Design and modelling of pollutant removal in stormwater constructed wetlands

This Thesis is submitted in partial fulfilment of the requirement for the degree of Doctor of Philosophy (Ph.D.) in Engineering

By

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DECLARATION AND STATEMENTS

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This work has not previously been accepted in substance for any degree and is not concurrently submitted in candidature for any degree.

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Dedication

To Jesse, Zachary, and Winnie.

Abstract

Growth in urban population, urbanisation and economic development have increased the demand for water, especially in water-scarce regions. Stormwater treatment has the potential to reduce water demand. Furthermore, the use of constructed wetlands (CWs) in the treatment of stormwater also has the benefit that CWs can lower peak flow discharges and hence lessen floods; as well as improve the aesthetics of urban landscapes. In this research study, 8 pilot-scale vertical flow constructed wetlands (VFCWs) were configured to examine the influence of design and operational variables on the performance of tidal-flow VFCWs. The rationale of the research was that tidal-flow operational strategy draws atmospheric oxygen in the VFCWs, thereby increasing the concentration of dissolved oxygen in the wetland system.

Moreover, a combination of dissolved oxygen and a fixed retention time of 24 hours enhances the removal of nutrients N and P. Therefore; the research was conducted in two major parts. The first part consisted of outdoor and laboratory experiments, which were carried out over a continuous period of 2 years at Cardiff School of Engineering, Cardiff University. The physical models of the VFCWs were configured from a series of media compositions and were fed with loads of influent stormwater to simulate various storm events over different catchment sizes. The performance of the VFCWs regarding total suspended solids, nutrients (N and P), and heavy metals were monitored during the experimental period. The data obtained were analysed using descriptive and inferential statistics. The second part of the study involved exploring the experimental data to develop artificial neural network models (ANNs) to predict pollutant removal in the VFCWs, an essential aspect of the design process. Accordingly, the outputs from the research show that the different designs of VFCWs significantly reduce priority pollutants in stormwater; and that pollutant removal is related to the design and operational variables.

Additionally, exploratory data analysis by principal components analysis (PCA) is relatively effective at reducing the dimensionality of input variables. Subsequently, the ANN models developed produced satisfactorily accurate generalisations of TN and TP removal, as measured by the different statistical indices. Generally, the good agreement between the predicted and experimental data suggests that ANNs can adequately predict TN and TP removal up to 4 months in advance. Furthermore, the ANNs had fewer inputs, indicating that monitoring costs and time can be reduced.

Glossary

IpH	Influent pH
ITR	Influent temperature
IEC	Influent electrical conductivity
ISS	Influent total suspended solids
IOP	Influent Orthophosphorus
ITP	Influent total phosphorus
IN2	Influent nitrite-nitrogen
IN3	Influent nitrate-nitrogen
IAM	Influent ammonia
ITN	Influent total nitrogen
Ife	Influent total iron
IZn	Influent total zinc
EpH	Effluent pH
ETR	Effluent temperature
EEC	Effluent electrical conductivity
ESS	Effluent total suspended solids
EOP	Effluent orthophosphorus
ETP	Effluent total phosphorus
EN2	Effluent nitrite-nitrogen
EN3	Effluent nitrate-nitrogen
EAM	Effluent ammonia
ETN	Effluent total nitrogen
EFe	Effluent total iron
EZn	Effluent total zinc
SSR	Total suspended solids removal
OPR	Orthophosphorus removal
TPR	Total phosphorus removal
AMR	Ammonia removal
TNR	Total nitrogen removal
FeR	Total iron removal
ZnR	Total Zinc removal
BFS	Blast furnace slag
CWs	Constructed wetlands
ANN	Artificial neural network
MLP	Multi-layer perceptron
NSE	Nash-Sutcliffe coefficient of efficiency
PCA	Principal component analysis
MSE	Mean squared error
RMSE	Root mean squared error
M5-60	Rainfall depth for 60 minute 5 years return period event
r Ratio	Ratio of rainfall depth
SAAR	Standard Average Annual Rainfall
WRAP SOIL	Winter Rain Acceptance Potential
PIMP	Proposed percentage of impermeable area

Table of Contents

List of figures

List of tables

Chapter 1 Introduction

According to the United Nations, over 55 % of the world's population lives in urban areas, a proportion that is expected to increase to 68 % by 2050. This gradual shift in the residence of the human population from rural to urban areas, combined with the global population growth is expected to add another 2.5 billion people to urban areas by 2050, with nearly 90 % of this increase taking place in Asia and Africa.

Most of these people will be living in overcrowded slums with inadequate, often non-existent, water and sanitation services due to the increase in water demand, especially in water-scarce regions. The primary drivers of high-water consumption are the competing demands for water for production, and wealth that affect technologies of economic output, patterns of food and other uses (Bernstein 2002).

