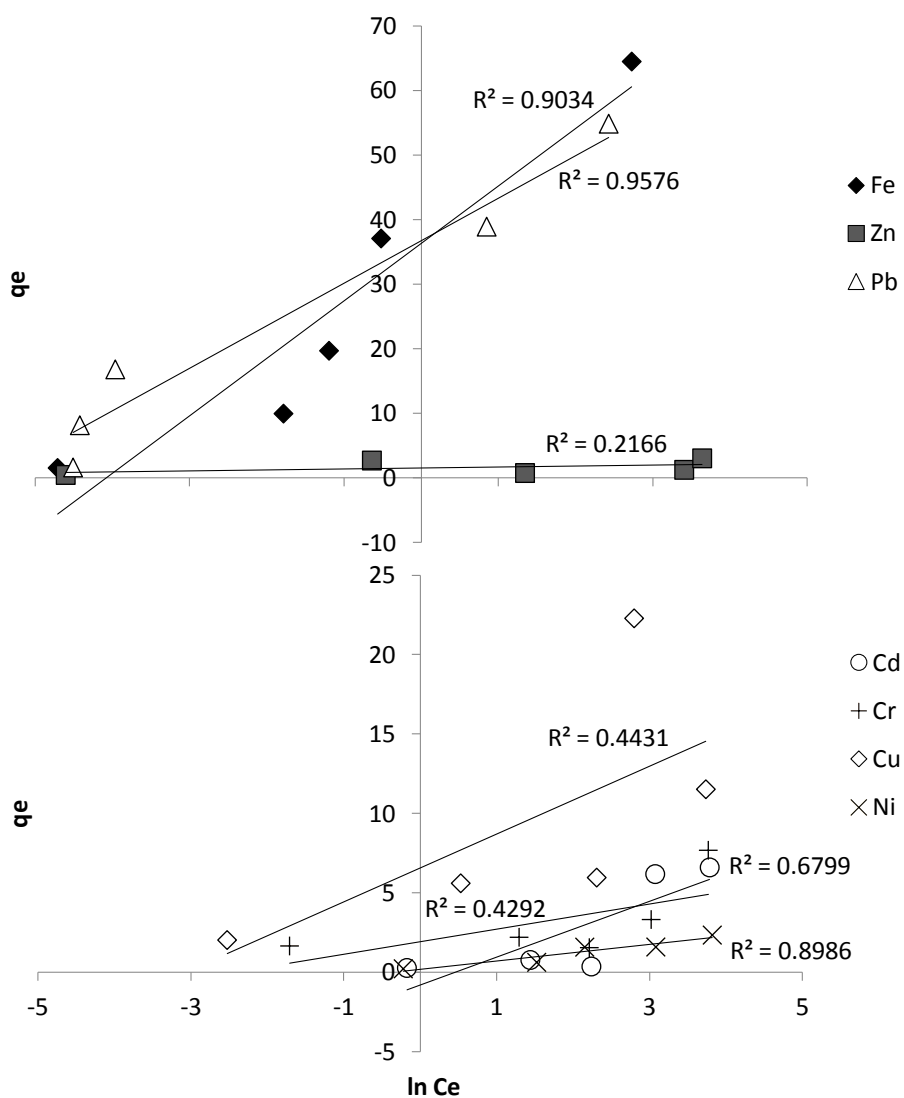


Figure 4-16 - Linearised Temkin isotherm plots for all metals (BFS)

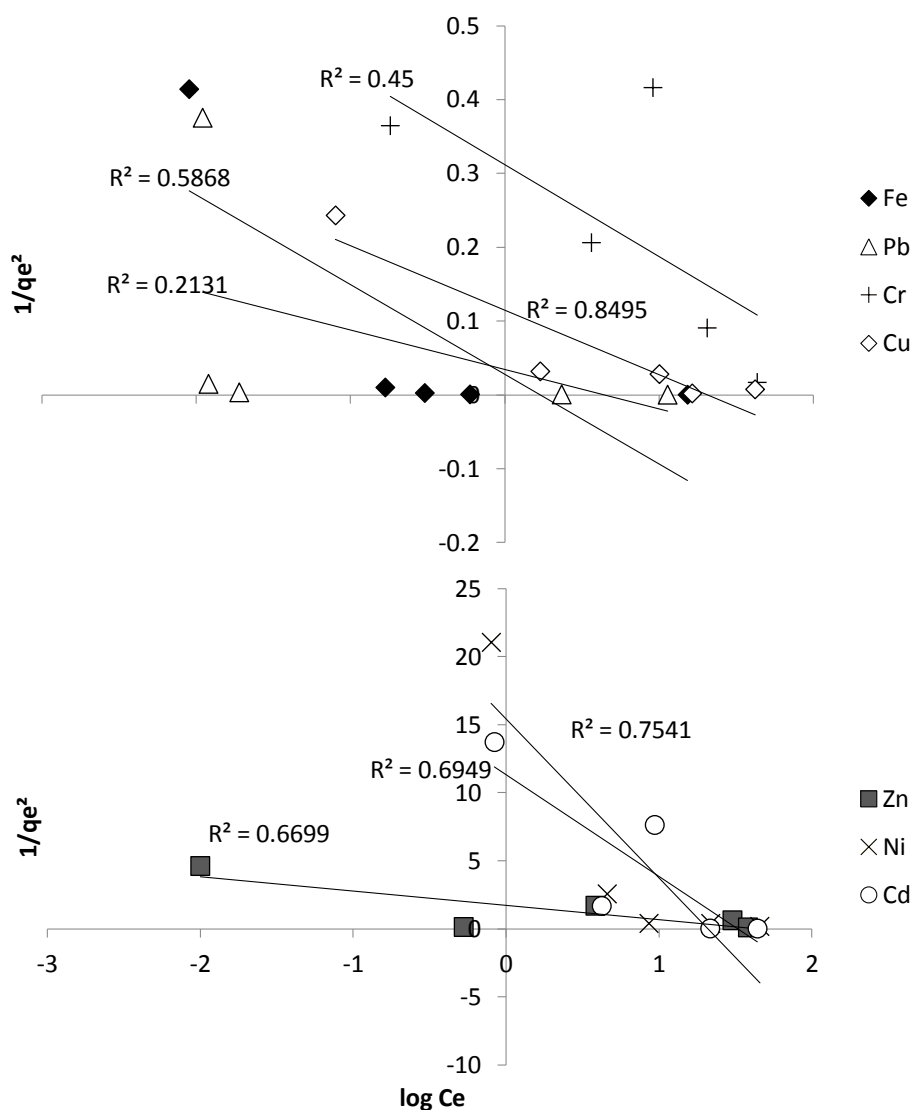


Figure 4-17 - Harkins-Jura isotherm plots for all metals (BFS)

4.4. Summary

The results of the batch adsorption experiments show that both loamy sand and BFS media are capable of effectively adsorbing the priority heavy metals investigated.

Elemental composition analysis found that both materials contained large fractions of Ca and Si, while BFS also contained notable percentages of Al and Mg. These findings can be used to increase understanding of removal of certain pollutants in chapter 5 (e.g., chemical precipitation of PO₄-P due to the large presence of Ca).

The adsorption rate of all metals to both adsorbents was quick, with the majority of the reaction taking place in the first 5 minutes of the experiment. The pseudo-second-order model was an extremely accurate representation of the dynamics of the metal adsorption process, with a near-perfect fit to the data for all metals and adsorbents. The well-fitting model therefore produced extremely reliable calculated q_e values when compared to the values determined from experimentation. The good fit of the model suggests that chemisorption controlled the rate of the adsorption of all metals to both adsorbents.

The adsorption capacities of loamy sand and BFS were determined for each metal through the application of adsorption isotherms to data obtained from the adsorption equilibrium experiments. Of the isotherms applied, the Langmuir isotherm was the better representation of loamy sand's capacity for Fe, Zn, Pb, and Cr, while its capacity for Ni was best represented by the Freundlich isotherm. The Temkin isotherm was the best representation of Cu, while Ni was best represented by the Harkins-Jura model. Cd adsorption to loamy sand was not adequately represented by any isotherm. The Langmuir isotherm was the better representation of BFS's capacity for Fe, Zn, Pb, Ni and Cu, while the Freundlich isotherm better represented its capacity for Cd. Cr adsorption to BFS was not adequately represented by either isotherm.

The loamy sand had a particularly high capacity for adsorption of Fe, Pb and Cu, significantly higher than alternative adsorbents reported in literature. The loamy sand's adsorption capacity for Zn also exceeded many alternative adsorbents, although was outperformed by carbon-based materials. The loamy sand had a lower capacity for Cr and Ni when compared to values reported in the literature. The BFS also had a particularly high adsorption capacity for Fe, Pb and Cu, and exceeded the loamy sand's capacity for these metals. However, despite its increased capacity, BFS has a lower affinity for Fe and Pb as determined by its lower b values. BFS's capacity for Zn adsorption was found to be comparable to literature values, while its capacity for Ni and Cd was generally lower than alternative adsorbents in similar studies.

The experiments were carried out using a single metal adsorbate solution in each case. Thus, it is possible that different results may have been produced with the use of a multi-metal adsorbate solution. This would have been more representative of the semi-synthetic stormwater used in the pilot-scale CW inflow, but was not investigated due to time and financial restraints.

5. Pilot-Scale Experiment Results

5.1. Introduction

This chapter is an analysis of the performance of the pilot-scale stormwater CWs. The effects of the three main design variables are studied and the pollutant removal processes of the systems are investigated. The three main design variables were:

1. The primary media
2. The wetland to watershed area ratio (WWAR)
3. The wetting and drying regime

Each pollutant group (TSS, heavy metals and nutrients) is considered and the effect of the three variables on pollutant reduction is analysed. The alternative physical and chemical properties brought about by a change in the CW media can affect such features as the level and sustainability of suspended solids and particulate pollutant removal, adsorption capacity, the pH in the system and the ability of the CW to support macrophytes. The WWAR determines the hydraulic and pollutant loading and therefore, it can impact on system hydraulics, which in turn can have an effect on pollutant removal performance and plant activity. Drying and subsequent re-wetting of soils can affect factors such as the chemical phase distribution of metals, soil structure (e.g., increased porosity, occurrence of fissures due to drying) and plant activity (Blecken *et al.*, 2009).

The objectives of this chapter are:

- To determine the pollutant removal performance of the 8 pilot-scale systems and compare with similar studies and systems to determine how effective the CWs were, relative to previously tested configurations.
- To determine the reasons why the key variables and operating conditions affect treatment performance, identifying any additional influencing factors (e.g., pH, temperature, time)

- To interpret the results of the experiment in order to determine the most effective configuration of the pilot-scale stormwater CW for treatment of TSS, heavy metals and nutrients

In order to determine whether each variable had a statistically significant effect on the treatment performance of the CWs, single-factor analysis of variance (ANOVA) tests were carried out on removal efficiency results for each contaminant (when possible) at a significance level of 0.05.

For most parameters (apart from TSS), data has not been displayed or analysed for the first few weeks of the experiment. It took some time to stabilise the operation of the system, thus the early period of results was not very reliable for metal and nutrient analysis. This is the reason that these early results have been omitted. Therefore, the data displayed gives the best representation of the performance of the pilot-scale stormwater CWs.

Where a significant relevant trend of change in contaminant concentration over time was identified, mean values of removal efficiency/effluent concentration have been compared between the first 10 weeks and the final 10 weeks of data recording. The reason that a period of 10 weeks was selected was the desire to use mean values over a significant period of time (> 2 months) to show that the CW was giving regular results that indicated a significant change in treatment performance.

In order to gain an appreciation of the quality of the treated stormwater and hence the performance of the CW systems, effluent pollutant concentrations were compared to water quality guidelines published by the UK Technical Advisory Group (TAG) regarding the Water Framework Directive (UK Technical Advisory Group on the Water Framework Directive, 2008). These are the standards used in the UK, but they do not specify limits for discharge, such as the effluent of CWs. This is because discharge pollutant limits are based on the watercourse into which they are discharged. The values of the upper pollutant concentrations in the pilot-scale CW effluent were thus calculated as those that meet the criteria for a watercourse with “good” ecological status. For each pollutant, several different limit values may exist depending on the type of watercourse, and so the lowest (and therefore the strictest)

value was used in this project in order to be conservative. For example, the lowest upper limit for Zn concentration in a watercourse with “good” ecological status is 0.008 mg/L. In order to comply with the standards, the discharge from the CWs must not increase the Zn concentration of the watercourse to > 0.008 mg/L. As all rivers are different, flow rates had to be assumed, and the values chosen for this study were extremely conservative.

Firstly, an extremely low flow rate was selected for the receiving watercourse, of 1000 m³/d. This is conservative as a low flow rate such as this would cause less dilution of the CW effluent. Secondly, the CW effluent flow rate was calculated by assuming that the entire volume of treated water exits the system within 15 minutes (this is also conservative). For the sake of these calculations, the maximum volume used in the 1.5% CW was used: 37.6 L. Discharged over 15 minutes, this produces a flow rate of 3.61 m³/d. These values were then used in the mass balance Equation 5.1 in order to determine the maximum allowable concentration for each pollutant in the CW discharge that would maintain “good” watercourse quality.

$$Q_w C_w + Q_{us} C_{us} = Q_{ds} C_{ds} \quad (5.1)$$

where: Q_w = discharge flow rate (m³/d)

C_w = discharge pollutant concentration (mg/L)

Q_{us} = upstream flow rate (m³/d)

C_{us} = upstream pollutant concentration (mg/L)

Q_{ds} = downstream flow rate ($Q_w + Q_{us}$) (m³/d)

C_{ds} = downstream pollutant concentration (mg/L)

Rearranging Equation 5.1 into Equation 5.2 allows calculation of the upper limit of concentration for each contaminant:

$$C_w = \frac{Q_{ds} C_{ds} - Q_{us} C_{us}}{Q_w} \quad (5.2)$$

The final assumption made for each pollutant was that the upstream concentration was 90% of the upper limit for “good” ecological status. Thus, for Zn:

$$Zn C_w = \frac{(1000 + 3.61)0.008 - 1000(0.9 \times 0.008)}{3.61} = 0.230 \text{ mg/L}$$

This method was applied to establish conservative upper limits of concentration for TSS, Zn, Cu, Pb, Cd, Cr, Ni, Fe, NH₄-N and PO₄-P. The UK TAG limits were used for C_w in all cases apart from TSS, for which the old freshwater fish directive limit of 25 mg/L was used (European Union, 2006). This value was chosen upon the recommendations of Natural Resources Wales, a branch of the UK Environment Agency. All limit values are shown in Table 5-5.

5.2. Inflow pollutant concentrations in semi-synthetic stormwater

Table 5-5 shows the target concentrations of the pollutants and the achieved concentrations. It was found that, for most pollutants, the addition of the natural sediment to dechlorinated tap water produced concentrations higher than the target values. Therefore, the only pollutant concentrations that required the addition of laboratory grade chemicals were Cd, Cr and Ni. It was therefore possible to achieve average inflow concentrations relatively close to the target values for these three pollutants. Average TSS inflow concentration is also close to the target value, as this was controlled by the addition of the appropriate amount of sediment to the inflow water volume in order to obtain the desired TSS value.

Filtered samples from the CW inflow and outflow were also analysed over a 7 week period during the experimental time frame. These results were then compared to the total metal concentration results in order to determine whether the metals were predominantly particulate or dissolved in nature. It was found that Cu, Cd, Cr and Fe were entirely particulate-associated in the inflow. A fraction of the total Zn concentration was dissolved (9% on average), as was the case with Ni (16% on average). Pb inflow was entirely particulate in most cases, apart from several cases where an extremely low dissolved concentration was detected (usually only 2-3% of the total Pb concentration).

Table 5-1 - Target and achieved inflow pollutant concentrations

Pollutant	Target inflow concentration (mg/L)	Mean achieved inflow concentration (mg/L)
TSS	180	179.5
Zn	0.35	0.54
Cu	0.07	0.15
Pb	0.16	0.21
Cd	0.005	0.004
Cr	0.025	0.03
Ni	0.04	0.09
Fe	2.9	3.88
TN	3	5.49
NH ₄ -N	-	1.27
NO ₂ -N	-	0.001
NO ₃ -N	-	0.18
TP	0.45	1.05
PO ₄ -P	-	0.90

5.3. ANOVA results

The results of the ANOVA tests have been compiled into 3 tables, one for each variable. These are presented as tables 5-2, 5-3 and 5-4.

Table 5-2 - ANOVA results for media comparison

Media comparison	Significance (for each contaminant)					
	TSS	Zn	Pb	Fe	TN	PO ₄ -P
CW1: CW4 (both LS)	$p < 0.01$	ns	ns	$p < 0.01$	ns	ns
CW1(LS):G	$p < 0.01$	$p < 0.01$	$p < 0.05$	ns	$p < 0.01$	$p < 0.01$
CW1(LS):BFS	$p < 0.01$	$p < 0.01$	ns	ns	ns	$p < 0.01$
CW4(LS):G	ns	$p < 0.01$	$p < 0.05$	$p < 0.01$	$p < 0.01$	$p < 0.01$
CW4(LS):BFS	ns	$p < 0.01$	ns	ns	ns	$p < 0.01$
G:BFS	$p < 0.05$	$p < 0.01$	$p < 0.05$	$p < 0.01$	$p < 0.01$	ns

* ns denotes "no significance", i.e. $p > 0.05$

Table 5-3 - ANOVA results for WWAR comparison

WWAR comparison	Significance (for each contaminant)			
	TSS	Zn	Fe	PO ₄ -P
CW1:CW4 (both 2.5%)	$p < 0.01$	ns	$p < 0.01$	ns
CW1(2.5%):5%	$p < 0.01$	ns	ns	$p < 0.01$
CW1(2.5%):1.5%	$p < 0.01$	$p < 0.05$	$p < 0.01$	ns
CW4(2.5%):5%	$p < 0.05$	ns	$p < 0.05$	$p < 0.01$
CW4(2.5%):1.5%	ns	$p < 0.05$	ns	ns
5%:1.5%	$p < 0.05$	$p < 0.05$	$p < 0.01$	$p < 0.01$

* ns denotes "no significance", i.e. $p > 0.05$

Table 5-4 - ANOVA results for wetting/drying regime comparison

WWAR comparison	Significance (for each contaminant)		
	TSS	Zn	Fe
CW1:CW4 (both WC)	$p < 0.01$	ns	$p < 0.01$
CW1:PDC	ns	$p < 0.01$	ns
CW1:EDC	$p < 0.01$	$p < 0.01$	$p < 0.01$
CW4:PDC	$p < 0.01$	$p < 0.01$	$p < 0.01$
CW4:EDC	ns	$p < 0.01$	ns
PDC:EDC	$p < 0.01$	ns	ns

* ns denotes "no significance", i.e. $p > 0.05$

5.4. TSS

Table 5-5 summarises the effluent concentrations and removal efficiencies achieved in all eight CW units. The results show that a good level of TSS removal was

achieved in all eight units, with average removal efficiencies in the range 85-94%. This level of TSS removal is comparable to other studies, with similar CW configurations, in which TSS reduction was considered successful (Blecken *et al.*, 2011; Scholz, 2003).

Figure 5-1 gives an indication of the variation in TSS removal efficiencies measured over the duration of the experiment. It should be noted that much of this variability is due to a gradual improvement in TSS removal over time. Overall, the variation in results of each CW within the 25th and 75th percentiles is relatively limited and the values of the results within these limits compare well to other studies with similar CW configurations (Blecken *et al.*, 2011; Scholz, 2003).

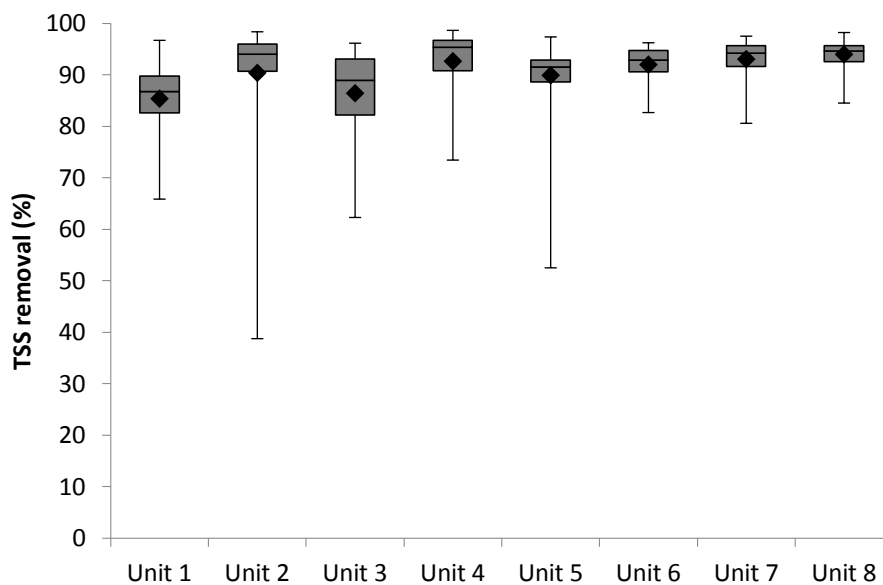


Figure 5-1 - Boxplot of TSS removal in all 8 CWs. Black diamonds represent mean removal efficiencies

5.4.1. Effect of CW media on TSS removal

Single factor ANOVA tests determined significant differences in TSS removal caused by the change in primary media (see Table 5-2). Also, importantly, there was a significant difference found between the results of the two loamy sand CWs. The two loamy sand units experienced significantly different mean removal efficiencies of 85% (unit 1) and 92% (unit 4). However, as both units' performances improved over time (see Figure 5-2), their removal efficiencies began to show signs of

convergence: the mean TSS removal efficiencies for the last 10 weeks of data recording were 93% and 97% for unit 1 and unit 4, respectively. Should the experiment have run for longer, it is possible that further convergence may have occurred. Nonetheless, it shows that variation in TSS removal efficiencies is possible between CWs with the same configuration and loading patterns.

The highest performing of the 8 CWs in terms of average TSS removal was unit 8, the BFS unit, with 94% removal efficiency and the lowest mean effluent concentration of 11.2 mg/L. As shown in Figure 5-2, the BFS CW achieved relatively consistent removal efficiencies over the length of the experiment, whereas there was a general improvement with the other three CWs.

The average removal efficiency of the gravel CW (unit 2) was 90%, with a mean effluent concentration of 18.5 mg/L. As was the case with the loamy sand CWs, the gravel unit's removal performance improved over time (see Figure 5-2). Over the final 10 weeks of data recording, its mean removal efficiency had increased to 97%.

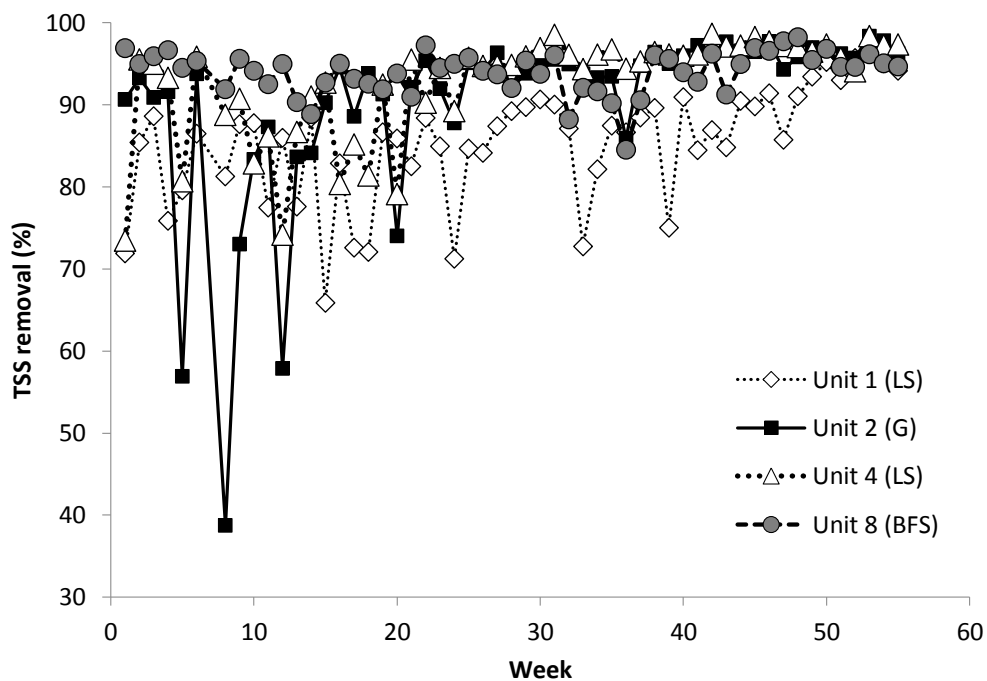


Figure 5-2 - TSS removal over time in units 1, 2, 4 and 8

Table 5-5 – Average pollutant concentrations and removal efficiencies

	Mean influent concentration (mg/L)	Upper discharge limit (mg/L)	Mean effluent concentration (mg/L) and (mean removal efficiency)							
			Unit 1	Unit 2	Unit 3	Unit 4	Unit 5	Unit 6	Unit 7	Unit 8
TSS	179.5	717.5	27.4 (85%)	18.5 (90%)	25.5 (86%)	15.3 (92%)	18.8 (90%)	15.4 (92%)	11.6 (94%)	11.2 (94%)
Zn	0.54	0.230	0.125 (76%)	0.026 (96%)	0.074 (85%)	0.121 (77%)	0.106 (80%)	0.071 (87%)	0.078 (86%)	<0.006 (>99%)
Cu	0.15	0.029	<0.0015 (>99%)	<0.005 (>96%)	<0.0014 (>99%)	<0.001 (>99%)	<0.001 (>99%)	<0.0015 (>99%)	<0.0013 (>99%)	<0.001 (>99%)
Pb	0.21	0.207	<0.019 (>91%)	<0.027 (>87%)	<0.019 (>91%)	<0.019 (>91%)	<0.019 (>91%)	<0.019 (>91%)	<0.019 (>91%)	<0.019 (>91%)
Cd	0.004	0.002	<0.0013 (>68%)	<0.0013 (>68%)	<0.0013 (>68%)	<0.0013 (>68%)	<0.0013 (>68%)	<0.0013 (>68%)	<0.0013 (>68%)	<0.0013 (>68%)
Cr	0.03	0.098	<0.001 (>96%)	<0.002 (>94%)	<0.001 (>96%)	<0.001 (>96%)	<0.001 (>96%)	<0.001 (>96%)	<0.001 (>96%)	<0.001 (>96%)
Ni	0.09	0.574	<0.005 (>94%)	<0.005 (>94%)	<0.005 (>94%)	<0.005 (>94%)	<0.005 (>94%)	<0.005 (>94%)	<0.005 (>94%)	<0.005 (>94%)
Fe	3.88	28.701	0.219 (95%)	0.293 (94%)	0.189 (96%)	0.090 (98%)	0.130 (97%)	0.106 (97%)	0.053 (99%)	0.051 (99%)
TN	5.49	-	1.41 (73%)	2.65 (52%)	1.63 (69%)	1.27 (76%)	1.85 (64%)	1.93 (63%)	1.23 (78%)	1.38 (74%)
NH ₄ -N	1.27	9.184	0.20 (84%)	0.12 (91%)	0.25 (80%)	0.15 (88%)	0.15 (89%)	0.18 (84%)	0.20 (84%)	0.08 (94%)
NO ₂ -N	0.001	-	<0.002 (-)	<0.002 (-)	<0.002 (-)	<0.002 (-)	<0.002 (-)	<0.002 (-)	<0.002 (-)	<0.002 (-)
NO ₃ -N	0.18	-	0.85 (-)	1.01 (-)	0.71 (-)	0.71 (-)	1.16 (-)	0.64 (-)	0.70 (-)	0.90 (-)
TP	1.05	-	0.25 (77%)	0.31 (71%)	0.24 (78%)	0.24 (77%)	0.18 (83%)	0.24 (77%)	0.24 (77%)	0.30 (72%)
PO ₄ -P	0.90	1.148	0.15 (83%)	0.22 (77%)	0.16 (82%)	0.16 (82%)	0.11 (88%)	0.14 (85%)	0.17 (82%)	0.23 (75%)

5.4.2. Effect of change in wetland-watershed area ratio on TSS removal

Single factor ANOVA tests found significant differences between TSS reduction for all configurations apart from unit 4 and the 1.5% WWAR CW (see Table 5-3). The 1.5% WWAR CW achieved a mean removal efficiency of 94%, outperforming the 2.5% WWAR CWs. The 5% WWAR CW achieved a mean removal efficiency of 90%.

The two 2.5% WWAR units experienced rather different mean removal efficiencies of 85% (unit 1) and 92% (unit 4). However, as both units' performances improved over time, their removal efficiencies began to show signs of convergence: the mean TSS removal efficiencies for the last 10 weeks of data recording were 93% and 97% for unit 1 and unit 4, respectively. Nonetheless, it shows that variation in TSS removal efficiencies is possible between CWs with the same configuration and loading patterns.

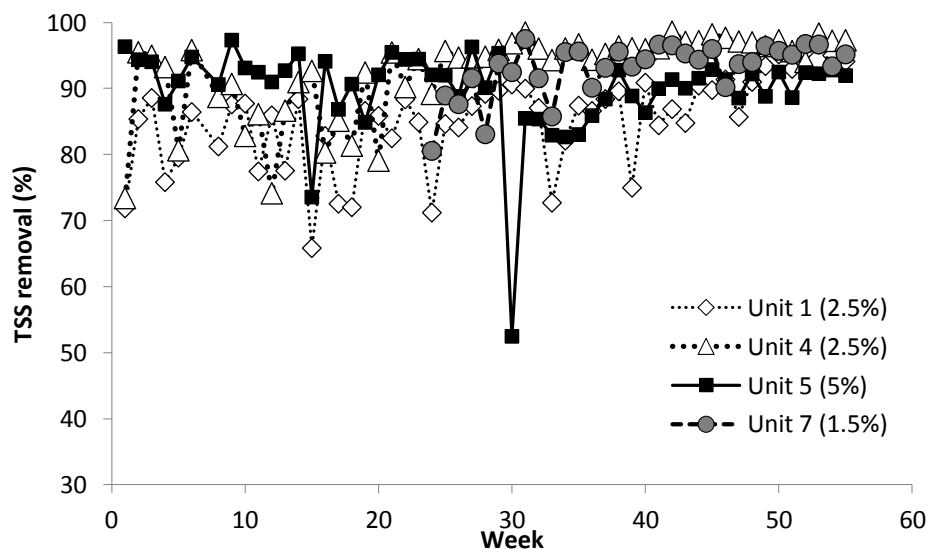


Figure 5-3 - TSS removal over time in units 1, 4, 5 and 7

After 45 weeks of running the systems, the weekly effluent TSS measurements of all 8 of the CWs consistently gave values greater than their mean values from the entire duration of the experiment. Thus, there was an improvement in TSS removal over time. Average removal efficiencies taken from the last 10 weeks of data recording

found that the 5% WWAR CW was now the poorest performing unit with a value of 92%. This is in comparison to a value of 95% for the 1.5% WWAR unit and values of 93% and 97% for the 2.5% WWAR CWs (units 1 and 4, respectively).

5.4.3. Effect of drying on TSS removal

Single factor ANOVA analysis (Table 5-4) found statistically significant differences between the effluent TSS concentrations of different wetting and drying regimes, although no significant differences could be found between units 1 (WC) and 3 (PDC), nor between units 4 (WC) and 6 (EDC).

The two WC CWs experienced rather different mean removal efficiencies of 85% (unit 1) and 92% (unit 4). However, as both units' performances improved over time, their removal efficiencies began to show signs of convergence: the mean TSS removal efficiencies for the last 10 weeks of data recording were 93% and 97% for unit 1 and unit 4, respectively. Nonetheless, it shows that variation in TSS removal efficiencies is possible between CWs with the same configuration and loading patterns. The variation between the two WC CWs complicates comparisons with the PDC and EDC CWs and no clear advantage/disadvantage of the wet conditions can be identified as a result of this.

The improvement in TSS removal over time was evident in all units. The PDC CW averaged a TSS removal efficiency of 94% over the final 10 weeks of data recording, and the EDC CW averaged 93%.

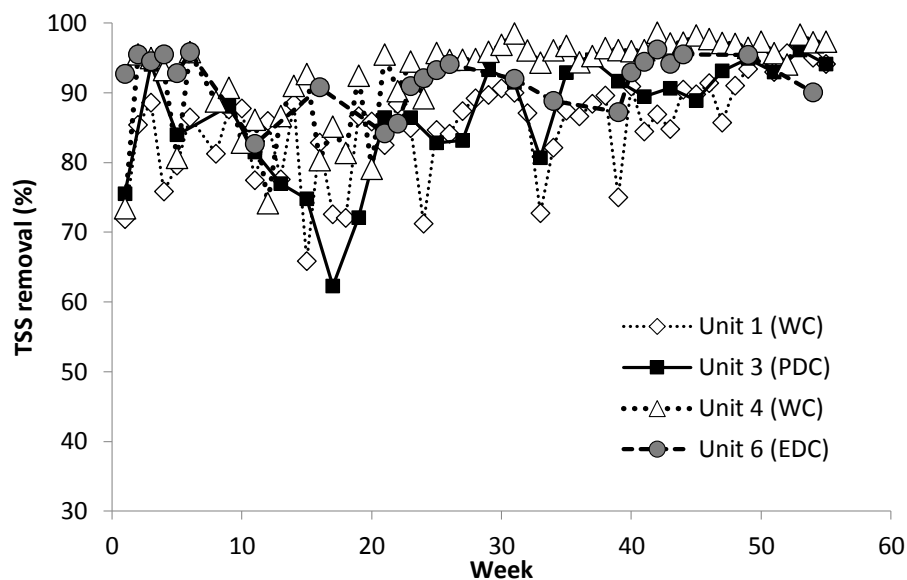


Figure 5-4 - TSS removal over time in units 1, 3, 4 and 6

5.4.4. Discussion – TSS Removal

There are several factors which may contribute to improved TSS removal over time in the loamy sand CWs. To appreciate these, it is important to understand the dominant solid removal mechanism in VF CWs with fine sand bed media: filtration (Kadlec and Wallace, 2009). Filtration is considered a combination of straining, sedimentation and adsorption processes. Straining involves the physical prevention of particles from travelling through the CW by the media, and is dependent on both the size of the pores and the suspended solids. Sedimentation is the process of solids travelling downwards via gravity and settling on a surface. Adsorption affects only very small solid particles near the substrate media. The solids are attracted to the media by electrostatic attraction, Van der Waals forces or bonding to zoogloal film on sand particles (Woodward and Ta, 1988). Due to the fact that the primary media in the loamy sand units consists mainly of sand particles, it is reasonable to suggest that straining and sedimentation play major roles in TSS removal in these systems. Adsorption may affect smaller particles, but this will not have a major effect on the overall TSS removal efficiency.

Given the knowledge of these solids removal mechanisms, several reasons are suggested for the improvement in TSS removal in the loamy sand CWs. Blecken *et al.* (2010) propose that “repacking and settling” of the CW media (caused by the

repeated loadings) would decrease pore sizes and hence improve solids retention. Higher early effluent TSS concentrations tend to be experienced as the CWs wash out fines from the media (Hatt *et al.*, 2007b). This may also explain the difference in results between the two loamy sand CWs. Despite best efforts to achieve a complete duplicate, it is possible that there was a greater percentage of fines present in the volume of loamy sand placed in unit 1 compared to unit 4. The loamy sand batch was mixed as well as possible, but this is something that was difficult to control. Hatt *et al.* (2007c) cites aggregation of solids over time as one way that resuspension of sediments can become reduced. Also, the authors report that previously settled solids can produce more adhesive surfaces on which incoming solids may be deposited.

The latter reason may also be relevant to the improvement in the performance of the gravel CW over time. The gravel CW was the only CW configuration in which the transition layer was also gravel instead of sand. The larger pore volume in the gravel transition layer is likely to have allowed more fine influent solids to pass through the system in the early stages of the experiment, and the build-up of solids over time was likely a factor in improving its TSS removal performance via the two mechanisms previously mentioned. Sedimentation is likely a major solids removal mechanism in the gravel CW. This would have occurred during loading as the water is moving down through the media, and also during the 24 hour flooded period. The long retention time with no flow allows plenty of time for suspended particles to settle on to the nearest surface.

The presence of a sand transition layer in the BFS CW may explain its superior performance over the gravel CW: despite both systems having similarly sized granular media, the sand transition layer helped to remove more solids than a gravel layer due to its larger surface area, thus producing a more consistent TSS removal performance over the duration of the experiment.

Overall, the BFS CW appears to be the most successful for TSS removal due to the slag's lower fines content than loamy sand, and the sand transition layer which helped to remove more influent fines than in the gravel CW. Therefore, because the BFS CW did not release or let through fine solids in the early stages of the experiment, it did not experience the "settling period" that the other configurations

required to develop their TSS removal mechanisms. However, it should be noted that the BFS CW did not perform statistically significantly better than unit 4, a loamy sand CW. Despite this, the fact that the BFS CW did not require time to mature and maintained high removal efficiencies over the course of the experiment makes it the most suitable media choice for TSS removal.

Prior to the start of the experiment it was expected that the loamy sand units would outperform the granular media units due to the smaller pore space in the loamy sand CWs, causing additional straining of solids. The likely reason that the media types are more closely matched in their removal performances is the 24 hour retention period. This allows additional time for suspended solids in all units to settle on to the nearest surface.

The reason that the 1.5% WWAR CW was the best performing configuration in this experiment may be due to the fact that, because it receives larger inflow volumes, it receives greater loads of incoming TSS. Therefore, more solids aggregate in the CW in a shorter period of time, thus reducing resuspension in the CW and providing adhesive surfaces on which incoming solids may be deposited (as reported by Hatt *et al.*, 2007c). Also, Blecken *et al.* (2010) propose that repeated loadings cause “repacking and settling” of the CW media, which decreases pore sizes and improves solids retention. The larger inflow volumes in the 1.5% WWAR CW may increase this effect.

Overall, the most suitable choice for TSS removal in terms of WWAR value was the 1.5% WWAR CW, as it matured more quickly than the other CWs and therefore produced a more consistent performance. All WWAR configurations improved with time and by the end of the experiment they were all performing at a high standard.

A direct comparison cannot be made between the WC CWs and the two CWs with enforced dry conditions. However, a comparison can be made between those two drier regimes, as a statistically significant difference was identified in the results of their effluent TSS concentrations. The PDC CW achieved a mean removal efficiency of 86%, while the EDC CW achieved a mean removal efficiency of 92%. It can also be observed in Figure 5-5 that the EDC CW achieved a higher TSS removal

efficiency in most effluent samplings over the lifetime of the experiment. Therefore extended drying conditions produced better TSS removal than partially dry conditions.

It is not possible to say which set of wetting/drying conditions is the most desirable for TSS removal. It was shown that extended drying conditions produced better TSS removal than partially dry conditions, but the variance in results of the two WC CWs means that a relationship between dry conditions and TSS removal cannot be determined.

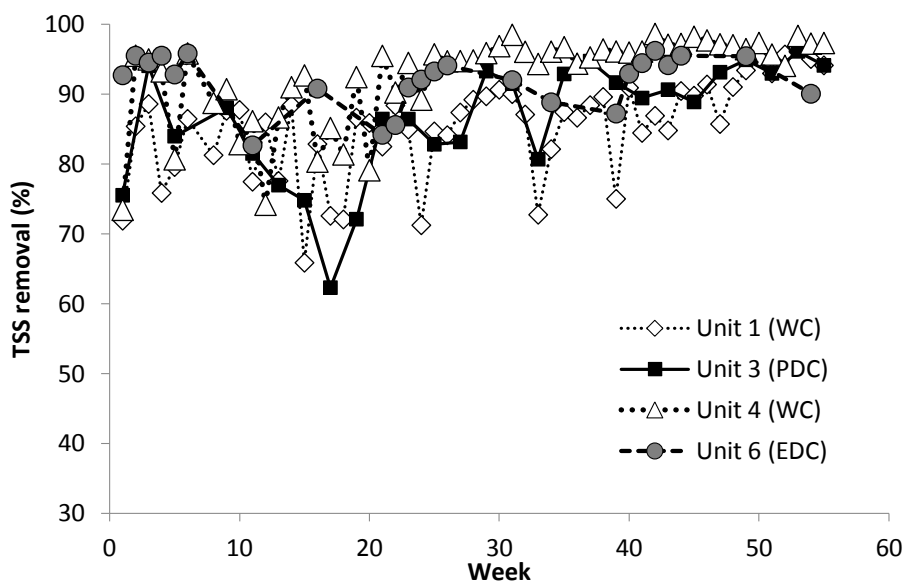


Figure 5-5 - TSS removal over time in units 1, 3, 4 and 6

5.5. Heavy metals

Table 5-5 summarises the average effluent concentrations and removal efficiencies achieved in all eight CW units. The results show that high heavy metal removal efficiencies were achieved in all units. The metal reductions are comparable to other studies with similar CW configurations in which metal reduction was considered highly successful (Blecken *et al.*, 2009b; Feng *et al.*, 2012). For Cu, Pb, Cd, Cr and Ni, the effluent concentrations were regularly too small to detect, and considered to be zero in these cases. Zn and Fe effluent concentrations were more consistently detectable and therefore easier to compare to other studies.

Mean Zn removal efficiencies ranged from 76% to above 99%, with mean effluent concentrations ranging from below the detection limit of 0.0064 mg/L to 0.12 mg/L. This compares well with previous laboratory-scale experiments (Hatt *et al.*, 2007a; 2007b; 2007c), and also matches other pilot-scale experiment results (Blecken *et al.*, 2009a; 2009b; 2011; Feng *et al.*, 2012) when taking the two highest removal efficiencies from this experiment (i.e. 96% and >99%). In general however, the mean Zn removal efficiencies are not quite as high as those values reported in the literature for similar pilot-scale sized stormwater CWs. All CWs successfully lowered Zn effluent concentrations to below the calculated discharge limit of 0.23 mg/L.

Mean Fe removal efficiencies are high, in the range 94-99%, and mean effluent concentrations range from 0.05-0.29 mg/L. This compares favourably with the results of similar pilot-scale stormwater CWs tested by Feng *et al.* (2012), in which the range of mean Fe removal efficiencies was 81-97% and the range of mean effluent concentrations was 0.25-1.2 mg/L. All CWs successfully lowered Fe effluent concentrations to below the calculated discharge limit of 28.7 mg/L.

5.5.1. Effect of CW media on heavy metal removal

As can be seen in Table 5-2, the experimental output showed that CW media had significant effects on Zn, Pb and Fe reduction. All Cd and Ni effluent concentrations were below the detection limits shown in Table 3-7, Effluent Cu and Cr concentrations were only detected at the beginning of the experiment in the gravel

CW unit. After 8 weeks of data recording, the gravel media CW stabilised and effluent Cu and Cr concentrations were typically below detection limits thereafter. The increase in removal efficiency in the gravel unit is attributed to its improved TSS removal over time.

5.5.1.1. Zinc

ANOVA test results (Table 5-2) show that there were significant differences between the 3 CW media types in terms of Zn removal.

Zn removal was successful in the BFS CW (unit 8), with all effluent concentrations being below the detection limit of 0.0064 mg/L. Unit 8 was indeed the highest performing CW throughout the duration of the experiment. This is unsurprising, as the influent Zn was mostly particulate in form and unit 8 successfully removed TSS to a high degree throughout the experiment.

Zn removal in the gravel unit (unit 2) was high, with a mean removal efficiency of 96% and mean effluent concentration of 0.03 mg/L. Removal efficiency stabilised in the gravel CW and showed improvement as the experiment progressed: developing from a mean removal efficiency of 91% in the first 10 weeks of data recording to 98% in the final 10 weeks.

Mean Zn removal efficiencies in the loamy sand CWs were 76% (unit 1) and 77%, and removal patterns became inconsistent during a certain period of the experiment. As Figure 5-6 shows, Zn removal efficiencies in loamy sand units decreased from week 25 onwards, before appearing to steadily increase again from week 45 for the remainder of the experiment. The horizontal dashed line shows the minimum removal efficiency achieved by either of the granular media CW units (value of 83% from the gravel media CW). Note that the removal efficiencies of the loamy sand CWs regularly drop below this value from week 29 onwards. Meanwhile, the other CWs are unaffected, with the gravel unit's performance improving over time.

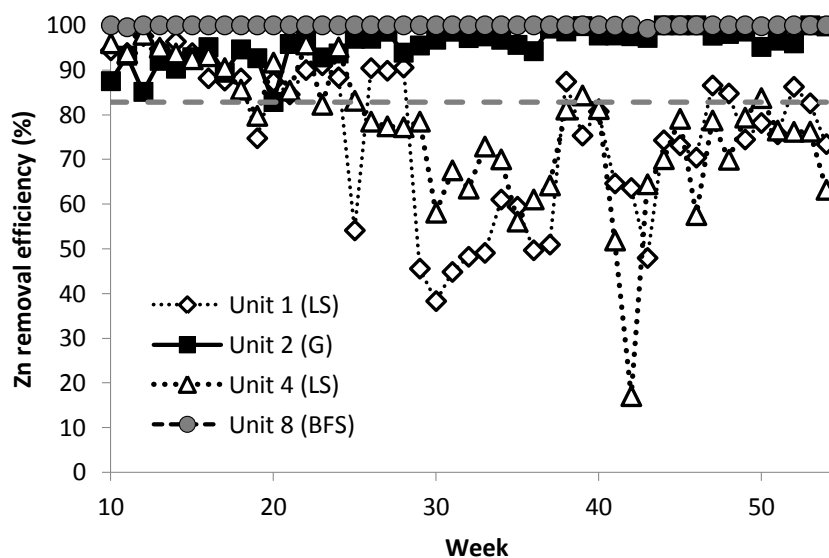


Figure 5-6 - Zn removal efficiency over time in units 1, 2, 4 and 8. Horizontal dashed line represents minimum removal efficiency achieved by any granular media unit

5.5.1.2. Lead

ANOVA tests found significant variations in Pb removal performance between the gravel and the other CW media (see Table 5-2). All Pb concentrations were below the detection limit (0.0195 mg/L) in the outflow of the loamy sand and BFS CWs. Low Pb concentrations were regularly detected in the effluent of the gravel CW for the first few weeks of the experimental run, but the number of detectable concentrations decreased over time and by the last 10 weeks of the experiment there were no detectable results. Therefore the performance of the gravel CW improved with time. This can be attributed to its improvement in TSS removal over time, as the Pb entering the system was almost entirely particulate in form.

5.5.1.3. Iron

The results of the ANOVA tests (Table 5-2) show that the choice of CW media had a significant effect on Fe removal. Correlation analysis found strong positive correlations between TSS effluent concentrations and Fe effluent concentrations in all four CWs ($R = +0.92$ for unit 1, $R = +0.96$ for unit 2, $R = +0.93$ for unit 4 and $R = +0.80$ for unit 8). Figure 5-7 shows the strong similarities in effluent TSS and Fe concentration trends. As discussed in section 5.4.4, the Fe entering the units was almost entirely particulate in form, and the strong correlations between effluent Fe

and TSS suggests that this is also the case in the outflow. Therefore, Fe removal performance is dependent on TSS removal performance and thus it is unsurprising that unit 8 was the best remover of Fe (mean 98.7% removal efficiency) as it was also the best remover of TSS.

Fe removal in the loamy sand CWs was good, with mean removal efficiencies of 94.6% (unit 1) and 98.6% (unit 4) and corresponding effluent concentrations of 0.22 mg/L and 0.01 mg/L. The mean unit 1 Fe effluent concentration over the last 10 weeks of data recording was 0.08 mg/L. The difference in removal performance between unit 1 and its duplicate, unit 4, was attributed to unit 4's higher TSS removal performance.

The average Fe removal efficiency in the gravel media CW was 93.8%, with a mean effluent concentration of 0.29 mg/L. These average figures were affected by relatively high effluent concentrations from the beginning of the experiment, which reduced over time. These high concentrations can be attributed to the early high TSS effluent concentrations in the gravel unit. The average gravel CW effluent concentration from the first 10 weeks of data recording was 0.81 mg/L (85.3% removal efficiency), but this reduced to a mean value of 0.03 mg/L (98.7% removal efficiency) for the final 10 weeks. The increase in removal efficiency in the gravel unit is attributed to its improved TSS removal over time.