Urbanisation influences the climatic conditions in the affected watersheds. As the catchments urbanise, water streams are drained, and the water basins degraded leading to modifications in the hydrology of the catchment. Furthermore, the filter capacity of the streams reduces mainly due to loss of wetlands and floodplains, and the channelisation of headwater streams (Sudduth et al. 2011; Violin et al. 2011).

Moreover, as previously vegetated areas are converted into hard surfaces such as rooftops, lawns, parking lots, and roadways, the total impervious area increases. Imperviousness not only reduces the infiltration capacity but also affects the storage of precipitation and the natural routes of water flow. These hydrological changes lead to an increase in surface run-off and a deterioration of water quality in the receiving watercourses (Bierwagen et al. 2010). Thus, the amount of water available for direct human consumption reduces significantly.

The link between urbanisation, population growth, and high demand for water is complicated. Unfortunately, an estimated 2.5 % of all the water is freshwater, of which less than 1 % of the usable freshwater is available for direct consumption. Accordingly, new sustainable ways of accessing water of desirable quality are needed for better sanitation, hygiene, production, and functioning of ecosystems.

Sustainable management of water resources encompasses practices that promote the minimisation of water consumption, treatment of wastewater, water reuse, and the reclamation and protection of water sources. This research focuses on wastewater treatment using constructed wetlands (CWs).

CWs are low-cost and efficient alternative technology for the treatment of many wastewater types including domestic sewage, agricultural wastewater, industrial effluents, mine drainage, landfill leachate, and urban-runoff or stormwater. Therefore, the rationale in this study is to design novel; cost-effective, tidal vertical flow subsurface CWs (VFCWs) for the treatment of stormwater. It is planned that the VFCWs will complement the drainage infrastructure so that water resources are protected from non-point pollution associated with urban stormwater run-off. In the UK, this water management strategy is known as Sustainable Urban Drainage Systems (SUDs). In Australia, a similar concept is referred to as Water Sensitive Urban Design (WSUD) as stated in Myers (2010), while in North America; stormwater management systems are classified as Low Impact Developments (LIDs) or Best Management Practices (BMPs). These water management concepts have numerous environmental benefits, including enhanced aesthetics of the urban landscape, reduction in water pollution, and mitigation of floods.

1.1 Population growth, urbanisation and climate change

Population dynamics and urbanisation are associated with the demand for water for production, energy, and food. An increase in population and economic development puts pressure on water resources. Notable negative impacts of rapid population growth and urbanisation include a deterioration in water quality due to the discharge of urban stormwater into watercourses (Arora and Reddy 2013); spatiotemporal dynamics of rainfall; and climate change (Fletcher et al. 2013).

Consequently, to mitigate the adverse effects of urbanisation on the environment and water resources, sustainable approaches are required to cope with the changing dynamics of the urban environment. Sustainable urban development promotes the needs of both the human population and the environment. Accordingly, sustainable approaches would include the treatment of municipal wastewaters, to ensure the provision of safe drinking water, sanitation, and hygiene. In this regard, wastewater treatment is a recognition that managing water quality, pre-development flow-regimes, and the natural water balance benefits the environment as well as enhances the liveability of the urban landscape (Fletcher et al. 2013).

1.2 Water, sanitation, and hygiene

UNFPA (2003) stated that some 2.6 billion people lack basic sanitation, with an estimated 1.1 billion living in areas with no access to safe water supplies. The scarcity of water is thus an issue of global concern. Moreover, many people die from adverse sanitation-related diseases. Unfortunately, these situations could become severe with increased urbanisation accelerating the deterioration in the quality of water sources. This cycle of pollution, water shortages, poor sanitation, and hygiene make water reuse a potential intervention.

1.3 Sustainable urban drainage systems

Although urban drainage systems are essential infrastructure, the application of SUDs has only attracted interest because of the multiple benefits associated with SUDs. The benefits include: improve water quality, restoring the natural flow of water and biodiversity (Rohr 2012; Cilliers 2015); recreational amenities in urban landscapes (Granger et al. 2008). SUDs also create greener spaces in cities and towns and therefore, help to integrate different habitats (Graham et al. 2012).

Wastewater treatment using SUDs differs from the conventional treatment systems in that SUDs can treat various volumes of wastewater, an essential aspect to mitigating effects of climate change, particularly the impacts of urbanisation on run-off and the receiving ecosystems (Boogaard 2015). SUDs can attenuate floods and the impact of non-point pollution resulting from stormwater discharges. However, as highlighted by Viavattene and Ellis (2012), many potential stakeholders do not understand the functioning of SUDs and therefore find it challenging to evaluate the performance of SUDs in comparison to the conventional wastewater treatment technologies. Thus, as water resources management shifts towards adaptability to the natural and human-made influences (climate change), it is vital to standardize design codes to enable performance assessments and increase the uptake of SUDs.

1.4 Stormwater treatment

Stormwater treatment is currently an area of research interest in many parts of the world. This is partly because of the increasing demand for water and hence the necessity for reliable water supply. Thus, stormwater treatment technologies have been developed to improve water quality and thus promote effective water resources planning (Luzi 2010; Pittman et al. 2011). These research developments continue to develop and now include constructed wetlands, advanced treatment technologies like disinfectants and microbiological systems, activated sludge, biofiltration and bioretention systems (Hatt et al. 2007a; Bratieres et al. 2008).

Wetlands are areas where water covers the soil or is present either at or near the surface of the soil all year or for varying periods during the year. Wetlands can be categorised as natural or constructed. Natural wetlands are areas that are either permanently or seasonally saturated in water, creating habitats for aquatic plants and conditions that encourage the development of wetland soils. Natural wetlands include marshes, swamps, forested wetlands, and coastal wetlands like mangroves. The application of wetlands in the treatment of wastewaters such as stormwater has gained importance in the water industry due to the environmental benefits and the relatively low operational and maintenance requirements of wetland systems.

1.4.1 Constructed wetlands (CWs)

Constructed wetlands (CWs) are simulated wastewater treatment systems consisting of shallow ponds and planted macrophytes aimed at removing pollutants from wastewater by physical, chemical, and biological processes that occur in natural wetlands (Vymazal and Kröpfelová 2008; Langergraber et al. 2009). Wastewater is treated as it flows through the wetland media and around the macrophytes, with reports indicating that vegetated wetlands increase pollutant removal (Tanner and Headley 2011). Generally, CWs are designed to control the water flow, retention time; and water levels.

In addition to removing pollutants, the ability of wetlands to retain large volumes of water and release it slowly makes wetlands important for controlling extreme weather conditions such as floods and droughts associated with climate change. Additionally, wetland vegetation, soils, and associated microbial assemblages act as biofilters capturing sediments, metals and transforming nutrients like phosphorus and nitrogen thereby contributing to improved water quality, water regulation, biodiversity, urban aesthetics and recreation. Thus, CWs can play an important role in urbanisation because CWs can continuously be retrofitted to suit the changing aspects of the urban landscape.

1.4.2 Design and operation of constructed wetlands

Many studies have reported that CWs are effective in removing environmental pollutants from a variety of wastewaters (Saeed and Sun 2012). However, the design and performance of CWs as an emerging technology remains a subject of debate, primarily because CWs are designed based on empirical findings (Zhang et al. 2014). Therefore, it is challenging to compare the performance of the different designs of CWs. Accordingly, the performance data from a CW design or operational strategy might not be appropriate in other contexts due to differences in operation and maintenance constraints linked to various wastewater treatments (Wallace 2006).

Consequently, the current design criteria are reliant on optimal factors like water depth, hydraulic load, retention time, and feeding mode, which subsequently causes variations in pollutant removal in various studies (Kadlec and Wallace 2009a). Furthermore, the mechanisms by which pollutants are removed in CWs are directly and indirectly affected by the internal and external environmental conditions of pH, temperature, oxygen, organic carbon, redox conditions and operational strategies.

Nevertheless, regulatory agencies, private and public groups interested in developing CWs ought to be able to derive estimates of performance from implemented design functions in similar situations. This is necessary because CWs can potentially add substantial value to urban spaces, going by reports that rentals for properties near water sources increase by 3-13 % (Ellis et al. 2003). Thus, such benefits can be derived from designs that favour retrofitting of required structures.

Equally, the concerns over open waterbodies that compensate for urbanisation are widespread. Therefore, CW designs that embrace barrier planting schemes could be applied to limit access to wetland areas with contaminated sediments. Additionally, designs that based on accurate estimates could avert excessive runoff and therefore limit incidences of flooding (Weiler and Scholz-Barth 2009). Thus, addressing these concerns could improve the uptake of CW technology.

1.4.3 Evaluation of the performance of constructed wetlands

CWs have been used in the treatment of industrial wastewaters, landfill leachate and groundwaters containing aromatic compounds, sulphated anthraquinones; hydrocarbons, cyanides, chlorinated volatile organics, and explosives. Pollutant removal has variously been reported as high; however, in some case studies the data reported did not include the effect of design features on performance, yet the pollutant removal in CWs often varies with the treatment conditions. Additionally, a better understanding of the functioning of CWs should include all the pollutant removal mechanisms involved, a recognition that wastewater treatment in CWs is of 'black-box' nature.

Therefore, several methods have been proposed to model contaminant removal and the performance of different CWs (Kadlec 2000; Rousseau et al. 2004; Stone et al. 2004; Jamieson et al. 2007; Stein et al. 2007). The assessment options depend on factors such as budget and technical constraints; as well as the environmental and social benefits of the different wetland systems.