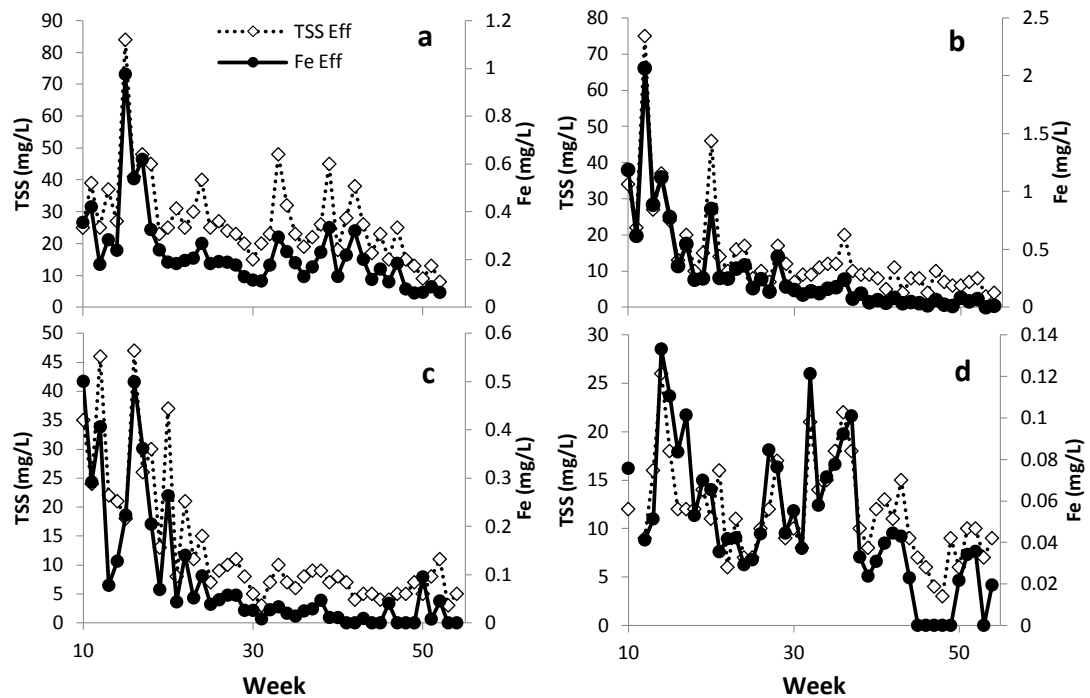


Figure 5-7 - Effluent TSS and Fe concentrations over time in (a) unit 1 (loamy sand), (b) unit 2 (gravel), (c) unit 4 (loamy sand), (d) unit 8 (BFS)

5.5.2. Effect of change in wetland-watershed area ratio on heavy metal removal

As can be seen in Table 5-3, the experimental output showed that WWAR had significant effects on Zn and Fe reduction. All Pb, Cd and Ni effluent concentrations were below the detection limits shown in Table 3-7. Effluent Cu and Cr concentrations were rarely detected, preventing any conclusions to be drawn on the effect of WWAR on their removal.

5.5.2.1. Zinc

The results of the single-factor ANOVA tests (Table 5-3) show that there were significant differences between the performance of the 1.5% WWAR CW compared to the other two configurations. The 1.5% WWAR CW was the highest performer in terms of Zn removal, with a mean removal efficiency of 86%. The 2.5% WWAR CWs produced the lowest mean removal efficiencies: 76% for unit 1 and 77% for unit 4. The 5% WWAR CW achieved a mean removal efficiency of 80%. As shown

in Figure 5-8, all four CWs in question experienced inconsistency in removal with a period of elevated effluent from week 29 to week 45, after which there appeared to be a steady improvement.

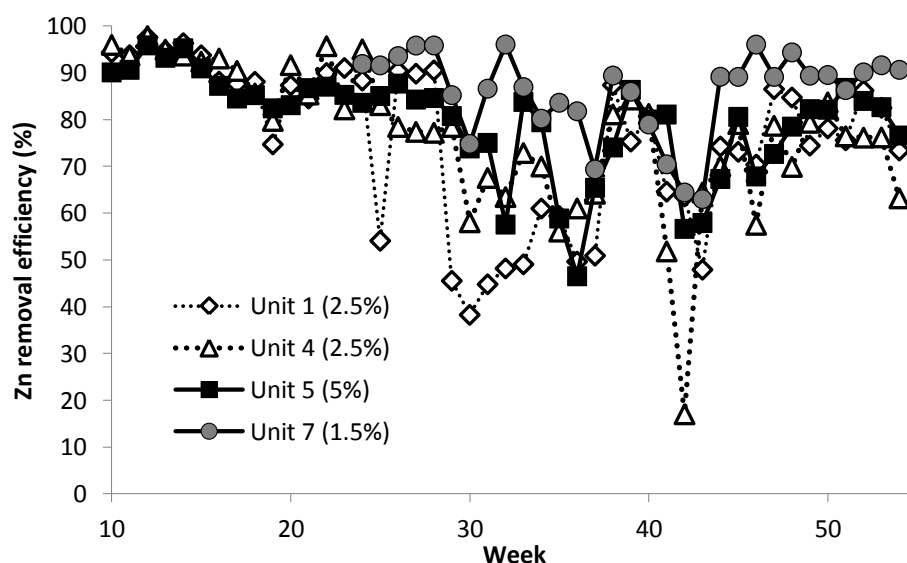


Figure 5-8 - Zn removal efficiency over time in units 1, 4, 5 and 7

5.5.2.2. Iron

ANOVA test results (Table 5-3) show that differing WWAR values had a significant effect on Fe removal. Correlation analysis found strong positive correlations between TSS effluent concentrations and Fe effluent concentrations in all four CWs ($R = +0.92$ for unit 1, $R = +0.93$ for unit 4, $R = +0.95$ for unit 5 and $R = +0.94$ for unit 7). Figure 5-9 shows the strong similarities in effluent TSS and Fe concentration trends. As discussed in section 5.2, the Fe entering the units was almost entirely particulate in form, and the strong correlations between effluent Fe and TSS suggests that this is also the case in the outflow. Therefore, Fe removal performance is dependent on TSS removal performance and thus it is unsurprising that the 1.5% WWAR CW was the best remover of Fe (mean 98.6% removal efficiency) as it was also the best remover of TSS. The average Fe removal efficiency in the 5% WWAR CW was 96.6%, with a mean effluent concentration of 0.13 mg/L. Fe removal in the 2.5% WWAR CWs was good, with mean removal efficiencies of 94.6% (unit 1) and 98.6% (unit 4) and corresponding effluent concentrations of 0.22 mg/L and 0.01

mg/L. The mean unit 1 Fe effluent concentration over the last 10 weeks of data recording was 0.08 mg/L. The difference in removal performance between unit 1 and its duplicate, unit 4, was attributed to unit 4's higher TSS removal performance.

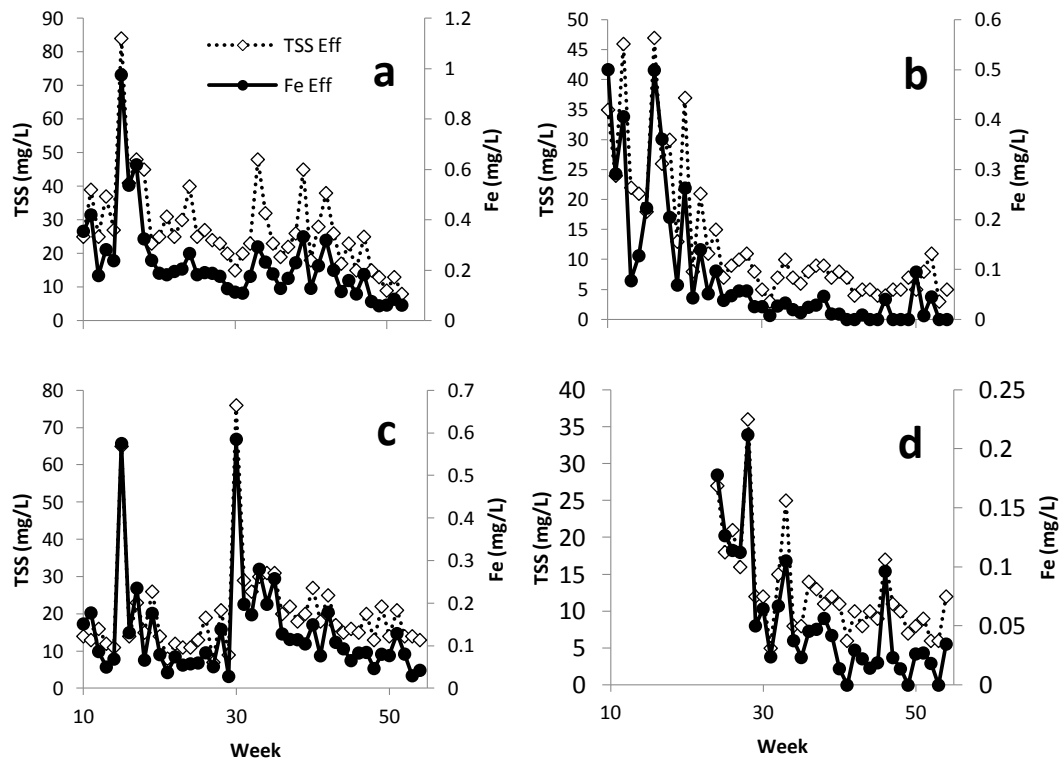


Figure 5-9 - Effluent TSS and Fe concentrations over time in (a) unit 1 (2.5% WWAR), (b) unit 4 (2.5% WWAR), (c) unit 5 (5% WWAR), (d) unit 7 (1.5% WWAR)

5.5.3. Effect of drying on heavy metal removal

As can be seen in Table 5-4, the experimental output showed that the wetting/drying regime had significant effects on Zn and Fe reduction. All Pb, Cd and Ni effluent concentrations were below the detection limits shown in Table 3-7. Effluent Cu and Cr concentrations were rarely detected, preventing any conclusions to be drawn on the effect of WWAR on their removal.

5.5.3.1. Zinc

The ANOVA test results (presented in Table 5-4) show that there was a significant difference in Zn removal efficiency results that arose from the WC CWs in comparison to the other two configurations. The EDC CW was the highest performer

in terms of Zn removal, with a mean removal efficiency of 87%. The PDC CW achieved a mean Zn removal efficiency of 85%, making it the second highest performer over the course of the experiment. The WC CWs produced the lowest mean removal efficiencies: 76% for unit 1 and 77% for unit 4. As can be seen in Figure 5-10, both of these units suffered a period of reduced removal efficiency as effluent Zn concentrations elevated between weeks 29 and 45, before appearing to re-stabilise for the remainder of the experiment. The horizontal dashed line shows the minimum removal efficiency achieved by either of the CW units with added dry periods (value of 72% from the PDC CW). Note that the removal efficiencies of both of the WC CWs regularly drop below this value between weeks 29 and 45. The CWs experiencing dry periods do not appear to have been affected to any significant extent during this same period.

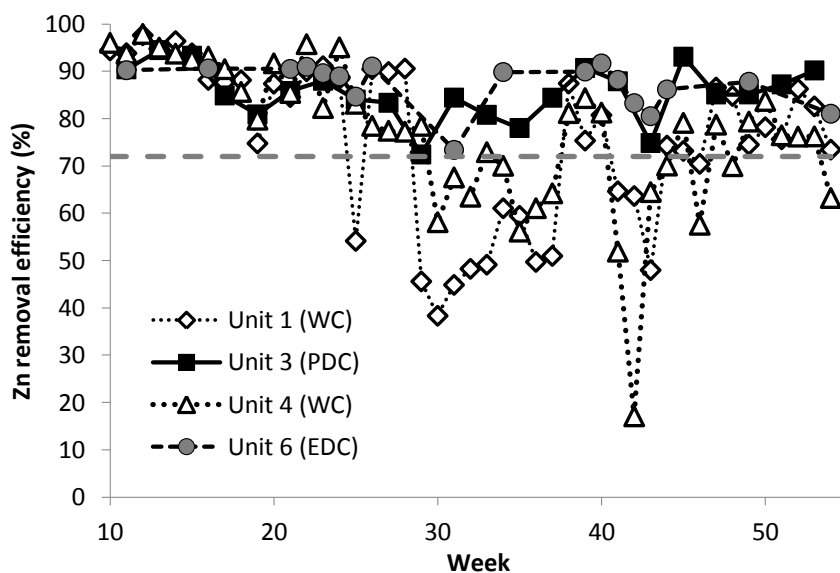


Figure 5-10 - Zn removal efficiency over time in units 1, 3, 4 and 6. Horizontal dashed line represents minimum removal efficiency achieved by any unit with added dry periods

5.5.3.2. Iron

ANOVA test results (see Table 5-4) show that differing wet and dry conditions had a significant effect on Fe removal in two separate cases between unit 1 (WC) and unit 6 (EDC), and between unit 4 (WC) and unit 3 (PDC). Correlation analysis found strong positive correlations between TSS effluent concentrations and Fe effluent concentrations in all four CWs ($R = +0.92$ for unit 1, $R = +0.93$ for units 3 and 4 and

$R = +0.83$ for unit 6). Figure 5-11 shows the strong similarities in effluent TSS and Fe concentration trends. As discussed in section 5.2, the Fe entering the units was almost entirely particulate in form, and the strong correlations between effluent Fe and TSS suggests that this is also the case in the outflow. Therefore, Fe removal performance is reflective of TSS removal performance. Fe removal was successful in the EDC CW. It exhibited a mean removal efficiency of 97.4% and mean effluent concentration of 0.11 mg/L. Its results were also relatively consistent over time. The average Fe removal efficiency in the PDC CW was 95.5%, with a mean effluent concentration of 0.19 mg/L. Fe removal in the WC CWs was good, with mean removal efficiencies of 94.6% (unit 1) and 98.6% (unit 4) and corresponding effluent concentrations of 0.22 mg/L and 0.01 mg/L. The mean unit 1 Fe effluent concentration over the last 10 weeks of data recording was 0.08 mg/L. The difference in removal performance between unit 1 and its duplicate, unit 4, was attributed to unit 4's higher TSS removal performance.

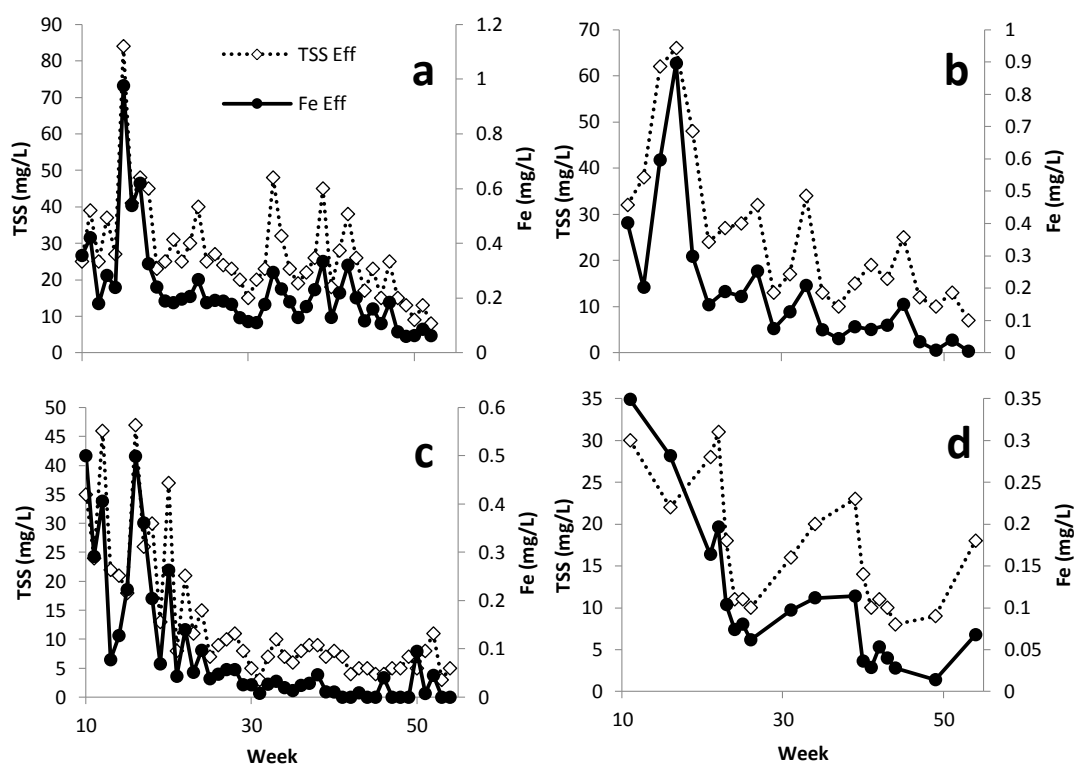


Figure 5-11 - Effluent TSS and Fe concentrations over time in (a) unit 1 (WC), (b) unit 3 (PDC), (c) unit 4 (WC), (d) unit 6 (EDC)

5.5.4. Discussion – Heavy metals removal

In general, it is theorised that solids removal mechanisms were extremely important in the reduction of heavy metals in the pilot-scale CWs. As the influent Zn was mostly particulate in form, or associated with solid particles (90% of influent Zn as determined by partitioning analysis), it is likely that the solids removal processes described in section 5.4.4 are the dominant Zn removal mechanisms in the CWs. This was determined to be in the main Zn removal mechanism in several other similar studies where influent Zn was mainly particulate (e.g., Blecken *et al.*, 2009b; Blecken *et al.*, 2011). It was found that all effluent Zn was dissolved in form; therefore the systems were extremely effective in removing particulate Zn.

There is a strong correlation between effluent TSS and Fe evident in all eight units (R^2 values in the range 0.64 to 0.92, see chapter 7), and this is typical of the relationship between these parameters in all eight units (see Figure 5-12 for the relationship between effluent TSS and Fe in units 1 and 2). Coupled with the fact that the influent Fe is entirely particulate in form, it is reasonable to suggest that typical solids removal mechanisms (settling, trapping, filtration and interception) are the main processes for Fe removal.

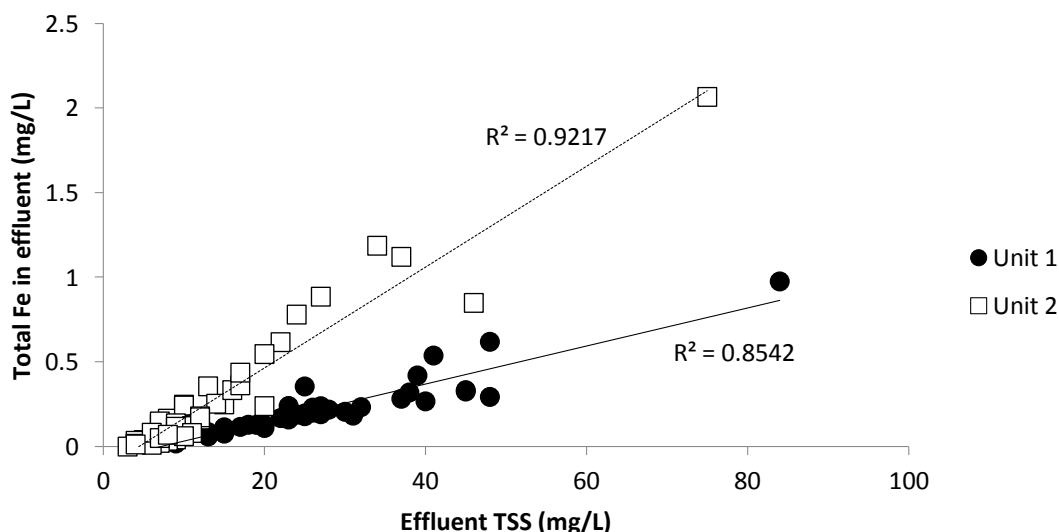


Figure 5-12 - Relationship between effluent TSS and Fe concentrations in effluent from units 1 and 2

For most metals, the choice of CW media did not have a significant effect on the CW performance and, where metals could be detected, removal patterns tended to reflect

the TSS removal performance of each media type. The major exception to this was Zn, where it was clearly identified that there was a lapse in performance in the loamy sand units over a period of 20 weeks.

The difference in Zn removal may be attributed to each media's ability to remove dissolved Zn. Partitioning analysis over a 7 week period from weeks 21 to 27 (inclusive) found that dissolved Zn concentrations increased from the influent to the effluent in all loamy sand CWs, but was reduced in the gravel media CW and completely removed in the BFS CW (see Figure 5-13).

Dissolved Zn is typically removed in CWs of this type via adsorption and microbial uptake in soils and organic matter, as well as plant uptake, precipitation and complexation by the media (Blecken *et al.*, 2009b; Feng *et al.*, 2012; Rieuwerts *et al.*, 1998). Batch adsorption analysis (see chapter 4) found that influent Zn, with the typical concentration used in this experiment, is adsorbed relatively quickly to loamy sand media (99.90% of original Zn concentration removed after 15 minutes) and BFS (99.82% of original Zn concentration removed after 15 minutes). Therefore both the loamy sand and BFS media have the demonstrated ability to effectively remove the majority of dissolved Zn by adsorption.

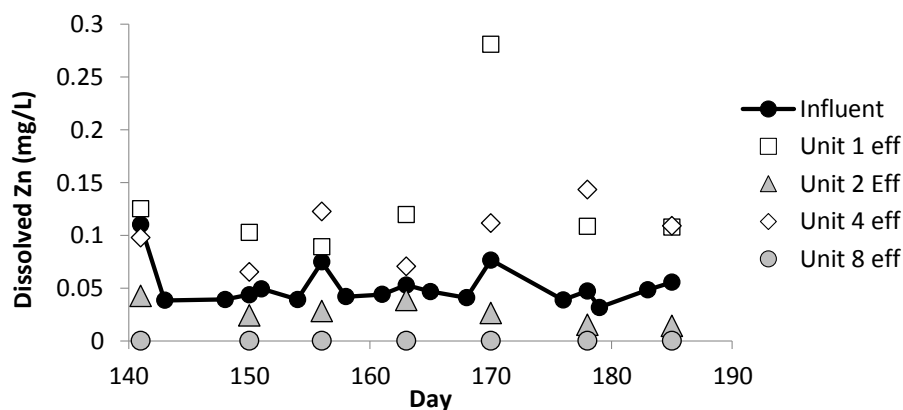


Figure 5-13 - Dissolved Zn concentrations vs time

The high performance of the BFS CW is likely attributable to its high pH (average value of 8.9) in comparison to the other CWs (average values of 6.9-7.6). In more alkaline conditions, dissolved Zn precipitates more readily (Rieuwerts *et al.*, 1998),

and thus it can then be effectively removed via the solids removal mechanisms that the BFS exhibited so successfully. Calcium (Ca) and magnesium (Mg) are recognised to be very effective adsorbents for heavy metals in neutral and alkaline conditions (Kim *et al.*, 2008), and elemental composition analysis of the BFS determined that it contained 24% Ca and 4% Mg (see chapter 4 for further details). Furthermore, the presence of sulphur in the BFS composition ($\approx 1\%$) may have contributed to its successful dissolved Zn removal, since Zn forms very insoluble compounds with sulphide and thus precipitates (Kadlec and Wallace, 2009). Therefore, it is unsurprising that the BFS unit was the best remover of dissolved Zn.

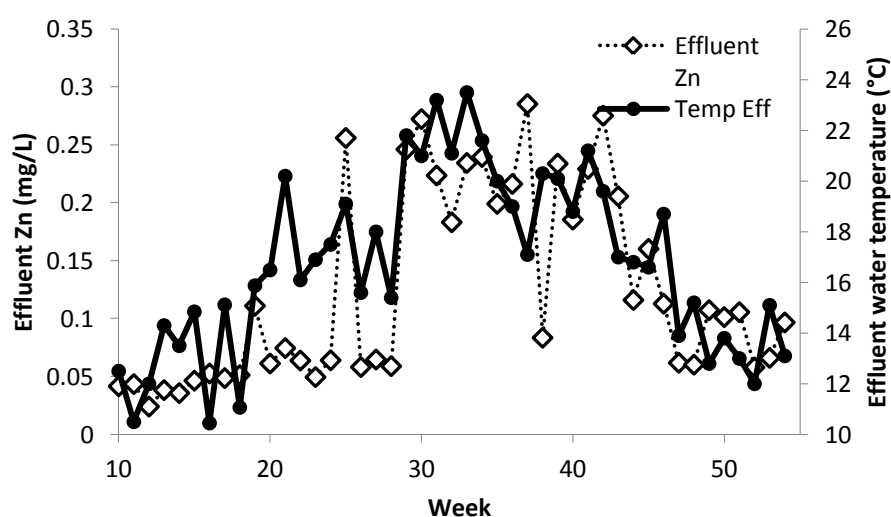


Figure 5-14 - Effluent Zn and water temperature over time in unit 1

It is important to note the timing of the increase in effluent Zn from the loamy sand CWs. The main dip in performance occurs from week 25 to 45 (see Figure 5-6). Week 25 began on the date 11/05/14 and week 45 on 19/10/14. This period is the British summertime, so it was considered that temperature may have contributed to the reduced Zn removal efficiencies. A relationship between effluent Zn concentration and effluent water temperature was thus identified, with a correlation coefficient of $R = +0.74$. Figure 5-14 shows the similarity in behaviour between these two components. Higher temperatures increase biological activity. Blecken *et al.* (2011) reported that, in stormwater CWs, higher biological activities occur at 20°C and above and therefore there is a higher turnover and decomposition of organic matter. This can lead to a release of dissolved organic matter (DOM) in the

outflow of the CW. Metals sorbed to organic matter in CW systems are not permanently immobilised (LeFevre *et al.*, 2014), and the release of DOM from the media will result in the release of associated sorbed metals. Martinez *et al.* (2003) report that Zn forms complexes with DOM and that increased temperature causes breakdown of DOM and increases the mobility of Zn in soil. This reason has been cited for the release of other metals which also bind to organic matter, in similar pilot-scale CW set-ups (e.g., Blecken *et al.*, 2011).

Figure 5-14 shows that Zn effluent concentrations are at their highest during the period of time when temperatures regularly reached 20°C. The increase in biological activity in the loamy sand CWs is evident from the plant growth experienced over this warm period. The *Typha latifolia* began to show the first visible signs of growth on 17/03/14 in the loamy sand CWs, before establishing themselves well during the spring and summertime (see Figure 3-1). During October 2014 there were visible signs that the plants were dying ahead of the winter (Figure 5-15), and by November they had turned completely brown (Figure 5-16).

The behaviour of the *Typha latifolia* in this period reflects the increase in biological activity in the loamy sand CWs, and therefore suggests that the release of DOM with associated sorbed Zn may be the source of the elevated Zn effluent concentrations. The BFS and gravel CWs did not successfully support the *Typha*, and do not contain high organic matter content within their media materials. Therefore, they would not have experienced the same increase in turnover and decomposition of organic matter that was experienced in the loamy sand CWs. This may explain why they did not experience the elevated effluent Zn concentrations.

Another factor in the increased Zn concentrations in the outflow of the loamy sand CWs may be directly related to the plant growth. Rieuwerts *et al.* (1998) reported that plant roots can slowly discharge organic substances which can act as complexing agents for metals, bringing adsorbed metals into solution. Therefore, previously adsorbed metals may have become mobilised when the plants were at their most active and thus ended up in the CW effluent. However, this would have been reflected in a change in pH, which was not identified. It is possible that the

effect was localised around the plant roots, but it is not possible to ascertain for certain in the experiment whether this was the case or not.



Figure 5-15 - Visible evidence of plant die off on 27/10/14



Figure 5-16 - Further visible plant die off on 18/11/14

The choice of WWAR value did not have a significant effect on the removal efficiency of most of the metals. The metals in the semi-synthetic stormwater were mainly particulate in form or bound to particles, so they were removed effectively by the physical mechanisms exhibited in the CWs, at which all four CWs performed well. The exception to the trend was Zn, where the 1.5% WWAR CW was clearly the strongest performer, but it is thought that this may be due to the fact that it had not been in operation as long as the other CWs, due to unforeseen operational difficulties delaying the commissioning of the CW until week 24 of the experiment. Week 24 began at the end of spring/start of summer. Therefore the 1.5% WWAR CW did not have as long as the other loamy sand CWs to grow its biological community. As explained above, this may have caused reduced release of DOM and therefore reduced release of associated dissolved Zn in the effluent (compared to the other CWs). Figure 5-8 shows that there was reduced Zn removal efficiency from the 1.5% WWAR during the summer period (suggesting that biological activity did increase), but that the removal did not drop as low as the other two CWs. This may have been due to reduced biological activity in comparison to the other CWs, caused by the late commissioning of the 1.5% WWAR.

The only significant effect on metals removal caused by drying was improved consistency of Zn removal during dry periods. The elevated effluent Zn concentrations exhibited in the WC CWs between weeks 29 and 45 did not occur in either of the units that were subjected to additional dry periods. Again, this is thought to be attributable to reduced biological activity occurring within the CWs due to their reduced intake of semi-synthetic stormwater and its nutrient content, which contributes to the biological community. Otherwise, metal removal patterns followed TSS removal patterns.

5.6. Nutrients

In order to fully understand the N transformation processes occurring within the pilot-scale CWs it is necessary to examine results for $\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$. The total of these concentrations is the inorganic fraction of TN. Therefore, subtracting this total from the TN values gives us the organic fraction of TN (see Equation 5.3). As mentioned earlier, inflow and outflow concentrations of $\text{NO}_2\text{-N}$

were typically below the detection limit of 0.002 mg/L. Therefore there is not a section devoted to it in this chapter, but the fact that NO₂-N concentrations were typically zero is still considered and used to bolster the understanding of the N transformation process in conjunction with the data for NH₄-N, NO₃-N and organic N.

$$\text{Organic N} = \text{TN} - (\text{NH}_4\text{-N} + \text{NO}_2\text{-N} + \text{NO}_3\text{-N}) \quad (5.3)$$

Total nitrogen removal improved over the duration of the experiment. The range of average removal efficiencies from the last 10 weeks of data recording of all units is 63-94%, with some units maturing more slowly than others. This compares favourably with the results of similar pilot-scale stormwater CWs, some of which experience an increase in TN concentrations in the effluent water. Zhang *et al.* (2011) report a range of 62-93% mean removal efficiencies, while the systems tested by Bratieres *et al.* (2008) produced a mean removal range of -241-79%.

NH₄-N removal was good in all units, with relatively consistent removal efficiencies and effluent concentrations experienced. Mean removal efficiencies of 80-94% were recorded, with mean effluent concentrations ranging from 0.08-0.25 mg/L. These values compare well with results of a similar pilot-scale CW tested by Zhang *et al.* (2011), who recorded mean removal efficiencies of 81-95%. The results from this experiment also compare favourably with those reported by Nanbaksh *et al.* (2007), who tested pilot-scale systems with a turf substrate. Mean NH₄-N removal efficiencies ranged from 81-89% in that experiment.

Increased NO₃-N concentrations from inflow to outflow are a common feature for VF CWs due to their excellent oxygen transfer efficiency, hence producing conditions that favour nitrification but not denitrification (which requires anoxic conditions to convert NO₃-N to N₂ gas by removing its oxygen components). Also, NO₃-N is very mobile in CW conditions, and thus is not easily sorbed to soil media (Li and Davis, 2014). Negative removal efficiencies have been found in many similar pilot-scale studies (e.g., Blecken *et al.*, 2010; Bratieres *et al.*, 2008; Nanbaksh *et al.*, 2007; Zhang *et al.*, 2011).

Mean TP removal efficiencies were in the range 71-83%, with effluent concentrations of 0.18-0.31 mg/L. The mean removal efficiencies compare well with results of a similar pilot-scale configuration reported by Bratieres *et al.* (2007), although some units in that study achieved TP removal of over 90% in a single instance. This was attributed to the use of *Carex appressa* as the CW plants, as it features an extensive root system plus small root hairs which provide extra surface area for adsorption. The CWs in this experiment are outperformed in terms of mean TP removal efficiency and mean effluent concentration by similar configurations set up by Blecken *et al.* (2010) and Zhang *et al.* (2011), although it is worth noting that a higher mean influent concentration was used in this experiment in comparison to those two, so a direct comparison cannot be made.

Influent analysis shows that 86% of influent P is in the dissolved inorganic PO₄-P form. Therefore TP is mostly dissolved, suggesting that solids removal mechanisms do not play the dominant role in its removal. However, the TSS removal mechanisms as discussed in section 5.4.4 played a part in removing the particulate fraction of TP which was identified during partitioning analysis.

Since the dissolved PO₄-P component of TP was the largest and most influential on its behaviour a focus is placed on this component to understand P removal in this chapter.

The PO₄-P removal efficiencies compare well to other similar pilot-scale systems reported by Bratieres *et al.* (2008) and Scholz & Hedmark (2010). There is much less variability in the range of removal efficiencies in the results of this experiment in comparison to the aforementioned papers. As with TP, the systems tested by Zhang *et al.* (2011) outperform this experiment, with a mean PO₄-P removal efficiency of 99%. All effluent PO₄-P concentrations were below the calculated discharge limit of 1.148 mg/L.

5.6.1. Effect of CW media on nutrient removal

5.6.1.1. Nitrogen

Single factor ANOVA tests identified significant differences in TN removal efficiency caused by the use of gravel CW media (see Table 5-2). No significant

difference was found in the performances of the loamy sand and BFS CWs. Total nitrogen removal improved over the duration of the experiment for all CWs, although it was a much slower improvement for the gravel media unit. Figure 5-17 shows the pollutograph of the influent N composition, and figures 5-19 to 5-22 show the corresponding effluent N composition pollutographs of the four CWs. The pollutographs show the change in TN concentrations and also the change in N composition from influent to effluent. It is apparent that there is an increasing TN removal efficiency as units 1, 4 (loamy sand) and 8 (BFS) mature. It can also be seen that there is an improvement in TN reduction in unit 2 (gravel), but that it is much slower than the other CWs and does not achieve the same removal performance by the end of the experimental run.

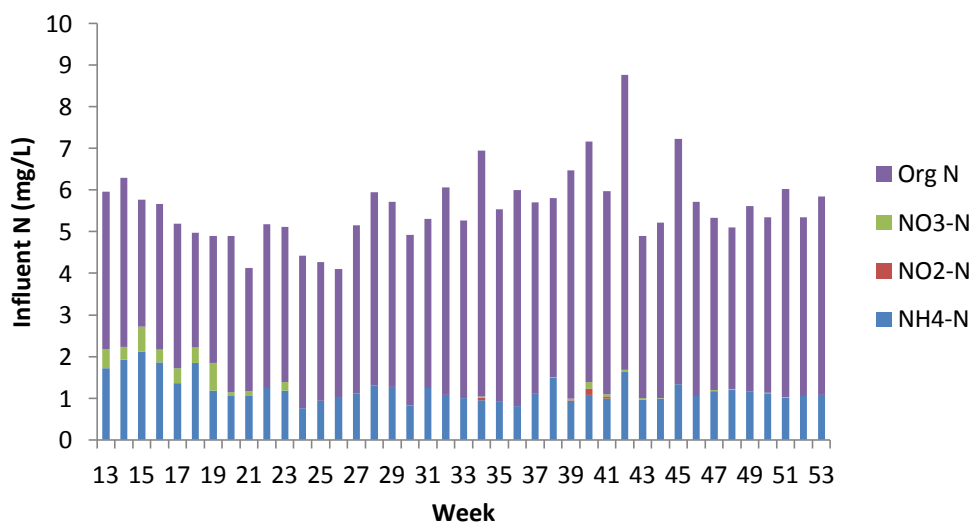


Figure 5-17 - Pollutograph showing influent N composition

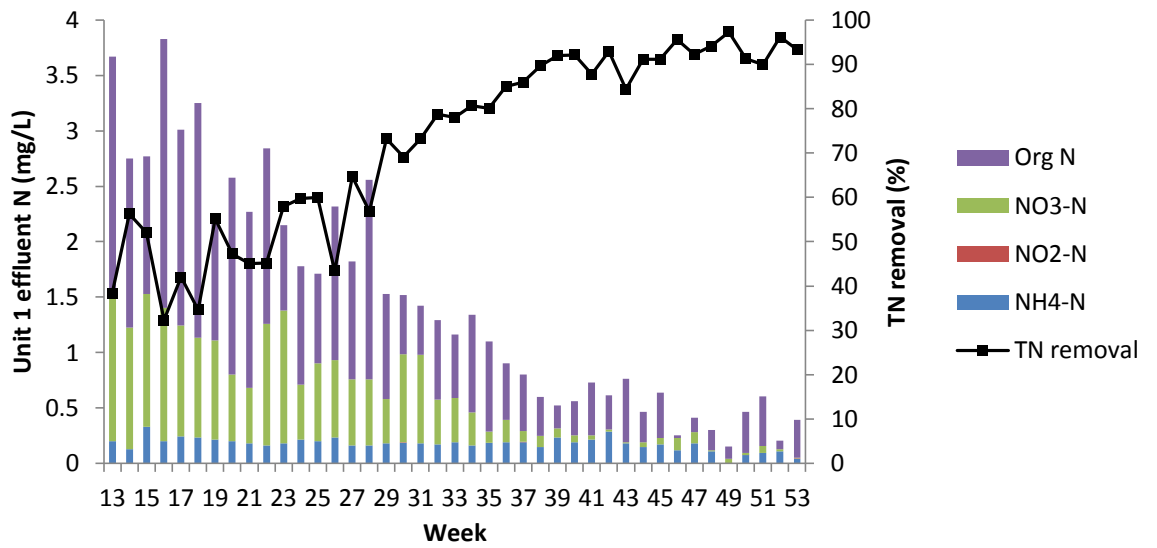


Figure 5-18 - Pollutograph showing N composition of unit 1 (loamy sand, 2.5% WWAR, WC) effluent

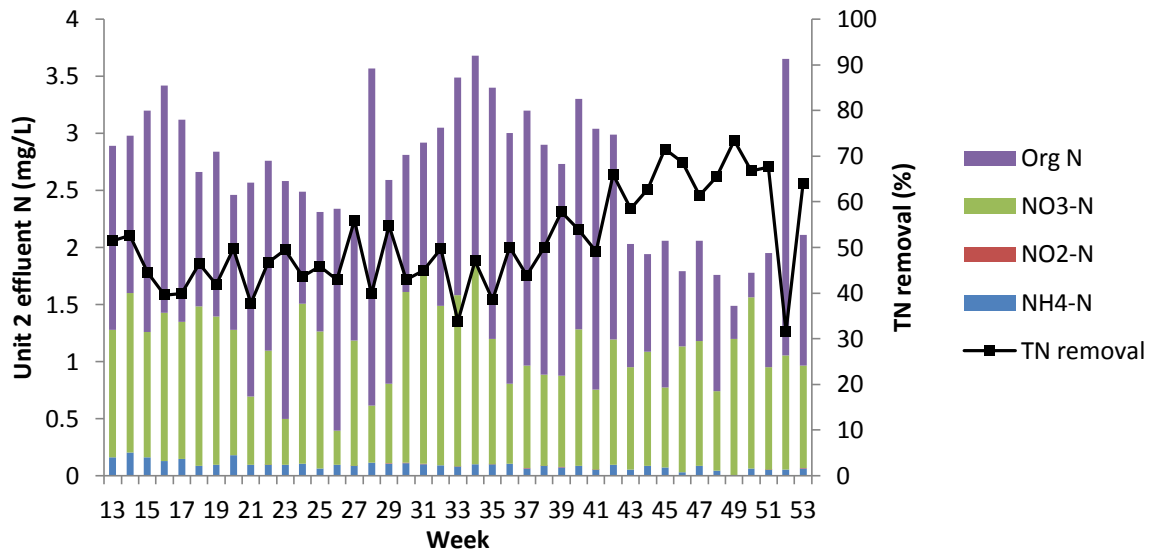


Figure 5-19 - Pollutograph showing N composition of unit 2 (gravel, 2.5% WWAR, WC) effluent

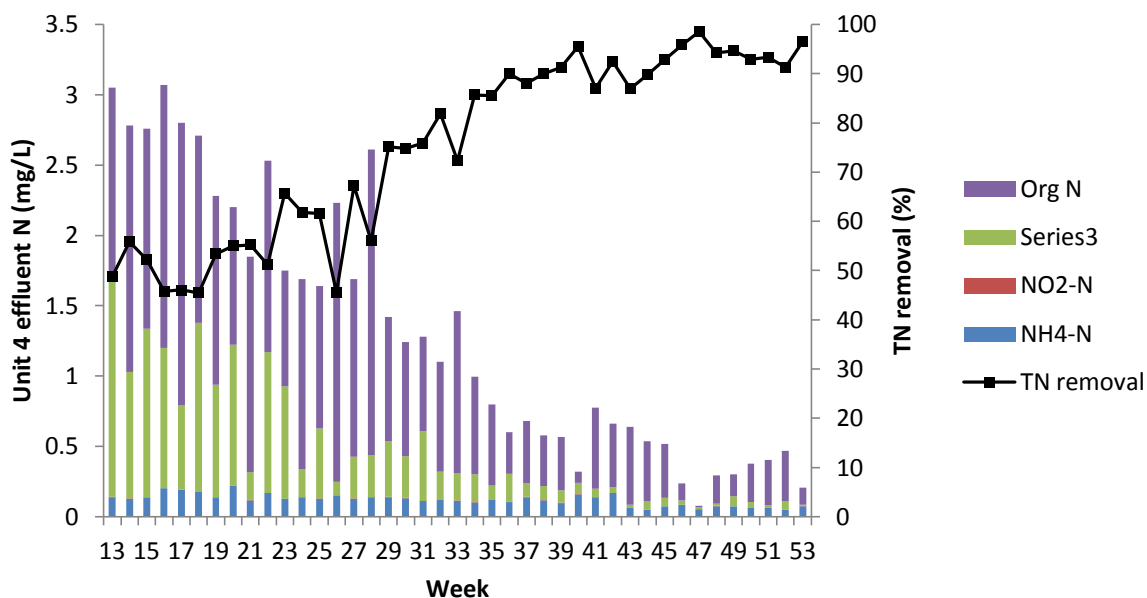


Figure 5-20 - Pollutograph showing N composition of unit 4 (loamy sand, 2.5% WWAR, WC) effluent

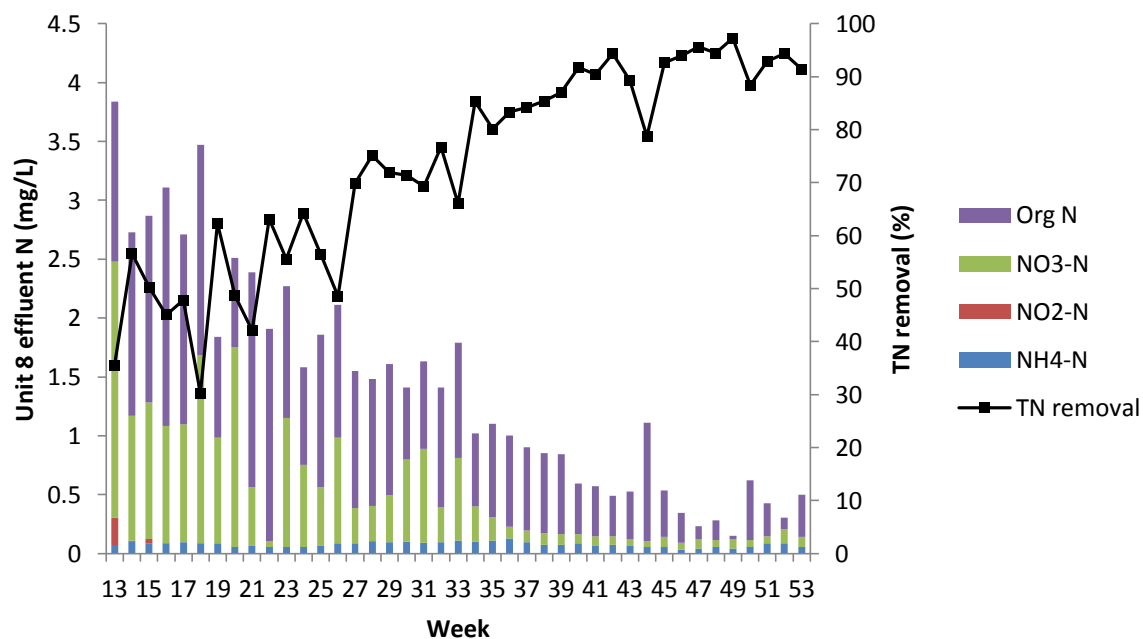


Figure 5-21 - Pollutograph showing N composition of unit 8 (BFS, 2.5% WWAR, WC) effluent

The initial effluent concentrations of the CWs were relatively similar. The mean TN removal efficiencies over the first 10 weeks of data recording were 45% (unit 1) and 51% (unit 4) for the loamy sand CWs, 45% for the gravel unit and 48% for the BFS

CW. There was therefore no obvious advantage to the use of any of the media types over the others during this start-up period.

As time passed it there was an improvement in the loamy sand and BFS CWs that was not being matched by the gravel CW. The mean TN removal efficiencies over the final 10 weeks of data recording were 94% (unit 1) and 94% (unit 4) for the loamy sand CWs, 62% for the gravel unit and 93% for the BFS CW. So the loamy sand and BFS units reached a very similar standard of removal, but the gravel CW clearly performs less effectively.

5.6.1.2. Phosphorus

Mean removal efficiencies in Table 5-5 give some indication of $\text{PO}_4\text{-P}$ removal between different media, with loamy sand outperforming gravel and BFS on average. Single factor ANOVA test results also highlight the significant differences in $\text{PO}_4\text{-P}$ removal efficiency between the loamy sand CWs and the gravel and BFS CWs (see Table 5-2).

There was an improvement in $\text{PO}_4\text{-P}$ removal over time in the loamy sand CWs, with a particularly notable increase in removal efficiency between weeks 33 and 42, as can be seen in Figure 5-22.

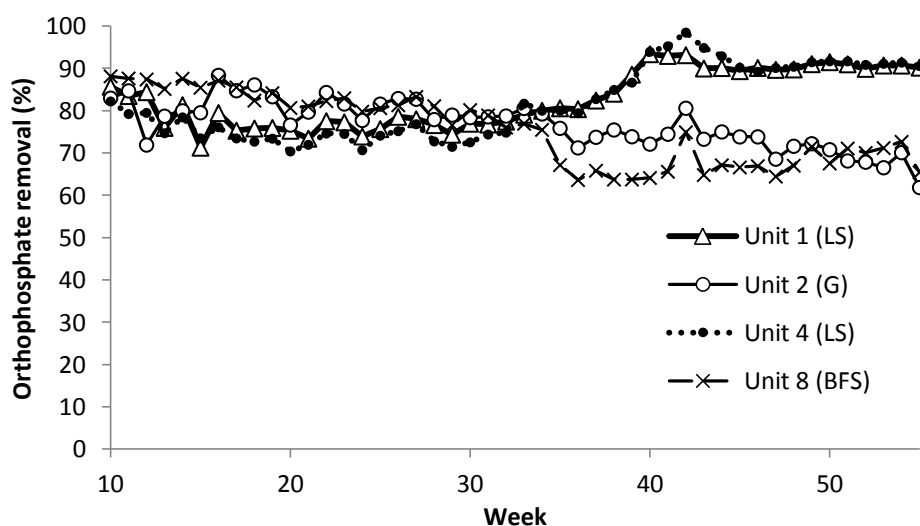


Figure 5-22 - $\text{PO}_4\text{-P}$ removal efficiencies over time for units 1, 2, 4 and 8

5.6.2. Effect of change in wetland-watershed area ratio on nutrient removal

5.6.2.1. Nitrogen

TN removal improved in all four WWAR CWs over the duration of the experiment. Since removal increased over time, the mean removal values in Table 5-5 are not very representative of the behaviour of the systems with regards to N.

Figure 5-17 shows the pollutograph of the influent N composition, and figures 5-19, 5-21, 5-24 and 5-25 show the corresponding effluent N composition pollutographs of the four CWs. The pollutographs show the change in TN concentrations and also the change in N composition from influent to effluent. It is apparent that there is an increasing TN removal efficiency as the units mature over time.