Thus, some evaluations of the performance of CWs focus on monitoring the influent – effluent quality rather than on the data of internal processes (Kumar and Zhao 2011). Regression analysis is then used to determine the significant relationships between the influent and effluents. Subsequently, regression models are created to predict effluent concentrations. However, the validity of the regression models is limited to the data used, making it difficult to compare the empirical regression equations of the CWs operated under different conditions (Hunt et al. 2011).

Similarly, other modelling techniques are available for evaluating the performance of CWs, and include the time-dependent retardation models (Shepherd et al. 2001),Tank-in-series (TIS) models (Kadlec and Knight 1996; Kadlec 2003); Monod models (Mitchell and McNevin 2001; Langergraber and Simunek 2005) and neural network models (Akratos et al. 2008; Akratos et al. 2009; May et al. 2009). Neural networks were applied to horizontal flow CWs to predict the removal of biochemical oxygen demand (BOD) and chemical oxygen demand (COD); ortho-phosphate (PO_4-P) and total phosphorus (TP); and for prediction of stormwater quality.

1.5 The scope of the research

This research addresses aspects of the design, operation and performance of tidal-flow VFCWs for treating urban stormwater. A total of 8 pilot-scale physical models is used as a reasonable representation of each design. The main part of this research consists of a series of experiments conducted using the research facilities at Cardiff School of Engineering, Cardiff University. The experiments are conducted in carefully considered test conditions and durations, using semi-synthetic stormwater made to simulate the local conditions. The data is analysed, and numerical models based on neural network approaches are reviewed, developed and optimised. ANN models developed are applied to the experimental results to demonstrate the capability of the ANNs to predict pollutant removal in the VFCWs.

Therefore, the outputs of this study highlight the effects of design and operational variables on the performance of VFCWs. Specifically, the tidal-flow with fixed retention time demonstrates the efficiency of the strategy on aerating VFCWs and for enhanced nitrogen removal. Similarly, the variable WWARs examined could facilitate CW design based on the cost-benefit analysis of land requirements; load volumes; media type; and pollutant removal. Equally, the prediction of the long-term performance of VFCW using neural networks could lead to reduced costs of maintenance, monitoring and evaluation. Ultimately, the success of VFCWs as a source control strategy at small and industrial scale, could provide alternative sources of non-portable water and hence reduce the demand for water demand, improve sanitation, and attenuate urban floods.

1.6 Structure of the thesis

This thesis is divided into 7 Chapters as outlined below:

Chapter 1 introduces the concept of global water scarcity and examines the links between population growth and urbanisation. Moreover, the causes of urbanisation and stormwater pollution about water management are explored; as well as the use of constructed wetlands for wastewater treatment. Moreover, the effect of design and operational variables on the performance of CWs is highlighted.

Chapter 2 presents the literature review exploring the criteria for the design of CWs, examining the application of CWs in stormwater management at the global, regional and the UK national context. Also, the monitoring and evaluation of the performance of CWs; and limitations to implementing CWs in urbanised catchments. Additionally, the gaps in the scientific body of knowledge, research and practice are identified to develop and promote evidence-based guidelines for the design optimised CWs. Finally, Chapter two ends with an outline of the research questions and objectives and hence the scope of the work undertaken.

Chapter 3 describes the research design, experimental materials, and methods for all the research work conducted in this study. Chapter Three explains how the pilot-scale CW Units were developed and the experimental investigations performed to address each research question identified in the literature reviews.

Chapter 4 presents the results of the experiments conducted as detailed in Chapter 3. The data analysed are presented in Tables and Figures to show the variations resulting from the effects of design and operational variables on the long-term operation of stormwater CWs.

Chapter 5 presents inferential statistical featuring the analyses of variances (ANOVA) undertaken to determine the effects of design and operational variables on the long-term performance of VFCWs treating urban stormwater. Consequently, the physical and chemical water quality of the influents and effluents are examined to establish treatment differences attributable to design and operational strategies.

Chapter 6 presents a novel modelling approach involving the integration of principal component analysis (PCA) and artificial neural networks (ANN) to develop models for predicting pollutant removal in VFCWs. A detailed process is presented showing how the large data dimensions are reduced to fewer but significant input variables. Furthermore, the application of a unique optimisation strategy, BFGS, to develop neural network models is discussed. Moreover, the ANN models built to predict TN and TP removal are examined.

Chapter 7 presents the conclusions and recommendations based on the literature reviews, experimental results, exploratory data analyses and numerical simulations.

Chapter 2 Literature review

The recent increase in the world population and rapid urbanisation are a matter of environmental concern. It is projected that in a few years, more than half the world's population will be living in urban areas. Urbanisation increases human interactions with the environment and hence environmental pollution. Some of the effects of urbanisation have included air pollution, increase in non-communicable diseases like heart diseases; high emissions of greenhouse gases; emergence of slums, and water scarcity; water pollution and hence the decline in the biodiversity of terrestrial and aquatic ecosystems; and modifications to the hydrological cycle: increased runoff rates and volumes, losses of infiltration and baseflow.