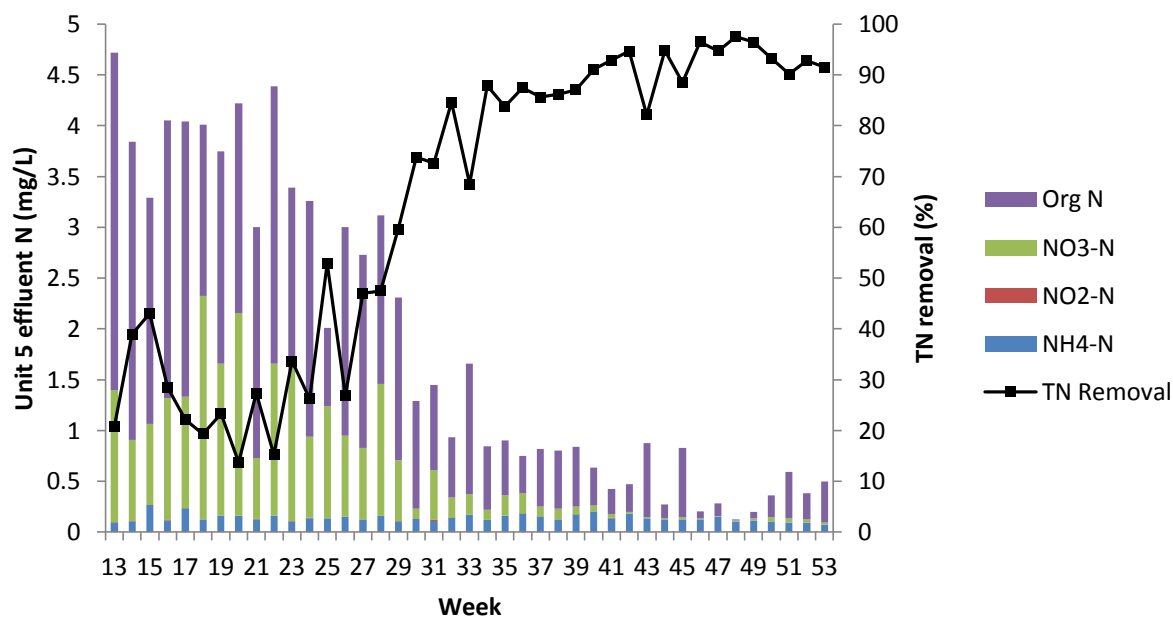


Figure 5-23 - Pollutograph showing N composition of unit 5 (5% WWAR, loamy sand, WC) effluent

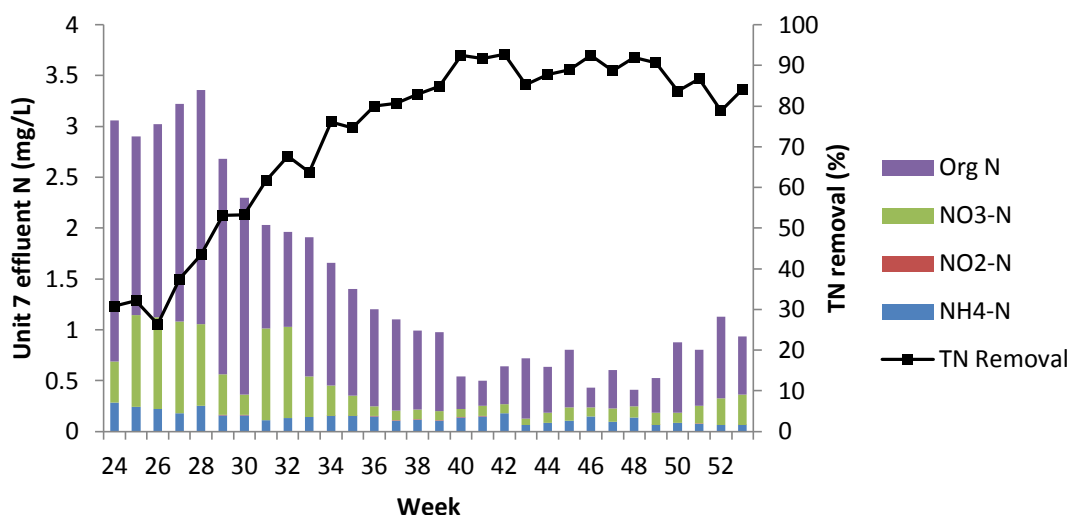


Figure 5-24 - Pollutograph showing N composition of unit 7 (1.5% WWAR, loamy sand, WC) effluent

The mean removal efficiencies from the final 10 weeks of data recording were 94% for both 2.5% WWAR CWs and the 5% WWAR CW, and 84% for the 1.5% WWAR. Thus it would appear that the 2.5% WWAR and 5% WWARs outperform the 1.5% WWAR CW by 10% removal efficiency. However, it should be noted that the 1.5% WWAR CW had not been in operation as long as the other CWs, due to unforeseen operational difficulties delaying the commissioning of the CW until week 24 of the experiment. Despite this, the CW was not at a disadvantage in comparison to the 5% WWAR CW, as the 1.5% WWAR CW's first TN removal efficiency reading was actually higher than the corresponding 5% WWAR CW result. However, this does not mean that the development of the biological community in the 1.5% WWAR CW was more advanced than in the 5% WWAR. Unfortunately, due to time restrictions, it was not possible to extend the running time to determine whether the 1.5% WWAR CW would eventually match the N removal performance of the other three systems. Single factor ANOVA tests found no significant difference in TN removal efficiencies between the three WWAR configurations, which suggests that WWAR did not significantly affect TN removal.

5.6.2.2. Phosphorus

Mean removal efficiencies in Table 5-5 give some indication of $\text{PO}_4\text{-P}$ removal between different WWAR values, with the 5% WWAR performing best on average. Single factor ANOVA tests identified significant differences in $\text{PO}_4\text{-P}$ removal

efficiency between the 5% WWAR CW and both other CWs, whereas no significant difference was found between the 2.5% and 5% WWAR CWs (see Table 5-3). To characterise these differences, it is necessary to examine how removal performances changed over time. All four CWs improved over time in terms of PO₄-P removal, with a particularly notable increase in removal efficiency for the 1.5% and 2.5% WWAR CWs between weeks 33 and 42, as can be seen in Figure 5-25. The performance of the 5% WWAR CW was more constant, performing at a high level (88% mean removal efficiency \pm 3% standard deviation) throughout the experiment. The 5% WWAR CW was not only the highest performer over the length of the experiment (see Table 5-5), but also during the final 10 weeks, achieving a mean PO₄-P removal efficiency of 92% in this period.

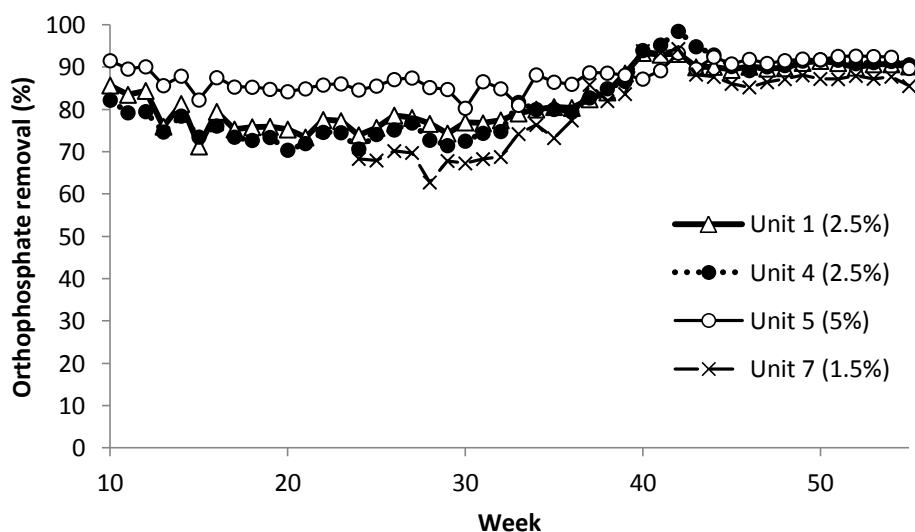


Figure 5-25 - PO₄-P removal efficiencies over time for units 1, 4, 5 and 7

The improvement undergone by the 1.5% WWAR CW did not match that of the 2.5% WWAR CWs. Despite relatively similar mean removal efficiencies from the whole duration of the experiment, effluent concentration values from the final 10 weeks of data recording show that the 1.5% WWAR CW could not reduce PO₄-P to the same level as the 2.5% WWAR CWs at the end of the project. In this 10 week period, the 1.5% WWAR CW was producing a mean PO₄-P effluent concentration of 0.12 mg/L, whereas both 2.5% WWAR CWs produced mean concentrations of 0.09 mg/L.

5.6.3. Effect of drying on nutrient removal

5.6.3.1. Nitrogen

TN removal improved in all four CWs. Since removal increased over time, the mean removal values in Table 5-5 are not entirely representative of the performance of the systems, although the order of relative performances between systems is correct (i.e., the WC CWs were the strongest performers and the EDC CW was the poorest performer). Single factor ANOVA tests found that there was no significant difference between the TN removal efficiencies produced by the three wetting/drying regimes.

Figure 5-17 shows the pollutograph of the influent N composition, and Figure 5-18, Figure 5-20, Figure 5-26, and Figure 5-27, show the corresponding effluent N composition pollutographs of the four CWs. The pollutographs show the change in TN concentrations and also the change in N composition from influent to effluent. It is apparent that there is an increasing TN removal efficiency as the units mature over time.

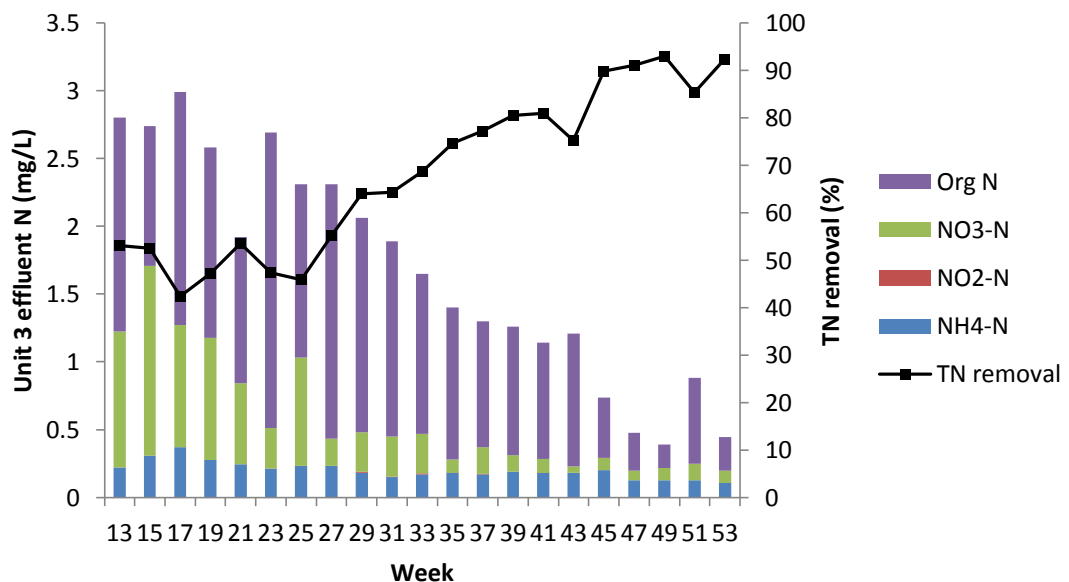


Figure 5-26 - Pollutograph showing N composition in unit 3 (PDC, loamy sand, 2.5% WWAR) effluent

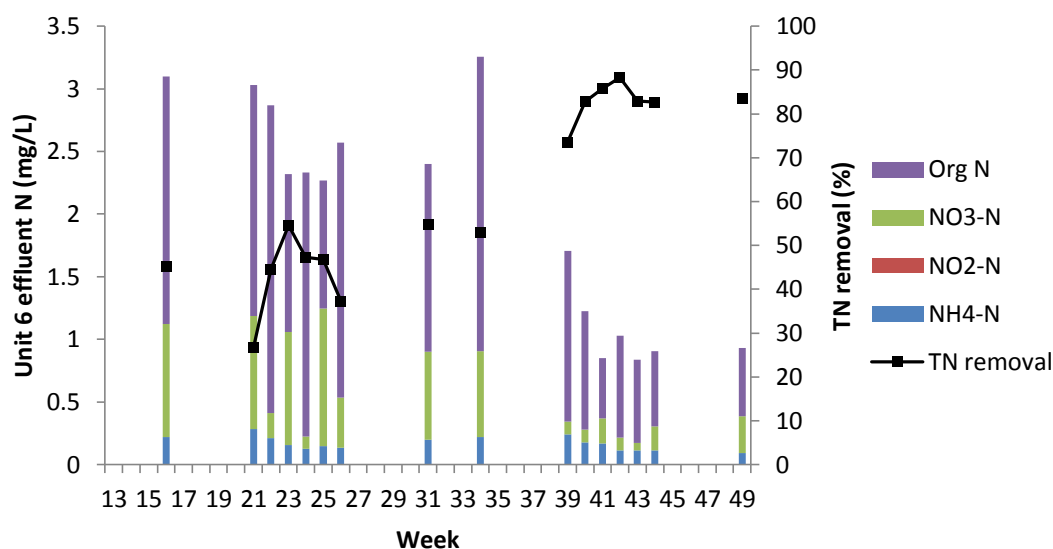


Figure 5-27 - Pollutograph showing N composition in unit 6 (EDC, loamy sand, 2.5% WWAR)

The mean TN removal efficiencies from the final 10 weeks of data recording were 94% for both WC CWs, 89% for the PDC CW and, and 80% for the EDC CW. Examination of the mean effluent NO₃-N concentrations for the final 10 weeks of data recording shows that significantly more NO₃-N was present in the EDC CW outflow (0.24 mg/L) compared to the PDC (0.09 mg/L) and WC CWs (0.05 mg/L and 0.04 mg/L for units 1 and 4, respectively). There was also significantly more organic nitrogen remaining in the EDC effluent (0.57 mg/L) compared to the PDC (0.36 mg/L) and WC CWs (0.24 mg/L for both units).

5.6.3.2. Phosphorus

Mean removal efficiencies in Table 5-5 give some indication of PO₄-P removal between different drying regimes (the EDC CW performing best on average) but there were changes in removal performances over time.

Single factor ANOVA tests found that there were no significant differences in PO₄-P removal efficiency caused by a change in wetting/drying regime. Figure 5-28 shows how closely matched the CWs were in terms of PO₄-P removal, particularly at the end of the experiment.

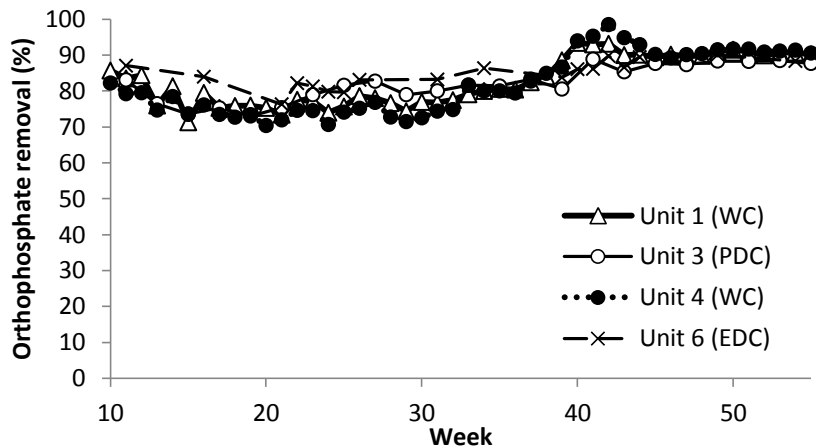


Figure 5-28 - PO₄-P removal efficiencies over time for units 1, 3, 4 and 6

5.6.4. Discussion – Nutrient removal

5.6.4.1. Nitrogen

The reason for the use of a tidal-flow regime in this experiment was to improve the denitrification ability of a VF CW system. At first, it seemed that denitrification was either unsuccessful or limited (due to the increased NO₃-N concentrations in the outflow), but the systems matured over time and NO₃-N effluent concentrations decreased, suggesting that the denitrification capabilities of the systems improved.

The variables investigated did not provide any alternative removal mechanism pathways for N, but they did affect how long it took for the systems to mature and hence affected the long-term reduction rates of N. There was therefore no obvious advantage to the use of any of the media types over the others during this start-up period (when NO₃-N removal was negative in all units). This would suggest that the differing physical properties of the CW media did not affect N removal at this stage, supporting the theory that biological removal was the main mechanism for N reduction in the CWs. As time passed it became obvious that there was an improvement in the loamy sand and BFS CWs that was not being matched by the gravel CW. Nitrification has been successful in the gravel unit (since NO₃-N concentrations have increased from influent to effluent), but denitrification is limited in comparison to the other CWs. It is no surprise that nitrification has been successful, as the granular nature of the gravel allows more air to enter the CW via

the larger pore space in the media. Overall, the gravel CW did not achieve any reduction in NO₃-N effluent concentrations over time, which suggests that the CW was unable to provide the anoxic conditions required for denitrification processes.

No significant conclusions can be drawn on the fact that the 1.5% WWAR CW produced poorer results in comparison to the other CWs since it was not running for the same length of time as them. Thus, they did not have equal lengths of time to mature. Single factor ANOVA tests found no significant difference in TN removal efficiencies between the three WWAR configurations, which suggests that WWAR did not significantly affect TN removal.

Taking a general view of the N removal patterns across all 8 CW units helps to understand the internal CW processes. Organic N was successfully reduced in the CWs, with removal efficiencies increasing over time. Taking unit 1 (see Figure 5-18) as an example: the average removal rate of organic N increased from 49% over the first 10 weeks of data recording to 95% over the final 10 weeks. Ammonification is the process by which organic N is mineralised and biologically transformed to NH₄-N. Thus, the ammonification capabilities of the CWs improved over time. Ammonification can occur under both aerobic and anaerobic conditions (Reddy and Patrick, 1984), so it was expected that the pilot-scale CWs would successfully reduce organic N concentrations. The organisms thought to be involved in ammonification are heterotrophic (U.S. EPA, 1993), stripping carbon from the organic N.

The improvement in organic N removal over time may be attributed to the increasing biological communities establishing themselves within the CWs as they mature. Thus, there is an increasing availability of heterotrophic microorganisms which increase the organic nitrogen removal efficiency. The increase in biological activity in the CWs benefits both ammonification and denitrification simultaneously (facultative heterotrophs also perform denitrification). This would explain the results from the wetting/drying regime tests, in which the main influence of drying conditions on nutrient removal is regarding the development of the biological communities in the pilot-scale CWs. Longer dry periods reduce the growth rate (due to decreased influent organic material), which causes less ammonification and

denitrification, thus contributing to a lower TN removal efficiency in comparison to systems experiencing more regular wet conditions.

Nitrification is the process by which $\text{NH}_4\text{-N}$ is converted to oxidised N. It is described by van de Graaf *et al.* (1996) as the biological formation of nitrate or nitrite from compounds which contain reduced nitrogen with oxygen as the terminal electron acceptor. Successful nitrification was indicated by the successful and consistent removal of $\text{NH}_4\text{-N}$ along with the increase in $\text{NO}_3\text{-N}$ concentrations from influent to effluent. This was expected prior to the beginning of the experiment, due to the tidal-flow dosing regime of the VF CW, which allows for good entry of air into the system between doses. This provides oxygen to the bed media ready to nitrify the $\text{NH}_4\text{-N}$ concentration present in the next dose.

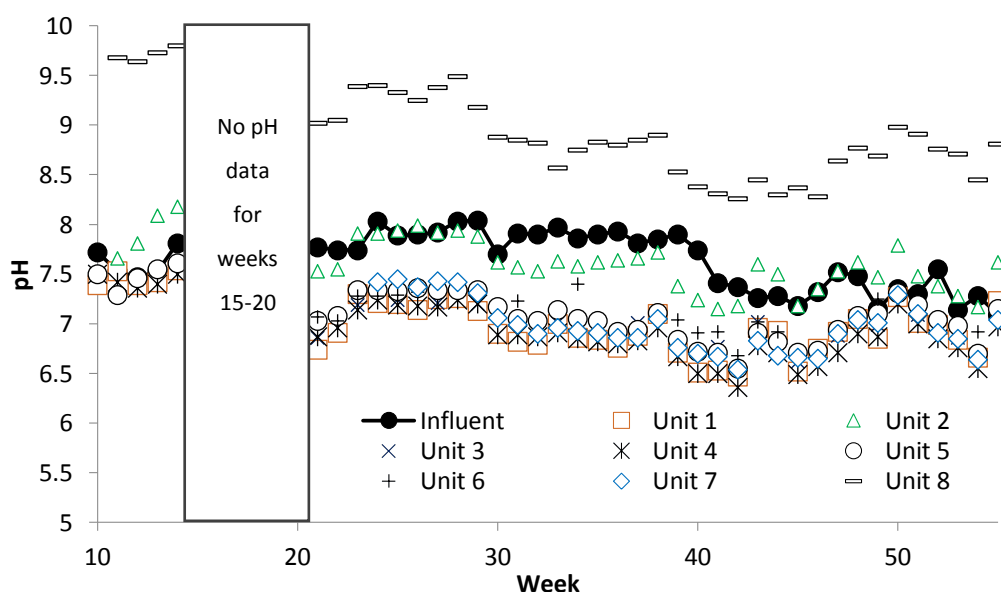


Figure 5-29 - pH values of influent stormwater and effluent from each unit

The oxygen supplied to the system is a key factor in the conversion of $\text{NO}_2\text{-N}$ to $\text{NO}_3\text{-N}$ during the nitrification process. The fact that $\text{NO}_2\text{-N}$ concentrations were consistently below detection limits suggests (in conjunction with results for $\text{NO}_3\text{-N}$) that the CWs were also effective in the secondary nitrification process, i.e., $\text{NO}_2\text{-N}$ was formed by oxidation of $\text{NH}_4\text{-N}$, but then oxidised further to $\text{NO}_3\text{-N}$, thus resulting in the detection of effluent $\text{NO}_3\text{-N}$ but not $\text{NO}_2\text{-N}$. Another potential indicator of the successful nitrification process is the reduction of pH in the majority

of the CWs (see Figure 5-30). When oxidation of $\text{NH}_4\text{-N}$ occurs, H^+ ions are produced, causing a decrease in pH (Lee *et al.*, 2009). The reason that this is not observable in the unit 8 effluent is probably due to the BFS media, which causes a highly alkaline effluent, despite the nitrification occurring.

The $\text{NH}_4\text{-N}$ concentrations remaining in the effluent may indicate that the systems do not have the ability to nitrify all the incoming $\text{NH}_4\text{-N}$. However, another contribution to the presence in the outflow may be due to the release of cell-bound nitrogen (NH_4^+) from bacteria that die while the CWs are drying out between doses (Scholz *et al.*, 2002).

The increase in $\text{NO}_3\text{-N}$ concentrations from inflow to outflow (along with the decrease in $\text{NH}_4\text{-N}$ concentrations and lack of $\text{NO}_2\text{-N}$ concentrations in the outflow) shows that the nitrification process has been very effective in the pilot-scale CWs.

As the systems mature over time, the growth of the biological community within the CWs is the likely reason behind the improvement in denitrification. Facultative heterotrophs perform denitrification: organisms that can use either nitrate or oxygen as terminal electron acceptors (Kadlec and Wallace, 2009). Thus, as the biological community increases there is a greater availability of facultative heterotrophs for denitrification. The growth of biofilm in the CW over time provides more anoxic zones in the inner biofilm layer where a high resistance to oxygen diffusion allows the heterotrophs to survive (Hu *et al.*, 2014).

The influence of the increasing biological activity in the systems can be observed in the results for the organic N and $\text{NO}_3\text{-N}$ removal, both of which improve over time. When organic N is ammonified it leaves a carbon molecule (Kadlec and Wallace, 2009). Carbon is a requirement for the denitrification process (Reddy and Patrick, 1984), so this molecule can now be used in the final phase of N reduction.

By the end of the experiment effluent $\text{NO}_3\text{-N}$ concentrations were extremely low for most loamy sand units and the BFS CW. For example, the last 10 weeks of data recording saw an average effluent concentration of 0.05 mg/L in unit 1, comparing favourably to other pilot-scale VF CWs which do not use a tidal-flow hydraulic regime (e.g., Blecken *et al.*, 2010; Bratieres *et al.*, 2008).

5.6.4.2. Phosphorus

Dissolved forms of P can be removed from stormwater by a range of mechanisms including plant uptake, sorption to substrate media, precipitation and microbial uptake (U.S. EPA, 2000b; Shenker *et al.*, 2005). Microbial uptake was not measured in the pilot-scale CWs. Plant uptake was unlikely to have had a strong contribution to the granulated media (gravel and BFS) CWs, as the plants struggled to establish themselves in these systems. This was apparent from visual observations, as the plants did not grow any larger than their original planting sizes, and lost their green colour and decreased in size over time. The plants established well in the loamy sand units, but died during the winter. Despite this, the PO₄-P removal efficiencies continued to improve, which suggests that one or more other removal mechanisms were dominant.

Adsorption of PO₄-P in CWs is usually associated with acidic conditions and the presence of oxyhydroxides of Fe and Al (Reddy and D'Angelo, 1997). None of the CWs exhibited acidic conditions over the duration of the experiment, and the Fe content of the loamy sand and BFS was low (4% and 2%, respectively). The BFS contained a considerable percentage of Al in its elemental composition (17%), but the alkaline conditions exhibited in the BFS CW makes it highly unlikely that PO₄-P was adsorbed to Al in that unit. It was therefore considered that adsorption was not a major P removal mechanism in the pilot-scale CWs.

The presence of calcium (Ca) in the CW media may have been a key factor in PO₄-P removal. The Ca contents of the loamy sand and BFS were high with respect to the content of other elements, at 27% and 24% respectively (see chapter 4 for details). Reddy and D'Angelo (1997) state two potential pathways of P removal, based on the type of soil in the CW. They state firstly that, in soils mainly formed of iron oxides, P can be readily immobilised via sorption and precipitation with ferric oxyhydroxide, and formation of ferric phosphate in the oxidised zones of the soil-water interface. They state secondly that, in calcareous CWs (such as the LS and BFS units), P can be precipitated as Ca mineral-bound phosphorus. This would suggest that, since the substrate media in the pilot-scale CWs features a large percentage of Ca, that precipitation is a dominant PO₄-P removal mechanism. Richardson and Craft (1993)

state that precipitation as insoluble Ca-phosphates is the dominant P transformation in CW soils at pH greater than 7. Mean effluent pH values for the loamy sand CWs were 7.0 for units 1, 3, 4 and 7 and 7.1 for units 5 and 6. The mean pH values of the gravel CW and BFS CW effluent were 7.6 and 8.9, while mean influent pH was 7.7. Thus, the high availability of Ca and the pH conditions suggest that chemical precipitation of $\text{PO}_4\text{-P}$ with Ca ions is a dominant removal mechanism in the pilot-scale CWs.

This theory is backed up by the decrease in $\text{PO}_4\text{-P}$ removal performance of the BFS CWs over time. A decrease in pH over time was also observed in the effluent of the BFS CW effluent (this corresponded with a decrease in influent pH over time), and a negative correlation between effluent $\text{PO}_4\text{-P}$ and pH was identified ($R = -0.84$). Figure 5-30 shows the similarity in behaviour between these two components (unfortunately, effluent pH data was unavailable from weeks 15 to 20). The high pH conditions produced by the use of BFS, along with its high Ca content (24%, see chapter 4), enhances soluble P precipitation processes (particularly at pH above 9.0 – Kadlec and Wallace, 2009). Therefore, a decreasing pH over time may have resulted in decreasing precipitation of $\text{PO}_4\text{-P}$, thus increasing effluent concentrations.

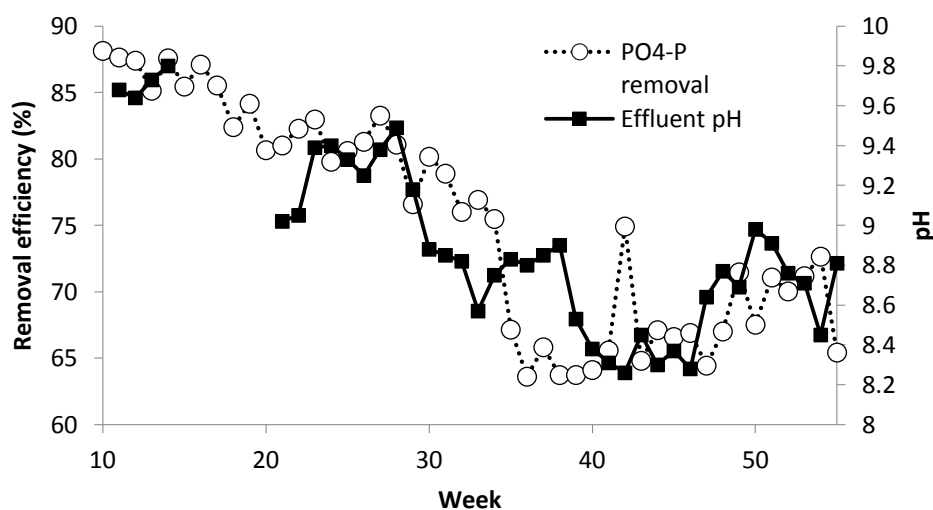


Figure 5-30 – $\text{PO}_4\text{-P}$ removal efficiency and effluent pH over time in unit 8 (BFS)

The only significant conclusions that can be drawn from the investigation of the effect of WWAR on nutrient removal are both regarding P reduction. These are: the

increased level of consistency offered by the high-performing 5% WWAR CW; and the reduced level of improvement over time of the 1.5% WWAR CW. Bratieres *et al.* (2008) also found that larger WWAR values produced better P removal. They proposed that, because the volume of flow through the larger surface area system (in this case the 5% WWAR CW) is smaller than the other CWs, a larger proportion of the water being washed through in any one dose is made up of water that had been retained in the CW soil from the dose before. Therefore, this water will have had a longer retention time, which may have enhanced P reduction. In this case, a larger proportion of the outflow will have received additional P reduction in comparison to the other CWs, thus reducing its overall P concentration.

Drying was not found to significantly affect P removal.

5.7. Summary

Table 5-6 shows the selection of the best performing variable for each different category of pollutant removal: TSS, heavy metals and nutrients. Where a dash is present, this indicates that there was no significant advantage found by using one particular configuration/set of operating conditions.

It is evident from the comparison of CW media that gravel is the least desirable option, as it is outperformed in both metal and nutrient removal (particularly the latter), and offers no significant advantage in terms of TSS removal. BFS was the ideal choice for TSS removal because there was no “settling period” associated with it, and it produced high TSS removal efficiency results from the beginning and throughout the experiment. Loamy sand is the best performer in terms of nutrient removal due to its advanced biological activity. However, this also appeared to lead to a release of DOM which caused a temporary increase in Zn effluent concentrations during warm temperatures. This effect was not experienced by the BFS and it effectively and consistently removed metals throughout the experiment. It should be emphasised at this point that both the loamy sand and BFS CWs performed well overall, and therefore the choice of media when designing a stormwater CW should be tailored to the pollutant which is considered to be of

greater threat in the target catchment, i.e., a BFS CW is more reliable for heavy metal removal, whereas a loamy sand CW will produce higher nutrient removal.

Table 5-6 - Best performing variable for each category of pollutant removal

	Media	WWAR	Wetting/drying regime
TSS removal	BFS	1.5% WWAR	-
Heavy metal removal	BFS	(1.5% WWAR)	PDC and EDC
Nutrient removal	Loamy sand	5% WWAR	WC

The comparatively higher performance of the 1.5% WWAR at heavy metals removal should be taken with caution, as it is believed that the reduced release of Zn may have been due its shorter life span and hence its reduced maturation compared to the other CWs. However, its TSS removal was the most successful, likely due to the quicker aggregation of solids in the system due to higher inflow volumes. Meanwhile, the 5% WWAR CW was the best performer in terms of P reduction. However, by the time all CWs had matured, the difference in removal performance in terms of both TSS and P reduction was not significant, so it can be said that all WWAR values tested in this project are viable options for CW design.

The release of dissolved Zn experienced during the summertime in loamy sand CWs was not experienced in the CWs that underwent drying regimes. Therefore, their overall Zn removal was superior to the WC CWs. However, it was found that drier conditions caused N removal to suffer. Thus, drying negatively affects the nitrogen removal performance of this CW design. But it should be noted that a good standard of N removal was still achieved in the EDC CW, and that its drought periods were quite extreme, much drier than would be expected in a real-life situation over this length of time. Therefore, it can be said that this CW design performs relatively well under dry periods and theoretically should be able to deal with periods of drought without a great negative impact on performance.

In conclusion, based on the results presented in this chapter, the most effective configuration of the pilot-scale systems for pollutant removal is a BFS CW that

receives regular inflow (wet conditions). The effect of the WWAR value was found to be of little importance overall.

6. Mechanistic Modelling Using HYDRUS CW2D

6.1. Introduction

This chapter focuses on the application of a numerical model for analysis of the constructed wetland systems. Black-box empirical models are often used to simulate CW systems of this type, but their validity is restricted to the values to which they have been calibrated for, and they cannot be used to investigate alternative events (Fournel *et al.*, 2013). Mechanistic models allow further investigation with alternative variables to occur, and also offer the benefit of allowing the determination of key CW components and processes that influence the model output. This is particularly relevant to the pilot-scale experiment in this project, since an understanding of the internal processes of the CWs is difficult to gain simply from influent and effluent data. Thus, this chapter details the application of a mechanistic model for analysis of the pilot-scale CWs with the aid of the HYDRUS CW2D wetland module. The main aims were:

- To test and validate a numerical model of the constructed wetland systems with emphasis on nutrient prediction
- To further the mechanistic understanding of the processes responsible for nutrient transformations in the CW and to aid future design by identifying the key parameters
- To investigate the effect of alternative variables that were not studied in the main experiment, using the numerical model

To the author's knowledge, since this type of CW operating regime has not been applied for stormwater treatment before, HYDRUS has not been used to model this type of system before either. This was reflected in the problem faced that HYDRUS is unable to simulate the fill and drain nature of the CW dosing regime in a single model, due to its inability to change boundary conditions over time. This part of the modelling was therefore approached manually, as explained in section 6.3.5.2. A further problem that had to be overcome was obtaining accurate soil hydraulic parameters for input to the numerical model without disrupting the pilot-scale CWs,

which were still running while the work of this chapter was being undertaken. This was achieved through a combination of careful sampling procedures and the construction of a small replica CW which was subjected to pre-conditioning in order to simulate the soil conditions of the pilot-scale CWs accurately, as described in section 6.3.3.

6.2. HYDRUS

The software selected to develop the numerical model was HYDRUS 2D. HYDRUS is a software package that is capable of simulating water, heat and solute transport in variably-saturated porous media. The package uses computational finite element models to simulate two-dimensional flow movement. The program numerically solves the Richards equation for saturated-unsaturated water flow and convection-dispersion type equations for heat and solute transport. HYDRUS was originally developed and released by the U.S. Salinity Laboratory in co-operation with the University of California Riverside, the International Groundwater Modeling Center (IGWMC), and PC-Progress Inc. HYDRUS was selected because of its ability to simulate variably-saturated media, its parameter optimisation algorithm for inverse estimation of soil hydraulic properties and, importantly, because of the availability of a special wetlands add-on module (CW2D), which allows for the simulation of aerobic and anoxic transformation processes for organic matter, nitrogen and phosphorus.

The water flow and solute transport capabilities of HYDRUS were utilised for this project and the governing equations through which the program carries out the modelling processes are described in the following sections, along with descriptions of the numerical analysis techniques adopted by HYDRUS and the components and processes of the CW2D module.

6.2.1. Water transport in HYDRUS

The governing equation for transient variably saturated flow used in the CW2D module is based on the modified Richards equation (Equation 6.1), which assumes isothermal uniform Darcian flow through rigid porous media, with insignificant influence from the air phase of the liquid flow.

$$\frac{\partial \theta(h)}{\partial t} = \frac{\partial}{\partial x_i} \left[K(h) \left(K_{ij}^A \frac{\partial h}{\partial x_j} + K_{iz}^A \right) \right] - S \quad (6.1)$$

where: $\theta(h)$ = Volumetric water content or soil water retention (L^3/L^3)

h = Pressure head (L)

S = Source/sink term (L^3/T)

x_i = Spatial coordinates ($i = 1,2$), (L)

K_{ij}^A = Components of the dimensionless anisotropy tensor K^A . For an

isotropic medium the diagonal elements of K_{ij}^A are one and the off-diagonal elements are zero.

t = Time (T)

$K(h)$ = Unsaturated hydraulic conductivity function (L/T)

L = Length unit after preference

T = Time unit after preference

HYDRUS uses van Genuchten's analytical models (1980) to calculate the unsaturated soil hydraulic properties $\theta(h)$ and $K(h)$ for Equation 6.1. These are shown in Equations 6.2 and 6.3.

$$\theta(h) = \begin{cases} \theta_r + \frac{\theta_s - \theta_r}{[1 + |\alpha h|^n]^m}, & h < 0 \\ \theta_s, & h \geq 0 \end{cases} \quad (6.2)$$

$$K(h) = K_s S_e^l \left[1 - \left(1 - S_e^{\frac{1}{m}} \right)^m \right]^2 \quad (6.3)$$

where:

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} \quad (6.4)$$

$$m = 1 - \frac{1}{n}, \quad n > 1 \quad (6.5)$$

K_s = saturated hydraulic conductivity. The following parameters are the van Genuchten (1980) parameters:

θ_r = Residual water content (L^3/L^3)

θ_s = Saturated water content (L^3/L^3)

α = Inverse of air-entry value or bubbling pressure (L^{-1})

n = Pore size distribution index

l = Pore connectivity parameter

6.2.2. Solute transport in HYDRUS

Solute transport in the HYDRUS CW2D model is based on the theory that the internal processes are similar to that of an activated sludge reactor. Thus, the mathematical structure of the CW2D multi-component solute transport model is based on the structure of activated sludge models proposed by Henze et al. (2000). Solute transport is described using the advection-dispersion equation (Equation 6.6), assuming constant pH, constant coefficients in the rate equations and constant stoichiometric factors.

$$\frac{\partial \theta}{\partial t} c_i + \frac{\partial \rho}{\partial t} s_i = \nabla(\theta D_i \nabla c_i) - \nabla(q c_i) + S c_{S,i} + r_i \quad (6.6)$$

where: $i = 1, 2, 3, \dots$ etc: No. of components

c_i = Concentration in the liquid phase (M/L^3)

s_i = Concentration in the solid phase (M/M)

ρ = Soil bulk density (M/L^3)

D_i = Effect dispersion tensor (L^2)

q = Volumetric flux density (L^3/L^2T)

$c_{S,i}$ = Concentration of source/sink (M/L^3)

r_i = Reaction time (M/L^3T)

M = Mass unit after preference

6.2.3. Numerical solution to governing flow and solute equations

HYDRUS solves the governing water flow and solute transport equations (equations 6.1 and 6.6) numerically via Galerkin-type finite element techniques. Depending on the size of the problem and the type of matrix utilised from the discretisation of the governing equations, solutions are obtained through the use of either the Gaussian elimination method, the conjugate gradient method or the ORTHOMIN method (Mendoza *et al.*, 1991).

6.2.4. CW2D solute transport: components and processes

There are 12 components (pollutants and bacteria) and 9 processes (biochemical transformations and degradation processes) that can be simulated in the CW2D module. Tables 6-1 and 6-2 list the components and processes (respectively). Note that organic P and N are accounted for in the COD components.

Table 6-1 - Components simulated in CW2D multi-component solute transport

HYDRUS Code	Component (measured in mg/L)
<i>SO</i>	Dissolved oxygen (O ₂)
<i>CR</i>	Readily biodegradable soluble COD
<i>CS</i>	Slowly biodegradable soluble COD
<i>CI</i>	Inert soluble COD
<i>XH</i>	Heterotrophic bacteria
<i>PO4P</i>	Orthophosphate-phosphorus (PO ₄ -P)
<i>XANb</i>	Autotrophic nitrite oxidising bacteria (<i>Nitrobacter</i> spp)
<i>XANs</i>	Autotrophic ammonia oxidising bacteria (<i>Nitrosomonas</i> spp)
<i>NO2N</i>	Nitrite nitrogen (NO ₂ -N)
<i>NO3N</i>	Nitrate nitrogen (NO ₃ -N)
<i>N2</i>	Elemental nitrogen (N ₂)
<i>NH4N</i>	Ammonium nitrogen (NH ₄ -N)

Table 6-2 - Processes simulated in CW2D multi-component solute transport

1. Hydrolysis: conversion of <i>CS</i> into <i>CR</i>
2. Aerobic growth of <i>XH</i> on <i>CR</i> (mineralisation of organic matter)
3. Anoxic growth of <i>XH</i> on <i>CR</i> (denitrification of <i>NO₂N</i>)
4. Anoxic growth of <i>XH</i> on <i>CR</i> (denitrification of <i>NO₃N</i>)
5. Lysis of <i>XH</i>
6. Aerobic growth of <i>XANs</i> on <i>NH₄N</i> (ammonium oxidation)
7. Lysis of <i>XANs</i>
8. Aerobic growth of <i>XANb</i> on <i>NO₂N</i> (nitrite oxidation)
9. Lysis of <i>XANb</i>

6.3. Materials and Methods

6.3.1. Physical models

2 of the 8 pilot-scale CWs were selected as the physical models which would be simulated by HYDRUS. These units 1 and 4 and were chosen because they were the control units (with standard configuration) in the experiment. Further details on the dimensions, configuration, components and loading regimes of the systems can be found in chapter 3.

6.3.2. Initial modelling considerations

In order to model CWs to analyse nutrient behaviour, HYDRUS requires two sets of input data: hydraulic properties and solute transport parameters.

Hydraulic parameters include the inflow volume, inflow rate and hydraulic properties of the CW media. The media hydraulic properties were obtained by laboratory tests (hydraulic conductivity, saturated water content) and the use of the HYDRUS module Rosetta Lite, which uses pedotransfer functions based on neural networks to provide soil hydraulic property estimates from its soil library based on inputs of alternative, easier to measure properties obtained from further laboratory tests (particle size distribution, bulk density and moisture content).

Calibration of the hydraulic values was possible with the use of the HYDRUS inverse solution function, which uses a “black-box” approach to provide soil

hydraulic parameter values based on measured influent and effluent flow rates. This was achieved with the aid of a “mini CW”, a small-scale model of the pilot-scale CWs using the same primary media in order to accurately determine hydraulic properties. The mini CW was required to avoid interrupting the operation of the pilot-scale CWs, since this procedure required the inflow water to run straight through the CW to outflow without being retained for 24 hours. The influent and effluent flow rates to the mini CW were measured, and the mini CW was modelled in HYDRUS, where the inverse solution tool was applied. The calibrated hydraulic parameters were then transferred to the HYDRUS model of the pilot-scale CWs.

Solute transport parameters include the pollutant concentrations of the inflow semi-synthetic stormwater and the background concentrations of the same pollutants in the CW. The inflow solute concentrations were obtained from the measurements taken from each inflow dose of semi-synthetic stormwater, carried out over the length of the experiment. The background concentrations were established by running the HYDRUS model through a large number of iterations. The first iteration used arbitrary values for the background solute concentrations, and the dosing regime was applied through the iteration cycles (one configuration for dosing and retention and a separate configuration for drainage and “rest” period, see section 6.3.5.2) until the background concentrations stabilised after the model had been subjected to a long period of dosing.

6.3.3. Soil laboratory tests and mini CW

Two of the most important soil hydraulic parameters, saturated hydraulic conductivity (K_s) and saturated water content (θ_s), were obtained from laboratory tests carried out on the loamy sand. Further laboratory tests were carried out to obtain input parameters for Rosetta Lite, which in turn provided estimated values for the rest of the soil hydraulic parameters. Calibration of soil properties in HYDRUS required accurate influent and effluent flow rates, which were also measured in the laboratory with the use of a specially constructed “mini CW”, described in section 6.3.3.1.



Figure 6-1- Extraction of soil samples from pilot-scale CWs

In-situ samples of the loamy sand from units 1 and 4 were extracted using a “category A” sampling method as outlined in BS EN ISO 22475-1:2006. This ensured minimal disturbance of the soil structure during sampling and handling. A thin-walled open-tube sampler was used, in accordance with section 6.4.2.3 of BS EN ISO 22475-1:2006. Initial observations indicated the accumulation of organic matter on the CW surfaces. Thus, the top 50 mm of top soil was removed prior to sample extraction. All handling, transport and storage of samples was carried out in accordance with clause 11 in BS EN ISO 22475-1:2006.

The wet sieve method was used to determine the particle size distribution (PSD) of the loamy sand samples and also a sample of excess loamy sand which was left over from the construction of the pilot scale CWs (adhering to 9.1 in BS 1377-2:1990). Samples were prepared according to 7.3 and 7.4.5 in BS 1377-1:1990.

The “linear measurement method” was adopted to determine the bulk density (ρ) of the in-situ loamy sand samples, adhering to BS 1377-2:1990. This method introduces a risk of human error in the physical measurement of sampling tube dimensions (necessary to determine the dimensions of the soil sample), thus an uncertainty of ± 2 mm was applied. This uncertainty equates to an approximate error of ± 0.05 g/cm³ in the final values of ρ . A mean value from six readings was taken in order to minimise the effect of the error. The mean value was also taken due to natural variance in ρ within the pilot-scale CWs.

Water moisture content (w) values of the in-situ loamy sand samples were determined using pressure plates in accordance with ASTM C1699-09 (“Standard Test Method for Moisture Retention Curves of Porous Building Materials Using

Pressure Plates”). Water was added to the samples until their saturated water content was exceeded by 10%. They were then subjected to 33 kPa of pressure for several days until equilibrium mass was reached. The w value of each sample was then determined as described in clause 3 of BS 1377-2:1990.

The saturated hydraulic conductivity (K_s) value of the loamy sand was determined by undertaking a permeability test using the constant head method in accordance with clause 5 of BS 1377-5:1990. Since the volume of soil required for the test was too great to remove from the pilot-scale CWs, the test was carried out on a sample of the excess loamy sand that was left over from the construction of the CWs.

It should be noted that PSD analysis had found this soil to contain a greater percentage of fines in comparison to the in-situ soil; therefore, before the excess loamy sand sample was tested, it was subjected to a hydraulic loading regime of its own to wash away its finer particles. The aim was to give the excess soil sample a more similar PSD to that of the in-situ soil. Therefore, the sample was loaded until the effluent ran clear (judged visually). Furthermore, in order to ensure that the void ratio of the excess soil sample was reflective of the in-situ CW soil, calculations were carried out to determine the compaction required to ensure that the excess soil sample had the same bulk density as the in-situ CW soil.

The K_s value was calculated using 4 different flow rates and their respective hydraulic gradients. A mean value was then taken to increase the accuracy of the result.

In order to calculate the θ_s value of the loamy sand, the dry density (ρ_d) and average particle density (ρ_s) were required. ρ_d was calculated from ρ and w using Equation 6.7 (equation 2.2.17 of BS 1377-1:1990).

$$\rho_d = \frac{100\rho}{100+w} \quad (6.7)$$

ρ_s was determined via a small pycnometer test on a sample of the extracted in-situ CW soil (according to clause 8, BS 1377-5:1990).

Knowledge of ρ_d and ρ_s allowed for the calculation of the soil’s void ratio, e , by Equation 6.8 (equation 2.2.28 in BS 1377-1:1990).

$$e = \frac{\rho_s}{\rho p_d} - 1 \quad (6.8)$$

The void ratio was then used to calculate θ_s via Equation 6.9 (equation 2.2.31 in BS 1377-1:1990).

$$\frac{100 \times e}{\rho_s} = \theta_s \quad (6.9)$$

6.3.3.1. Mini CW flow rates

The mini CW was constructed from the same loamy sand used in the construction of the pilot-scale CWs. It was constructed in the soil laboratory using a hydraulic consolidation cell, as described in clause 5 of BS 1377-5:1990. The dimensions of the cell are shown in Figure 6-2. A 6 cm gravel drainage layer was included. A 2 mm mesh was also placed between the gravel and the loamy sand to act as a transition layer, preventing large particles from washing through the system. Experience dictated that both the gravel and the 2 mm mesh would have significantly higher permeability values than that of the loamy sand and thus they would not have a significant effect on the results of the flow test.

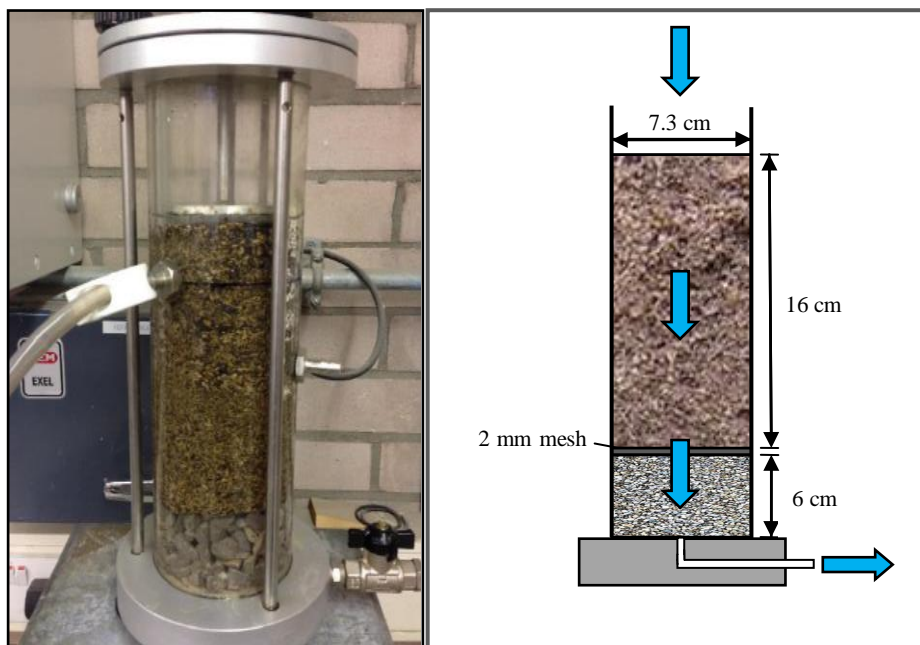


Figure 6-2 - Mini CW

The soil conditions of the in-situ pilot-scale CWs were replicated by compacting the loamy sand in the conductivity cell to the appropriate density (determined from the

results of the bulk density test). The mini CW was also subjected to a pre-testing loading regime in order to wash away finer particles contained in the loamy sand, so that its PSD was more similar to that of the in-situ loamy sand.