Additionally, stormwater runoff carries pollutants that include sediment, nutrients, bacteria (from animal and human waste), pesticides, trace metals, and by-products of petroleum. Thus, unlike pollution from industrial and sewage treatment plants, stormwater occurs over many areas (diffuse) and carries natural and anthropogenic pollutants. When stormwater enters the urban drainage system, the pollutants in the runoff can degrade the water quality of the receiving waters, hence increasing not only the likelihood of water pollution and water shortages but also flooding.

Pollutant loading from point and non-point sources increases with an increase in human activities; and varies considerably with weather conditions especially for non-point pollution (Jining and Yi 2009). While it is recognised that non-point loadings can vary, minimal effort has been made to identify non-point sources that are significant regarding pollutant load and impact on receiving waters. This is because estimating the pollutant loads associated with non-point sources remains highly challenging.

Surveys conducted in the urban catchments of the UK found that discharges from surface water sewers caused deterioration in the water quality of the receiving water courses. The impact on the water quality was reported to impair the use of the watercourse downstream of the outfall. Furthermore, the land use and the catchment area were found to influence the impacts: reductions in water quality were more likely to occur downstream of outfalls from large catchments, while industrial and highway outfalls had the highest impacts (Payne and Hedges 1990).

Shen et al. (2012) presented a research overview about agricultural non-point pollution in China, and it was found that the nutrients nitrogen (TN) and phosphorus (TP) contributed 44.5 % and 26.7 % respectively to the total pollutant loads in Lake Dianchi. It was also pointed out that the models used to estimate non-point sources were mostly for developed countries, and therefore not suitable for developing countries like China. However, the models developed in the context of China were equally described as simple and unreliable.

Clearly, the sources and transport of pollutants together with the effects of the pollutants on the environment and public health remain an area of research interest over the past years. In recent times, the pollutant list has increased to include pesticides, hormones and other synthetic chemicals regarded as posing an emerging problem. Additionally, as watersheds urbanise, the changes in the land-use create more impervious areas and hence disrupt the drainage network. Consequently, the stormwater runoff response to rainfall is much faster, leading to shorter times of concentration and reduced recession times. Moreover, water quality and urban hydrology have been impacted as sanitary sewers are currently either separate or combined with stormwater sewers (Fletcher et al. 2013). Therefore, there is a need to mitigate the effects of urbanisation on the environment. This will require new adaptive management actions that promote sustainable urban development and environmental protection. The implementation of the approach could be based on ecohydrological methods and hence a change in concepts in environmental sciences, the global economy, engineering, and education systems.

2.1 Sustainable water management

The growing pressure on the earth's water resources – from population and economic growth, climate change, pollution, and other challenges – has significant impacts on our social, economic, and environmental sustainability. As a result, many countries have taken steps to safeguard water sources through policy and technology. In the USA, The Clean Water Act (CWA) established the structure for regulating discharges of pollutants into the waters of the United States and regulating quality standards for surface waters. Under the CWA, the US Environment Protection Agency (EPA) sets wastewater standards for industry and the water quality criteria for pollutants in surface waters(Ashley et al. 2007; Hough and Robertson 2009). The EPA also implements an Urban Waters Initiative which focuses on investing in water infrastructure, enforcement and prevention of harmful runoff.

Similarly, within Europe, the EU Water Framework Directives (WFD) recognises that water pollution from non-point sources is an issue of concern. Consequently, the EU has emphasized controlling diffuse pollution associated with stormwater runoff from roads and housing areas (Ellis et al. 2003). The WFD contains legislation that promotes sustainable use of water by detailing how urban surface drainage is managed, as well as sets limits on direct discharges of runoff to water sources.

In addition to the EU Water Framework Directives (WFD), the UK has specific laws concerning sustainable water management. The Flood and Water Management Act 2010 reviewed the approach to combating floods from building flood defences to improving flood risk management (Butler et al. 2010). Thus, drainage systems in new developments are approved by local authorities after consultation with regulatory agencies affected by the likely discharge. Moreover, to control surface drainage in new developments, the use of SUDs is recommended. Additionally, the UK “Future Water” strategy, promotes rainwater harvesting, and SUDs to retain runoff before discharge into water courses, and to reduce peak flows and the likelihood of stormwater pollution (Butler et al. 2010).

2.2 Urban wastewater treatment in the UK

Urban wastewater, often called sewage, is defined in the WFD as the mixture of domestic wastewater from kitchens, bathrooms and toilets, the wastewater from industries discharging to sewers and rainwater run-off from roads and other impermeable surfaces such as roofs, pavements and roads draining to sewers. Without treatment of wastewater, discharges to sewers and the stormwater run-off contaminated with metals, oils and other pollutants from urban areas draining to sewers would have significant adverse impacts on the water environment.