Three effluent flow rate tests were carried out on the mini CW in order to obtain a mean cumulative effluent flow graph for comparison to the results of the HYDRUS model. The top 6 cm of the consolidation cell contained no loamy sand, to allow for ponding of inflow. The mini CW inflow volume was calculated based on the maximum volume of water that the consolidation cell could hold during a dosing event without overflowing. This volume was found to be 0.25 L.

In each effluent flow rate test, 0.25 L of inflow was applied and cumulative effluent measurements were taken every 5 seconds.

Influent flow rate measurements were also carried out on the mini CW. The time between the application of the 0.25 L inflow dose and the complete drainage of the ponding volume into the mini CW media was measured. Three influent flow rate tests were carried out in order to achieve a mean value.

6.3.4. Influent pollutant concentrations

Influent pollutant concentration values of the semi-synthetic stormwater were measured throughout the experiment. These concentrations were thus available as input values for HYDRUS.

The CW2D module models 12 components in its solute transport equations. These are shown in Table 6-1. Values for all 12 components are required prior to running the model. Of the 12 components, $\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{PO}_4\text{-P}$ were measured in the pilot-scale CW experiment. The mean influent concentrations of $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$ and N_2 were < 0.002 mg/L, < 0.01 mg/L and 0 mg/L respectively, so the HYDRUS input parameters of *NO2N*, *NO3N* and *N2* were set as 0. Influent and effluent concentrations of $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ were consistently detectable and therefore provided weekly removal efficiencies, so these two parameters were the focus of the investigation.

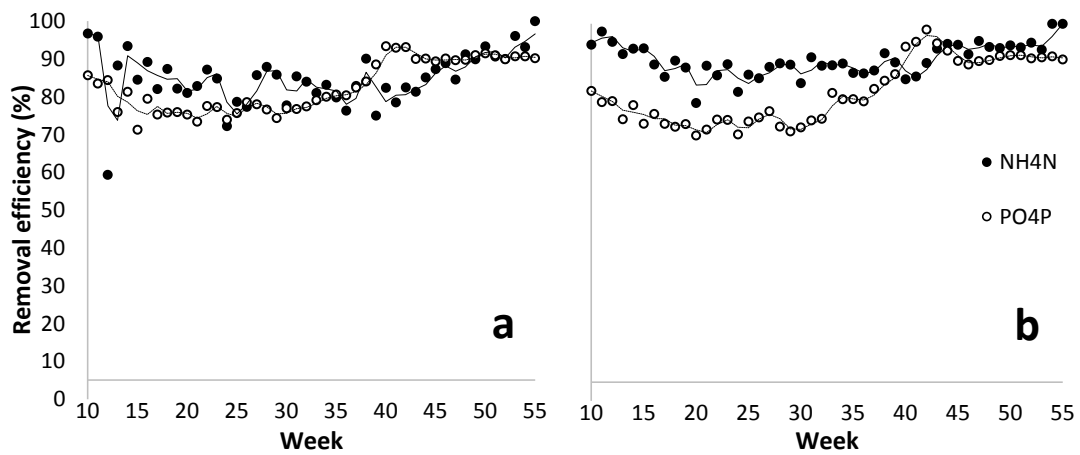


Figure 6-3 - Removal efficiency of NH₄-N and PO₄-P in pilot scale CWs 1 (a) and 4 (b)

Removal rates of NH₄-N and PO₄-P varied over the course of the experiment, but graphical analysis (see Figure 6-3) found that they appeared to stabilise between weeks 44 and 54, particularly in unit 4. Therefore it was decided that the NH₄-N and PO₄-P removal efficiencies obtained from the HYDRUS model would be validated against the removal efficiency values obtained from these 11 weeks, given in Table 6-3.

Table 6-3 - NH₄-N and PO₄-P removal rates in units 1 and 4 (weeks 44-54)

	NH ₄ -N		PO ₄ -P	
	Unit 1	Unit 4	Unit 1	Unit 4
Average influent (mg/L)	1.113		0.997	
Unit average removal rate (%)	89.97	94.01	90.36	91.02
Average removal rate (%)	91.99		90.69	

Concentrations of *SO*, *CR*, *CS*, *CI*, *XH*, *XANs* and *XANb* (see Table 6-1) were not recorded in the pilot-scale experiment. Influent concentrations of heterotrophic (*XH*) and autotrophic (*XANs* and *XANb*) bacteria were set to zero, as HYDRUS assumes that they are immobile. It is recommended to set the influent dissolved oxygen (*SO*) concentration to 1 mg/L (Simunek *et al.*, 2014) because dissolved oxygen levels quickly stabilise within the model to their saturated value of 9.08 mg/L.

Values for *CR*, *CS* and *CI* were estimated from literature. Ghunmi (2011) states that BOD_u (ultimate) can be assumed to equal total biodegradable soluble COD and,

therefore, equals the sum of *CS* and *CR*. Ghunmi also states that BOD_u can be determined by dividing BOD_5 by 0.7. Karlsson (2012) assumes that *CR* can be substituted for BOD_5 , *CS* can then be calculated if COD is known and also that *CI* can be calculated from subtracting *CR* and *CS* from total COD. Thus, according to the literature, influent *CR*, *CS* and *CI* can all be determined from COD and BOD_5 values. Since neither of these parameters were measured in the semi-synthetic stormwater, literature values were obtained from Duncan (1999). As detailed in chapter 3, this study is the most up-to-date extensive study of urban stormwater pollutant concentrations worldwide, and thus it was the most suitable reference for estimating these parameters. These values were then used to calculate the *CR*, *CS* and *CI* input values for HYDRUS.

The full list of CW2D solute transport components and the selected input values is shown in Table 6-4.

Table 6-4 - CW2D solute transport component input concentrations

Component	Input concentration (mg/L)
<i>SO</i>	1
<i>CR</i>	18
<i>CS</i>	7.714
<i>CI</i>	82.286
<i>XH</i>	0
<i>PO4P</i>	0.997
<i>XANb</i>	0
<i>XANs</i>	0
<i>NO2N</i>	0
<i>NO3N</i>	0
<i>N2</i>	0
<i>NH4N</i>	1.113

6.3.5. HYDRUS modelling

Modelling in HYDRUS was conducted in 3 stages. These were:

1. Simulation of the mini CW. Model calibration through the use of HYDRUS's inverse solution to estimate improved values of the loamy sand hydraulic properties.
2. Simulation of the pilot-scale CWs. Firstly hydraulically only, then with the addition of the CW2D wetland module to simulate nutrient ($\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$) removal efficiencies and validate against real data.
3. Use of the validated model to test further variables to determine their effect on removal rates.

6.3.5.1. Mini CW simulation

A 2D axisymmetrical vertical-flow loamy sand profile was constructed in HYDRUS to the dimensions of the mini CW (described in section 6.3.3.1). The model was run over a 24 hour simulation period. Water flow parameters were initially calculated by inserting the results of the PSD, bulk density and moisture content tests into Rosetta Lite, which gave input values for θ_r , θ_s , α , n , K_S and l . The Rosetta values for θ_s and K_S were then replaced with the values obtained from experiments to increase model accuracy.

The influent flow rate (as determined in section 6.3.3.1) was converted to a precipitation rate: 132.738 cm/hr applied over 2.7 minutes over the surface of the mini CW model. "Precipitation" in HYDRUS simply refers to the inflow on the surface of a soil profile, when that surface is set as an "atmospheric" boundary. Thus, the upper boundary of the mini CW profile was designated an "atmospheric" boundary condition; the vertical sides of the profile had "no flux" conditions; and the lower boundary was designated as "free drainage" to simulate the conditions of the mini CW.

Finite element mesh discretisation was set to 10 in the horizontal direction and 20 in the vertical direction. In order to account for the high-magnitude changes in water pressure that were expected at the top of the mini CW profile, a scaling factor distribution was applied to the model so that the vertical mesh discretisation was finer with increasing height. This can be seen in Figure 6-4. The mesh discretisation of 10x20 was deemed suitable to produce quality output while preventing extremely

long run times that would have been caused by further discretisation. A similar mesh arrangement was used for a much larger sized CW in a similar study by Langergaber and Simunek (2005), so the discretisation was deemed appropriate.

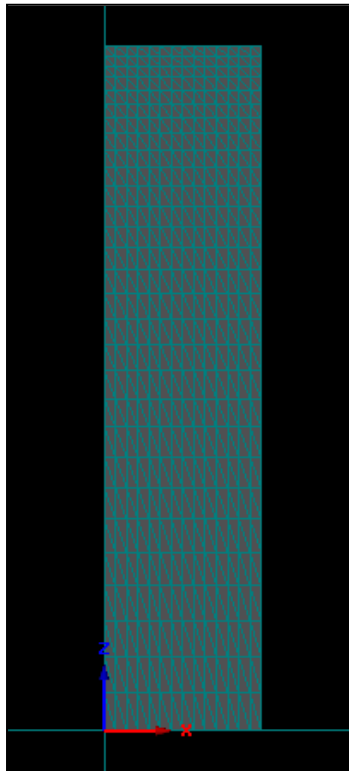


Figure 6-4 - Finite element mesh as displayed in HYDRUS

The initial water content was set to an arbitrary value of 8% in the model. The initial water content value specification is unimportant as it is merely a starting point, and the model adjusts the water content value when the inflow is applied. The model was run for a simulated time of 24 hours, with the inflow being applied at time $t = 0$. After the simulation, the final modelled water content values throughout the mini CW were saved and imported into a duplicate model as the initial water content values. This duplicate model was then run with the same flow parameters as the original and its final water conditions were saved and imported into a second duplicate model. The process was repeated until the model's initial water content had stabilised.

HYDRUS's inverse solution function was then used to calibrate the water flow parameters in the model. The data obtained from effluent flow rate measurements of

the mini CW (section 6.3.3.1) was used to calibrate the model. This was carried out stage by stage, first adjusting the van Genuchten parameter, l , then α and n , then θ_r and θ_s and then K_s .

6.3.5.2. Pilot-scale CW simulation

A 2D axisymmetrical vertical-flow loamy sand profile was constructed in HYDRUS to the dimensions of the pilot-scale CWs (dimensions described in chapter 3). Since HYDRUS does not have the capability to simulate a boundary condition that changes at a certain point in time (e.g., from “no flux” to “free drainage” to represent the opening of a tap after a certain period of time), two separate model configurations were required to adequately represent the pilot-scale CWs. In the first configuration (A), an “atmospheric” condition was applied to the upper boundary of the profile, while the lower boundary was given a “no flux” condition. In the second configuration (B) the lower boundary was assigned a “free drainage” condition. Thus, the configuration A was used to represent the dosing and retention period, and ran for a simulated time of 24 hours, while configuration B was used to simulate the release period and time between doses of 24 hours, in which time the physical CWs were left to drain. In order to simulate the pilot-scale CWs, configuration A was first run to simulate a dose and the 24-hour retention period, and then its final water content and solute concentration values were manually imported into a separate model running configuration B. Then the final values of the drainage period simulated by configuration B were imported into another configuration A model, to simulate the second dose. This cycle was carried out manually until the flow and solute transport results stabilised. This was an extremely time-consuming process due to the manual work required, but it was the only way in which to simulate the tidal flow dosing regime of the pilot-scale CWs.

Calibrated hydraulic properties of the loamy sand (as determined from the method in section 6.3.5.1) were applied to the pilot-scale CW. The 22.5 L inflow volume was simulated by applying an initial precipitation event of 132.738 cm/hr across the CW surface over 0.135 hours to model configuration A.

As with the mini CW, a 10 x 20 finite element mesh was applied to the model (both configurations), with discretisation finer towards the atmospheric boundary.

Preliminary simulations found problems with overflow errors, due to the fact that only the loamy sand layer of the pilot-scale CW was being modelled. In the physical models, the sand transition layer and the gravel drainage layer provided additional water retention capacity. Since these layers were not modelled in HYDRUS (due to the lack of supporting hydraulic data for each material), there was insufficient volume in the model to hold the full 22.5 L of inflow. A temporary “virtual” layer with estimated hydraulic parameters was created to solve this problem hydraulically, but it was discovered during the solute transport modelling that the virtual layer was not a sufficiently accurate representation of the sand and gravel used in the physical models. Time restrictions meant that it was unfeasible to carry out full analysis of the hydraulic parameters of the gravel and sand used in the physical models (as had been done for the loamy sand), so the decision was taken to remove the virtual layer from the HYDRUS model and reduce the inflow volume to 10 L. This then prevented the overflow error.

Initial water content conditions were determined by the same method as outlined in section 6.3.5.1. This same iterative process was used to establish the initial background solute concentrations in the model media. In the first iteration, the pollutant concentrations were set to the concentrations found in the semi-synthetic stormwater. Initial immobile heterotrophic and autotrophic bacteria concentrations were set to 1 mg/L as recommended in the HYDRUS User Manual (Simunek *et al.*, 2014).

6.3.5.3. Use of validated model to test further variables

Results of the validated HYDRUS simulation of the pilot-scale CW (see section 6.4.2.2) influenced the selection of which further variables to test using the model. It was found that, during the final 12 hours of retention, NH₄-N reduction was minimal. Results indicated that 92% NH₄-N removal was achieved in 24 hours, but that 80% removal may still be possible in half the retention time, potentially increasing the overall efficiency of the CW by enabling it to treat greater quantities

of stormwater in a given time period. Therefore the focus on further testing was placed on the potential reduction of treatment cycle time through reduced retention time and drainage time.

The two different retention periods investigated were 6 hours and 12 hours. Unfortunately, due to time restrictions, it was not possible to investigate any more retention times because of the excessive time required to manually carry out the model iterations. 6 hours was chosen as the results in 6.4.2.2 show that, after 6 hours, the majority of NH₄-N had been removed from the CW (86%). 12 hours was chosen as the results in 6.4.2.2 show that minimal further reduction in NH₄-N was observed in the final 12 hours of retention (>2%).

The new drainage time values were based on the cumulative effluent volumes of the 6-hour and 24-hour retention time models. It was deemed reasonable to assume that once 95% of the original inflow had drained from the CW then it would be able to receive a new load. Therefore, the new drainage times were the approximate time it took for 95% of the original inflow volume to drain from the model.

Initial water content and background solute concentration conditions were set as the final values obtained from the 24 hour retention time model developed in section 6.3.5.2. This was deemed suitable as the model had run for 45 iterations and represented a 90 day mature wetland. Thus, it was expected that background solute concentrations in the 6- and retention time simulation would stabilise more quickly using the mature wetland's final conditions rather than restarting with the original initial background solute concentrations that were applied in the 24-hour retention time model. For the 12-hour model, the final water content and background solute concentration conditions of the 6-hour retention model were used as initial conditions.

6.4. Results

6.4.1. Results of soil laboratory tests

PSD test results for both the in-situ loamy sand sample from the pilot-scale CW and the excess loamy sand are shown in Table 6-5.

The in-situ CW soil contained approximately 0.8% fines, compared to the excess soil's 2.3%. This is likely due to the smaller particles being washed out of the CW during the experiment. The PSD results of the in-situ soil were used as input to Rosetta Lite.

The results of PSD analysis showed that, for the excess soil to be used in the mini CW configuration, it first had to undergo a loading regime of its own to wash away its fine particles. This would give the excess soil sample a more similar PSD to that of the in-situ soil. Therefore, the mini CW was loaded until the effluent ran clear (judged visually).

Table 6-5 – PSD results: percentage of sample (%) passing through sieve

Sieve size (mm)	Sample	
	Excess loamy sand	In-situ pilot-scale CW loamy sand
2	59.5	61.2
1.18	46.6	42.5
0.6	31.1	22.6
0.425	22.4	13.7
0.3	15	7.5
0.212	9.8	4.2
0.15	6.9	2.7
0.063	2.3	0.8

Results from the bulk density tests are shown in Table 6-6. In order to minimise the effect of human error, numerous identical tests were run concurrently and the mean value was taken as the final value. There was enough equipment available to conduct 6 tests. The values are generally in the range expected for sandy soils (1.3-1.8 g/cm³ (Cresswell and Hamilton, 2002)) The mean value of $\rho = 1.67 \text{ g/cm}^3$ was used for input to Rosetta Lite.

Table 6-6 - Bulk density of in-situ CW soil from units 1 and 4

Sample no.	Bulk density (g/cm ³)
1	1.73
2	1.88
3	1.50
4	1.70
5	1.65
6	1.58
Mean	1.67

Results of the water moisture content analysis of the in-situ CW soil are shown in Table 6-7. In order to minimise the effect of human error, numerous identical tests were run concurrently and the mean value was taken as the final value. There was enough equipment available to conduct 3 tests. Results were relatively consistent across all three samples. The mean value of $w = 7.36\%$ was used for input to Rosetta Lite.

Table 6-7 - Moisture content of in-situ CW soil samples at 33 kPa

Sample no.	Moisture content (%) at 33 kPa
1	7.37
2	6.91
3	7.81
Mean	7.36

The saturated hydraulic conductivity analysis gave a result of $K_s = 4.5 \times 10^{-4}$ m/s.

Dry density was calculated as $\rho_d = 1.36$ and average particle density was found to be $\rho_s = 2.61$ for the in-situ CW soil. The void ratio was thus calculated as 0.92 as per Equation 7.8.

$$e = \frac{\rho_s}{\rho_d} - 1 = \frac{2.61}{1.36} - 1 = 0.92$$

Saturated water content was thus calculated to be $\theta_s = 35.2\%$ as per Equation 6.9.

$$\theta_s = \frac{100 \times e}{\rho_s} = \frac{100 \times 0.92}{2.61} = 35.2\%$$

The influent flow rate to the mini CW was measured as $5555.6 \text{ cm}^3/\text{hr}$.

The cumulative effluent flow was recorded (mean values taken from 3 runs) for comparison to the HYDRUS model output. This can be observed in Figure 6-5.

6.4.2. HYDRUS modelling results

6.4.2.1. Mini CW simulation results

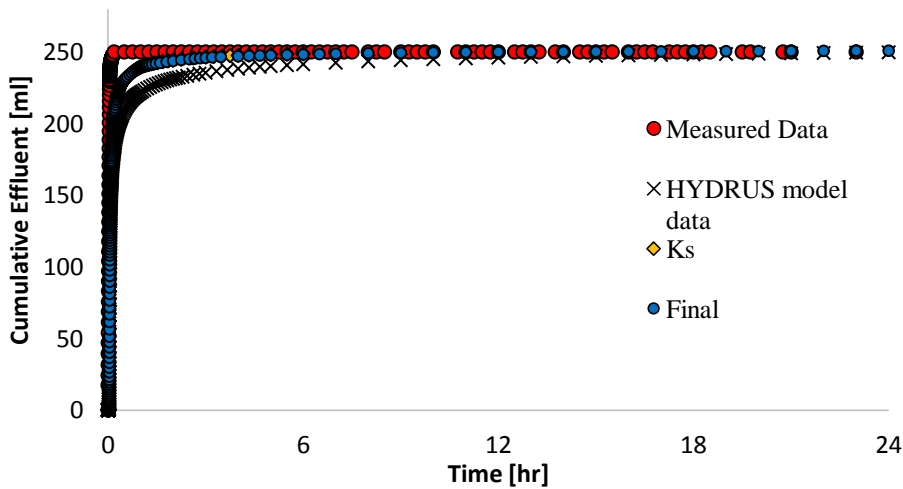


Figure 6-5 - Cumulative effluent flow from mini CW physical and numerical models

The cumulative effluent flow results from the mini CW HYDRUS model are shown in Figure 6-5 plotted alongside the measured cumulative flow from the physical model. The graph shows that the effluent flow rate of the HYDRUS model was not as high as that of the physical model. Thus, it was apparent that calibration of the hydraulic parameters of the model loamy sand was required through the use of HYDRUS's inverse solution function (as explained in section 6.3.5.1).

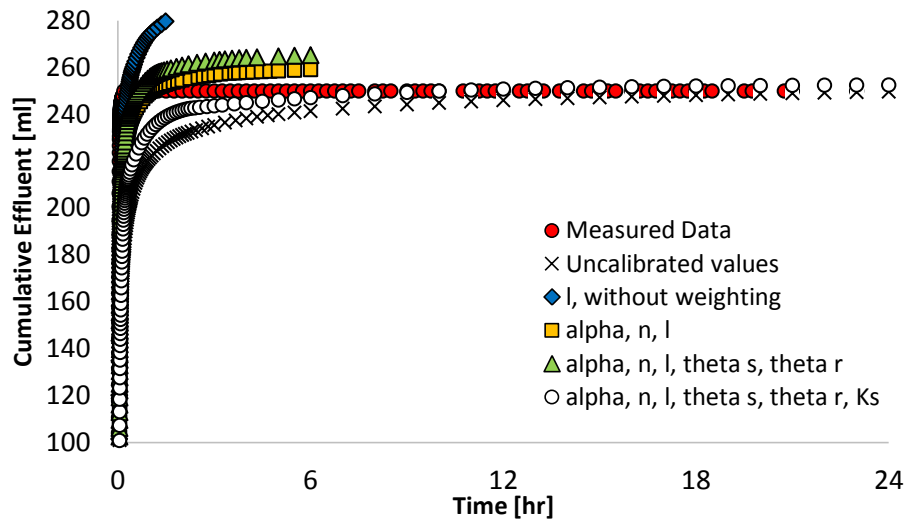


Figure 6-6 - Cumulative effluent flow results of measured data (red) and HYDRUS mini CW model output, per calibrated parameter

The results of the step-by-step adjustment through the use of the inverse solution are shown in Figure 6-6. Initially the van Genuchten parameter l was calibrated, increasing the effluent flow rate as desired, but also increasing the cumulative effluent flow volume too much, exceeding the 250 mL inflow volume. As a result, weighting factors were applied to the cumulative effluent data used in HYDRUS's inverse solution so that the program would treat any data after 2.7 mins as more significant than any previous data. It was predicted that this would prevent the HYDRUS model's cumulative flow results from exceeding 250 mL. This worked partially, as when α , n and l were calibrated next, there was a significant improvement observed between the calibrated and measured data.

When θ_r and θ_s were calibrated, the cumulative effluent results showed a greater difference to the measured results (as shown in Figure 6-6). The final parameter to be calibrated was K_S , a critical parameter for model accuracy (Simunek *et al.*, 2014). Given the importance of K_S , it was decided to re-calibrate the previous van Genuchten parameters after K_S had been calibrated. The cumulative effluent flow results for the final calibrated model can be seen in Figure 6-6, showing a significant improvement on the results obtained using the original hydraulic input parameters. Table 6-8 shows both the original and calibrated model loamy sand hydraulic properties.

Table 6-8 - Initial and calibrated hydraulic parameters of loamy sand

Parameter	Initial value	Calibrated value
θ_r (L^3/L^3)	0.0511	0.048535
θ_s (L^3/L^3)	0.3517341	0.3515583
α (L^{-1})	0.0301	0.0023951
n (-)	3.0983	7.8137
K_S (L/T)	163.615	176.48
l (-)	0.79812	0.79812

6.4.2.2. Pilot-scale CW simulation results

Background concentration and effluent removal efficiency results for NH_4-N and PO_4-P obtained from the HYDRUS model of the pilot-scale CW are shown in Figure 6-7 and Figure 6-8. The removal efficiency values are compared to the average removal efficiency value for both contaminants.

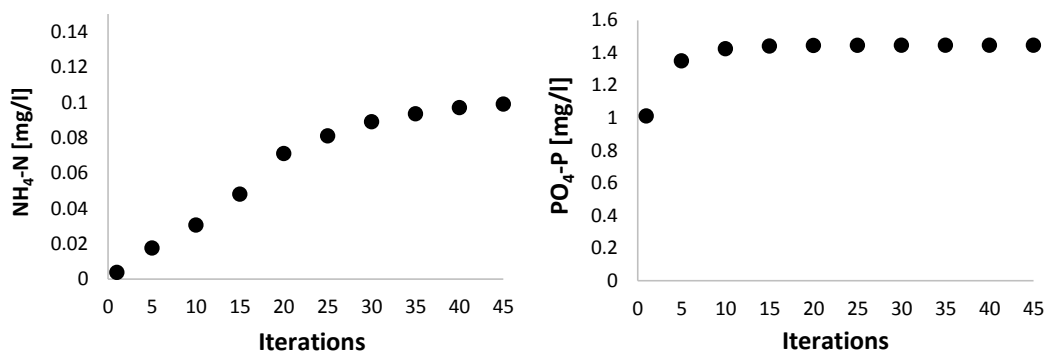


Figure 6-7 - Stabilisation of background NH_4-N and PO_4-P concentrations

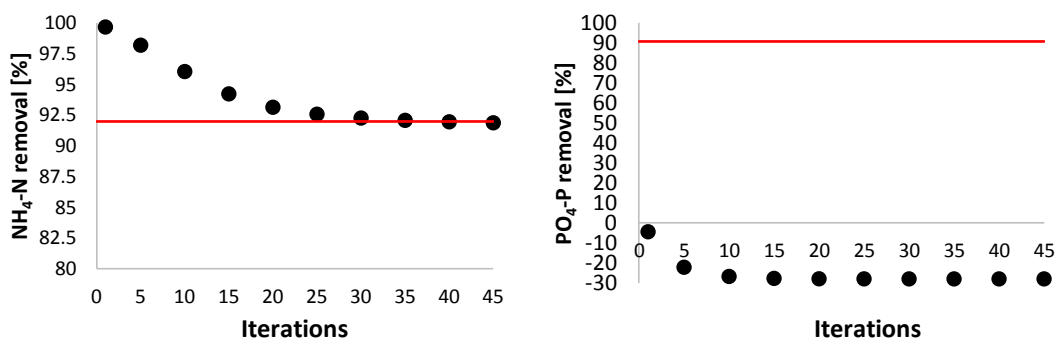


Figure 6-8 - Stabilisation of NH_4-N and PO_4-P removal efficiencies – red line denotes average removal efficiency measured in physical models

Background contaminant concentrations (Figure 6-7) and removal efficiencies (Figure 6-8) stabilised after 45 iterations. The change in removal between iterations 40 and 45 was < 0.1% for both contaminants.

NH₄-N removal stabilised at 91.87%, compared to the average measured value of 91.99%, demonstrating a very successful valid model in terms of simulation of NH₄-N removal. PO₄-P removal stabilised at -27.99%, compared to the average measured value of 90.69%, thus demonstrating an unsuccessful model in terms of simulation of PO₄-P removal.

Figure 6-9 shows the distribution of NH₄-N concentrations in the modelled pilot-scale CW over the duration of a single 24 hour retention period. It can be observed that the highest concentrations are observed just after loading (0.01 - 0.06 hours) and over time these concentration reduce due to oxidation (transforming the NH₄-N into oxidised N). It can be observed that, by 6 hours, NH₄-N concentrations have reduced significantly. Also, there is no clear visual difference in NH₄-N concentrations between 12 hours and 24 hours. Therefore, the majority of the NH₄-N oxidation has occurred within the first 6 hours after dosing, and very little takes place during the final 12 hours. These visual observations influenced the decisions taken in section 6.3.5.3 to investigate 6-hour and 12-hour retention times.

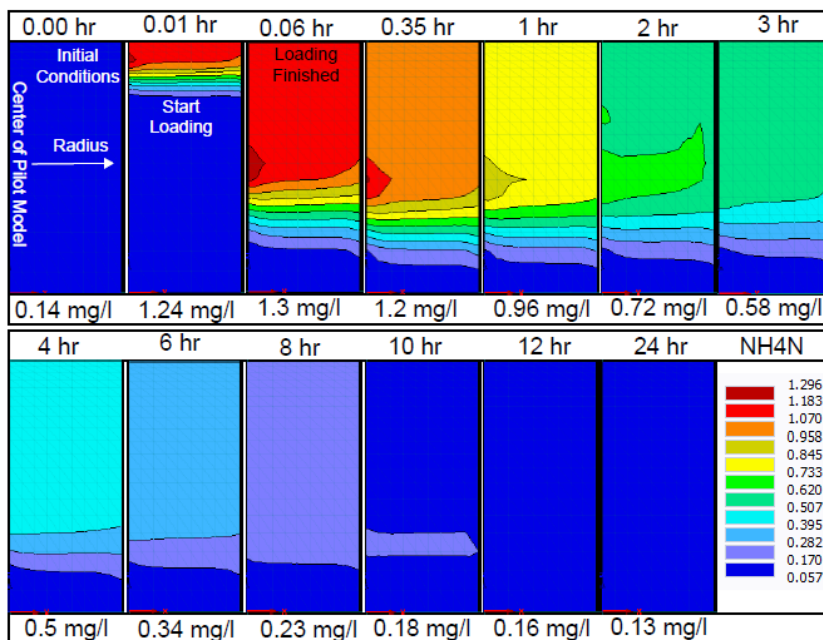


Figure 6-9 - NH₄-N concentrations in the modelled pilot-scale CW over the duration of a retention period

6.4.2.3. Use of validated model to test further variables – results

The 6-hour retention time HYDRUS model took 45 iterations for solute concentrations to stabilise and the NH₄-N removal efficiency to reach a constant rate, while the 12-hour model took 35 iterations.

Table 6-9 shows the results of the retention time tests. The results show that the majority of NH₄-N is removed in the first 6 hours of retention (86.08%), while very little is removed in the final 12 hours (1.08%). This suggests that retaining influent stormwater in a CW for a set period of time is beneficial to NH₄-N reduction, but that the retention time need not exceed 6 hours.

Table 6-9 - NH₄-N removal efficiency achieved at different retention times

Retention time (hours)	NH ₄ -N removal (%)
6	86.08
12	90.79
24	91.87

Figure 6-9 shows the cumulative outflow (expressed as a percentage of inflow) of the HYDRUS models over time during a single drainage period. It can be observed that, after approximately 7.5 hours, 95% of the inflow volume has drained from the system. Thus, the new drainage time applied to the 6- and 12-hour retention time HYDRUS models was 7.5 hours, with a view to shortening the turnaround between dosing events.

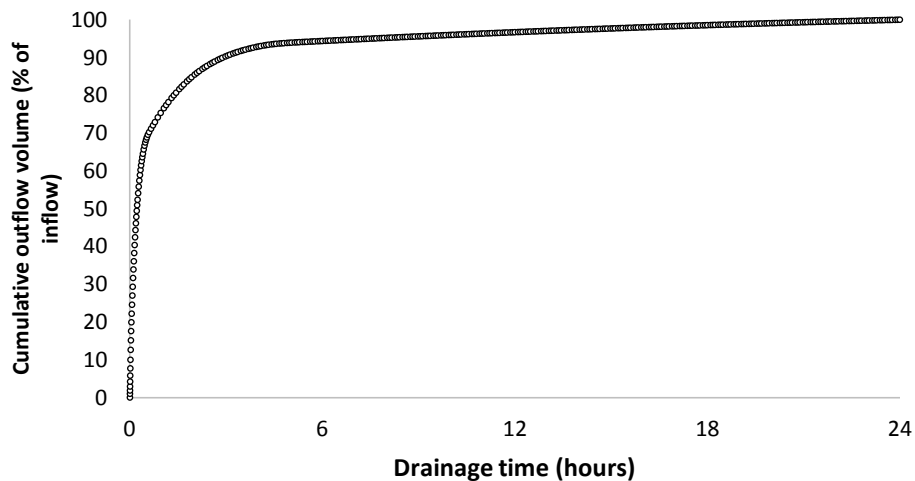


Figure 6-10 - Cumulative effluent of HYDRUS over the course of a drainage period

Table 6-10 shows the results of the optimisation of the 6- and 12- hour retention time models. The results show that, of the retention and drainage times investigated, the shorter the time used, the greater the $\text{NH}_4\text{-N}$ removal rate, with the theory being that shorter overall cycle times allow for more cycles to take place, thus increasing the $\text{NH}_4\text{-N}$ removal achievable in a given time period.

Table 6-10 - Retention/drainage time optimisation results

Retention time (hrs)	Drainage time (hrs)	Total cycle time (hrs)	Influent $\text{NH}_4\text{-N}$ (mg/L)	Removal efficiency (%)	$\text{NH}_4\text{-N}$ removed (mg/L)	$\text{NH}_4\text{-N}$ removal rate (mg/L/hr)
24	24	48	1.13	91.87	1.023	0.021
24	7.5	31.5	1.13	91.87	1.023	0.032
12	7.5	19.5	1.13	90.79	1.010	0.052
6	7.5	13.5	1.13	86.08	0.958	0.071

6.5. Discussion

Results from the soil laboratory tests provided the necessary input data required to create a good hydraulic model of the pilot-scale CWs using HYDRUS. This was aided by the use of HYDRUS's inverse solution function, which increased the accuracy of the model during calibration.

The model was then run with solute transport, using influent contaminant concentration values from the physical pilot-scale CW experiment along with literature values as input values. This provided results which indicated a successfully validated model in terms of $\text{NH}_4\text{-N}$ removal, but not in terms of $\text{PO}_4\text{-P}$.

The success in creating a valid model for $\text{NH}_4\text{-N}$ removal suggests that the main processes responsible for $\text{NH}_4\text{-N}$ reduction in the pilot-scale CWs are those that are simulated in HYDRUS, specifically the oxidation of ammonium by the autotrophic bacteria, *Nitrosomonas spp* (process 6 in Table 6-2). The model could then be used to determine the benefits of a tidal-flow regime to $\text{NH}_4\text{-N}$ removal and to optimise the retention and drainage times.

There are several reasons which may account for the lack of accuracy in the prediction of $\text{PO}_4\text{-P}$ removal. Nutrient removal in CWs is achieved through physical, chemical and biological processes, but HYDRUS does not model physical processes. It was identified in chapter 5 that precipitation processes are likely to play a significant role in the removal of $\text{PO}_4\text{-P}$ in the pilot-scale CWs, but this cannot be modelled in HYDRUS because the formed precipitates that are subsequently removed by physical processes cannot be simulated. This is thought to be a major reason for the lack of model accuracy in terms of $\text{PO}_4\text{-P}$ removal.

Adsorption was also identified as a $\text{PO}_4\text{-P}$ removal mechanism in chapter 5. HYDRUS has the ability to model adsorption processes, but due to the unavailability of adsorption coefficient data for the loamy sand, this was not included in the model. However, two checks were run using estimated adsorption coefficient values. The first set of values was obtained from washed sand (0-4 mm). It was found that the inclusion of these adsorption coefficients had no effect on effluent $\text{PO}_4\text{-P}$ concentrations. The second set of values were exaggerated coefficient values, simply used to check whether the inclusion of adsorption coefficient values in the modelling process would have any effect on the effluent $\text{PO}_4\text{-P}$ concentration results. It was found again that there was no effect on the effluent values.

Plant uptake has some contribution to $\text{PO}_4\text{-P}$ reduction in many CWs, but plants were not modelled in the HYDRUS model. The reason that plants were not included

in the model is that, during the time period being investigated (weeks 44-54), the plants in the pilot-scale CWs were dead. Therefore, it is assumed that plant uptake in the physical models did not provide the difference in removal efficiencies. It is possible that the dead plant roots and matter provide additional surface area for adsorption processes, but there is no way to quantify this contribution.

It should also be noted that heat transport has not been simulated in the HYDRUS model. Heat can affect adsorption and precipitation processes (Kadlec and Wallace, 2009), so neglecting its effect may have had an influence on the PO₄-P results.

The results of the retention/drainage time optimisation for NH₄-N removal through the use of the validated HYDRUS model showed that a higher removal rate could be achieved with a 6-hour retention time and 7.5 hour drainage time (total cycle time of 13.5 hours). Rainfall is stochastic, so the volume of stormwater entering the CW in practice is entirely dependent on the depth of rainfall in a given time period. Therefore, it is unrealistic to propose a continual recurring treatment cycle of 13.5 hours. However, the results do show that, in times of heavy rainfall, the retention time can be shortened to as little as 6 hours, and drainage time minimised to 7.5 hours in order to treat greater quantities of incoming stormwater via more cycles in a short period with little negative effect on removal efficiency.

It should be recognised that these results apply only to the pilot-scale CWs investigated, and that field conditions cannot be predicted from this study alone. Nevertheless, the findings have value in that it has furthered understanding of the general relationship between retention time and NH₄-N removal in a tidal-flow stormwater CW of this type. Also, the study has demonstrated the major role played by autotrophic bacteria (*Nitrosomonas spp.*) in NH₄-N removal in CWs of this type and the potential importance of physical processes – such as precipitation - to PO₄-P reduction in tidal-flow stormwater CWs.

6.6. Summary

In conclusion, a valid model was created for the simulation of NH₄-N reduction in the pilot-scale stormwater CWs. This confirmed that the oxidation by autotrophic bacteria (*Nitrosomonas spp.*) was the main removal mechanism of NH₄-N reduction

in the pilot-scale CWs. The model demonstrated that retaining stormwater in a CW enhances $\text{NH}_4\text{-N}$ reduction, and allowed further investigation of optimal retention and drainage times that can increase the $\text{NH}_4\text{-N}$ removal efficiency in times of large demand for stormwater treatment (e.g., extended rainfall periods). The optimum retention time was found to be 6 hours, while the optimum drainage time was found to be 7.5 hours.

The model could not be validated for $\text{PO}_4\text{-P}$ reduction. This was due to the fact that it was not possible to simulate the $\text{PO}_4\text{-P}$ reduction processes occurring in the pilot-scale CWs in HYDRUS, based on the data that was available.

7. Statistical Analysis and Predictive Model Development for Stormwater Constructed Wetlands

7.1. Introduction

This chapter details the use of statistical analysis to identify influential factors and important relationships between parameters in the pilot-scale stormwater CWs and the development of regression models for CW performance prediction. Stormwater treatment in CWs involves a combination of complex physical, chemical and biological processes, and thus it is difficult to determine exactly what mechanisms are occurring within the systems. Statistical analysis is an excellent way of identifying significant relationships between pollutants and environmental conditions in CWs. This provides knowledge of the key parameters that influence the internal water quality treatment processes in the systems. Given the large range of parameters investigated, and the overall size of datasets due to the length of the project and number of CW units, the process of investigating the effect of the parameters one at a time is time-consuming and may also result in the overlooking of certain relationships due to the scale of the work and the variety of parameters involved.

Multivariate statistical analysis can be used as a tool to identify relationships within large amounts of data and is therefore an excellent adjunct to general performance investigations. PCA can highlight non-hypothesized relationships between variables. Specifically, the use of PCA means that researchers are not limited to investigating processes they had predicted, and can further increase their understanding of pollutant behaviour in CWs.

The use of regression models for performance prediction requires the knowledge of a range of parameters from the CWs. However, many important priority pollutants in stormwater are relatively expensive or difficult/time consuming to measure, requiring laboratory work involving the addition of reagents, digestion procedures,

preservation and other such measures. This causes strains on both time and budget when trying to analyse the performance of a stormwater treatment system. Therefore, the regression models described in this chapter were designed to predict values of parameters that are difficult/expensive to measure from known values of parameters that are considered easier/relatively inexpensive to measure. Large amounts of influent and effluent data from the pilot-scale CWs were subjected to principal component analysis (PCA), simple linear regression and multiple regression analysis (MRA). The main objectives of this chapter were:

- To identify, through the use of PCA, statistically significant relationships between stormwater parameters that are deemed expensive/difficult to measure and those that are deemed inexpensive/easier to measure
- Develop simple linear regression models that can be used for the prediction of expensive/difficult to measure parameters based on known values of inexpensive/easier to measure parameters and analyse the quality of models produced
- Develop multiple regression models that can be used for the prediction of expensive/difficult to measure parameters based on known values of inexpensive/easier to measure parameters and analyse the quality of models produced
- Use the identified relationships and models produced to further understanding of pollutant behaviour in tidal-flow stormwater CWs

The development of mathematical models such as those described in this chapter is of paramount importance to ensure cost-effective characterisation of controlling processes in stormwater CWs. The results can help to reduce costs and sampling efforts dramatically. Models designed specifically for wetland-type ecosystems such as the (k-C)* model (Kadlec and Knight, 1996), Monod-type models (Mitchell and McNevin, 2001) and the activated sludge-based model used in HYDRUS CW2D (Langergraber, 2006 – see chapter 6) are extremely useful tools to predict and understand CW behaviour, but are often complicated and require both specific software and the measurement of a great deal of variables in order to produce

reliable predictions. In recent years, several studies have adopted regression modelling as a simple way of simulating dependencies between variables in CWs (e.g., Scholz, 2003; Tomenko *et al.*, 2007; Hijosa- Valsero *et al.*, 2011), with notable success. For example, Tomenko *et al.*, produced a multiple regression model capable of predicting effluent BOD concentration with a model fit of $R^2 = 0.89$ (i.e., a model that explains 89% of the entire dataset).

PCA is an exploratory data analysis method that uses the correlation structure between multiple constituents to produce a small number of new variables that contain most of the information in the original dataset (Olsen *et al.*, 2012). PCA is often applied to water sample datasets in order to determine the influencing factors on the water quality. For example, Mendiguchía *et al.* (2004) used PCA to improve the understanding of the physico-chemical characteristics of the Guadalquivir River in Spain, finding that the river could be split into four different zones with separate water quality characteristics. Olsen *et al.* (2012) conducted PCA on a collection of surface water samples in the Illinois River watershed in order to pinpoint the main sources of contamination in the watershed. This was achieved by comparing the groupings of samples by certain contaminants in the PCA and comparing the samples to their geographic distance downstream of known potential polluting sources (e.g., runoff from fields with applied poultry waste). Thus, when applied with a good understanding of water contaminants and typical influential factors, PCA can be a useful tool to understand the particular relationships occurring in a system.

7.2. Materials and methods

7.2.1. Data and variable selection

Data was obtained from the pilot-scale stormwater CWs as detailed in chapter 3. Effluent concentrations of TSS, TN, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, TP, $\text{PO}_4\text{-P}$, Fe, Zn, Pb, Ni, Cd, Cr and Cu were used for both PCA and regression analysis, alongside effluent values for pH, temperature and EC. Time (measured in weeks) was also considered in the regression analysis (see section 7.3.3). Furthermore, influent

concentrations were used to provide removal efficiency values for TSS, nutrient and metal reductions, which were also incorporated into the regression analysis.

Regression modelling uses one or more “predictor” variables to predict the value of a “response” variable (Draper and Smith, 1998). Thus, with a good model, you can predict the value of one parameter if you know the value of another. In addition to developing understanding pollutant removal processes in stormwater CWs, one of the aims of the modelling process was to create models that use predictor variables that are easy or relatively inexpensive to measure, to predict values for those variables which may be more difficult or expensive to measure. Thus, the parameters chosen for the predictor variables were TSS, pH, temperature, EC and time. TSS can be measured via standard methods (APHA *et al.*, 2012) with relatively basic equipment and does not require digestion or the addition of reagents, etc., thus it is inexpensive to determine. pH, temperature and EC can all be measured easily at the influent/effluent point in a stormwater CW, using a hand-held probe.

The response variables were therefore TN, NH₄-N, NO₃-N, NO₂-N, TP, PO₄-P, Fe, Zn, Pb, Ni, Cd, Cr and Cu. All of these parameters required ICP analysis or the addition of reagents to determine their values, with some also requiring preservation with acid, which also required neutralising the sample prior to analysis. These reasons were sufficient to categorise these parameters as more difficult or expensive to measure.

7.2.2. Principal component analysis

The PCA process involves reducing the dimensionality of a dataset which contains a large number of interrelated variables, without the loss of important information in the dataset. Thus, most of the variation in the dataset is retained. The information is transformed into a number of principal components (PCs): a new, uncorrelated set of variables which are put in order so that the first few explain most of the variation that was present in all of the original variables (Jolliffe, 2002). The first PC (PC-1) explains the maximum variance of the dataset, and the explained variance associated with each PC decreases from PC-1 to the last significant PC (Adams, 2004; Settle *et al.*, 2007).

The minimum number of PCs that should be selected to analyse the PCA output is dependent on the amount of explained variance that the researcher wants to account for. It is recommended that the number of PCs selected should explain > 70% of the variance in the dataset (Jolliffe, 2002). Thus, this minimum value was used in the analysis.

For PCA, a dataset must be prepared as a matrix consisting of variables represented by columns and objects by rows. PCA was conducted on each CW unit in this project and thus the effluent samples were designated as the rows for the matrix. The columns were the variables TSS, pH, temperature, EC, TN, NH₄-N, NO₃-N, NO₂-N, TP, PO₄-P, Fe, Zn, Pb, Ni, Cd, Cr and Cu. PCA requires a full dataset to work, which posed a problem since there was missing pH and EC data for weeks 15-20 (inclusive). Thus, for each CW, PCA was carried out twice. The first run incorporated all of the previously mentioned variables but excluded the sample results from weeks 15-20. This allowed for relationships involving pH and EC to be identified. The second PCA run then allowed for relationships between other variables to be identified based on the maximum amount of available data.

Some of the variables used in this study were measured in different units to the others, or varied in magnitude. For example, a typical TSS value was 15-30 mg/L, whereas a typical Fe value was >0.1 mg/L, while EC was measured in mS and temperature is measured in °C. Thus, the data had to be subjected to pre-treatment before analysis in order to eliminate scale effects. For data of this type, a combination of two common transformation techniques is recommended. The first is standardisation, in which the values in one column (i.e. the array of values of one variable) are divided by the standard deviation of the column, thus giving all variables equal weighting by adapting their standard deviation to 1.0 (Kokot *et al.*, 1998). The second technique is mean centering, in which the mean value of each variable is subtracted from each value in its column. This ensured that the PCA was not affected by the scale of the variables, and focussed only on their variance.

PCA was carried out on the computer software package The Unscrambler X 10.3, produced by CAMO software. The program gave useful visual output in the form of

two main graphs: scores plots and loadings plots. This is one of the most useful aspects of PCA: the ability to visually interpret the output information. The scores plot shows the PCA output arrangement of the objects (samples) relative to the PCs, and can be displayed in a number of ways to show how the objects are affected by the variables (see section 7.3.1.2 for an example of this). The loadings plot shows the relationships between variables, and can be viewed alongside to the scores plot to understand where certain objects may have been affected by certain variables. In a loadings plot, the angle between variable vectors indicates the strength of correlation between them. A more acute angle indicates positive correlation, whereas a more obtuse angle indicates negative correlation. Thus, a 90° angle indicates zero correlation. The numerical values of the loadings for each variable are also paramount, as the higher the loading value the more effect that variable is having on the dataset. Thus, for a significant relationship to be occurring between variables, they must both have adequate loading value. The loadings and scores plots can also be combined in a biplot.

PCA allowed the identification of potentially significant relationships between variables. A list of these relationships was the product of PCA, and the relationships were subsequently subjected to correlation analysis to determine whether they could be deemed statistically significant. Further information on PCA can be found in useful publications such as Davis (2002), Jackson (2003) and Shaw (2003).

7.2.3. Correlation and regression analysis

Correlation analysis was carried out on the raw data in order to identify relationships between variables that the PCA had identified as carrying potential significance. This was done with the use of Microsoft Excel: variables were plotted against one another on a scatter graph and the coefficient of determination (R^2) was determined from the linear trendline of the plot. The R^2 value is a measure of the strength and direction of the linear relationship between the two variables, so it is an indicator as to whether a significant linear relationship exists (Dobson, 2002). R^2 values range from 0 to 1: the closer to 1 the R^2 value is, the stronger the linear relationship, with $R^2 = 0$ denoting no linear relationship. An R^2 value of above 0.59 was considered a valid linear

relation in this project (as in Scholz, 2003), and so those variable pairs that produced this value were selected for outlier elimination and modelling. The scatter plots were arranged so that the predictor variable (in this case, the cheaper/easier/quicker to measure parameter) was plotted on the x-axis and the response variable (more expensive/difficult/time-consuming parameter) on the y-axis. This ensured that the plots were ready for linear regression analysis.

The scatter graphs were used to visually identify any obvious outlying data points. This is a subjective process, based on distance from the linear best-fit trendline of the scatter graph. Data was only eliminated when it was judged that a single point was clearly an outlier. An example of this is shown in Figure 7-1. It can be seen that the circled data point in graph (a) is a clear outlier, and thus it was removed. Note the improvement in R^2 value with the elimination of the outlier.

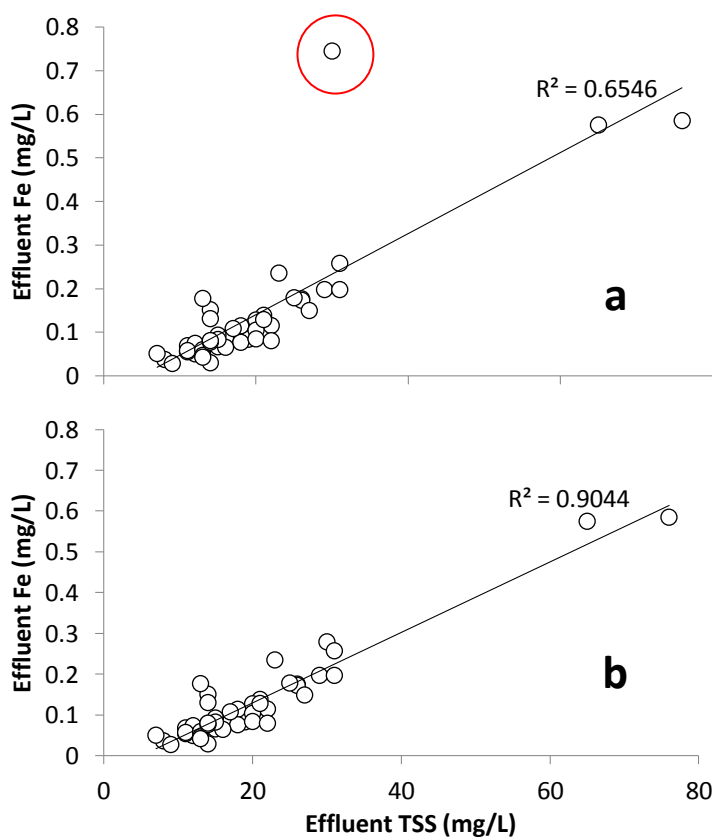


Figure 7-1 - Elimination of outlier: (a) shows identification of outlying data point, (b) shows the chart with the outlier eliminated, improving the R^2 value of the trendline

Both simple and multiple regression analysis (MRA) was conducted on the data. Simple regression analysis is a statistical process which describes the relationship between a dependent “response” variable and a single independent “predictor” variable. A simple regression model aids the understanding of how the response variable is affected by variation in the predictor variable. The equations of the linear trendlines in those relationships with the desired R^2 values were used to determine the constants for the simple regression models, which took the form of the straight-line equation, shown in Equation 7.1:

$$y = ax + b \quad (7.1)$$

where: y = response variable

a = predictor variable constant (gradient of linear trendline)

x = predictor variable

b = model constant (y-axis intercept)

Multiple regression is simply a regression problem where the number of parameters is greater than or equal to 2, and is not simple linear regression (Christensen, 1987). Models with multiple predictor variables are in the form shown in Equation 7.2.

$$y = a_1x_1 + a_2x_2 + \dots + a_nx_n + b \quad (7.2)$$

where: n = number of predictor variables

a_n = constant for predictor variable x_n

x_n = predictor variable n

MRA was conducted using the regression function in Microsoft Excel’s Data Analysis Toolpak. If more two or more predictor variables were found to have significant R^2 values in correlation with the same response variable, they were incorporated into the MRA. A 95% confidence interval was applied in the analysis. Thus, the significance of the F value for each model was checked to ensure that it was below 0.05 (for 95% confidence) to ensure that the model represented a statistically significant relationship. The F value is given as part of the output of the

regression function in Microsoft Excel. The P values of each predictor value are also given, and these were checked to determine the significance of each variable in the model. Again, if any predictor variable's P value exceeded 0.05 then it was not deemed statistically significant, and so it was omitted from the model. The adjusted R² value for a multiple regression model is also given in the regression function in Microsoft Excel, and this was taken as an indication of the fit of the model to the data.

7.3. Results and discussion

7.3.1. Principal component analysis

PCA was successfully applied to the datasets and provided very useful output. Examples of the loadings and scores plots used to identify potentially significant relationships between variables are displayed and discussed in sections 7.3.1.1 and 7.3.1.2, and the selected variable relationships for each CW unit are given in section 7.3.1.3.

The number of PCs that explained >70% of variance in the dataset for units 2, 3, 5, 6, 7 and 8 was three, while PC-4 also required examination for unit 1. Only the first two PCs were required to explain > 70% of variance in unit 4. For example, for the second PCA run of the unit 2 dataset: PC-1 explained 53% of variance; PC-2 explained 14% of variance; and PC-3 explained 11% of variance. Thus, the total explained variance was 78% and analysis of these three components was required to identify significant relationships.

7.3.1.1. Loadings plots

Figure 7-2 shows an example of two loadings plots identical to those produced from Unscrambler X, but recreated on Microsoft Excel for formatting reasons. Plot (a) shows the loadings plot for the first PCA run on unit 8 (including variables pH and EC, excluding weeks 15-20). It can be seen that there is a general grouping between TSS, NH₄-N and Fe, which indicates acute angles between these vectors (as shown) and suggests there is a potentially significant relationship between these variables. Since neither pH nor EC feature in this variables group, it was checked in the second

PCA run (plot (b) in Figure 7-2) with the benefit of all the available valid data for those variables. There is also a grouping between pH, NO₃-N and TN. Furthermore, significantly obtuse angles between this group and both PO₄-P and TP suggest that there may be a relationship between these variables also. Note also a grouping in plot (b) of TN, NO₃-N and NO₂-N, that was ignored because there was no predictor variable present in this group. The loadings of the variables in these selected groups are high enough (relative to the rest of the loadings) to suggest that the relationships may be significant, and thus they are selected for correlation analysis. All loadings plots for the first two principal components are available in Appendix 1.

7.3.1.2. Scores plots

Figure 7-3 shows two versions of the same scores plot for the unit 8 dataset. The loadings plot for the same unit is shown in Figure 7-2b, and it was suggested in the previous section that a significant relationship between TSS and Fe might be present, due to the close proximity of these variables on the loadings plot and their relatively high loading values. Thus, the scores plot can be arranged to show how these variables may show their similarities across the samples from the original dataset.

From Figure 7-2b it can be seen that both Fe and TSS are located on the area between the negative PC-1 and positive PC-2 axes of the loadings plot. Figure 7-3 shows that the samples that exhibited the highest values for both parameters are also situated in this area. Both parameters also have their lowest values in the area between the positive PC-1 and negative PC-2 axes. Thus, the general distribution of high to low values for both variables is very similar, suggesting that there may be a significant relationship occurring.

This visual inspection was carried out for all potential relationships after groupings had been identified in the loadings plots. As mentioned previously, this is one of the main benefits of PCA: the ability to visually interpret the data and identify potential patterns in this way. This means that non-hypothesized relationships may be discovered in addition to expected relationships.

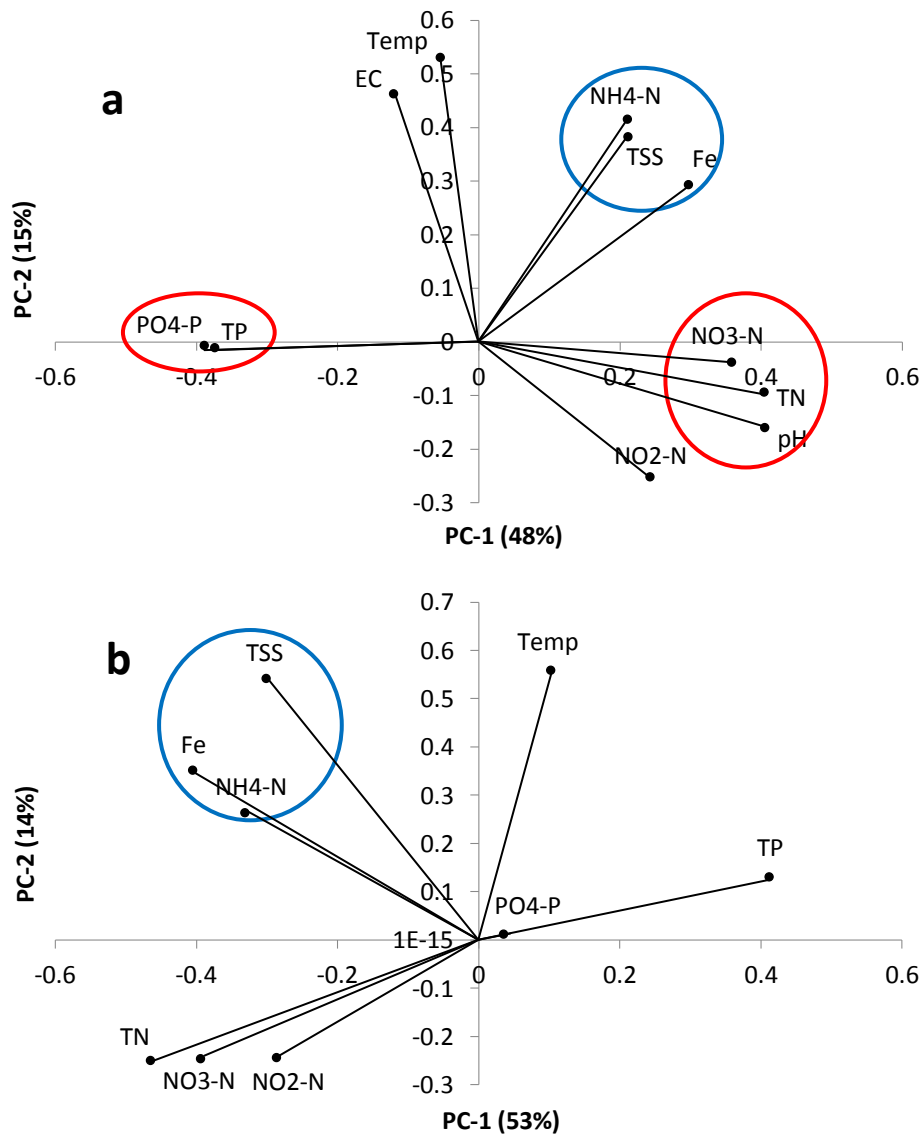


Figure 7-2 - PCA loadings plots for pilot-scale CW 5 (a) including pH and EC, excluding weeks 15-20, (b) excluding pH and EC, including weeks 15-20

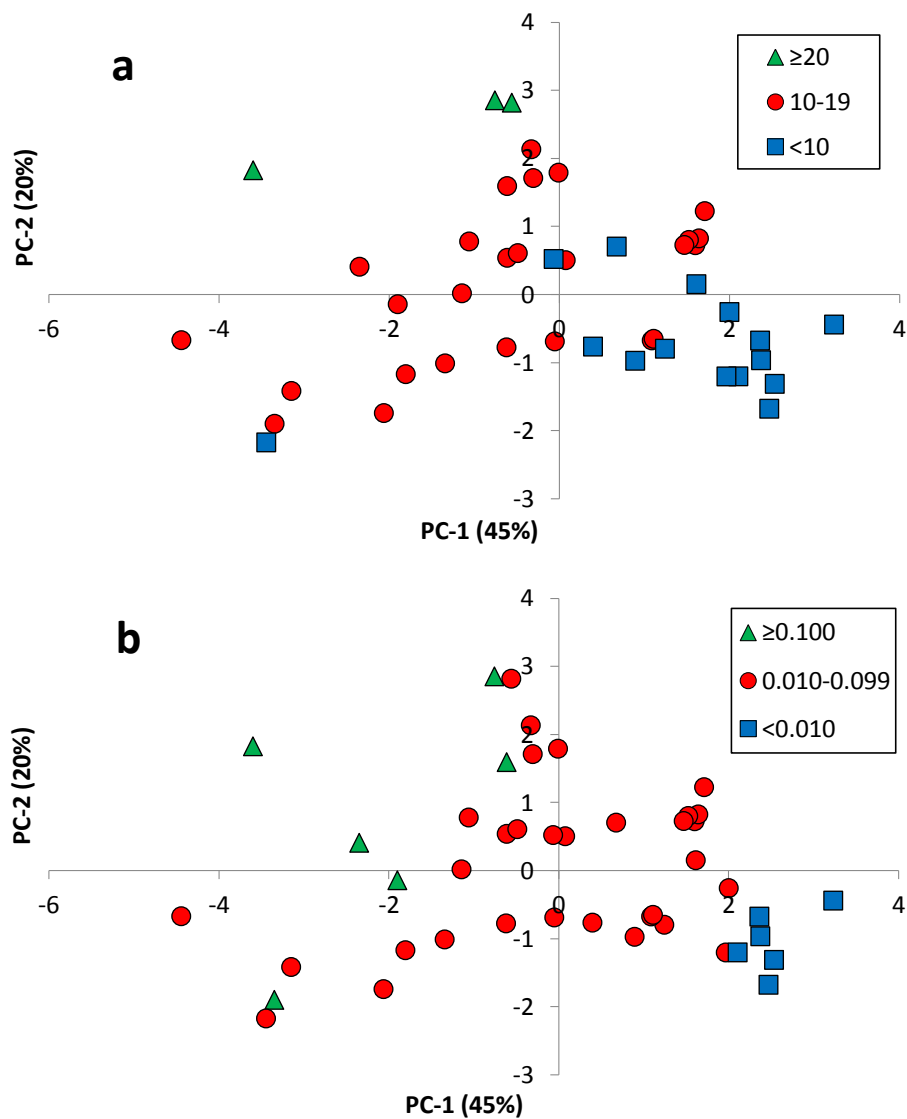


Figure 7-3 - PCA output: scores plots for CW 8, (a) showing effluent TSS ranges in mg/L, (b) showing effluent Fe concentration ranges in mg/L

Table 7-1 - Variables with potentially significant relationships as identified from PCA of effluent samples, in all 8 pilot-scale CWs

Unit 1	Unit 2	Unit 3	Unit 4
TSS & Fe	TSS & Fe	TSS & Fe	TSS & Fe
pH & TN	TSS & Zn	TSS & NH ₄ -N	TSS & TN
pH & Zn	TSS & Pb	TSS & NO ₃ -N	TSS & NO ₃ -N
EC & Zn	TSS & Cu	Temp & Zn	pH & TN
EC & TN	TSS & NH ₄ -N	EC & TN	pH & NO ₃ -N
Temp & Zn	pH & TP	EC & TP	pH & Fe
	pH & PO ₄ -P	EC & PO ₄ -P	Temp & NO ₂ -N
		EC & Fe	
Unit 5	Unit 6	Unit 7	Unit 8
TSS & Fe	TSS & Fe	TSS & Fe	TSS & Fe
pH & TN	TSS & NH ₄ -N	TSS & TN	pH & TN
pH & NO ₃ -N		TSS & NH ₄ -N	pH & NO ₃ -N
pH & Zn		TSS & PO ₄ -P	pH & TP
EC & NH ₄ -N			pH & PO ₄ -P

7.3.1.3. Selected relationships between variables

The potentially significant relationships identified in the PCA are shown in Table 7-1. These relationships were then further examined in order to determine their statistical significance by correlation analysis (see section 7.3.2). Only relationships involving one of TSS, pH, EC or temperature as one parameter and one of TN, NH₄-N, NO₃-N, NO₂-N, TP, PO₄-P, Fe, Zn, Pb, Ni, Cd, Cr or Cu as the other were selected, in order to arrange the parameters into predictor and response variables ready for regression analysis.

7.3.2. Correlations

Those pairs of variables that were found to have a coefficient of determination value of $R^2 > 0.59$ are shown in Table 7-2, along with their respective R^2 values. As detailed in section 7.2.3, correlations with time and TSS removal efficiency were also investigated at this stage, and the results are also given in Table 7-2. Examples of selected scatter plots involved in the correlation analysis can be seen in Figure

7-4. The scatter plots for all relevant variable pairs (after outlier elimination) are presented in Appendix 2.

The results in Table 7-2 show that several parameters can be predicted using the values of alternative cheaper/easier to measure parameters in all 8 pilot-scale stormwater CWs. The accuracy with which these parameters varies, with the lowest acceptable R^2 value being 0.51 for effluent $\text{NH}_4\text{-N}$ prediction from effluent EC in unit 5, and the highest R^2 value being 0.92 for effluent Fe prediction from effluent TSS concentration in unit 2.

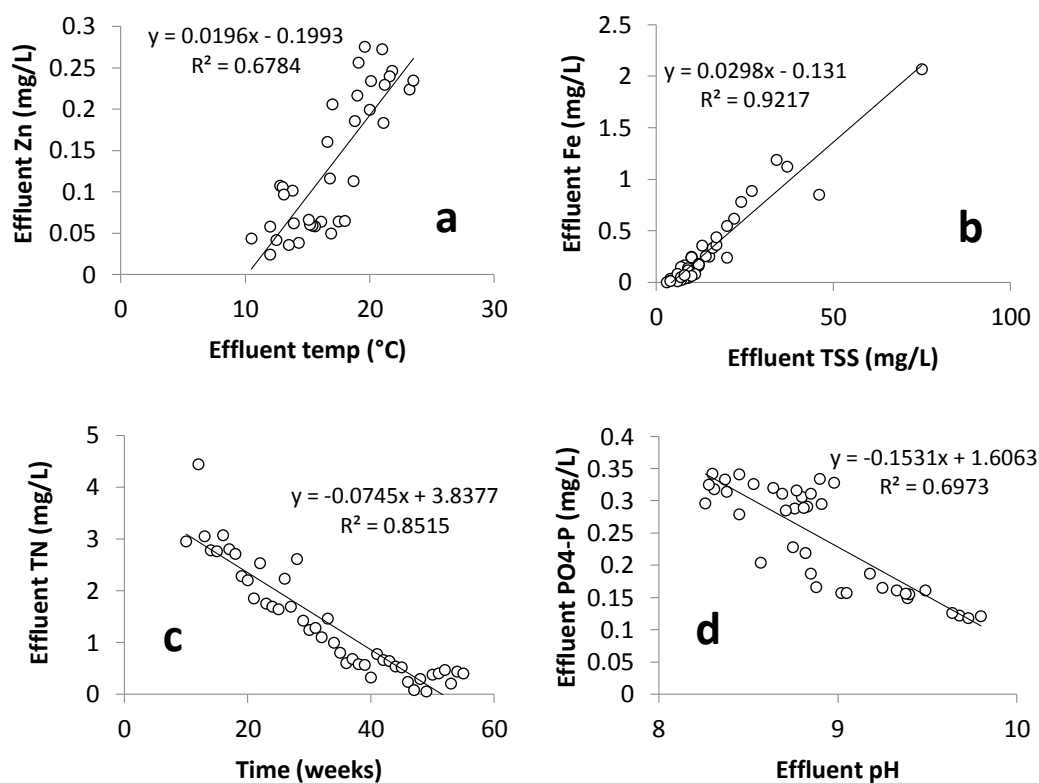


Figure 7-4 - Selected scatter plots showing determination coefficients (R^2) and linear regression model equations, from (a) unit 1 (b) unit 2 (c) unit 4 (d) unit 8

As the results of Table 7-1 show, the majority of the significant relationships identified through correlation analysis involved either TSS removal efficiency or effluent TSS concentration. This highlights the importance of sediment removal to reduce concentrations of other pollutants in stormwater CWs. Partitioning analysis

(described in chapter 5) found that heavy metals were predominantly particulate in form or associated with particulates, so it is no surprise that their behaviour should correlate well with TSS measurements. The reason that Fe and Zn feature more than the other heavy metals in the correlation analysis is that for most of the effluent readings taken, the concentrations of Pb, Ni, Cd, Cr and Cu had been successfully reduced to below detection limits and thus correlations with TSS could not be formed.

The decision to include time as a predictor variable was taken not only due to its ease of measurement, but also because of the observation that the behaviour of the nutrients in the CW effluent appeared to change over time. In some units, effluent N decreased over the duration of the project, whereas in some units effluent P appeared to increase over time (full details of nutrient behaviour observations over time can be found in chapter 5). Thus, significant relationships were found between time and several nutrient forms in CW units 2, 3, 4, 5, 6, 7 and 8. This shows that the systems were constantly changing over the length of the experiment and emphasises the importance of CW maturation time on nutrient reduction.

Other notable relationships include that between Zn and temperature in unit 1, which is thought to be due to a release of dissolved organic matter containing sorbed Zn when temperatures increased during the summer. This is discussed in chapter 5. Statistically significant relationships were found between EC and TN, TP and PO₄-P in unit 3, but it should be noted that there was significantly less data available for correlation analysis when dealing with EC, pH or temperature in unit 3. This is due to a combination of the fact that effluent sampling was only possible every second week in unit 3 (due to the dosing regime) and the fact that pH, EC and temperature data was unavailable until week 21. Likewise, it should also be noted that the correlations for unit 6 were also performed on a relatively small dataset due to its dosing regime (extended dry periods resulting in many weeks without effluent sampling).

7.3.3. Regression models

7.3.3.1. Simple linear regression models

Examples of the results of simple linear regression analysis can be viewed for selected pairs of variables in Figure 7-4. Table 7-2 shows the model constants, a and b , for all of the simple linear regression models, and selected model-fit diagrams are shown in Figure 7-5. In total, 56 simple regression models were produced from the analysis.

Of the simple linear models produced, five have R^2 values greater than 0.9, denoting an excellent fit to the data. Four of these models use effluent TSS concentrations as a predictor variable to determine metal concentrations: effluent Fe, Zn and Cu in unit 2 and effluent Fe in unit 5. This is an unsurprising result, given that partitioning analysis determined that, in all CW units, metals were predominantly particulate in form or associated with particles. Furthermore, the partitioning analysis found that all metals were entirely particulate in form/associated with particles in the effluent of unit 2. The other model with $R^2 > 0.9$ is the prediction of TN with using time in unit 3. Again, this was unsurprising as the steady reduction of TN over time was clear to see over the course of the experiment.

Twenty of the simple regression models have R^2 values of $0.8 < R^2 < 0.9$, demonstrating a very good fit to the data. Again, the majority of these models are based on the prediction of metals from TSS, and nutrients from time. In unit 7, a model for the prediction of TN from pH was developed. This relationship may be due to the effect of improved nitrification in the system as the CW matured over time, since nitrification has been observed to lower pH (Kadlec and Wallace, 2009).

Eleven of the simple regression models have R^2 values of $0.7 < R^2 < 0.8$, demonstrating a good fit to the data. Again, these mainly show relationships between metals and TSS, and nutrients and time. Relationships between $\text{NH}_4\text{-N}$ and TSS are also drawn in units 2 and 3, suggesting that effluent $\text{NH}_4\text{-N}$ may be associated quite heavily with particulates.

Statistical Analysis and Predictive Model Development for Stormwater Constructed Wetlands

Table 7-2 - Results of simple linear regression analysis: variables, constants and determination coefficients

CW Unit	y	x	a	b	R ²	CW Unit	y	x	a	b	R ²
1	Fe eff	TSS eff	0.0112	-0.0799	0.8542	4	Fe eff	TSS R.E.	-1.9867	1.9403	0.7755
	Fe eff	TSS R.E.	-1.8796	1.8312	0.6274		TN eff	TSS eff	0.0786	0.4085	0.6709
	Zn eff	Temp eff	0.0196	-0.1993	0.6784		TN eff	TSS RE	-14.882	15.281	0.6589
2	Fe eff	TSS eff	0.0298	-0.131	0.9217	5	TN eff	Time	-0.0745	3.8377	0.8515
	Fe eff	TSS R.E.	-5.1769	5.0724	0.8557		NO ₃ -N eff	TSS eff	0.037	-0.035	0.6282
	Zn eff	TSS eff	0.0022	-0.0055	0.9139		NO ₃ -N eff	TSS RE	-7.0171	6.9758	0.6236
	Zn eff	TSS R.E.	-0.3839	0.3804	0.8479		NO ₃ -N eff	Time	-0.0346	1.5357	0.7183
	Pb eff	TSS eff	0.006	-0.0553	0.8830	6	Fe eff	TSS eff	0.0086	-0.0423	0.9079
	Pb eff	TSS R.E.	-1.061	1.0094	0.8525		Fe eff	TSS R.E.	-1.4541	1.4281	0.7917
	Cu eff	TSS eff	0.0009	-0.0083	0.9066		NO ₃ -N eff	pH eff	2.0925	-14.317	0.5900
	Cu eff	TSS R.E.	-0.1631	0.1556	0.8401		NO ₃ -N eff	Time	-0.0495	2.2008	0.7149
	NH ₄ -N eff	TSS eff	0.0034	0.0498	0.8675		Fe eff	TSS eff	0.0067	-0.024	0.8624
	NH ₄ -N eff	TSS R.E.	-0.6179	0.6703	0.7721		Fe eff	TSS R.E.	-1.2556	1.2305	0.8186
3	Fe eff	TSS eff	0.012	-0.1162	0.8582	7	NH ₄ -N eff	TSS eff	0.0086	0.0437	0.8641
	Fe eff	TSS R.E.	-2.1798	2.0689	0.8109		NH ₄ -N eff	TSS R.E.	-1.4743	1.5252	0.8411
	Fe eff	EC eff	1.0711	-0.4986	0.7129		Fe eff	TSS eff	0.0071	-0.0370	0.8878
	TN eff	EC eff	13.021	-5.6588	0.7123	8	Fe eff	TSS R.E.	-1.1497	1.1219	0.8393
	TN eff	Time	-0.0675	3.9639	0.9046		TN eff	pH eff	3.136	-20.269	0.8314
	NH ₄ -N eff	TSS eff	0.0034	0.1082	0.7656		TN eff	Time	-0.0804	4.6044	0.6203
	NH ₄ -N eff	TSS R.E.	-0.6386	0.7470	0.7592		NH ₄ -N eff	TSS eff	0.0070	0.0507	0.6373
	NH ₄ -N eff	Time	-0.0042	0.3388	0.6738		NH ₄ -N eff	TSS R.E.	-1.1811	1.2377	0.6559
	NO ₃ -N eff	TSS eff	0.0205	-0.1087	0.6641		NH ₄ -N eff	Time	-0.0052	0.3387	0.6369
	NO ₃ -N eff	TSS R.E.	-3.7298	3.6030	0.6270		Fe eff	TSS eff	0.0058	-0.0181	0.6974
	NO ₃ -N eff	Time	-0.0272	1.2850	0.7438		TN eff	pH eff	2.0524	-16.926	0.6084
	TP eff	EC eff	1.167	-0.4093	0.5984		TN eff	Time	-0.0817	4.238	0.8032
	PO ₄ -P eff	EC eff	0.5167	-0.129	0.6965		TP eff	pH eff	-0.1689	1.8225	0.6618
PO ₄ -P eff	Time	-0.0024	0.2392	0.8114	PO ₄ -P eff	pH eff	-0.1531	1.6063	0.6973		
4	Fe eff	TSS eff	0.011	-0.0512	0.8585	PO ₄ -P eff	Time	0.0055	0.0472	0.7601	

Note: "R.E." denotes "removal efficiency, "eff" denotes "effluent"

The remaining twenty simple regression models have R^2 values of $0.59 < R^2 < 0.7$. This indicates that the model has a significant fit to the data, and therefore is useful to gain an appreciation of some of the potentially influential parameters in the prediction of the response variables. However, it is not recommended to use these models for reliable prediction alone. Many of these relationships were found to be useful when incorporating a second predictor variable into models for MRA (see section 7.3.3.2).

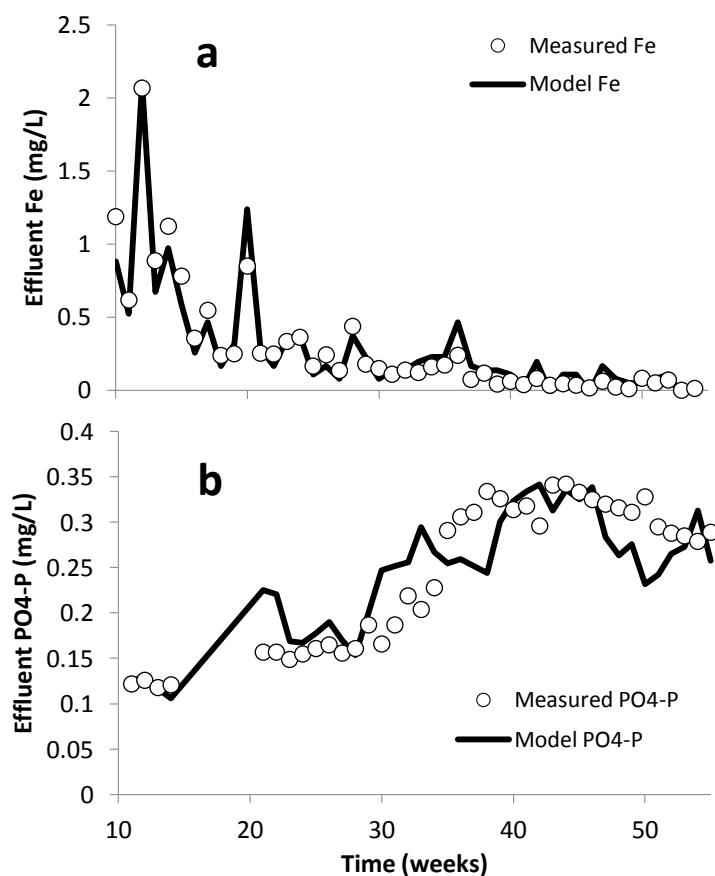


Figure 7-5 - Selected examples of model-fit diagrams: (a) $Fe\ eff = 0.0298(TSS\ eff) - 0.131$ ($R^2 = 0.9217$), unit 2 (b) $PO_4\text{-}P\ eff = -0.1531(pH\ eff) + 1.6063$ ($R^2 = 0.6973$), unit 8

In unit 3, EC was found to be a predictor variable for statistically significant relationships with Fe, TN, TP, and $PO_4\text{-}P$. However, these four models should not be

considered as reliable as the others, due to a combination of the fact that effluent sampling was only possible every second week in unit 3 (due to the dosing regime) and the fact that EC data was unavailable until week 21. Thus, it is recommended that these three models are not treated with the same level of reliability as the others. Similar care should be taken when interpreting the models developed from the results of unit 6, which also had a significantly reduced dataset due to its dosing regime (extended dry periods).

7.3.3.2. Multiple regression models

10 multiple regression models were developed from the MRA, producing two model structures. The first type uses 2 predictor variables while the second uses 3 predictors. The variables, model constants and R² values for those models that satisfied the F and P value conditions described in section 7.2.1 are given in Table 7-3 (two predictor variables) and Table 7-4 (three predictor variables).

Table 7-3 - Variables, constants and R² values for multiple regression models with 2 predictor variables

CW unit	y	x ₁	x ₂	a ₁	a ₂	b	Adjusted R ²
1	Fe eff	TSS eff	TSS R.E.	0.0164	1.0889	-1.15142	0.8784
2	Fe eff	TSS eff	TSS R.E.	0.0480	3.3466	-3.4805	0.9301
	Zn eff	TSS eff	TSS R.E.	0.0036	0.2516	-0.2573	0.9221
3	Fe eff	TSS eff	EC	0.0067	0.3794	-0.2296	0.9530
4	Fe eff	TSS eff	TSS R.E.	0.0171	1.1798	-1.2276	0.8649
5	NO ₃ -N eff	Time	TSS R.E.	-0.0373	0.8033	-3.9263	0.7433
7	TN eff	Time	pH	-0.0292	2.4410	-14.3239	0.8620
	NH ₄ -N eff	Time	TSS Eff	-0.0033	0.0043	0.2123	0.7795
8	PO ₄ -P eff	Time	pH	0.0036	-0.0727	0.7634	0.8118

The inclusion of TSS removal efficiency as a predictor variable was found to produce models with improved R² values compared to the simple regression models for effluent Fe concentration prediction in units 1, 2, and 4, and effluent Zn prediction in unit 2. The inclusion of TSS removal efficiency was in fact initially taken with all units, producing improved R² values for Fe predictions, but MRA for units 3, 5, 6, 7 and 8 found that the P values for the TSS removal efficiency variables exceeded 0.05, so they were not deemed statistically significant for 95% model confidence. There were multiple cases for various other parameters where a multiple

regression model was created that produced an improved R^2 value, but P values of one or more variables showed them to be statistically insignificant to the model. Therefore, many multiple regression models were rejected through the desire to achieve 95% model confidence. The F and P values for all multiple regression models are shown in Table 7-5.

The addition of time as a second predictor variable produced four statistically significant models with improved adjusted R^2 values: effluent $\text{NO}_3\text{-N}$ prediction in unit 5 from time and TSS removal efficiency; effluent TN prediction in unit 7 from time and effluent pH; effluent $\text{NH}_4\text{-N}$ prediction from time and effluent TSS concentration; and effluent $\text{PO}_4\text{-P}$ prediction in unit 8 from time and effluent pH. Figure 7-6 shows a model-fit chart of $\text{PO}_4\text{-P}$ prediction in unit 8, comparing the multiple regression model to the simple model that predicted effluent $\text{PO}_4\text{-P}$ from pH alone. The improvement in fit to the measured data can be seen visually with the inclusion of time as a second response variable. The production of these models highlights the importance of the maturation process in stormwater CWs, showing that the systems were constantly changing over the length of the experiment, impacting on nutrient effluent concentrations. Therefore, although time is a useful predictor variable for these models, it is not possible to foresee what changes in nutrient behaviour may arise beyond the timescale of this experiment, as time as a factor does not directly influence this and therefore cannot be used to measure nutrient fluctuations.

As was the case with the simple regression models, the model for unit 3 should not be regarded to be as reliable as the other multiple regression models, since it was developed from significantly less input data. This was due to a combination of the fact that the effluent sampling was only possible every second week (due to the dosing regime) and the fact that EC data was unavailable until week 21. However, the model still highlights important relationships between Fe and the two variables. The P-value of effluent TSS (3.66×10^{-8}) was much lower than that for EC (0.0028), which shows that TSS is the most significant influence on the effluent Fe concentration by a very large margin. Still, the relationship between effluent Fe and

EC may suggest that some of the effluent Fe may have been present in dissolved form, since EC measures dissolved solids. Further experimentation to collect a more significant volume of data for EC in unit 3 would help to ascertain whether this relationship is fully valid or not.

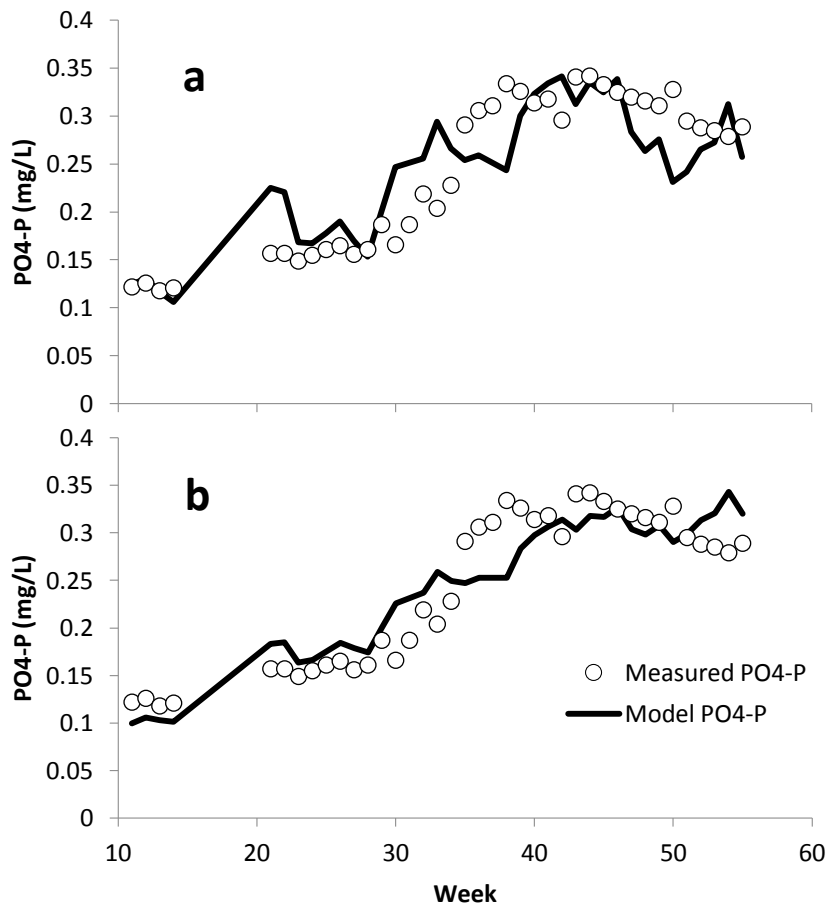


Figure 7-6 - Model fit of PO₄-P prediction in unit 8 with (a) only pH as a predictor variable ($R^2 = 0.6973$), (b) pH and time as predictor variables (adjusted $R^2 = 0.8118$)

The single model that incorporated three predictor variables used time, effluent TSS and TSS removal efficiency to predict effluent NH₄-N concentrations in unit 2. As mentioned previously, time was identified as having a relationship with effluent nutrient patterns in the pilot-scale CWs. The improvement in model fit with the combination of effluent TSS, TSS removal and time as predictor variables when

compared to the simple model of effluent NH₄-N prediction from effluent TSS alone can be seen in Figure 7-7.

Table 7-4 - Variables, constants and R² values for multiple regression models with 3 predictor variables

CW unit	y	x ₁	x ₂	x ₃	a ₁	a ₂	a ₃	b	R ²
2	NH ₄ -N eff	Time	TSS eff	TSS R.E.	-0.0010	0.0059	0.5819	-0.4917	0.9285

Again, several other models with three predictor variables were produced which increased R² values in comparison to the simple regression models or two-variable models for the same response parameter. However, the P values of one or more predictor variables in these models were found to be greater than 0.05, so the models were rejected because they did not offer 95% confidence. The F and P values for all multiple regression models are shown in Table 7-5.

Adjusted R² values for the multiple regression models give an indication of the quality of the model. For example, the R² value of 0.93 for the model in Table 7-4 indicates that 92.85% of the variance in results can be described by the model. Thus, it is an excellent fit of model. Three more multiple regression models have excellent R² values of above 0.9, while four models have 0.8 < R² < 0.9, showing a very good fit. The two remaining multiple regression models have R² values of 0.74 and 0.78, which, while they do not match the performance of the other models, still denotes good models. It is unsurprising that these models do not describe their relevant results as well as some of the other models, because they are used to predict effluent NO₃-N and NH₄-N from time and TSS. Despite the fact that these variables clearly have a statistically significant influence on effluent NO₃-N and NH₄-N concentrations, it is also known that other factors - that were unable to be measured - are important. Specifically, biological transformation of N is a key process in the CWs (see chapters 5 and 6), and so the availability of oxygen and denitrifying facultative heterotrophs are both examples of typical variables that would have been likely to significantly influence effluent NO₃-N and NH₄-N concentrations. Had these been measured and incorporated into the models, it is likely that the R² values would be greater. In contrast, R² values for the prediction of effluent Fe and Zn

concentrations in unit 2 were very high, which was also unsurprising due to the fact that partitioning analysis determined that these metals were entirely particulate/associated with particles in the outflow of unit 2. Despite having the highest R^2 value (0.953), the effluent Fe prediction model for unit 3 should not be considered as reliable as the other models as it used significantly less input data. However, as the statistical analysis has shown, the model is still good, and can be used to get an idea of the system behaviour.

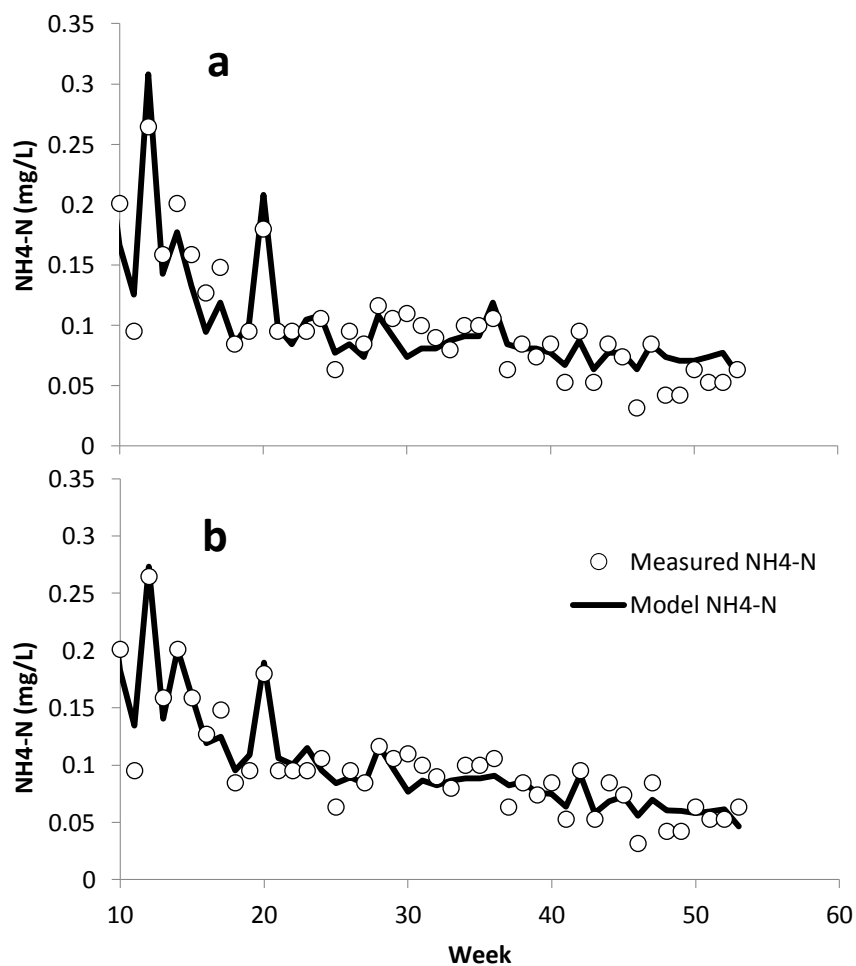


Figure 7-7 - Model fit of NH₄-N prediction in unit 2 with (a) only effluent TSS as a predictor variable ($R^2 = 0.8675$), (b) effluent TSS, time and TSS removal efficiency as predictor variables (adjusted $R^2 = 0.9233$)

The F-values shown in Table 7-5 confirm that all of the multiple regression models presented are statistically significant to 95% confidence, since $F < 0.05$.

Furthermore, the highest F-value is 1.1×10^{-9} (for $\text{NH}_4\text{-N}$ prediction in unit 7), an extremely low value which adds confidence to the use of these models.

Similarly, the P-values are extremely low and, in all but three models, all variables are statistically significant to a minimum of 99% confidence. In units 2 and 4, TSS removal efficiency as a predictor variable is statistically significant to >98% and >95% confidence respectively, and in unit 5 pH as a predictor is statistically significant to >98% confidence. In each model, one predictor variable is always far more statistically significant than the other(s): e.g., effluent TSS always has a much lower P-value than TSS removal efficiency for effluent metal concentration predictions. Thus the simple regression models that use these predictor variables for their respective response variables can be considered very reliable. The MRA has simply refined these models to give improved fits to the data.

Table 7-5 – Statistical significance of multiple regression models and their predictor variables (F and P values)

CW Unit	Response variable	Significance F	Predictor variables	P-values
1	Fe eff	2.3×10^{-20}	TSS eff TSS R.E.	3.4×10^{-12} 0.00212
2	Fe eff	2.03×10^{-25}	TSS eff TSS R.E.	1.5×10^{-8} 0.009947
	Zn eff	1.96×10^{-24}	TSS eff TSS R.E.	4.95×10^{-8} 0.0134
	$\text{NH}_4\text{-N}$ eff	1.6×10^{-23}	Time TSS eff TSS R.E.	0.00012 4.8×10^{-9} 0.00032
3	Fe eff	9.18×10^{-10}	TSS eff EC eff	3.66×10^{-8} 0.002819
4	Fe eff	2.08×10^{-19}	TSS eff TSS R.E.	1.55×10^{-6} 0.048416
5	$\text{NO}_3\text{-N}$ eff	8.8×10^{-12}	Time pH	3.8×10^{-6} 0.016
7	TN eff	6.8×10^{-12}	Time pH	0.00909 2.3×10^{-7}
	$\text{NH}_4\text{-N}$ eff	1.1×10^{-9}	Time TSS eff	0.00013 0.00017
8	$\text{PO}_4\text{-P}$ eff	3.3×10^{-14}	Time pH	1.5×10^{-5} 0.00117

7.4. Summary

It was found that many of the more expensive/difficult to measure parameters measured from the pilot-scale stormwater CWs were able to be successfully predicted by the development of regression models which required only the knowledge of relatively less expensive/easier to measure parameters.

Potential relationships between these two categories of parameters were identified in all eight CWs through PCA and then confirmed through correlation analysis. The majority of these relationships involved TSS (particularly with metals), which highlights the significant role that sedimentation and filtration plays in pollutant removal in stormwater treatment systems of this type. There were also several strong relationships identified between nutrient concentrations and time.

Fifty-six simple regression models were developed based on the significant relationships identified in the correlation analysis. Of these, five can be considered excellent fits to the data. A further twenty models can be considered as very good fits to the data: these twenty-five models are therefore recommended for reliable prediction of expensive/difficult to measure parameters in the stormwater CWs. These models predict either effluent metal concentrations from TSS data or effluent nutrient concentrations from time, with one exception in unit 7: TN prediction from pH.

Ten multiple regression models were developed based on the significant relationships identified in the correlation analysis. Of these, four can be considered excellent fits to the data. A further four can be considered as very good fits to the data. Seven of these eight models are recommended for reliable prediction of expensive/difficult to measure parameters in the stormwater CWs. The excluded model, which predicts Fe from TSS and EC in unit 3, was based on a smaller dataset in comparison to the other models and therefore should not be treated with the same level of reliability. The remaining models, with R^2 values of 0.74 and 0.78, can be considered good fits to the data, and can provide adequately approximate predictions of effluent $\text{NO}_3\text{-N}$ concentrations in unit 5 and effluent $\text{NH}_4\text{-N}$ concentrations in unit 7 in order to get an idea of behaviour of these pollutants in the systems. Most of the

models predict either metal removal from effluent TSS concentration and TSS removal or nutrient removal from time and pH. One multiple regression model was developed that incorporates three predictor variables (time, effluent TSS concentration and TSS removal efficiency) in order to model effluent $\text{NH}_4\text{-N}$ concentrations in unit 2.

The development of the regression models helped to further understand some of the internal processes and mechanisms in tidal-flow stormwater CWs, and this should serve as a guide for any future work as to which parameters are important in these processes. Firstly, TSS was extremely important for many parameters, particularly metals. Effluent metal concentrations were extremely heavily influenced by effluent TSS concentrations and TSS removal efficiencies. Therefore, efficient solids removal is paramount for the effective removal of heavy metals in this type of system. TSS was also found to have a significant influence on effluent concentrations of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ in some units, which suggests that, while biological transformation is the dominant process governing their behaviour, some of these ions can be associated with particulates also. Secondly, time was of large significance when modelling nutrient predictions. Effluent nutrient concentrations were continually changing over time, and thus it should be noted that these parameters need to be regarded carefully when analysing CW behaviour, particularly as the CW matures and adapts. Even beyond the initial plant establishment period, effluent nutrient concentrations continue to change, e.g., the increase of $\text{PO}_4\text{-P}$ with time. The importance of pH should also be noted: in the multiple regression model developed for unit 7, pH decrease may reflect the increase in nitrification as the system's biological community develops. Meanwhile, in the model for unit 8, pH decrease over time may have caused a decrease in $\text{PO}_4\text{-P}$ removal through precipitation, as conditions become less suitable for this process.

8. Conclusions

8.1. Summary

This thesis concerned the design and assessment of novel constructed wetland systems for stormwater treatment. The systems were specifically designed with a tidal-flow regime in order to target the reduction of nitrate concentrations to a greater extent than exhibited in other stormwater CW configurations, while maintaining high pollutant removal efficiency capabilities with regard to a range of stormwater priority pollutants. The study aimed to assess the effectiveness of the CWs, understand the internal CW processes and develop models to demonstrate the potential of the system. This was achieved by fulfilling the two main research aims:

1. Design and assess a novel configuration of vertical flow CWs for stormwater treatment.
2. Develop models to further the understanding and accurately predict the performance of the CW system and investigate the processes occurring within..

The main conclusions from the research carried out to fulfil these aims are presented in the following section.

8.2. Conclusions

8.2.1. Design and assessment of pilot-scale CWs

Eight pilot-scale stormwater CWs were set up at the School of Engineering, Cardiff University, to experimentally assess the long-term pollutant removal capabilities of the novel tidal-flow CW design. The performance of the systems was considered successful when compared to results of similar pilot-scale CWs that operated without tidal flow. N removal was enhanced by the system design, after the CWs had matured over time. Similarly, TSS, P and metal removal (with the exception of Zn) matched or outperformed alternative system designs. The experimental assessment identified physical processes, such as straining and sedimentation, as major removal mechanisms for TSS and heavy metal reduction. The main pathway of N removal

was identified as biological transformation, while chemical precipitation is thought to have played a key role in P reduction.

The three design variables (CW media, WWAR and wetting/drying regime) were found to have significant impacts on the removal of different pollutants. BFS was the most effective media for the removal of TSS and heavy metals since it did not require a settling period, while loamy sand is the preferred material for nutrient reduction due to its advanced biological activity. Smaller WWAR values improved TSS removal, possibly due to an increased rate of solids aggregation in the system, whereas nutrient removal was enhanced by larger values. However, after the CWs had matured, all WWAR configurations provided relatively similar results. CWs with enforced drought periods showed improved Zn removal, as the release of Zn bound to DOM associated with increased biological activity was not evident in their effluents. This is likely because the reduced inflow to the systems resulted in reduced nutrient intake and thus reduced biological growth. For the same reason, the WC CW exhibited the best N removal due to its superior biological development.