In Europe, agriculture is thought to contribute to between 50 – 80 % of N and P loading into Europe’s freshwaters. Agriculture is, therefore, an essential source of N and P loading into surface water and groundwater (Lankoski and Ollikainen 2011). Thus, the 1991 EU Nitrates directive requires the EU Member States to reduce nitrate loading from agriculture to ground and surface waters. Therefore, the discharge of wastewater into the water environment is regulated by the EU Water Framework Directive 2000/60/EC (WFD).

The WFD focuses on integrating all aspects of the water environment so that water management is effective and sustainable. The WFD established a framework for the protection of water bodies in all Member States to reach "good status" objectives. It contains crucial legislation such as the Nitrates Directive, which aims to reduce water pollution caused or induced by nitrates from agricultural sources, and to prevent further pollution, through several measures; and the EU Urban Waste Water Treatment Directive (91/271/EEC) seeks to protect the water environment for aquatic life, recreation, a resource for drinking water, sanitation, industry, and commerce. Article 16 of the EU Urban Wastewater Treatment Directive requires the EU Member States to regularly produce reports on the collection and treatment of urban wastewater, and the re-use and disposal of the residual sewage sludge.

The EU Urban Wastewater Treatment Directive was transposed into UK Law and became the "Urban Waste Water Treatment (England and Wales) Regulations 1994". Accordingly, the UK/EU Directives (91/271/EEC) requires that urban wastewater is adequately treated to reduce pollutants such as nitrogen, phosphorus, and heavy metals before discharge into the water environment. However, with the current wastewater treatment technologies, nutrient outflow concentrations are far from the required quality standards of the European Union for sensitive areas (10–15 mg N/l and 1–2 mg P/l), hence the need for efficient, cost-effective and sustainable methods for urban wastewater treatment.

2.3 Pollutants in stormwater run-off

The primary focus in stormwater quality studies has been about sediments, organic matter, nutrients and heavy metals. However, recently, both pathogens and emerging organic compounds (EOCs) have been included. EOCs include industrial derived compounds and polyaromatic hydrocarbons (PAHs) such as pesticides and herbicides (Eriksson et al. 2007; Aryal and Lee 2009; Aryal et al. 2010).EOCs occur at ultra-trace concentrations in the water environments and hence require special analytical techniques such as mass spectrometry, gas or liquid chromatography, and tandem combinations like GC/MS/MS (Karnjanapiboonwong et al. 2011; Blair et al. 2013; Metcalfe et al. 2013).

Similarly, minerals and organic pollutants were identified as contaminants of concern in urban environments (Lundy et al. 2012; Schmitt et al. 2015). This and other publications show that stormwater quality and the subsequent pollutant loads to the environment is related to the degree of imperviousness (car-parks, roof-tops, roads) and natural processes such as atmospheric deposition. Nevertheless, the data relating to priority pollutants in the environment is variable. Thus, data such as the production and transfer processes as well as characteristics of pollutants and pollutant loads are needed to develop management strategies that meet the requirements of under the Urban Wastewater Treatment Directive and the Water Framework Directive (2000/60/EEC) (Kafi et al. 2008).

Table 2-1 shows the priority pollutants monitored in the European Union and the UK, together with effluent pollutant concentrations and their respective per cent removals. The data shows that stormwater CWs reduced priority pollutants carried in stormwater and hence improved the water quality of the receiving watercourses. However, the data show variations in removal efficiency, which suggests that pollutant reduction was higher in some treatment systems than in others. Equally, extreme seasonal variations in performance could be inferred from the BOD_5 data as high as 388 mg/l (Adeola et al. 2009) associated with propylene glycol in the de-icing fluids used during winter at London Heathrow Airport. Nonetheless, average BOD_5 concentrations in stormwater runoff are usually below 18 mg/l (Pontier et al. 2001). More importantly, the performance data presented in Table 2-1 is only limited to pollutants prioritised in the UK and EU and is based on the presence of the pollutants in stormwater run-off and on the effects of the pollutants on aquatic life and public health.

Table 2-1 Combined list of priority pollutants in UK and Europe(Lucas et al., 2015)

Pollutant Group	Pollutant	UK Priority (Mitchell, 2005)	EU Priority (Eriksson et al., 2007)	Removal Efficiency (%)	Effluent Concentration (mg/l)	Refs
Basic Parameters	Biochemical Oxygen Demand (BOD_5)	✓	✓	24 - 76	0.6 - 388	1,2,3,4,5,6
	Chemical Oxygen Demand (COD)	✓	✓	39 - 54	1 - 135	
	Suspended Solids (SS)	×	✓	18 - 94	2 - 172	
	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	1,3,4,5,7,8, 9,10
	Chromium (Cr)	✓	✓	53 - 84	0.001	
	Copper (Cu)	✓	✓	32 - 97	BDL - 0.224	
	Iron (Fe)	✓	×	10	0.4 - 4.3	
	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, 12
	Pendimethalin	×	✓	58	<0.00001	
	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 *tert*-butyl ether	×	✓	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
[1]Scholes et al. (1999), [2]Adeola et al. (2009), [3]Terzakis et al. (2008), [4]Birch et al. (2004), [5]Kao et al. (2001), [6]Pontier et al., (2001), [7]Meiorin (1989), [8]Shutes et al (2001), [9]Shutes (2001), [10]Bulk & Slak (2003), [11]Miller et al. (2002), [12]Maillard et al. (2011), [13]Schaad et al. (2008)
✓ = priority pollutant, × = not a priority pollutant, BDL = below detection limit (reported in reference as 0)