Further understanding of the stormwater CWs was gained by laboratory-based analysis of the loamy sand and BFS. Elemental composition analysis showed significant fractions of Ca in both materials. This backed the theory that $\text{PO}_4\text{-P}$ was likely being reduced in part by chemical precipitation. Furthermore, the presence of notable fractions of Mg in the BFS indicates good heavy metal adsorptive capacity of the material. Batch adsorption tests determined the metal adsorption characteristics of the media, finding that the adsorption rate of all metals to both media types was quick with the majority of the reaction taking place within 5 minutes. The reaction rate was well described by the pseudo-second-order model, which indicates that chemisorption was the controlling factor in the adsorption rate of all metals to both media types.

The experimental design and methodology can serve as a blueprint for further investigation into the use of tidal-flow CWs for stormwater treatment, hence enhancing the body of knowledge for stormwater treatment.

8.2.2. Model development

The successful application of the mechanistic HYDRUS model deepened understanding of the stormwater CWs, confirming that oxidation of $\text{NH}_4\text{-N}$ by autotrophic bacteria (*Nitrosomonas spp.*) was the main removal mechanism for this parameter. This confirmed that biological transformation was the biggest influence on N behaviour in the systems, and showed that a reliable model can be constructed using HYDRUS to predict N behaviour under different conditions. As such, the model showed that the retention time for N removal in the systems could be cut to an optimum 6 hours, while, if required, the drainage time could also be reduced to 7.5 hours. The work carried out with HYDRUS also demonstrated how to set up a tidal-flow wetland regime in the program, by overcoming a limitation of the software: the fact that time-variable boundary conditions cannot be established. This model set-up can now be used and possibly improved on by future researchers to investigate tidal flow CWs for stormwater treatment.

Statistical analysis of the data gleaned from the pilot-scale stormwater CWs was used to develop predictive models for effluent pollutant concentrations. Furthermore, the models predict concentrations of more expensive/difficult to measure pollutants from the knowledge of relatively less expensive/easier to measure parameter concentrations/values. A combination of PCA and correlation analysis identified statistically significant relationships and both simple and multiple regression models were developed from the data. In total, 56 simple regression models and 10 multiple regression models were developed. The relationships between parameters discovered in the statistical analysis also further enhanced the understanding of internal CW processes. The importance of TSS removal was reinforced, while the effect of pH on $\text{PO}_4\text{-P}$ removal was highlighted and pH as an indicator of nitrification in one unit was a useful sign of increased biological development. These findings bolstered the theories developed from general observation of the pilot-scale CW experiments.

8.3. Recommendations for further work

1. With the successful pollutant reduction performance achieved by the pilot-scale CWs, a field-scale physical model would be the next logical step. A HDPE pipe size of 400 mm internal diameter was used for this study, but the

same manufacturer produces a range of pipe sizes up to 3500 mm internal diameter. A prototype using a unit of this size would better represent field conditions, with the application of larger inflows to represent larger catchment areas. A long-term study of 2 years would be relatively easy to set up having learned the lessons of this study, which was the first of its kind conducted at the School of Engineering, Cardiff University. The new study may also benefit from the improved understanding of the application of HYDRUS to tidal-flow CWs that was presented in this study. This would aid experimental design, e.g., implementing the optimum retention and drainage times for NH₄-N removal.

2. This study has demonstrated that tidal-flow CWs can be used to effectively reduce a range of priority pollutants from stormwater runoff. However, stormwater flows are stochastic, so inflow batch doses to the systems cannot be expected in such a regime as was exercised in the experimental side of this project. Therefore, further research to engineer a way of adapting tidal flow CWs to deal with the stochastic nature of rainfall is required. This could perhaps be achieved through the design of a forebay to the CW that releases the inflow when a certain volume is reached. Whatever design is investigated, it would be a crucial step to the implementation of these potentially valuable stormwater treatment systems.
3. Any future experimental work carried out on pilot-scale or field-scale tidal-flow stormwater CWs would benefit from the continuous measurement of dissolved oxygen and redox potential in the systems. It is felt that measurement of these parameters would have given a greater understanding of the N transformation process in the tidal-flow CWs, indicating the times during the inflow/outflow cycle at which oxygen concentrations were highest/lowest, impacting on oxidation and nitrification/denitrification processes.
4. The batch adsorption results presented in chapter 4 are based on the use of a single metal adsorbate solution in each case. Thus, it is possible that different results may have been produced with the use of a multi-metal adsorbate solution. This would have been more representative of the semi-synthetic

stormwater used in the pilot-scale CW inflow (and indeed real stormwater), but was not investigated due to time and financial restraints. Thus a simple series of batch adsorption tests using multi-metal adsorbate solution would further refine the understanding of metal adsorption to the media used in the CWs.

5. Despite a wide range of stormwater priority pollutants having been addressed in this study, stormwater can contain a great deal of alternative pollutants. Additional research to determine the capability of the tidal-flow CW design to reduce contaminants such as polycyclic aromatic hydrocarbons (PAHs), various herbicides and oil and grease would be of great benefit. This research is essential if there is to be potential for the wider implementation of tidal-flow stormwater CWs.

References

- Adams, 2004. *Chemometrics in analytical spectroscopy*, 2nd ed. Cambridge: Royal Society of Chemistry.
- Adeola, S.O., Revitt, D.M., Shutes, R.B.E., Garelick, H., Jones, H. and Jones, C., 2009. Constructed wetland control of BOD levels in airport runoff. *International Journal of Phytoremediation*, 11(1), 1-10.
- APHA (American Public Health Association), AWWA (American Water Works Association), and WEF (Water Environment Federation), 2012. *Standard Methods for the Examination of Water and Wastewater* (22nd ed). Washington DC: American Public Health Association.
- Artola, A., Martin, M., Balaguer, M. and Rigola, M., 2000. Isotherm model analysis for the adsorption of Cd(II), Cu(II), Ni(II), and Zn(II) on anaerobically digested sludge. *Journal of Colloid and Interface Science*, 232(1), 64-70.
- Austin, D., Lohan, E. and Verson, E., 2003. "Nitrification and denitrification in a tidal vertical flow wetland pilot", in *Proceedings of the Water Environment Federation Technical Conference 2003, Los Angeles, California*.
- Babatunde, A.O. and Zhao, Y.Q., 2010. Equilibrium and kinetic analysis of phosphorus adsorption from aqueous solution using waste alum sludge. *Journal of Hazardous Materials*, 184(1-3), 746-752.
- Baldizón, M.E., Dolmus, R., Quintana, J., Navarro, Y. and Donze, M., 2002. Comparison of conventional and macrophyte-based systems for the treatment of domestic wastewater. *Water Science and Technology*, 45(1), 111-116.
- Birch, G.F., Matthai, C., Fazeli, M.S. and Suh, J.Y., 2004. Efficiency of a constructed wetland in removing contaminants from stormwater. *Wetlands*, 24(2), 459-466.
- Blecken, T-B., Marsalek, J. And Viklander, M., 2011. Laboratory study of stormwater biofiltration in low temperatures: Total and dissolved metals removals and fates. *Water, Air and Soil Pollution*, 219(1-4), 303-317.

- Blecken, G.T., Zinger, Y., Deletic, A., Fletcher, T.D., Hedström, A. and Viklander, M., 2010. Laboratory study on stormwater biofiltration: Nutrient and sediment removal in cold temperatures. *Journal of Hydrology* 394(3-4), pp. 507-514.
- Blecken, T-B., Zinger, Y., Deletic, A., Fletcher, T.D. and Viklander, M., 2009a. Impact of submerged zone and a carbon source on heavy metal removal in stormwater biofilters. *Ecological Engineering*, 35(5), 769-778.
- Blecken, T-B., Zinger, Y., Deletic, A., Fletcher, T.D. and Viklander, M., 2009b. Influence of intermittent wetting and drying conditions on heavy metal removal by stormwater biofilters. *Water Research*, 43(18), 4590-4598.
- Bratieres, K., Fletcher, T.D., Deletic, A. and Zinger, Y., 2008. Nutrient and sediment removal by stormwater biofilters: A large-scale design optimisation study. *Water Research*, 42(14), 3930-3940.
- Brix, H., 1993. Wastewater treatment in constructed wetlands: system design, removal processes and treatment performance. In: Moshiri, G.A. ed. *Constructed Wetlands for Water Quality Improvement*. Boca Raton, Florida: CRC Press Inc, pp. 9-23.
- Bulc, T. and Slak, A.S., 2003. Performance of constructed wetland for highway runoff treatment. *Water Science and Technology*, 48(2), 315-322.
- Butler, D., Memon, F.A., Makropoulos, C., Southall, A. and Clarke, L., 2010. *WaND Guidance on water cycle management for new developments*. London: Construction Industry Research & Information Association (CIRIA), Report C690.
- Carleton, J.N., Grizzard, T.J., Godrej, A.N. and Post, H.E., 2001. Factors affecting the performance of stormwater treatment wetlands. *Water Research*, 35(6), 1552-1562.
- Chen, Z.B., Kusch, P., Reiche, N., Borsdorf, H., Kästner, M. and Köser, H., 2012. Comparative evaluation of pilot scale horizontal subsurface-flow constructed wetlands and plant root mats for treating groundwater contaminated with benzene and MTBE. *Journal of Hazardous Materials*, 209(1), 510-515.

- Choi, J.W., Chung, S.G., Hong, S.W., Kim, D.J. and Lee, S.H., 2012. Development of an environmentally friendly adsorbent for the removal of toxic heavy metals from aqueous solution. *Water, Air and Soil Pollution*, 223(4), 1837-1846.
- Christensen, R., 1987. *Plane Answers to Complex Questions: The Theory of Linear Models*. Springer-Verlag New York Inc.
- Constructed Wetland Association, 2008. Constructed Wetlands Database Version 11.01.
- Cooper, P., 2007. The constructed wetland association UK database of constructed wetland systems. *Water Science and Technology*, 56 (3), 1-6.
- Cooper, P.F., Job, G.D., Green, M.B. and Shutes, R.B.E., 1996. *Reed beds and constructed wetlands for wastewater treatment*. Swindon: WRc Publications.
- Cresswell, H.P. and Hamilton, G.J., 2002. Particle Size Analysis. In: N.J. McKenzie, H.P. Cresswell and K.J. Coughlan, eds. *Soil Physical Measurement and Interpretation for Land Evaluation*. Victoria: CSIRO Publishing, 224-239.
- Dada, A.O., Olalekan, A.P., Olatunya, A.M. and Dada, O., 2012. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk. *Journal of Applied Chemistry*, 3(1), 38-45.
- Dantas, T.N.D.C., Neto, A.A.D. and Moura, M.C.P.D.A., 2001. Removal of chromium from aqueous solutions by diatomite treated with microemulsion. *Water Research*, 35(9), 2219-2224.
- Davis, A.P., Shokouhian, M., Sharma, H. and Minami, C., 2006. Water quality improvement through bioretention media: nitrogen and phosphorus removal. *Water Environment Research*, 73(1), 5-14.
- DEFRA. 2008. *Future Water* [Online]. Norwich: The Stationery Office. Available at: <http://www.defra.gov.uk/publications/2011/06/16/pb13562-future-water/> [Accessed: 20/02/12].
- DEFRA, 2012. *Consultation on implementation of the Sustainable Drainage Systems (SuDS) provisions in Schedule 3 of the Flood and Water Management Act*

- 2010: *Summary of Consultation Responses* [online]. Available from: <http://www.defra.gov.uk/consult/files/suds-consult-sum-resp.pdf/> [Accessed 10 January 2013].
- Demirbas, A., Pehlivan, E., Gode, F., Altun, T. and Arslan, G., 2005. Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) from aqueous solution on Amberlite IR-120 synthetic resin. *Journal of Colloid and Interface Science*, 282(1), 20-25.
- Demirbas, E., Dizge, N., Sulak, M.T. and Kobya, M., 2009. Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon. *Chemical Engineering Journal*, 148(2-3), 480-487.
- Department of Transport, Local Government and Regions, 2001. *Vegetative treatment systems for highway runoff. Design manual for Roads and Bridges*. London: HMSO, Advice Note, Volume 4, Section 2. Part 1, Highways Agency 103/01.
- Dobson, J.A., 2002. *An Introduction to Generalized Linear Models*, 2nd Ed. Chapman & Hall/CRC. Florida.
- Draper, N.R., and Smith, H., 1998. *Applied Regression Analysis*, 3rd Ed. John Wiley and Sons, USA.
- Duncan, H. 1999. *Urban Stormwater Quality: A Statistical Overview*. Melbourne: Cooperative Research Centre for Catchment Hydrology, Monash University.
- Dussailant, A., 2012. Stormwater Management. *Water & Sewerage Journal*, 2012(2), 39.
- Ellis, J.B., Shutes, R.B.E. and Revitt, M.D., 2003. *Constructed Wetlands and Links with Sustainable Drainage Systems* [online]. Bristol: Environment Agency. Available from: <https://eprints.mdx.ac.uk/6076/1/SP2-159-TR1-e-p.pdf/> [Accessed 22 February 2012].
- Eriksson, E., Baun, A., Scholes, L., Ledin, A., Ahlman, S., Revitt, M., Noutsopoulos, C. and Mikkelsen, P.S., 2007. Selected stormwater priority pollutants - a European perspective. *Science of the Total Environment*, 383(1-3), 41-51.

References

- European Commission. 2012. *Introduction to the new EU Water Framework Directive* [Online]. Available at: http://ec.europa.eu/environment/water/water-framework/info/intro_en.htm [Accessed: 15th March 2013].
- European Union, 2006. *Directive 2006/44/EC of the European Parliament and of the Council of 6 September 2006 on the quality of fresh waters needing protection or improvement in order to support fish life* [online]. Available from: <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2006:264:0020:0031:EN:PDF> [Accessed 23rd April 2015]
- FAWB. 2009a. *Biofiltration Filter Media Guidelines (Version 3.01)*. Melbourne: Facility for Advancing Water Biofiltration. Available from: http://graie.org/SOCOMA/IMG/pdf/FAWB_Filter_media_guidelines_v3_June_2009-2.pdf [Accessed 5 May 2012].
- FAWB. 2009b. *Condition Assessment and Performance Evaluation of Biofiltration Systems. Practice Note 2: Preparation of Semi-Synthetic Stormwater*. Melbourne: Facility for Advancing Water Biofiltration. Available from: <http://www.monash.edu.au/fawb/products/fawb-adoption-guidelines-appendices.pdf> [Accessed 10 May 2012].
- Feng, W., Hatt, B.E., McCarthy, D.T., Fletcher, T.D. and Deletic, A., 2012. Biofilters for stormwater harvesting: Understanding the treatment performance of key metals that pose a risk for water use. *Environmental Science and Technology*, 46(9), 5100-5108
- Flood and Water Management Act 2010. 2010 legislation, c.29. UK: The Stationery Office Limited. Available from: http://www.legislation.gov.uk/ukpga/2010/29/pdfs/ukpga_20100029_en.pdf [Accessed 12 Feb 2012].
- Foo, K.Y. and Hameed, B.H., 2010. Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, 156(1), 2-10.

- Fournel, J., Forquet, N., Molle, P. and Grasmich, A., 2013. Modelling constructed wetlands with variably saturated vertical subsurface-flow for urban stormwater treatment. *Ecological Engineering*, 55, 1-8.
- Ghunmi, L.A., Zeeman, G., Fayyad, M. and van Lier, J.B., 2011. Grey water biodegradability. *Biodegradation*, 22(1), 163-174.
- Giæver, H. M., 2003. Experience and results from the northernmost constructed wetland in Norway. *Advances in Ecological Sciences*, 11, 215-236.
- Gottschall, N., Boutin, C., Crolla, A., Kinsley, C. and Champagne, P., 2007. The role of plants in the removal of nutrients at a constructed wetland treating agricultural (dairy) wastewater, Ontario, Canada. *Ecological Engineering*, 29(2), 154-163.
- Gregoire, C., Elsaesser, D., Huguenot, D., Lange, J., Lebeau, T., Merli, A., Mose, R., Passeport, E., Payraudeau, S., Schütz, T., Schulz, R., Tapia-Padilla, G., Tournebize, J., Trevisan, M. and Wanko, A., 2009. Mitigation of agricultural nonpoint-source pesticide pollution in artificial wetland ecosystems. *Environmental Chemistry Letters*, 7(3), 205-231.
- Grüneberg, B. and Kern, J., 2001. Phosphorus retention capacity of iron-ore and blast furnace slag in subsurface flow constructed wetlands. *Water Science and Technology*, 44(11-12), 69-75.
- Gupta, S.S. and Bhattacharyya, K.G., 2011. Kinetics of adsorption of metal ions on inorganic materials: A review. *Advances in Colloid and Interface Science*, 162(1-2), 39-58.
- Halcrow/UPRC, 2000. *Protection of the water environment using balancing facilities. Final Field Studies Report*. Reading: Halcrow & Urban Pollution Research Centre, Middlesex University, Environment Agency Thames Region.
- Hares, R.J. and Ward, N.I., 2004. Sediment accumulation in newly constructed vegetative treatment facilities along a new major road. *Science of the Total Environment*, 334, 473-479.

- Hatt, B.E., Deletic, A. and Fletcher, T.D., 2006. Integrated treatment and recycling of stormwater: a review of Australian practice. *Journal of Environmental Management*, 79, 102-113.
- Hatt, B.E., Deletic, A. and Fletcher, T.D., 2007a. Stormwater reuse: designing biofiltration systems for reliable treatment. *Water Science and Technology*, 55(4), 201-209.
- Hatt, B.E., Fletcher, T.D. and Deletic, A., 2007b. Hydraulic and pollutant removal performance of stormwater filters under variable wetting and drying regimes. *Water Science and Technology*, 56(12), 11-19.
- Hatt, B.E., Fletcher, T.D. and Deletic, A., 2007c. Treatment performance of gravel filter media: Implications for design and application of stormwater infiltration systems. *Water Research*, 41(12), 2513-2524.
- Henderson, C., Greenway, M. and Phillips, I., 2007. Removal of dissolved nitrogen, phosphorus and carbon from stormwater by biofiltration mesocosms. *Water Science and Technology*, 55(4), 183-191.
- Henze, M., Gujer, W., Mino, T. and van Loosdrecht, M.C.M., 2000. Activated sludge models ASM1, ASM2, ASM2D and ASM3, *IWA Scientific and Technical Report No. 9*. London: IWA Publishing.
- Hijosa-Valsero, M., Sidrach-Cardona, R., Martín-Villacorts, J., Valsero-Blanco, M.C., Bayona, J.M. and Bécares, E., 2011. Statistical modelling of organic matter and emerging pollutants removal in constructed wetlands. *Bioresource Technology*, 102(8), 4981-4988.
- Ho, Y.S. and McKay, G., 1999. The sorption of lead(II) ions on peat. *Water Research*, 33(2), 578-584.
- Hu, Y., Zhao, Y. and Rymaszewicz, A., 2014. Robust biological nitrogen removal by creating multiple tides in a single bed tidal flow constructed wetland. *Science of the Total Environment*, 470-471(1), 1197-1204.
- I.C.E., 2012. *The State of the Nation: Water* [online]. Available from: <http://www.ice.org.uk/getattachment/86d84a07-f7d6-4027-b477-e751b845aaa5/State-of-the-Nation-Water.aspx> [Accessed 29 August 2012].

- Idris, S.M., Jones, P.L., Salzman, S.A. and Allinson, G., 2012. Performance of the Giant Reed (*Arundo donax*) in Experimental Wetlands Receiving Variable Loads of Industrial Stormwater. *Water Air and Soil Pollution*, 223(2), 549-557.
- Jackson, J.E., 2003. *A User's Guide to Principal Components*. John Wiley & Sons, New York.
- Jang, A., Seo, Y. and Bishop, P.L., 2005. The removal of heavy metals in urban runoff by sorption on mulch. *Environmental Pollution*, 133(1), 117-127.
- Jeyakumar, R.P.S. and Chandrasekaran, V., 2014. Adsorption of lead(II) ions by activated carbon prepared from marine green algae: Equilibrium and kinetic studies. *International Journal of Industrial Chemistry*, 5, 1-10.
- Joliffe, I.T., 2002. *Principal Component Analysis*, 2nd Ed. Springer-Verlag New York Inc.
- Jordau, C.P., Fernandes, R.B.A., Ribiero, K.L., Nascimento, B.S. and Barros, P.M., 2009. Zn(II) adsorption from synthetic solution and kaolin wastewater onto vermicompost. *Journal of Hazardous Materials*, 162(2-3), 804-811.
- Kadlec, R.H. and Knight, R.L., 1996. *Treatment Wetlands*. 1st ed. CRC Press, Boca Raton.
- Kadlec, R. H., Axler, R., McCarthy, B. and Henneck, J., 2003. Subsurface treatment wetlands in the cold climate of Minnesota. *In: Ü. Manssen and P. Jenssen*, eds. *Constructed Wetlands for Wastewater Treatment in Cold Climates*. Southampton: WIT Press, 19-51.
- Kadlec, R.H. and Wallace, S., 2009. *Treatment Wetlands*. 2nd ed. Boca Raton: CRC Press.
- Kao, C.M., Wang, J.Y., Lee, H.Y., and Wen, C.K., 2001. Application of a constructed wetland for non-point source pollution control. *Water Science and Technology*, 44(11-12), 585-590.
- Karthikeyan, G., Muthulakshmi Andal, N. and Anbalagan, K., 2005. Adsorption studies of iron(III) on chitin. *Journal of Chemical Sciences*, 117(6), 663-672.

- Kim, H., Seagren, E.A. and Davis, A.P., 2003. Engineered bioretention for removal of nitrate from stormwater runoff. *Water Environment Research*, 75(4), 355-367.
- Kim, D.H., Shin, M.C., Choi, H.D., Seo, C.I. and Baek, K., 2008. Removal mechanisms of copper using steel-making slag: adsorption and precipitation. *Desalination*, 223(1-3), 283-289.
- Kobyas, M., 2004. Removal of Cr(VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: kinetic and equilibrium studies. *Bioresource Technology*, 91(3), 317-321.
- Kokot, S., Grigg, M., Panayiotou, H. and Phuong, T.D., 1998. Data interpretation by some common chemometrics methods. *Electroanalysis*, 10(16), 1-8.
- Korkusuz, E.A., Beklioğlu, M. and Demirel, G.N., 2007. Use of blast furnace granulated slag as a substrate in vertical flow reed beds: Field application. *Bioresource Technology*, 98(11), 2089-2101.
- Langergraber, G., 2006. Simulation of the treatment performance of outdoor subsurface flow constructed wetlands in temperate climates. *Science of the Total Environment*, 380(1-3), 210-219.
- Langergraber, G., Pressl, A., Leroch, K., Rohrhofer, R. and Haberl, R., 2010. Comparison of single-stage and a two-stage vertical flow constructed wetland systems for different load scenarios. *Water Science and Technology*, 61(5), 1341-1348.
- Langergraber, G. and Simunek, J., 2005. Modeling variably saturated water flow and multicomponent reactive transport in constructed wetlands. *Vadose Zone Journal*, 4(4), 924-938.
- Lee, C., Fletcher, T.D. and Sun, G., 2009. Nitrogen removal in constructed wetland systems. *Engineering in Life Sciences*, 9(1), 11-22.
- LeFevre, G. H., Paus, K. H., Natarajan, P., Gulliver, J. S., Novak, P. J., and Hozalski, R. M., 2014. Review of Dissolved Pollutants in Urban Storm Water and Their Removal and Fate in Bioretention Cells. *Journal of Environmental Engineering*, 141(1), CID: 04014050.

- Li, H. and Davis, A.P. 2009. Water Quality Improvement through Reductions of Pollutant Loads Using Bioretention. *Journal of Environmental Engineering-Asce*, 135(8), 567-576.
- Liu, Y., 2006. Some considerations on the Langmuir isotherm equation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 274 (1-3), 34-36.
- Lu, C. and Chiu, H., 2006. Adsorption of zinc(II) from water with purified carbon nanotubes. *Chemical Engineering Science*, 61(4), 1138-1145.
- Mæhlum, T. and Jenssen, P.D., 2003. Design and performance of integrated subsurface flow wetlands in a cold climate. *In: Ü. Manssen and P. Jenssen, eds. Constructed Wetlands for Wastewater Treatment in Cold Climates.* Southampton: WIT Press, 69-86.
- Maillard, E., Payraudeau, S., Faivre, E., Grégoire, C., Gangloff, S. and Imfeld, G., 2011. Removal of pesticide mixtures in a stormwater wetland collecting runoff from a vineyard catchment. *Science of the Total Environment*, 409(11), 2317-2324.
- Martin, P., Turner, B., Dell, J., Pratt, C., Campbell, N., Payne, J. and Reed, B., 2000. *Sustainable urban drainage systems: A design manual for England & Wales.* London: Construction Industry Research & Information Association (CIRIA), Report C522.
- Martinez, C.E., Jacobsen, A.R. and McBride, M.B., 2003. Aging and temperature effects on DOC and elemental release from a metal contaminated soil. *Environmental Pollution*, 122(1), 135-143.
- Mathialagan, T., and Viraraghavan, T., 2002. Adsorption of cadmium from aqueous solutions by perlite. *Journal of Hazardous Materials*, 94(3), 291-303.
- Mays, P.A. and Edwards, G.S., 2001. Comparison of heavy metal accumulation in a natural wetland and constructed wetlands receiving acid mine drainage. *Ecological Engineering*, 16(4), 487-500.
- Meiorin, E. C., 1989. Urban Runoff Treatment in a Fresh/Brackish Water Marsh in Fremont, California. *In: D.A. Hammer, ed. Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural.* Chelsea, Michigan: Lewis Publishers Inc., 677-685.

- Mendiguchía, C., Moreno, C., Galindo-Riaño, M.D. and García-Vargas, M., 2004. Using chemometric tools to assess anthropogenic effects in river water: A case study: Guadalquivir River (Spain). *Analytica Chimica Acta*, 515(1), 143-149.
- Mendoza, C.A., Thierrien, R. and Sudicky, E.A., 1991. *ORTHOFEM User's Guide, Version 1.02*. Ontario: Waterloo Centre for Groundwater Research.
- Met Office, 2011. *Weather extremes: Temperature* [online]. Available from: <http://www.metoffice.gov.uk/climate/uk/extremes/#temperature/> [Accessed 25 April 2012].
- Meyer, D., Molle, P., Esser, D., Troesch, S., Masi, F. and Dittmer, U., 2013. Constructed Wetlands for Combined Sewer Overflow Treatment – Comparison of German, French and Italian Approaches. *Water* 5(1), 1-12.
- Miller, P.S., Mitchell, J.K., Cooke, R.A. and Engel, B.A., 2002. A wetland to improve agricultural subsurface drainage water quality. *Transactions of the ASAE*, 45(5), 1305-1317.
- Mitchell, C. and McNevin, D., 2001. Alternative analysis of BOD removal in subsurface flow constructed wetlands employing Monod kinetics. *Water Research*, 35(5), 1295-1303.
- Mitchell, G., 2005. Mapping hazard from urban non-point pollution: a screening model to support sustainable urban drainage planning. *Journal of Environmental Management*, 74(1), 1-9.
- Moore, T.L.C. and Hunt, W.F., 2012. Ecosystem provision by stormwater wetlands and ponds – A means for evaluation? *Water Research*, 46(20), 6811-6823.
- Nakamiya, K., Hashimoto, S., Ito, H., Edmonds, J.S., Yasuhara, A. and Morita, M., 2005. Microbial treatment of bis (2-ethylhexyl) phthalate in polyvinyl chloride with isolated bacteria. *Journal of Bioscience and Bioengineering*, 99(2), 115-119.
- Nanbakhsh, H., Kazemi-Yazdi, S. and Scholz, M., 2007. Design comparison of experimental storm water detention systems treating concentrated road runoff. *Science of the Total Environment*, 380(1-3), 200-228.

- Nelson, E.A., Specht, W.L. and Knox, A.S., 2006. Metal removal from water discharges by a constructed wetland. *Engineering in Life Sciences*, 6(1), 26-30.
- New Jersey Department of Environmental Protection, 2004. *New Jersey Stormwater Best Practices Manual Chapter 9.2: Standar for Constructed Stormwater Wetlands* [online]. Available from: http://www.njstormwater.org/bmp_manual/NJ_SWBMP_9.2%20print.pdf [Accessed 14 March 2013].
- Nieto, L.M., Alami, S.B.D., Hodaifa, G., Faur, C., Rodríguez, S., Giménez, J.A. and Ochando, J., 2010. Adsorption of iron on crude olive stones. *Industrial Crops and Products*, 32(3), 467-471.
- Nuttall, P.M., Boon, A.G. and Rowell, M.R., 1997. *Review of the design and management of constructed wetlands*. London: Construction Industry Research & Information Association (CIRIA), Report R180.
- Office for National Statistics, 2010. *Population Estimates for UK, England and Wales, Scotland and Northern Ireland - Mid 2010* [online]. Available from: <http://www.ons.gov.uk/ons/rel/pop-estimate/population-estimates-for-uk--england-and-wales--scotland-and-northern-ireland/mid-2010-population-estimates/index.html> [Accessed 7 March 2012].
- Ogbonna, A.C., Abii, T.A. and Onwu, F.K., 2014. Equilibrium studies on biosorption of lead, cadmium and nickel ions using cassava waste biomass. *Journal of Chemical and Pharmaceutical Research*, 6(12), 418-432.
- Olsen, R.L., Chappell, R.W. and Loftis, J.C., 2012. Water quality sample collection, data treatment and results presentation for principal components analysis – literature review and Illinois River watershed case study. *Water Research*, 46(9), 3110-3122.
- Pandhare, G.G., Trivedi, N., Pathrabe, R. and Dawande, S.D., 2013. Adsorption of cadmium(II) and lead(II) from a stock solution using neem leaves powder as a low-cost adsorbent. *International Journal of Innovative Research in Science, Engineering and Technology*, 2(10), 5752-5761.

- Parab, H., Joshi, S., Shenoy, N., Lali, A., Sarma, U.S. and Sudersanan, M., 2006. Determination of kinetic and equilibrium parameters of the batch adsorption of Co(II), Cr(III) and Ni(II) onto coir pith. *Process Biochemistry*, 41(3), 609-615.
- Patrulea, V., Negrulescu, A., Mincea, M.M., Pitulice, L.D., Spiridon, O.B. and Ostafe, V., 2013. Cu(II) adsorption on chitosan. *BioResources*, 8(1), 1147-1165.
- Pontier, H., Williams, J.B. and May, E., 2001. Metals in combined conventional and vegetated road runoff control systems. *Water Science and Technology*, 44(11-12), 607-614.
- Potgieter, J.H., Potgieter-Vermaak, S.S. and Kalibantonga, P.D., 2006. Heavy metals removal from solution by palygorskite clay. *Minerals Engineering*, 19(5), 463-470.
- Prabakaran, R. and Arivoli, S., 2012. Adsorption kinetics, equilibrium and thermodynamic studies of Nickel adsorption onto Thespesia Populnea bark as biosorbent from aqueous solutions. *European Journal of Applied Engineering and Scientific Research*, 1(4), 134-142.
- Rahman, R.A. and Anuar, N., 2009. Pentachlorophenol Removal via Adsorption and Biodegradation. *World Academy of Science, Engineering and Technology*, 31, 190-195.
- Ramos, R.L., Jacome, L.A.B., Barron, J.M., Rubio, L.F., and Coronado, R.M.G., 2002. Adsorption of zinc(II) from an aqueous solution onto activated carbon. *Journal of Hazardous Materials*, 90(1), 27-38.
- Reddy, K.R. and Patrick, W.H., 1984. Nitrogen transformations and loss in flooded soils and sediments. *CRC Critical Reviews in Environmental Science and Technology*, 13(4), 273-309.
- Reddy, K.R. and D'Angelo, E.M., 1997. Biogeochemical indicators to evaluate pollutant removal efficiency in constructed wetlands. *Water Science and Technology*, 35(5), 1-10.

- Reed, S.C., Middlebrooks, E.J. and Crites, R.W., 1998. *Natural systems for Waste Management and Treatment*, 2nd Ed., McGraw-Hill Professional, New York.
- Revitt, M., Shutes, B. and Scholes, L., 1999. The use of constructed wetlands for reducing the impacts of urban surface runoff on receiving water quality. In: J.B. Ellis, ed. *Impacts of Urban Growth on Surface Water and Groundwater Quality*. Wallingford: Int Assoc Hydrological Sciences, 349-356.
- Richardson, C.J. and Craft, C.B., 1993. Effective phosphorus retention in constructed wetlands: fact or fiction? In: Moshiri, G.A., (ed.), *Constructed Wetlands for Water Quality Improvement*. Lewis Publishers. Boca Raton, Florida, USA, 271-282.
- Ricordel, S., Taha, S., Cisse, I. and Dorange, G., 2001. Heavy metals removal by adsorption onto peanut husks carbon: characterization, kinetic study and modelling. *Separation and Purification Technology*, 24(3), 389-401.
- Rieuwerts, J.S., Thornton, I., Farago, M.E. and Ashmore, M.R., 1998. Factors influencing metal bioavailability in soils: preliminary investigations for the development of a critical loads approach for metals. *Chemical Speciation and Bioavailability*, 10(2), 61-75.
- Robati, D., 2013. Pseudo-second-order kinetic equations for modelling adsorption systems for removal of ions using multi-walled carbon nanotube. *Journal of Nanostructure in Chemistry*, 3(55), [online: <http://www.jnanochem.com/content/3/1/55>]
- Rose, E.P. and Rajam, S., 2012. Equilibrium study of the adsorption of iron (II) ions from aqueous solution on carbons from wild jack and jambul. *Advances in Applied Science Research*, 3(2), 1889-1894.
- Schaad, D.E., Chambers, W., Halley, J. and Denson, S., 2008. Design and performance of multipurpose constructed wetland and flow equalization basin. *Journal of Environmental Engineering*, 134(2), 118-125.
- Scholes, L.N.L., Shutes, R.B.E., Revitt, D.M., Purchase, D. and Forshaw, M., 1999. The removal of urban pollutants by constructed wetlands during wet weather. *Water Science and Technology*, 40(3), 333-340.

- Scholz, M., 2003. Performance predictions of mature experimental constructed wetlands which treat urban water receiving high loads of lead and copper. *Water Research*, 37(6), 1270-1277.
- Scholz, M., 2004. Treatment of gully pot effluent containing nickel and copper with constructed wetlands in a cold climate. *Journal of Chemical Technology and Biotechnology* 79(2), pp. 153-162.
- Scholz, M. and Hedmark, Å., 2010. Constructed wetlands treating runoff contaminated with nutrients. *Water, Air & Soil Pollution*, 205(1-4), 323-332.
- Scholz, M. and Xu, J., 2002. Comparison of constructed reed beds with different filter media and macrophytes treating urban stream water contaminated with lead and copper. *Ecological Engineering*, 18(3), 385-390.
- Scholz, O., Gawne, B., Ebner, B. and Ellis, I., 2002. The effects of drying and re-flooding on nutrient availability in ephemeral deflation basin lakes in western New South Wales, Australia. *River Research and Applications*, 18(2), 185-196.
- Schueler, T.R., 1992. *Controlling urban runoff: a practical manual for planning and designing urban BMPs*. Washington Council of Governments, Washington DC.
- Sekar, M., Sakthi, V. and Rengaraj, S., 2004. Kinetics and equilibrium adsorption study of lead(II) onto activated carbon prepared from coconut shell. *Journal of Colloid and Interface Science*, 279(2), 307-313.
- Settle, S., Goonetilleke, A. and Ayoko, G.A., 2007. Determination of surrogate indicators for phosphorus and solids in urban stormwater: Application of multivariate data analysis techniques. *Water, Air and Soil Pollution*, 182(1-4), 149-161.
- Shaw, P.J.A., 2003. *Multivariate Statistics for the Environmental Sciences*. Arnold, London.
- Shenker, M., Seitelbach, S., Brand, S., Haim, A. and Litaor, M.I., 2005. Redox reaction and phosphorus release in re-flooded soils of an altered wetland. *European Journal of Soil Science*, 56(4), 515-525.

- Shutes, B., Ellis, J.B., Revitt, D.M. and Scholes, L.N., 2005. Constructed wetlands in UK urban surface drainage systems. *Water Science and Technology*, 51(9), 31-37.
- Shutes, B. and Raggatt, L. 2010. *Development of generic Best Management Practice (BMP) Principles for the management of stormwater as part of an integrated urban water resource management strategy* [online]. SWITCH. Available from: http://www.switchurbanwater.eu/outputs/pdfs/W2-2_GEN_RPT_D2.2.5_BMP_principles_for_SWM.pdf/ [Accessed 3 April 2012].
- Shutes, R.B.E., 2001. Artificial wetlands and water quality improvement. *Environment International*, 26(5-6), 441-447.
- Shutes, R.B.E., Revitt, D.M., Scholes, L.N., Forshaw, M. and Winter, B., 2001. An experimental constructed wetland system for the treatment of highway runoff in the UK. *Water Science and Technology*, 44(11-12), 571-578.
- Simunek, J., van Genuchten, M. T. and Sejna, M., 2014. *The HYDRUS software package for simulating the two- and three-dimensional movement of water, heat and multiple solutes in variably saturated media. User Manual, 2.04.*
- Soda, S., Hamada, T., Yamaoka, Y., Ike, M., Nakazato, H., Saeki, Y., Kasamatsu, T. and Sakurai, Y., 2012. Constructed wetlands for advanced treatment of wastewater with a complex matrix from a metal-processing plant: Bioconcentration and translocation factors of various metals in *Acorus gramineus* and *Cyperus alternifolius*. *Ecological engineering*, 39, 63-70.
- Sun, G., Zhao, Y. and Allen, S., 2005. Enhanced removal of organic matter and ammoniacal-nitrogen in a column experiment of tidal flow constructed wetland system. *Journal of Biotechnology*, 115(2), 189-197.
- Swires, C., 2009. *Pilot Constructed Treatment Wetland and Natural Media Filter* Masters Thesis. University of Tennessee.
- Taylor, M. 2006. *An Assessment of Iron and Steel Slag for treatment of Stormwater Pollution*. Hamilton: Landcare Research.
- Terzakis, S., Fountoulakis, M.S., Georgaki, I., Albantakis, D., Sabathianakis, I., Karathanasis, A.D., Kalogerakis, N. and Manios, T., 2008. Constructed

- wetlands treating highway runoff in the central Mediterranean region. *Chemosphere*, 72(2), 141-149.
- Tomenko, V., Ahmed, S. and Popov, V., 2007. Modelling constructed wetland treatment system performance. *Ecological Modelling*, 205(3-4), 355-364.
- Tóth, J., 2002. *Adsorption: Theory, Modelling and Analysis*. Marcel Dekker, Inc., New York.
- Tryball, R.E., 1980. *Mass Transfers Operations*, 3rd ed. McGraw, New York.
- Uhl, M. and Dittmer, U., 2005. Constructed wetlands for CSO treatment: an overview of practice and research in Germany. *Water Science and Technology*, 51(9), 23-30.
- UK Technical Advisory Group on the Water Framework Directive, 2008. *Proposals for Environmental Quality Standards for Annex VII Substances* [online]. Available from: http://www.wfduk.org/sites/default/files/Media/Environmental%20standards/Specific%20pollutants%20proposals_Final_010608.pdf [Accessed 11th August 2013].
- United Nations, 2009. *Core Publications: Agenda 21* [online]. Available from: <http://www.un.org/esa/dsd/agenda21> [Accessed: 15 January 2012].
- U.S. EPA, 1993. *Design Manual: Nitrogen control*. EPA 625/R-93/010, United States Environmental Protection Agency, Office of Research and Development: Washington D.C.
- US EPA, 2000a. *A Handbook of Constructed Wetlands, Volume 5: Stormwater*. Washington: United States Environmental Protection Agency. Available from: <http://yosemite.epa.gov/water/owrccatalog.nsf/065ca07e299b464685256ce50075c11a/27d2b544e85d1d8285256d83004fdb0c!OpenDocument/> [Accessed 14 April 2012].
- US EPA, 2000b. *Constructed Wetlands Treatment of Municipal Wastewater*. EPA 625/R-99/010, United States Environmental Protection Agency, Office of Research and Development, Cincinnati, Ohio. Available from:

-
- <http://water.epa.gov/type/wetlands/restore/upload/constructed-wetlands-design-manual.pdf> [Accessed 6 June 2012].
- US EPA, 2000c. *Guiding principles for constructed treatment wetlands: Providing water quality and wildlife habitat*. EPA 843/B-00/003, United States Environmental Protection Agency, Office of Wetlands, Oceans and Watersheds, Washington D.C. Available from: <http://water.epa.gov/type/wetlands/constructed/upload/guiding-principles.pdf> [Accessed 3 June 2012].
- Vadivelan, V. and Kumar, K.V., 2005. Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. *Journal of Colloid and Interface Science*, 286(1), 90-100.
- Van de Graaf, AA., de Bruijn, P., Robertson, L.A., Jetten, M.S.M. and Kuenen, J.G., 1996. Autotrophic growth of anaerobic, ammonium-oxidising microorganisms in a fluidized bed reactor. *Microbiology*, 142(8), 2187-2196.
- Van Genuchten, M., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Science Society of America Journal*, 44(5), 892-898.
- Van Hullebusch, E.D., Peerbolte, A., Zandfoort, M.H. and Lens, P.N.L., 2005. Sorption of cobalt and nickel on anaerobic granular sludges: isotherms and sequential extraction. *Chemosphere*, 58(4), 493-505.
- Vijayaraghavan, K., Jegan, J., Palanivelu, K. and Velan, M., 2005. Biosorption of cobalt(II) and nickel(II) by seaweeds: batch and column studies. *Separation and Purification Technology*, 44(1), 53-59.
- Vinod, V., Kailash, D., Suresh, C. and Madan, L., 2012. Adsorption studies of Zn(II) ions from wastewater using *Calotropis procera* as an adsorbent. *Research Journal of Recent Sciences*, 1, 160-165.
- Vymazal, J., 2001. *Transformations of Nutrients in Natural and Constructed Wetlands*. Backhuys Publishers, Leiden, The Netherlands.
-

- Vymazal, J., 2009. The use of constructed wetlands with horizontal sub-surface flow for various types of wastewater. *Ecological Engineering*, 35(1), 1-17.
- Vymazal, J. and Kröpfelová, L., 2008. *Wastewater Treatment in Constructed Wetlands with Horizontal Sub-Surface Flow*. Springer.
- Walker, D.J. and Hurl, S., 2002. The reduction of heavy metals in a stormwater wetland. *Ecological Engineering*, 18(4), 407-414.
- Werker, A.G., Dougherty, J.M., McHenry, J.L. and Van Loon, W.A., 2002. Treatment variability for wetland wastewater treatment design in cold climates. *Ecological Engineering* 19(1), 1-11.
- Wittgren, H.B. and Mæhlum, T., 1997. Wastewater Treatment Wetlands in Cold Climates. *Water Science and Technology*, 35(5), 45-53.
- Wong, T.H.F., Breen, P.F., Somes, N.L. and Lloyd, S.D., 1999. *Managing Urban Stormwater Using Constructed Wetlands* [online]. Clayton, Victoria: Cooperative Research Centre (CRC) for Catchment Hydrology and Department of Civil Engineering, Monash University. Available from: http://www.superfloats.com/reference_library/wetland/GUIDELINES/managing%20urban%20stormwater%20using%20constructed%20wetlands.pdf/ [Accessed 2 May 2012].
- Woods-Ballard, B., Kellagher, R., Martin, P., Jefferies, C., Bray, R. and Shaffer, P., 2007. *The SUDS manual*. London: Construction Industry Research & Information Association (CIRIA), Report C697.
- Woodward, C.A. and Ta, C.T., 1988. Developments in modelling slow sand filtration. In: Graham, N.J.D. (ed.). *Slow Sand Filtration: Recent Developments in Water Treatment Technology*. John Wiley & Sons, New York, 349-366.
- Yu, B., Zhang, Y., Shukla, A., Shukla, S.S. and Dorris, K.L., 2000. The removal of heavy metal from aqueous solutions by sawdust adsorption – removal of copper. *Journal of Hazardous Materials*, 80(1-3), 33-42.
- Yu, L.J., Shukla, S.S., Dorris, K.L., Shukla, A. and Margrave, J.L., 2003. Adsorption of chromium from aqueous solutions by maple sawdust. *Journal of Hazardous Materials*, 100(1-3), 53-63.

- Zhang, Z., Rengel, Z., Liaghati, T., Antoinette, T. and Meney, K., 2011. Influence of plant species and submerged zone with carbon addition on nutrient removal in stormwater biofilter. *Ecological Engineering*, 37(11), 1833-1841.
- Zinger, Y., Fletcher, T.D., Deletic, A., Blecken, G.T. and Viklander, M., 2007. Optimisation of the nitrogen retention capacity of stormwater biofiltration systems. NOVATECH 2007, Lyon, France.
- Züst, B. and Schönborn, A., 2003. Constructed wetlands for wastewater treatment in cold climates: Planted soil filter Schattweid - 13 years' experience. In: Ü. Manssen and P. Jenssen, eds. *Constructed Wetlands for Wastewater Treatment in Cold Climates*. Southampton: WIT Press, 53-68.

Appendices

Appendix 1 – Loadings plots from PCA analysis

Appendix 2 – Scatter plots from correlation analysis

Appendix 1 – Loadings plots from PCA analysis

The numerical output data from Unscrambler X was extracted and used in Microsoft Excel to produce these charts. All significant relationships were identified in the analysis of the first two principal components, hence only these components are displayed here. For each unit, two charts are shown (with the exception of unit 7). The first chart shows the results of the first PCA analysis, which used a reduced dataset but included pH and EC. The second chart shows the results of the second PCA analysis, which used a full dataset for all variables but excluded pH and EC.

Unit 1

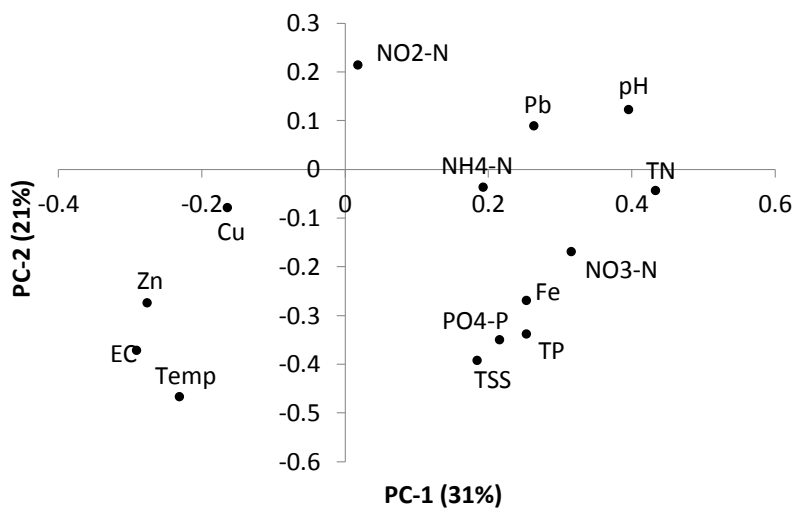


Figure A1.1 - First PCA run, unit 1

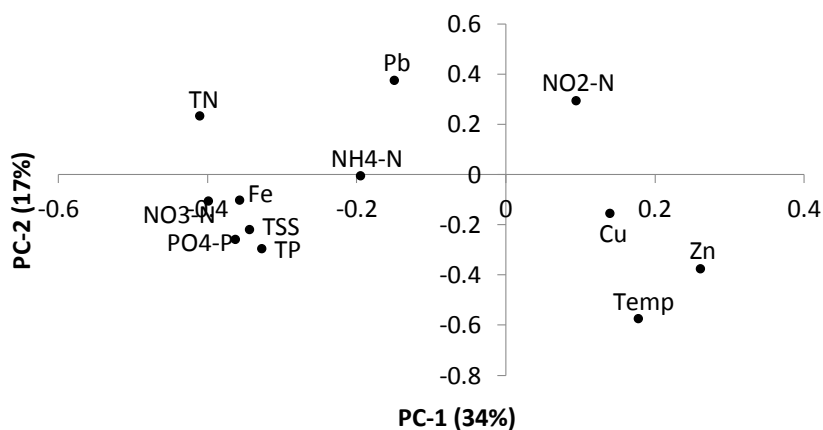


Figure A1.2 - Second PCA run, unit 1

Unit 2

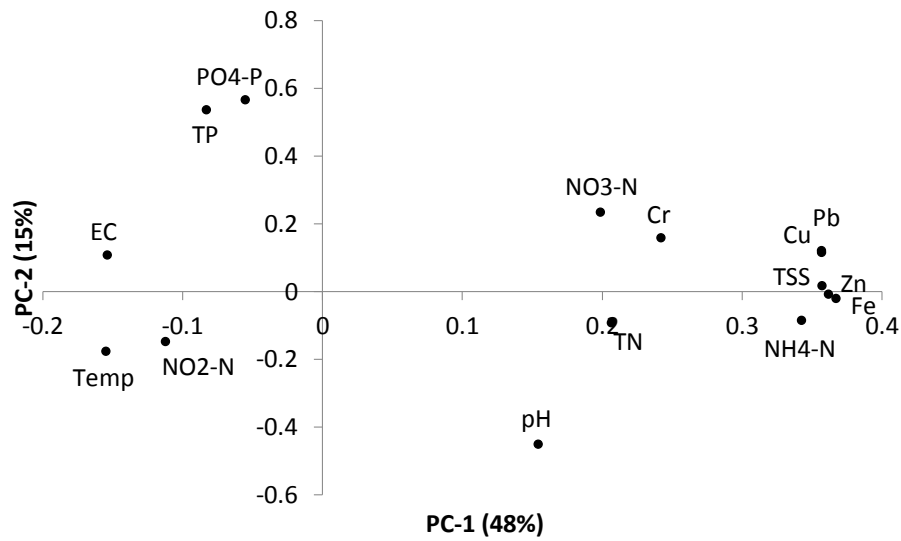


Figure A1.3 - First PCA run, unit 2

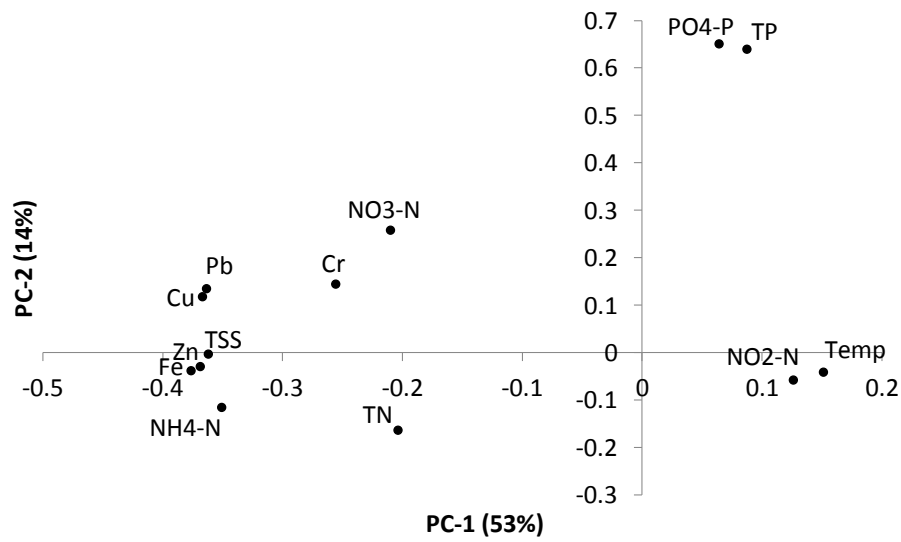


Figure A1.4 - Second PCA run, unit 2

Unit 3

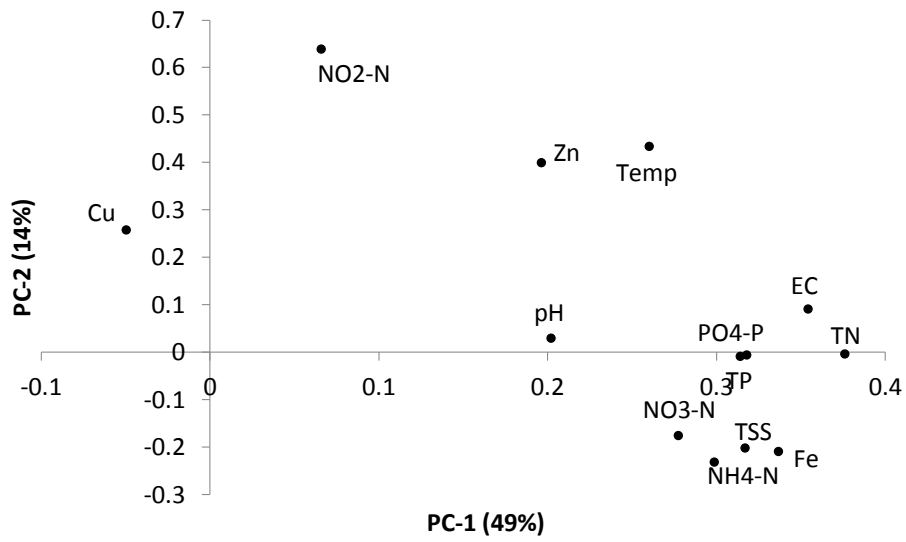


Figure A1.5 - First PCA run, unit 3

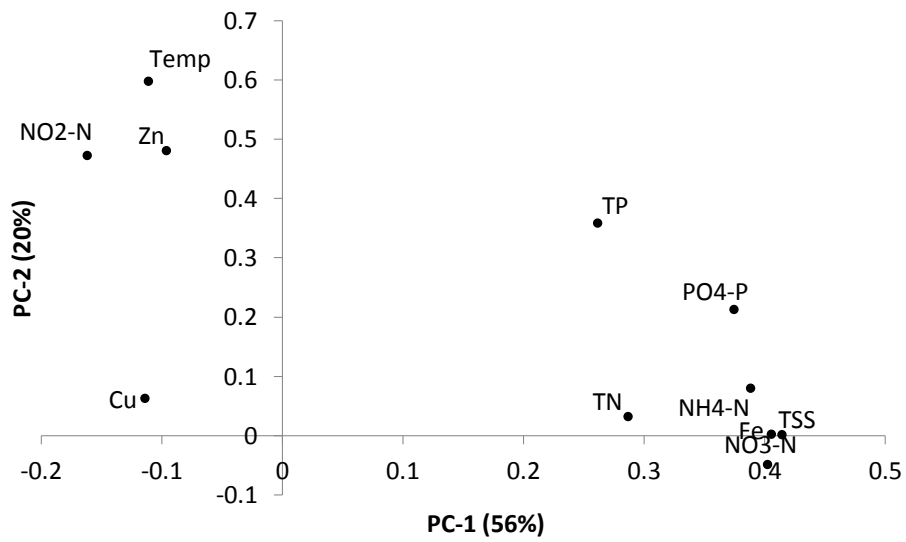


Figure A1.6 - Second PCA run, unit 3

Unit 4

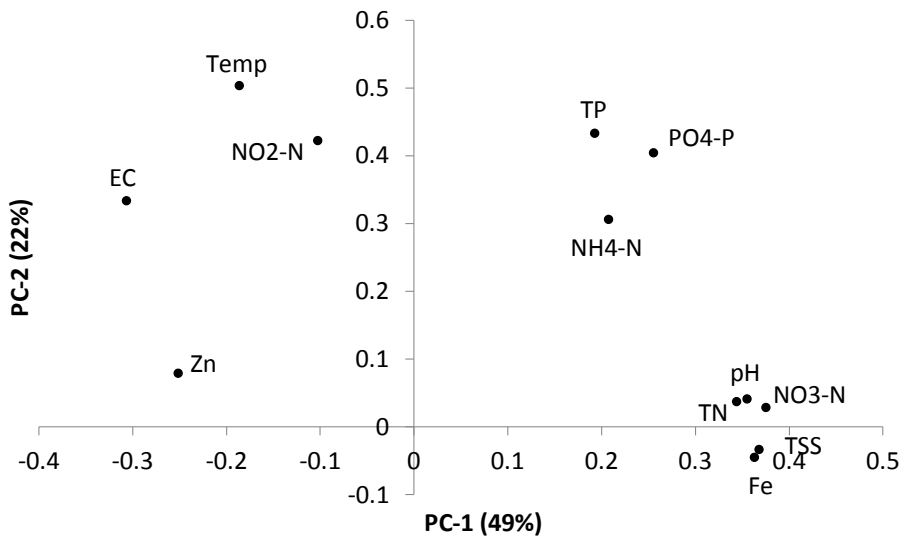


Figure A1.7 - First PCA run, unit 4

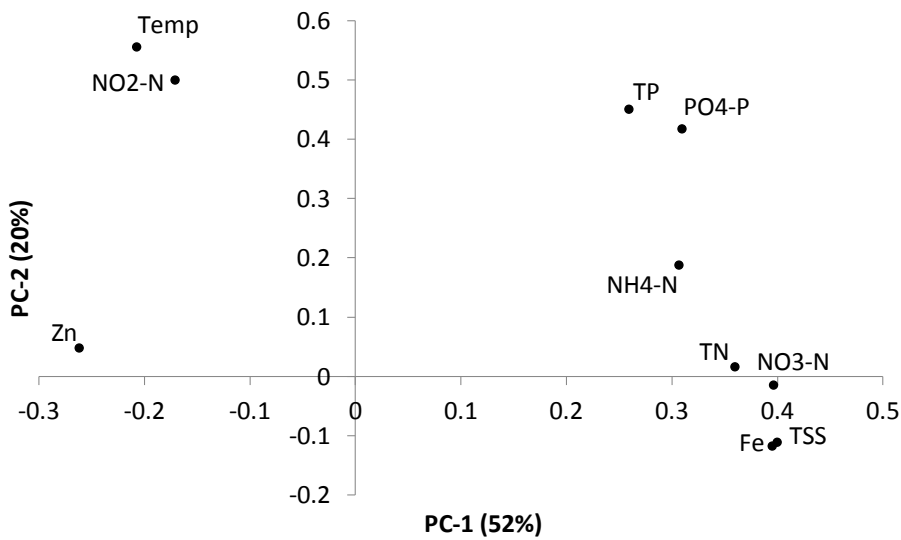


Figure A1.8 - Second PCA run, unit 4

Unit 5

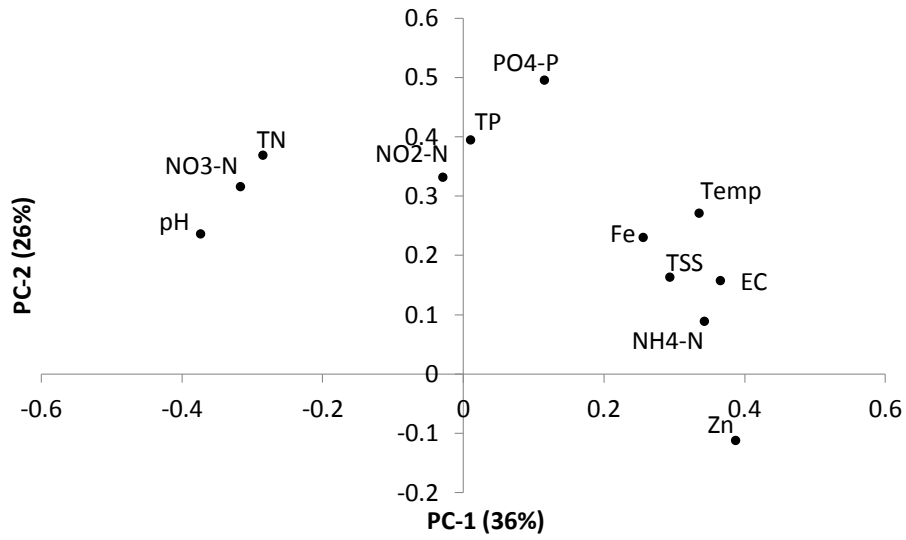


Figure A1.9 - First PCA run, unit 5

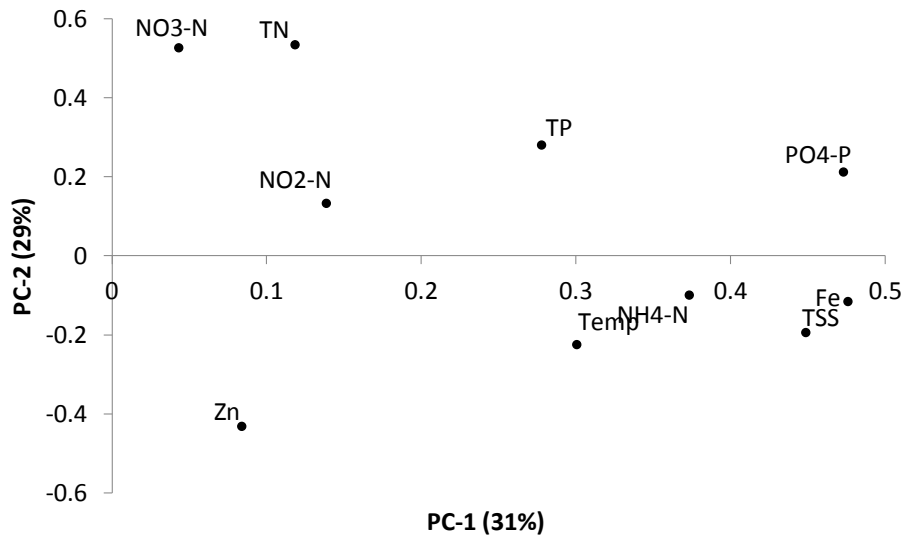


Figure A1.10 - Second PCA run, unit 5

Unit 6

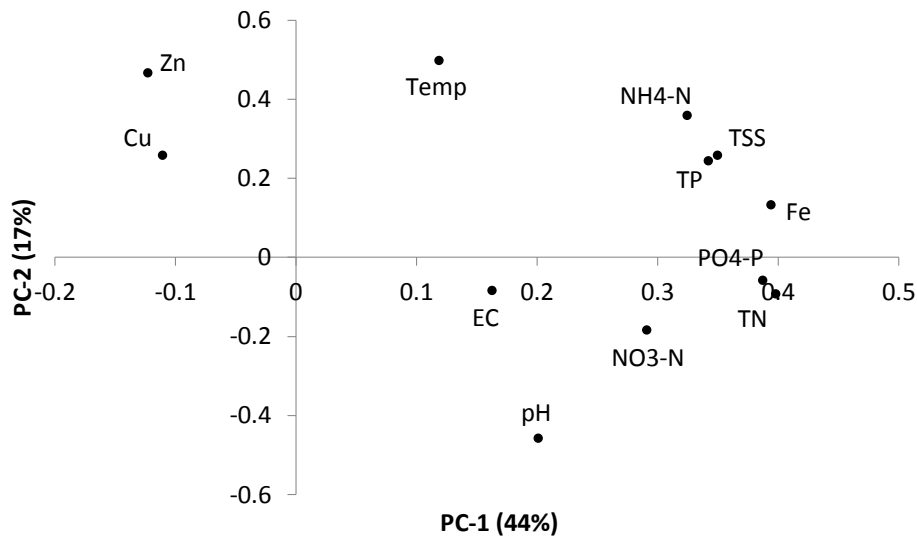


Figure A1.11 - First PCA run, unit 6

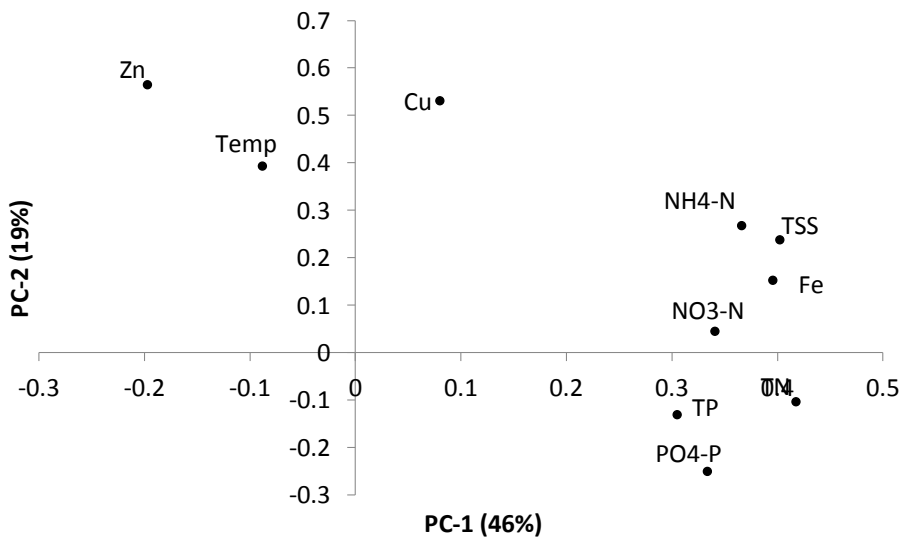


Figure A1.12 - Second PCA run, unit 6

Unit 7

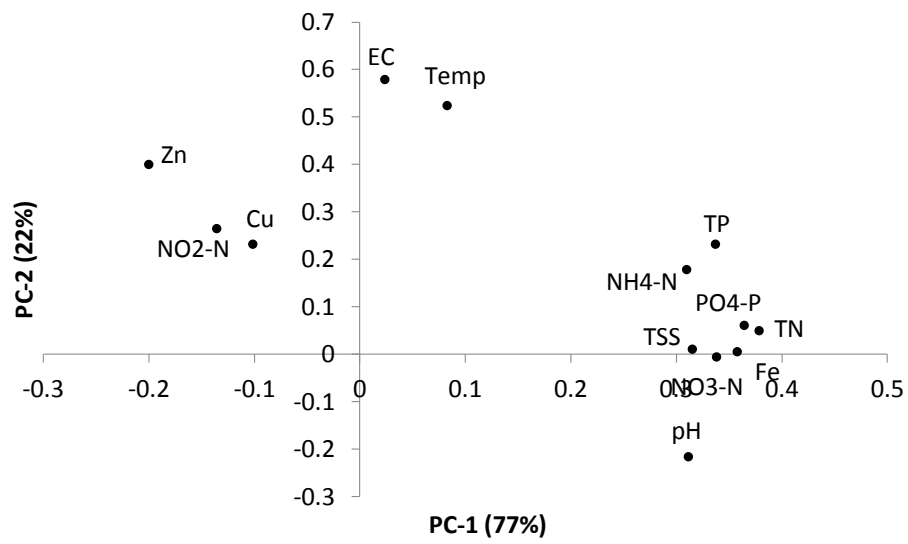


Figure A1.13 – Unit 7 PCA output

Unit 8

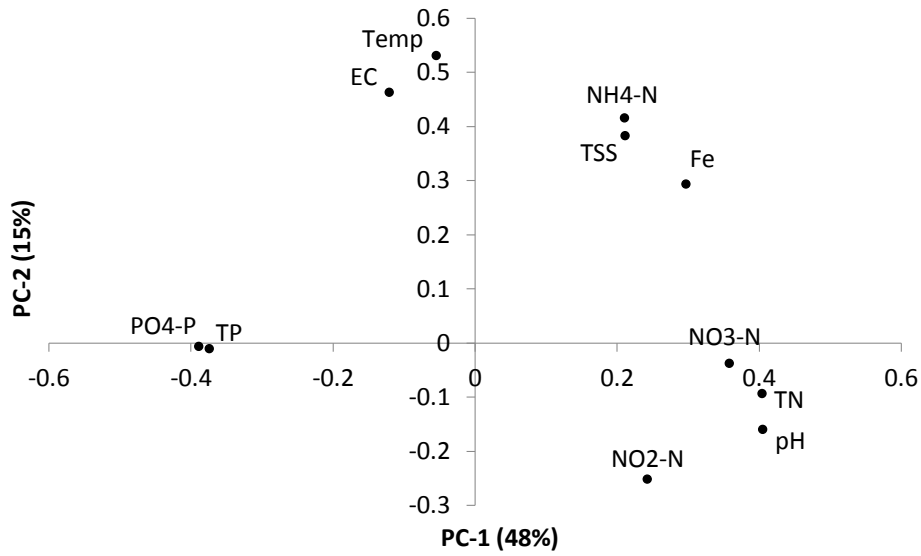


Figure A1.14 - First PCA run, unit 8

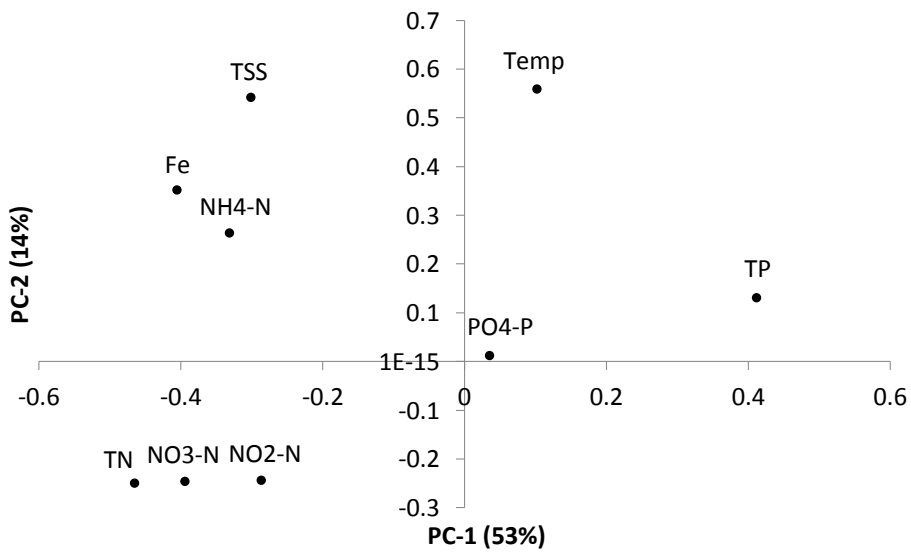
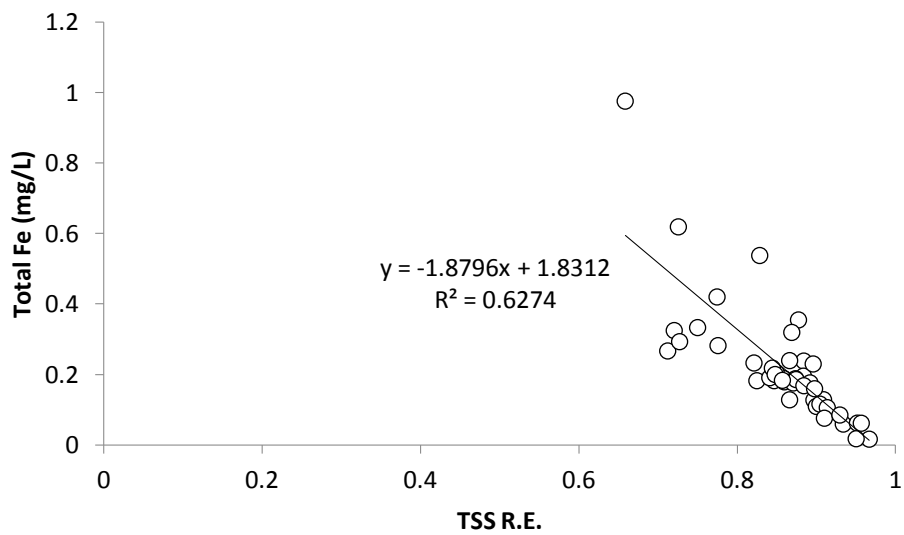
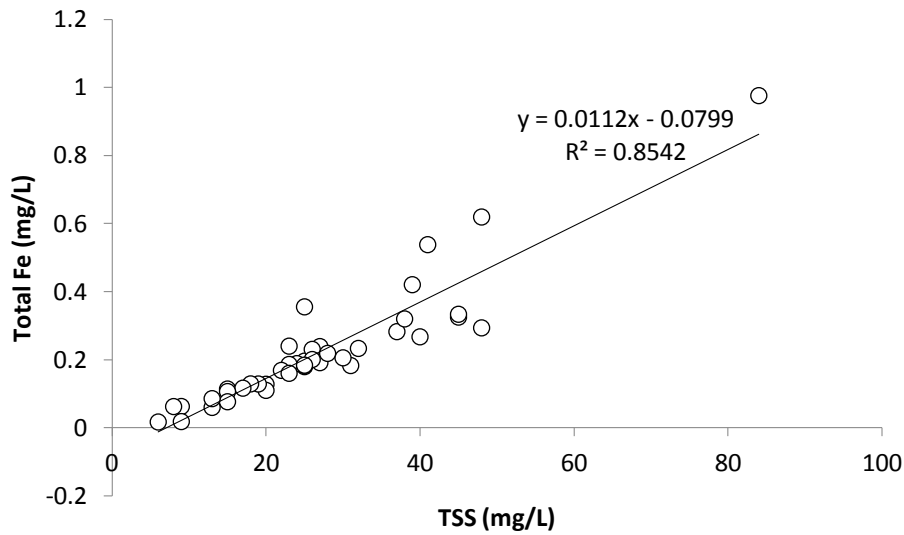


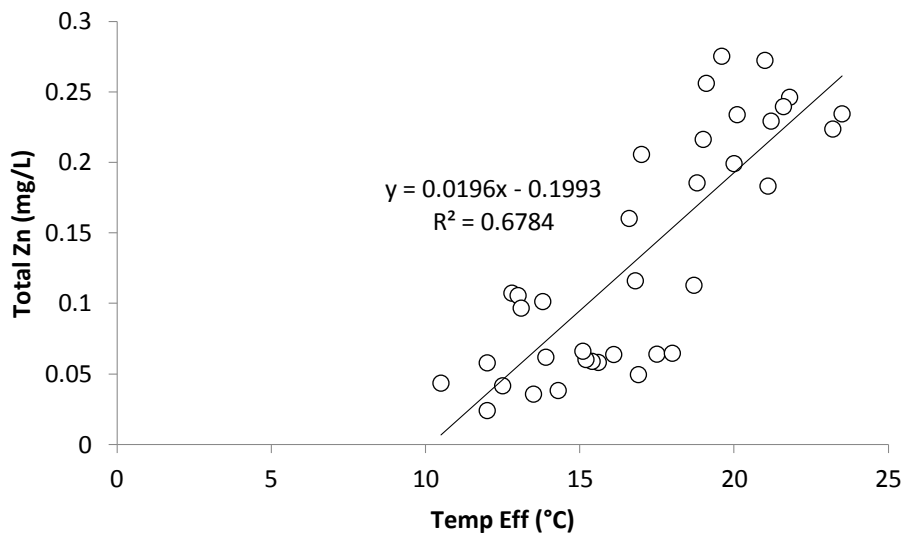
Figure A1.15 - Second PCA run, unit 8

Appendix 2 – Scatter plots from correlation analysis

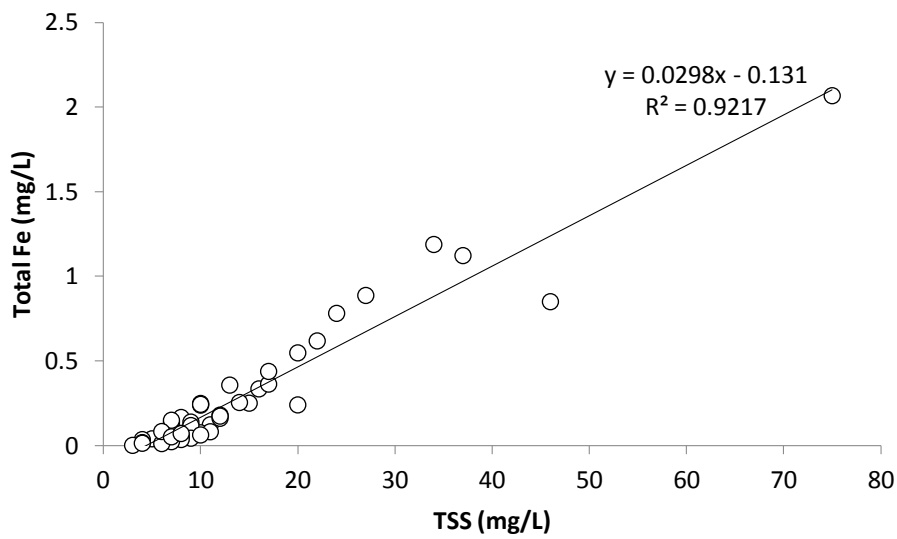
The scatter plots showing significant relationships between variables in the pilot-scale CW effluent are given in this section, after outlier elimination. Figures are not individually titled as there is sufficient information given by the axes on the charts.

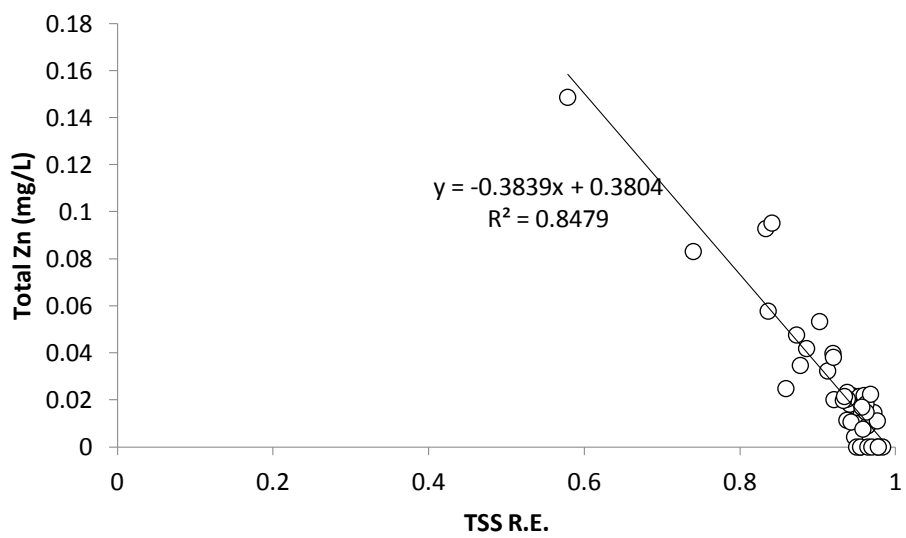
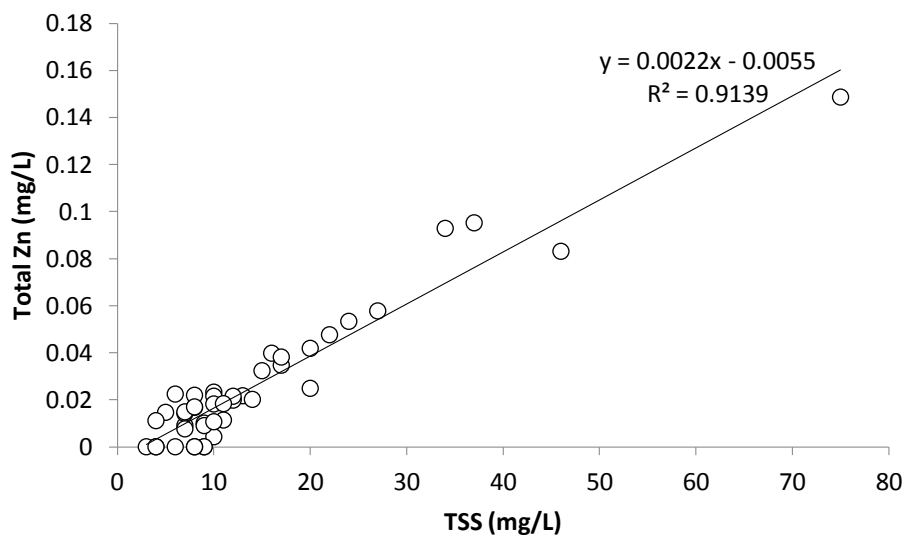
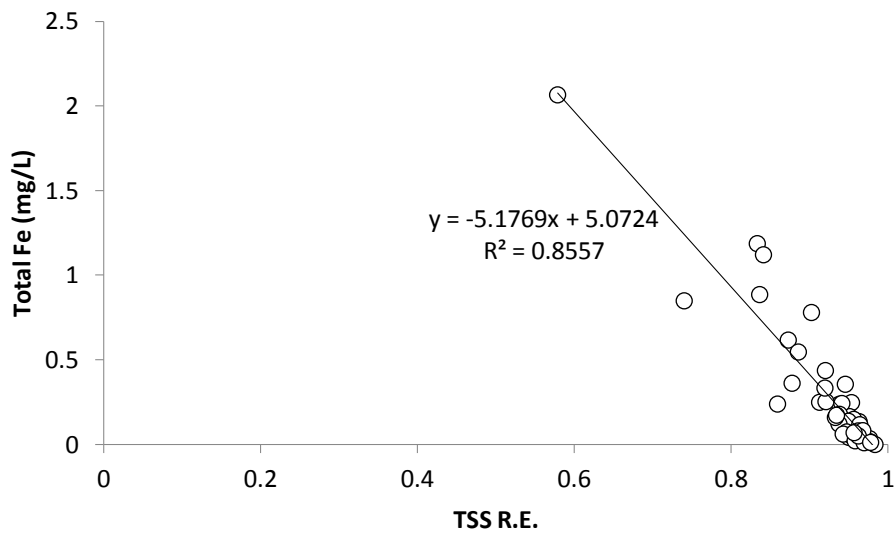
Unit 1

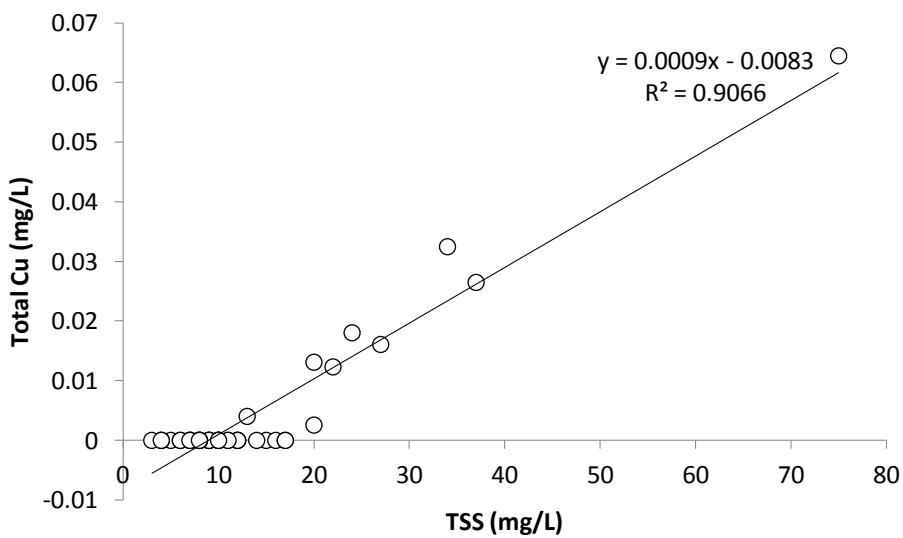
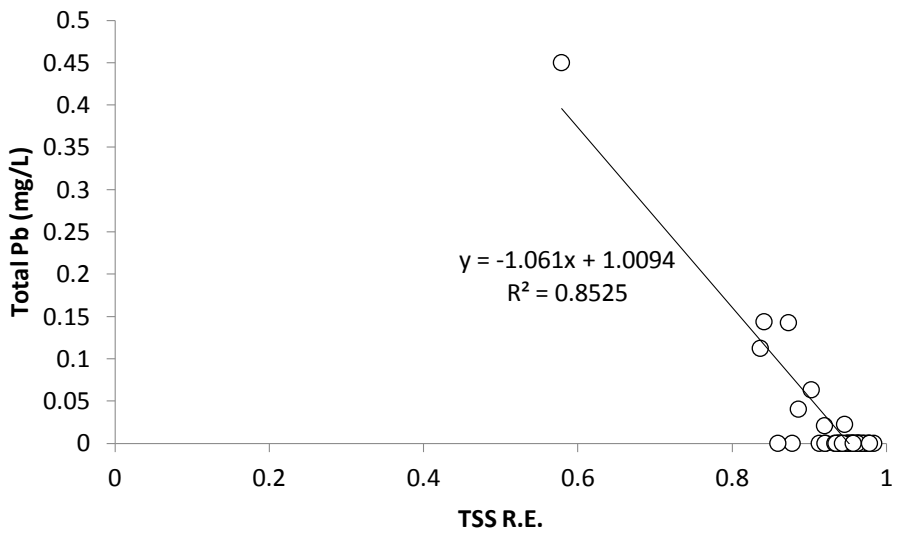
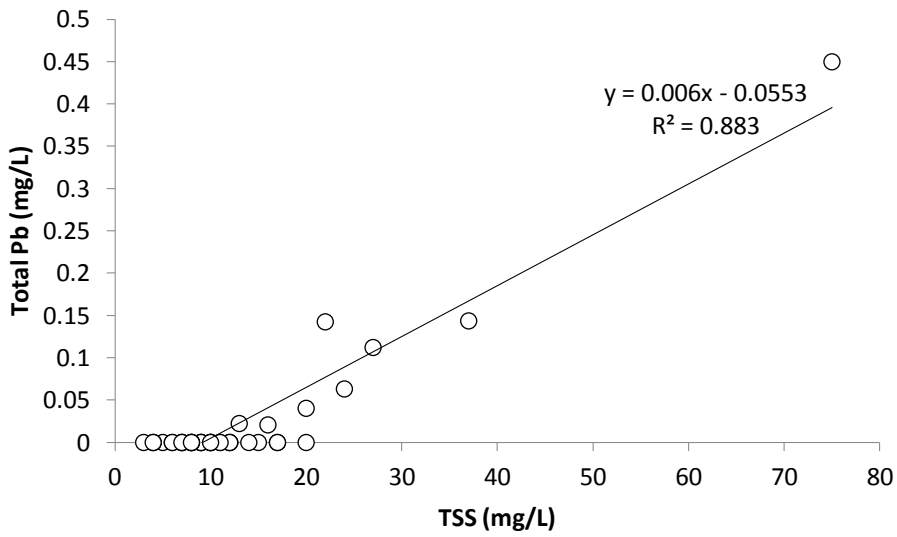


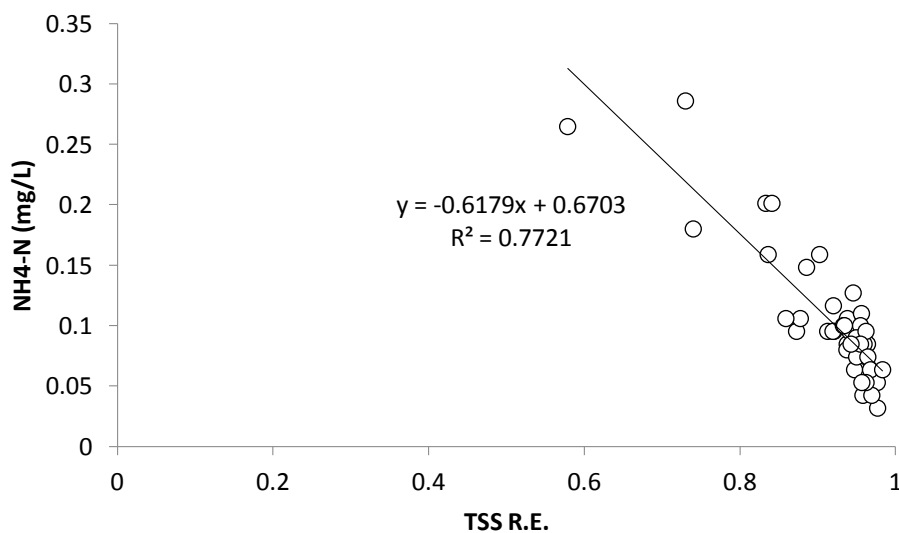
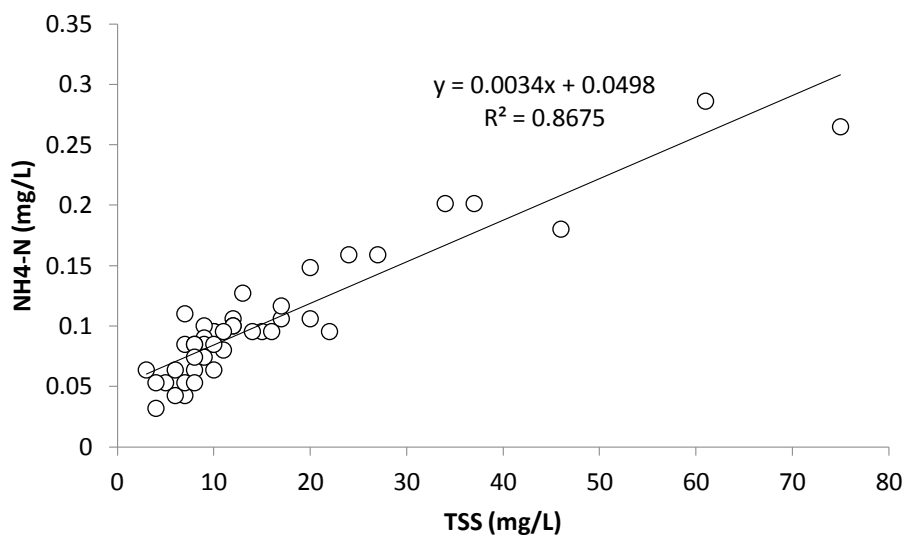
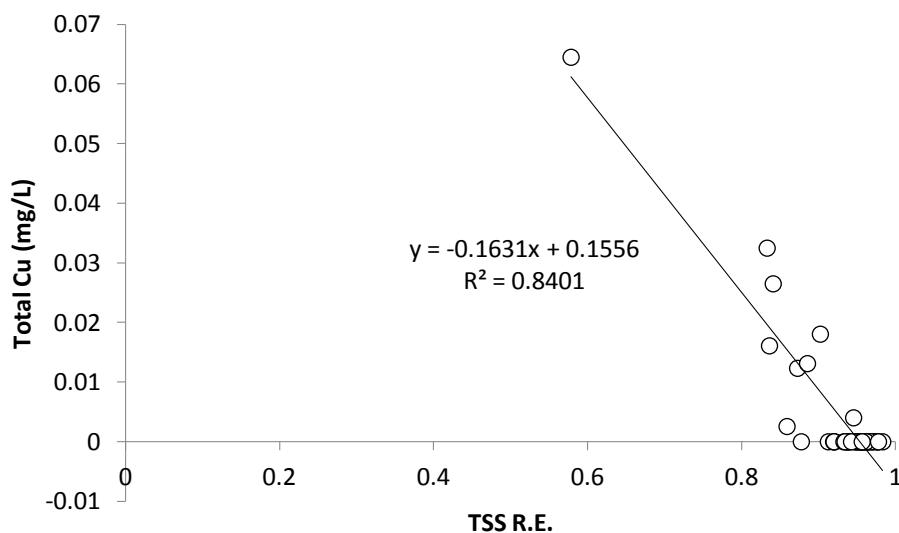


Unit 2

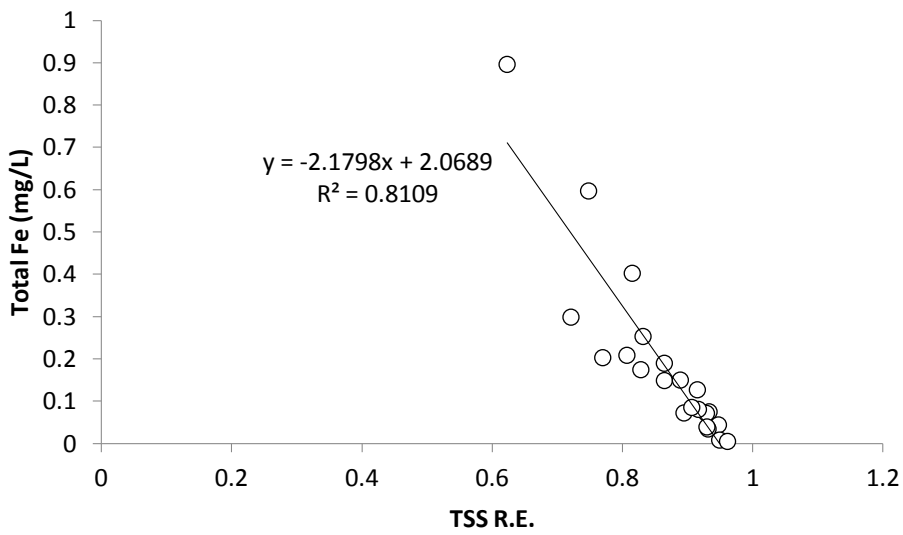
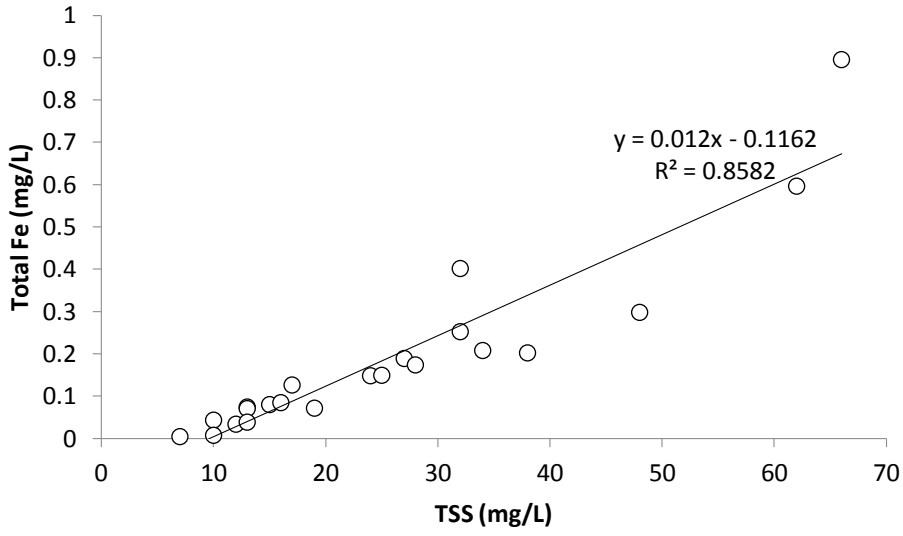


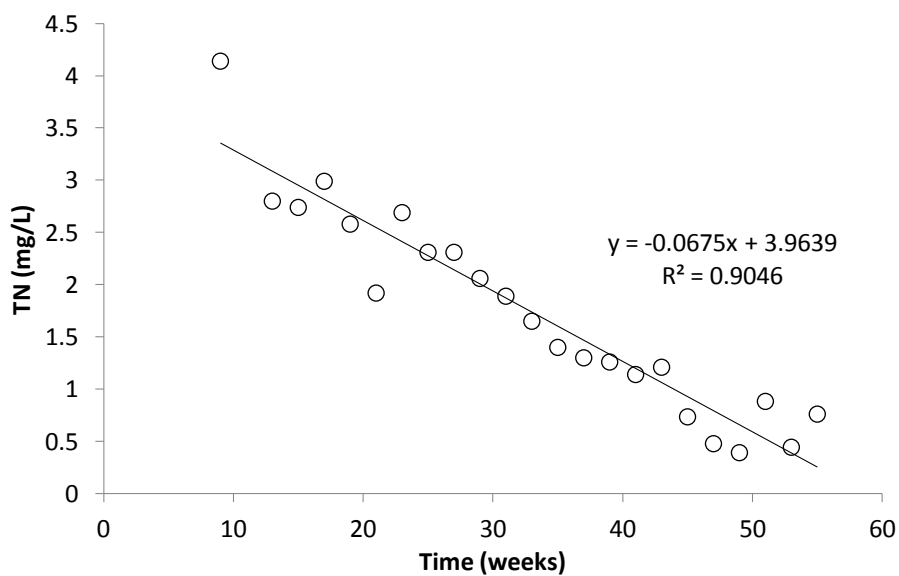
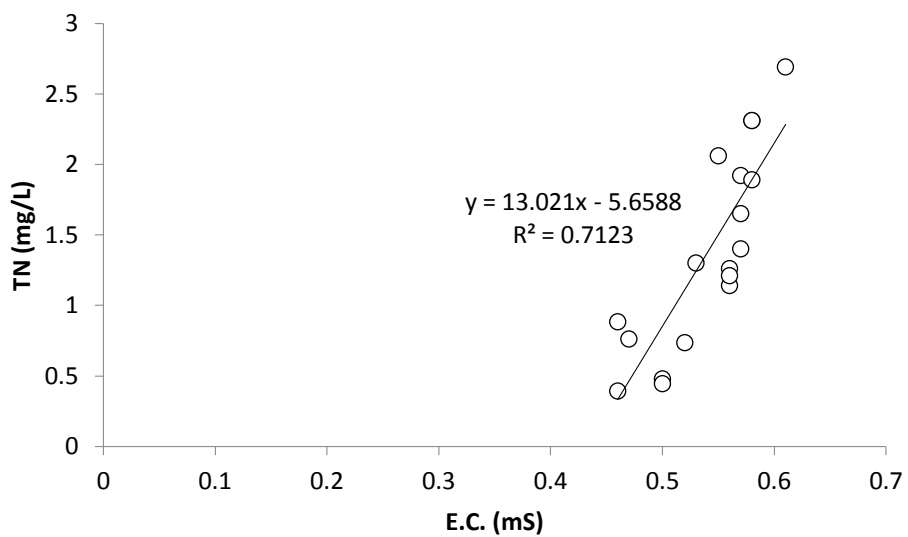
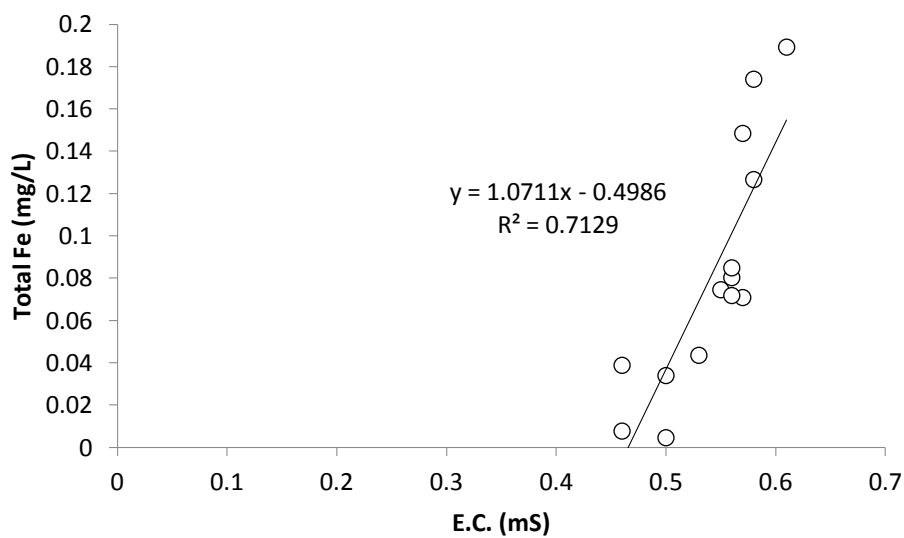