2.3.1 Nitrogen (N)

Nitrogen in urban runoff contributes to the eutrophication of receiving waters around the world. While phosphorus is normally the limiting nutrient in fresh water, N may also be of concern (Taylor et al. 2005). However, although considerable data exist on the concentration of nitrogen in urban runoff (Duncan 1999), there are less on its composition. Taylor et al. (2005) characterised the composition of nitrogen in urban stormwater in Melbourne (Australia), and reported that about 80 % of the N in urban stormwater is in dissolved forms. The particulate form of N in stormwater is broken down once it enters wastewater treatment systems. The decomposition of particulate N into dissolved substances subsequently increases the percentage of previously dissolved matter. Dissolved N forms include nitrite-N, nitrate-N, and ammonia-N, and can be incorporated into organic matter forming organic N. The main forms of N and transformations are shown (Figure 2-1).

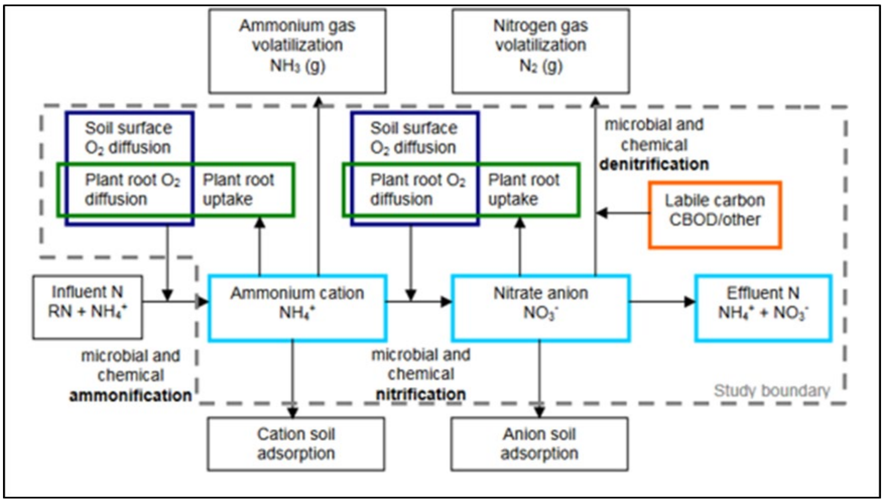


Figure 2-1 Nitrogen transformations in a subsurface flow CWs (Fuchs 2009).

2.3.1.1 Nitrogen transformations

Nitrogen is an essential nutrient in the biogeochemical cycles of CWs. Nitrogen exists in two forms namely: organic N and inorganic N. Organic N comprises compounds such as nucleic acids, amino acids, proteins, and urea. Ammonia (NH_3), ammonium $(NH_4)^+$, nitrite $(NO_2)^-$, nitrate $(NO_3)^-$, dinitrogen (N_2), nitric oxide (NO) and nitrous oxide (N_2O) are forms of inorganic N. Figure 2-2 shows compositions and transformations of nitrogen. Thus, nitrogen removal in CWs is dependent on the nature of N species present in the wastewater.

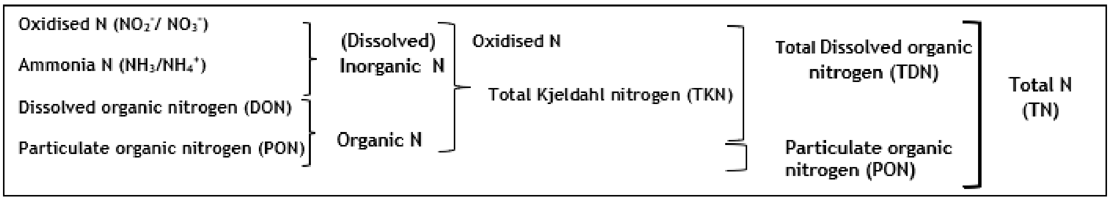


Figure 2-2 Nitrogen compositions and transformations (Taylor et al. 2005)

Nitrogen together with nutrients like phosphorus, can under favourable conditions of pH and temperature contribute to the eutrophication of water resources. Eutrophication manifests itself as algal blooms. Upon death, algal blooms decompose causing reduced levels of dissolved oxygen and in the affected watercourse. However, nitrogen can be removed from CWs in the form of Ammonia-N, mostly volatilisation and adsorption, while particulate N is eliminated by sedimentation. Equally, nitrogen can undergo different biological transformations like ammonification, nitrification, denitrification, plant uptake, biomass assimilation, and anaerobic ammonium oxidation (ANAMMOX) and subsequently gets removed in CWs treating wastewater containing N compounds.