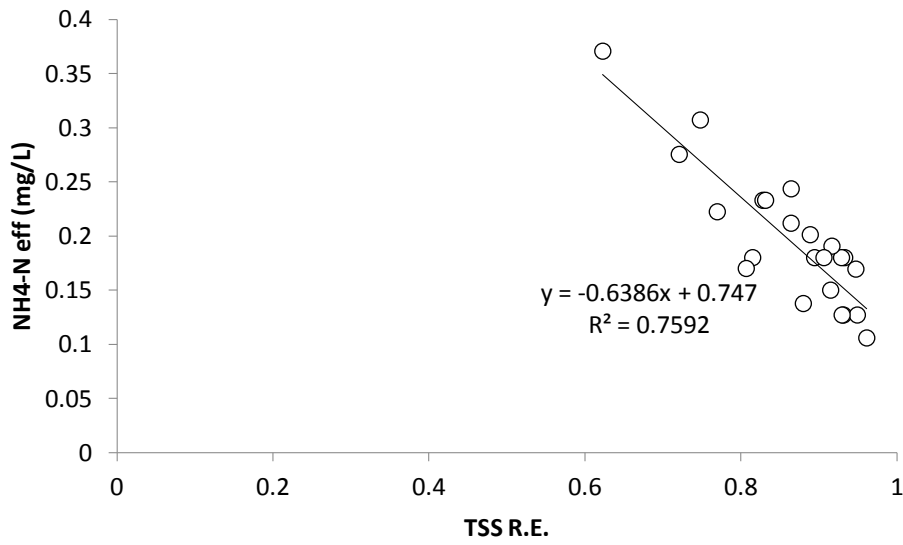
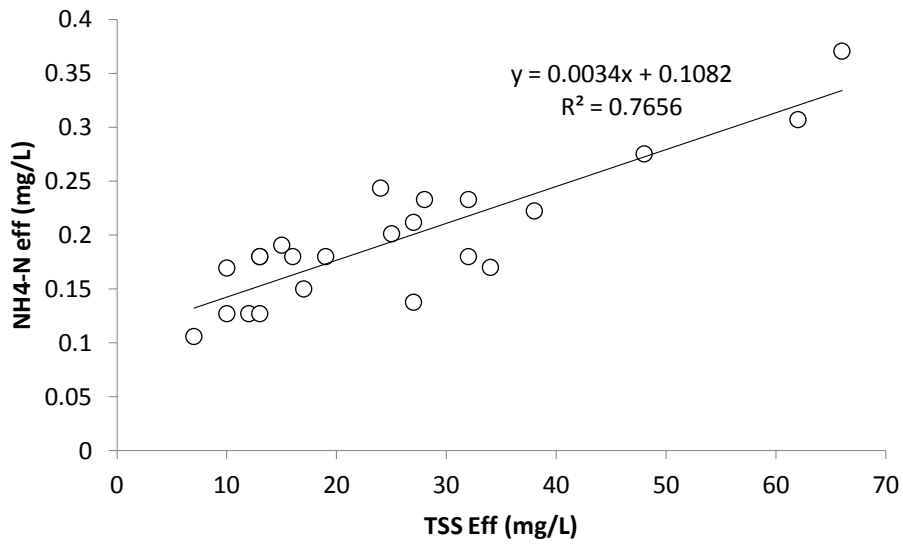


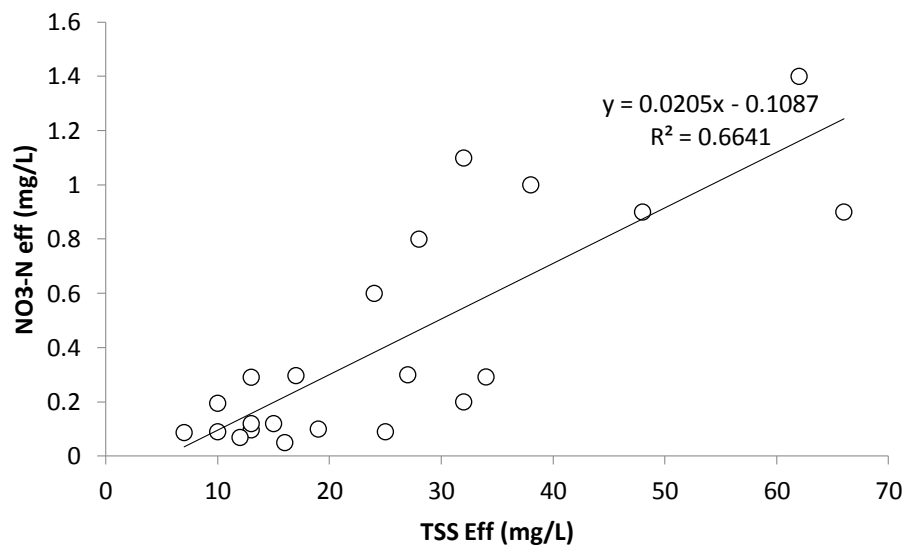
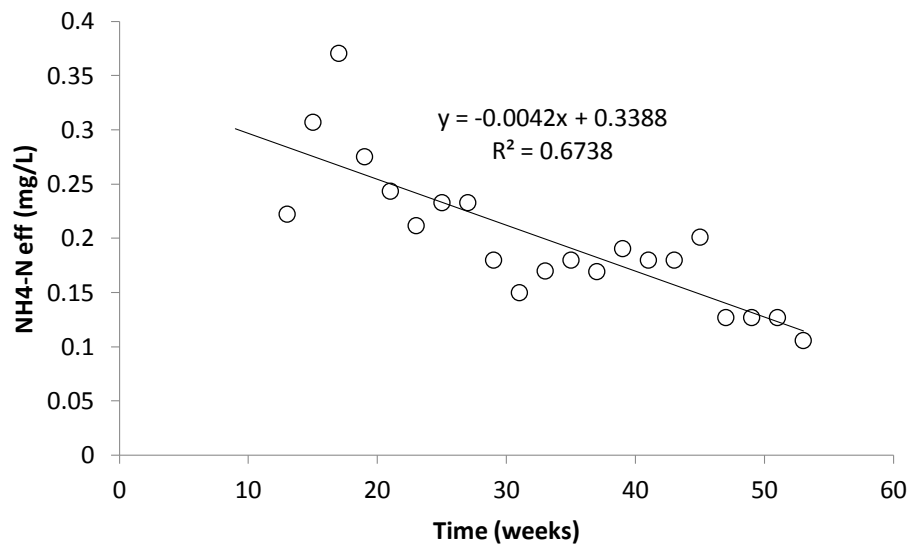


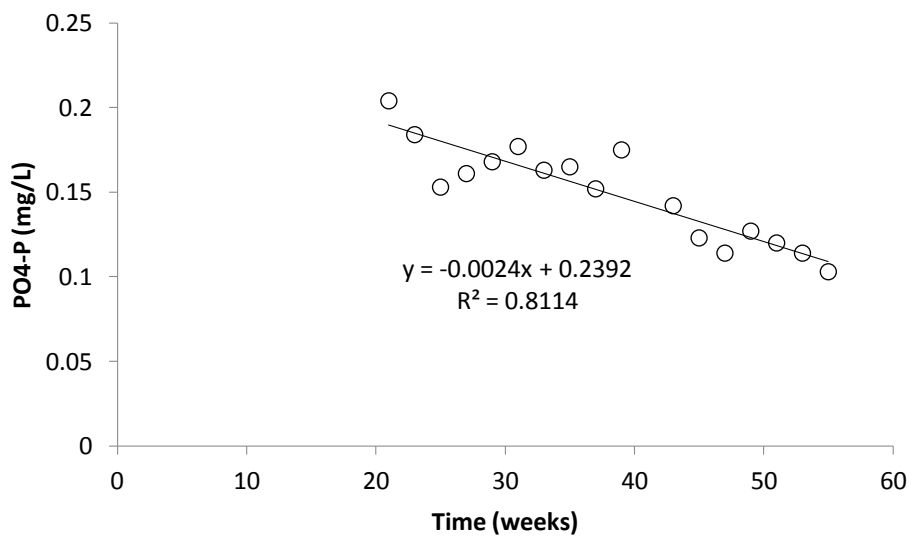
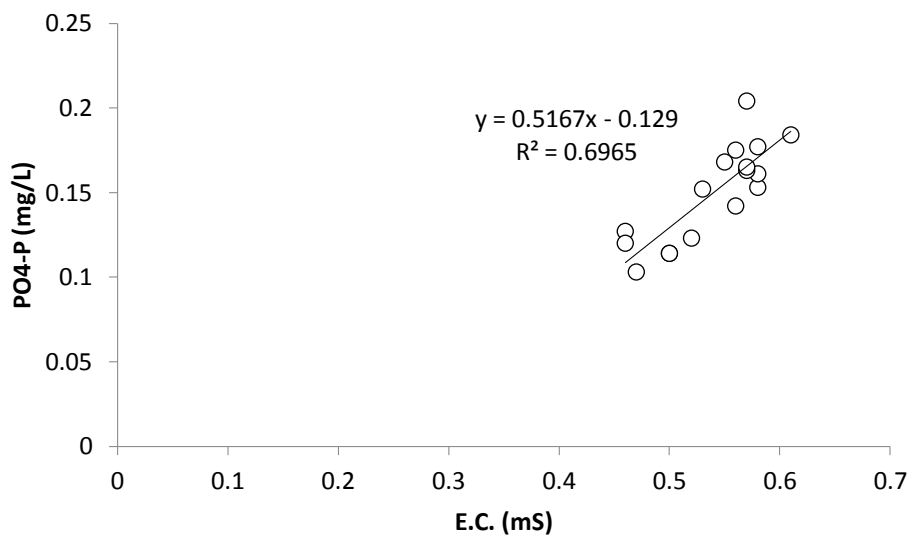
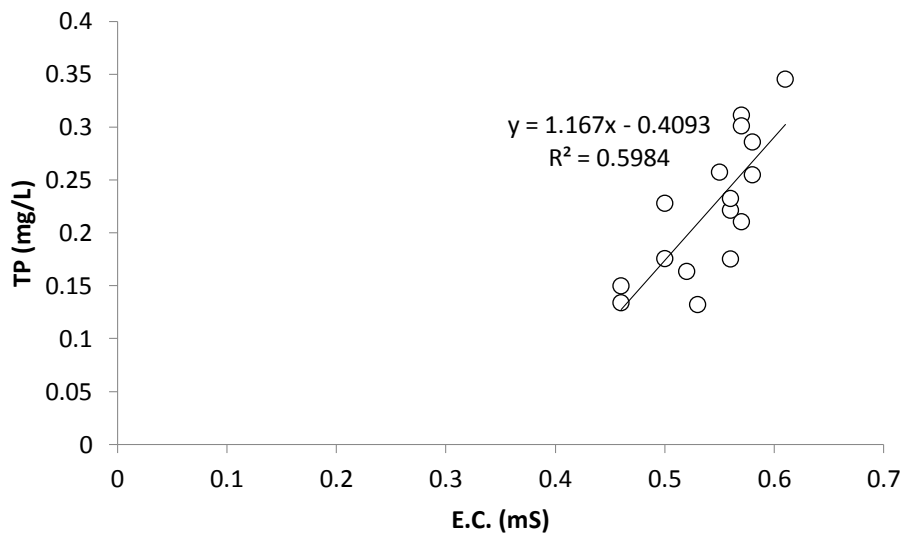
Unit 3



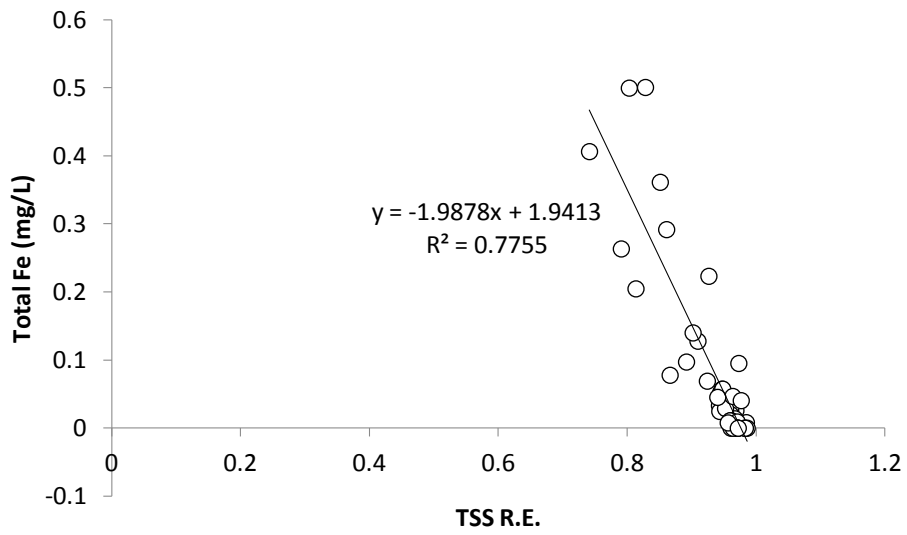
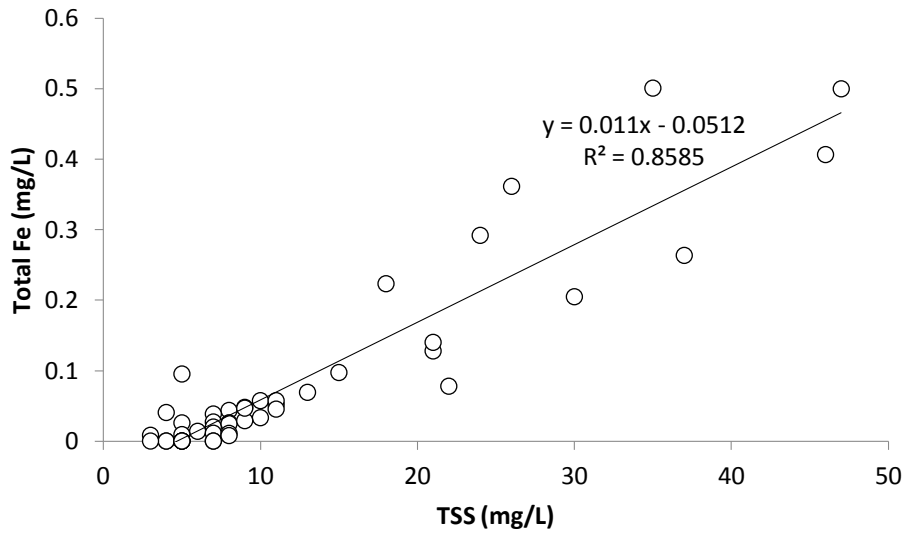


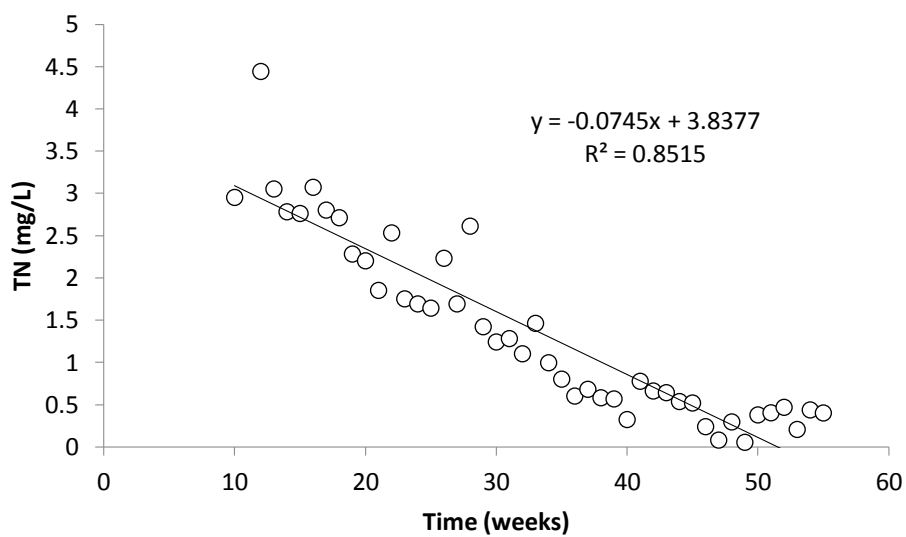
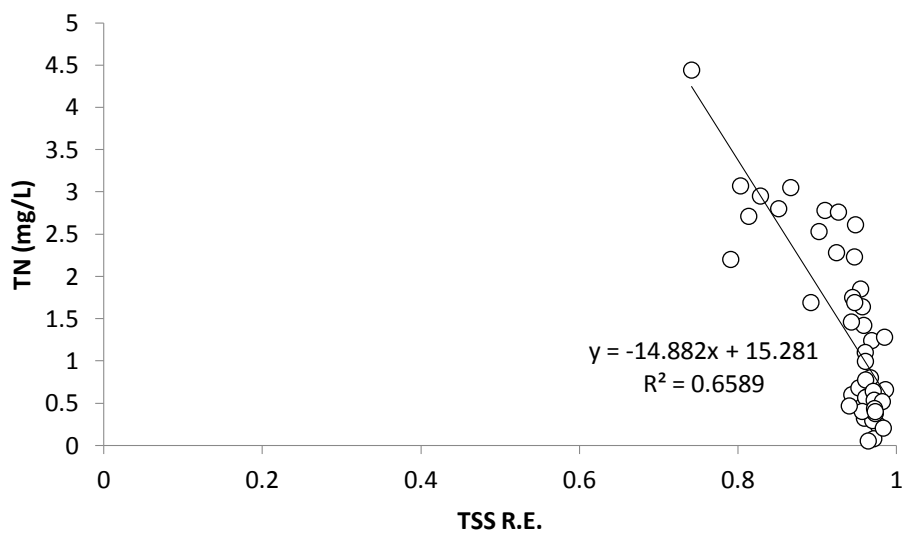
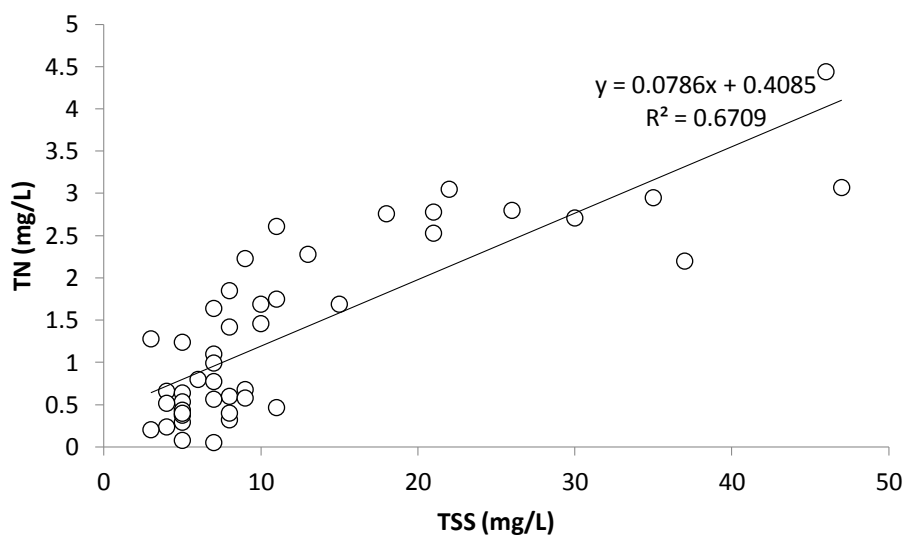


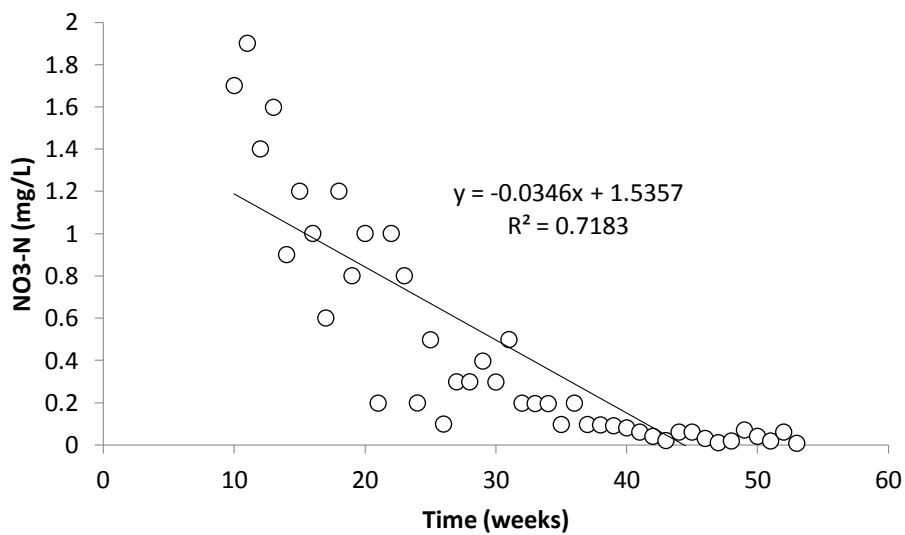
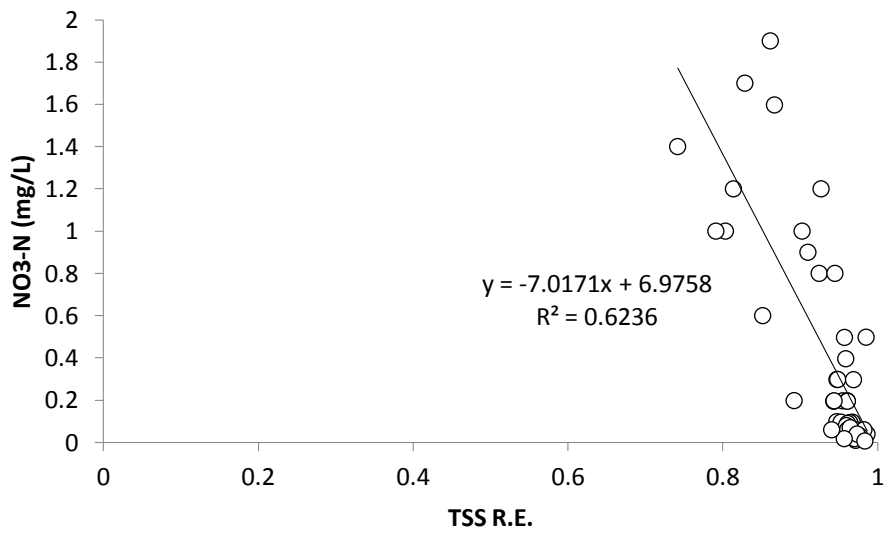
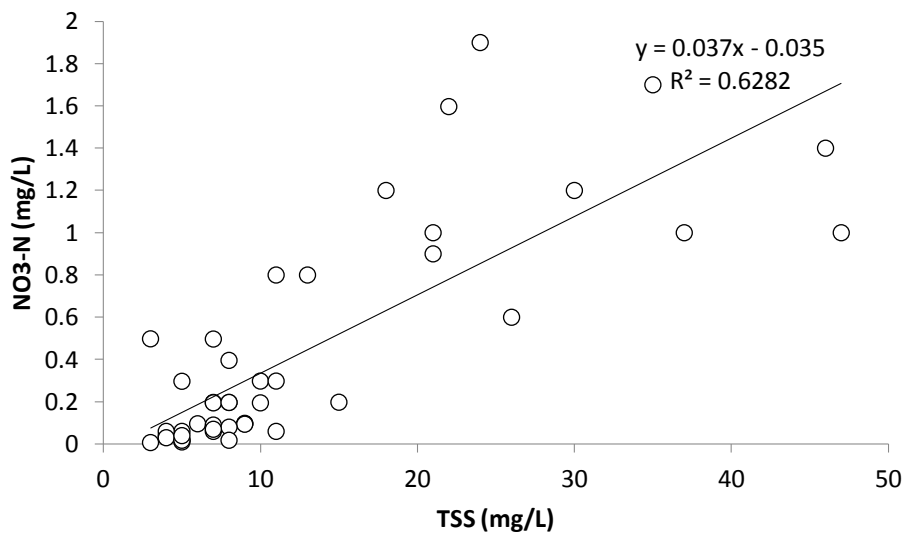




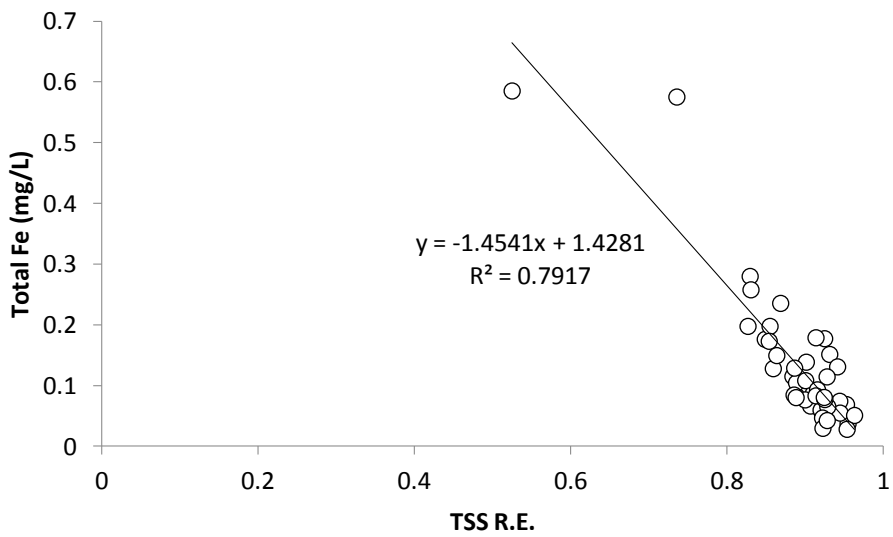
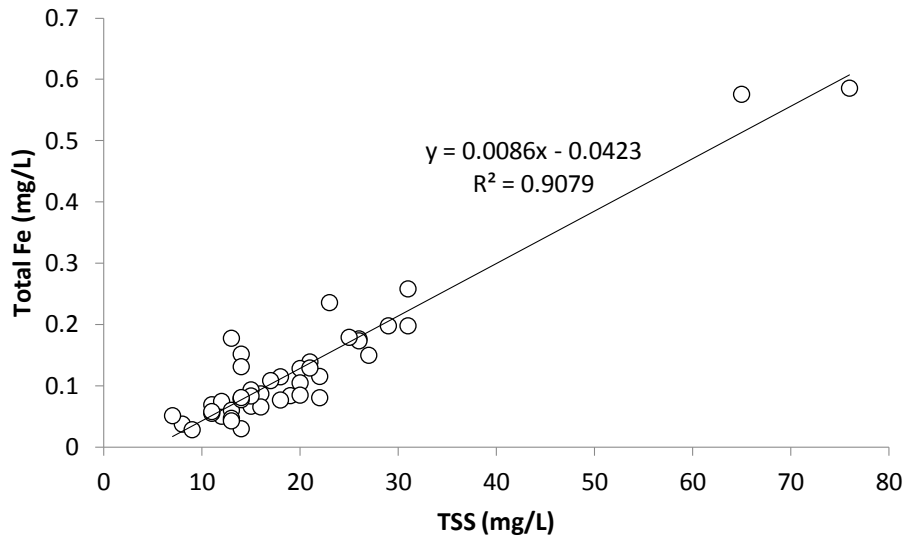
Unit 4

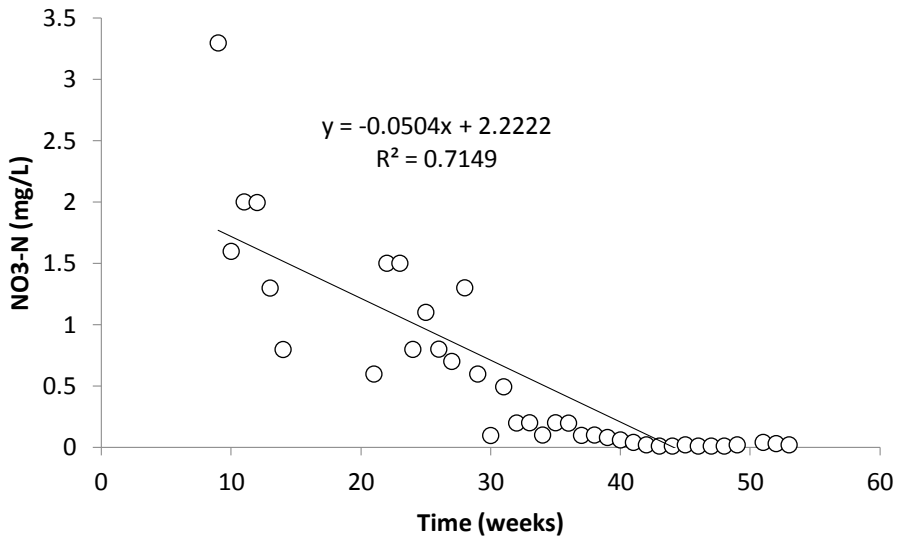
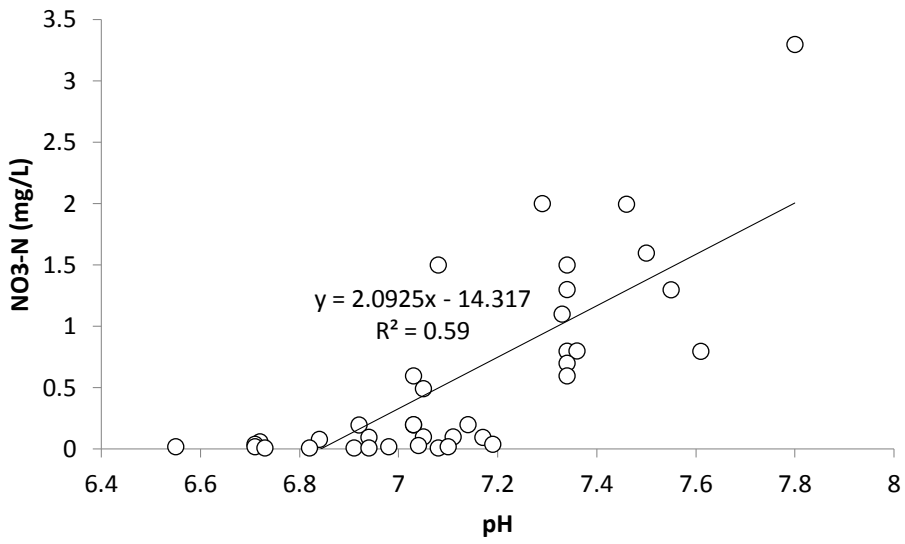




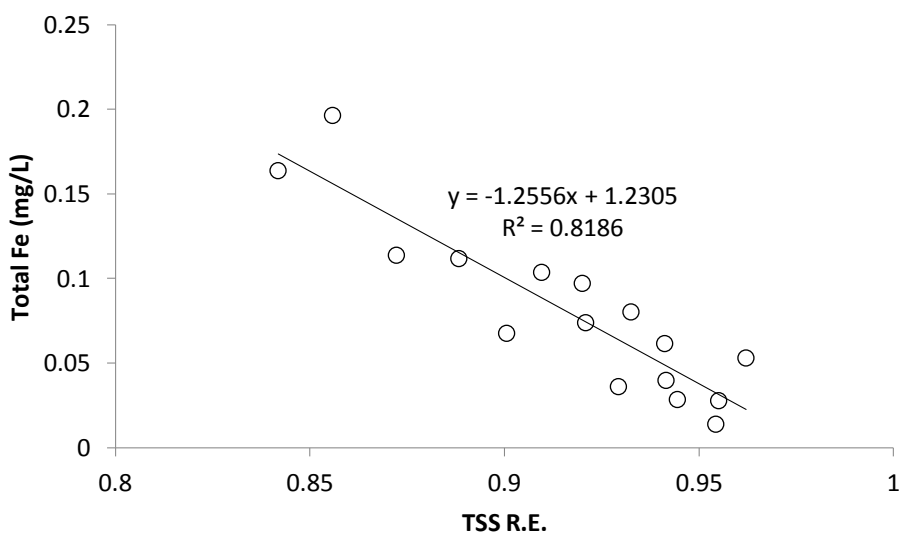
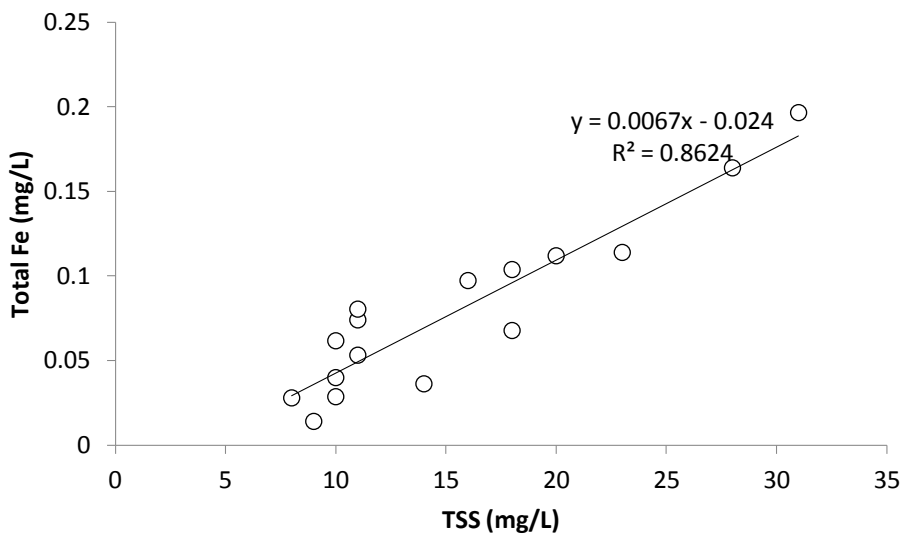


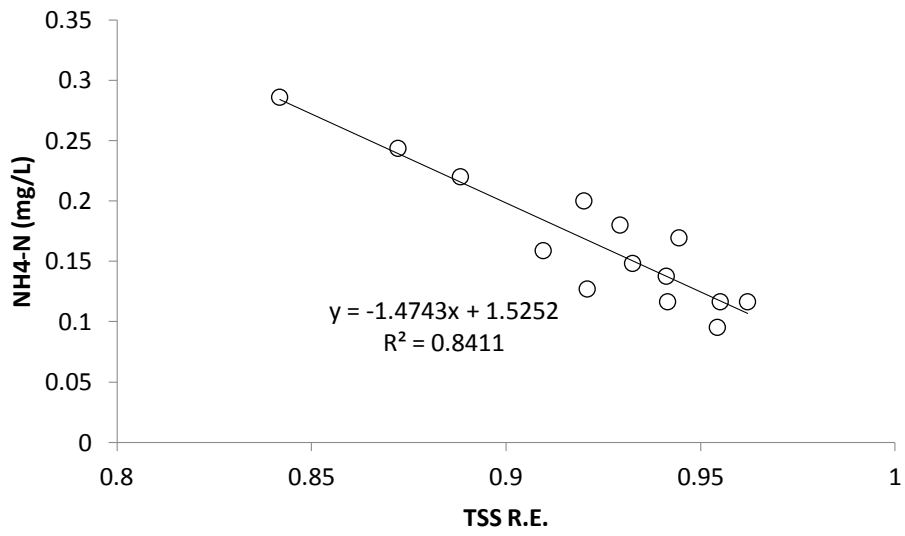
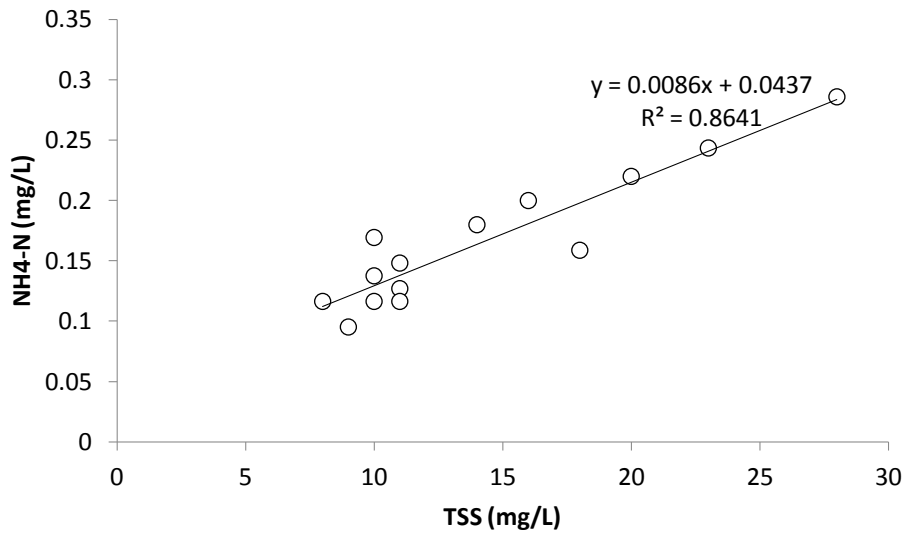
Unit 5



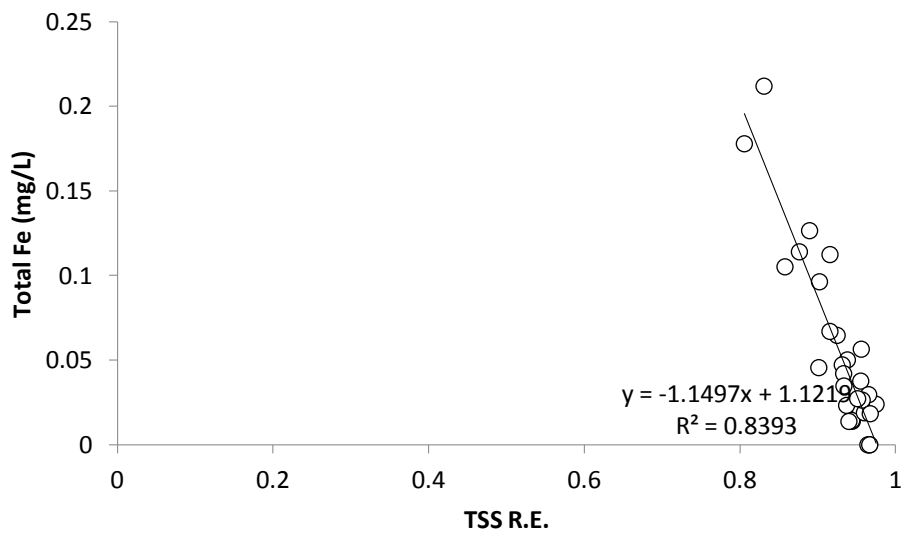
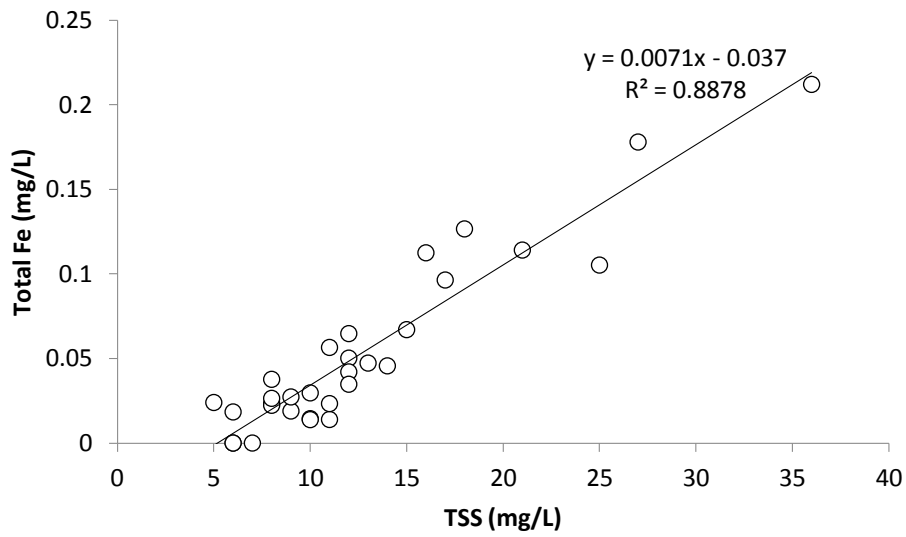


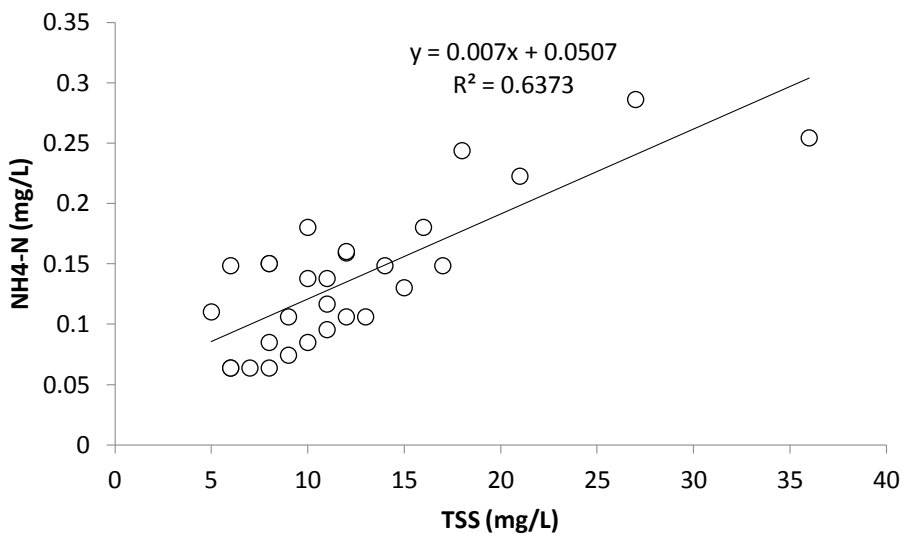
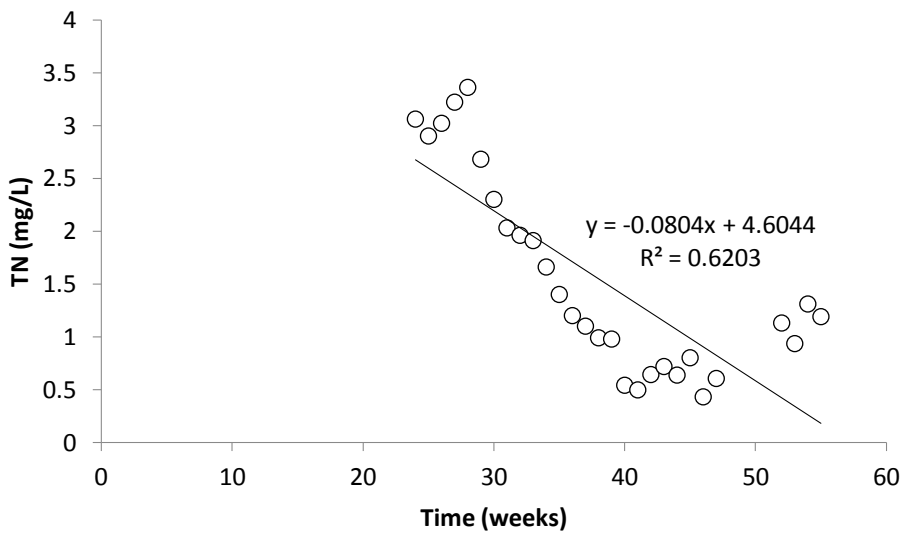
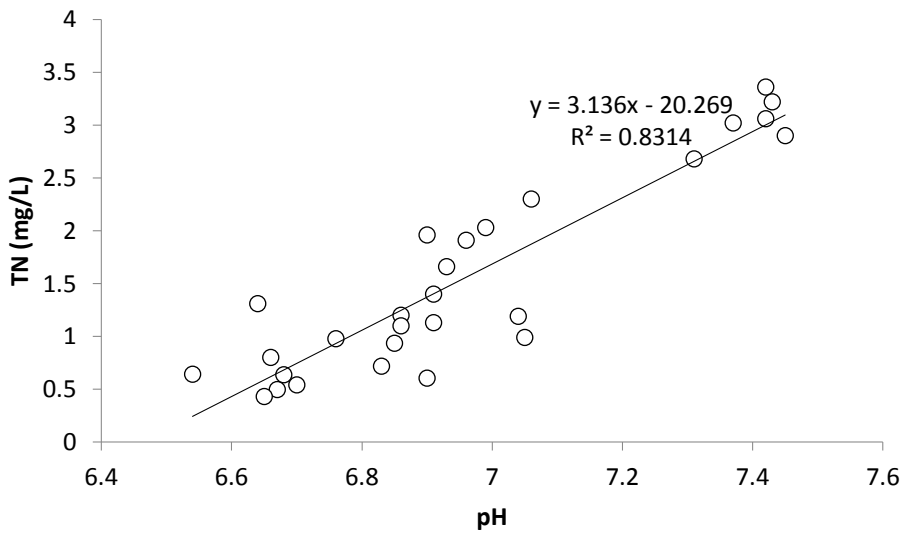
Unit 6

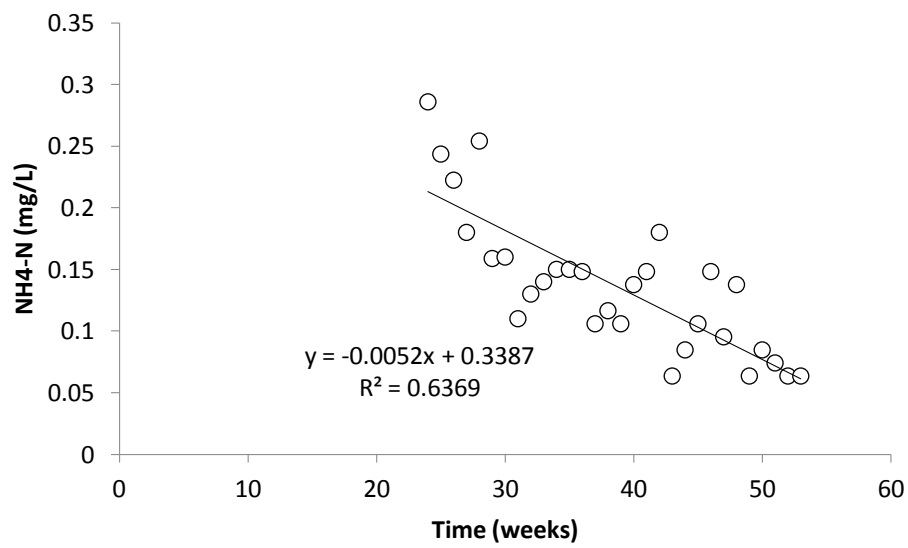
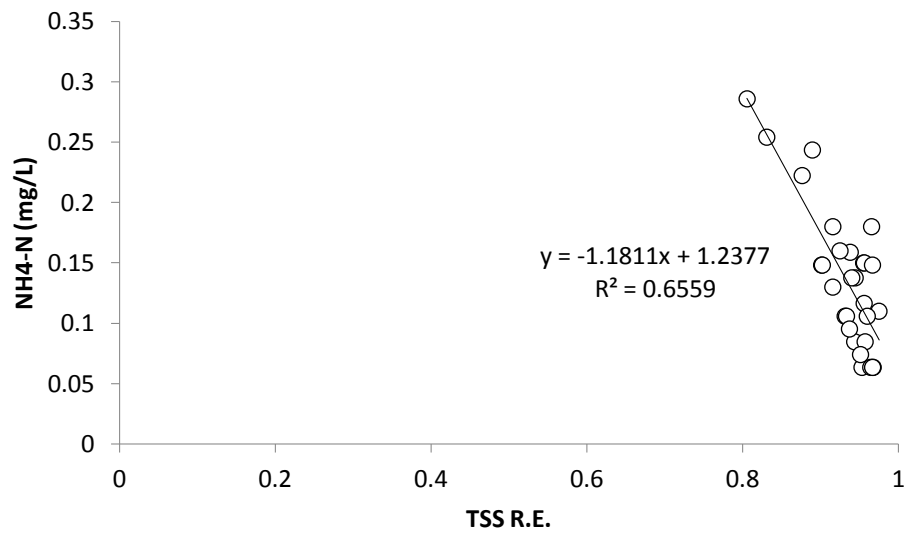




Unit 7







Unit 8