2.3.1.2 Ammonification: Nitrogen mineralisation

The process of ammonification results from the breakdown of organic matter such as dead animals and plants or waste materials like manure. This breakdown is accomplished by scores of microorganisms which utilise dead organic material for energy. Ammonia and related compounds are produced as metabolic by-products of ammonification. The by-products of ammonification are involved in other processes like volatilisation, adsorption, plant uptake, and nitrification.

Ammonification occurs in the aerobic environments of soil so that bacteria and other micro-organisms involved have enough oxygen. Other factors that can influence ammonification include carbon to nitrogen ratio (C/N), temperature, pH, soil structure and nutrient availability (Morató et al. 2014).

In CWs, ammonification decreases with depth, due to the decline in aerobic conditions. Consequently, ammonification is higher and faster in the upper zones of the CWs than in the lower zone where anaerobic conditions dominate (Kadlec 2000; Morató et al. 2014). Ammonification encompasses several deamination processes whose optimal pH is in the range 6.5-8.5 and at temperatures of 40-60 °C (Hammer 1989; Hammer and Knight 1994; Vymazal 2007).

2.3.1.3 Nitrification

Nitrification is an essential step in the nitrogen cycle because it is how organic matter degradation is related to fixed nitrogen loss. Ammonium released by ammonification is oxidised to nitrate by nitrification and can then be reduced to dinitrogen gas by denitrification, resulting in net loss of fixed nitrogen from the system. Whether organic matter degradation results into net ammonium release depends mostly on the availability and quality of organic substrate and interactions among the microbial communities involved in nitrogen and organic matter cycling. In sediments, the nitrogen cycle relies on the supply of organic matter and oxygen from overlying water. During nitrification, ammonia is converted to nitrates by nitrifying bacteria (Kadlec and Knight 1996). Nitrification requires oxygen and certain bacteria of the species N*itropira*, *Nitrosococcus*, *Nitrosomonas* and *Nitrobacter*. These bacteria can be aerobic, autotrophic or chemoautotrophic and depend on aqueous carbon dioxide as a carbon supply source (Morató et al. 2014). The oxidation of ammonia to nitrate provides the required energy (Vymazal 2007). Nitrification reduces the ammonia-N concentration, while nitrate-N concentrations increase according to the equations below:

$NH_3\,(aq) + O_2\,(g) + 2H^+\,(aq) + 2e^- \rightarrow NH_2OH\,(aq) + H_2O\,(l)$ 2-1

$NH_2OH\,(aq) + H_2O\,(l) \rightarrow 5H^+\,(aq) + NO_2^-\,(aq) + 4e^-$ 2-2

$\frac{1}{2}O_2\,(g) + 2H^+\,(aq) + 2e^- \rightarrow H_2O\,(l)$ 2-3

Combining equations 2-1, 2-2, and 2-3 gives equation 2-4:

$NH_3\,(aq) + 1.5O_2\,(g) \rightarrow H^+\,(aq) + NO_2^-\,(aq) + H_2O\,(l)$ 2-4

$NO_2^- + 0.5\,O_2 \rightarrow NO_3^-(aq)$ 2-5

Nitrification is a two-step process involving autotrophic bacteria in aerobic conditions (Kadlec and Knight 1996; Vymazal 2007). The most common bacterial type involved in converting ammonia-N to nitrite-N (nitritation) is *Nitrosomonas*, an ammonium oxidising bacteria (AOB). Similarly, nitrite-N is converted to nitrate-N (nitritation) under aerobic conditions by *Nitrobacter,* a nitrite oxidising bacteria (NOB). During nitritation, oxygen is the electron acceptor (Lee et al. 2009). Like ammonification, nitrifying bacteria occur in the surface layers of the wetland and decrease with depth as the upper zones have aerobic conditions whereas, in the lower zones, the conditions are anaerobic.

2.3.1.4 Denitrification

Chemical fertiliser inputs and soil organic-matter mineralisation are the primary sources of $(NH_4\text{-}N)^+$ in the environment. Denitrification is the microbial process of reducing nitrate and nitrite to gaseous forms of nitrogen, principally nitrous oxide (N_2O) and nitrogen (N_2). A broad range of micro-organism can denitrify (Bratieres et al. 2008; Davis et al. 2010). Denitrification is a response to changes in the oxygen (O_2) concentration of their immediate environment. Only when O_2 is limited will denitrifies switch from aerobic respiration to anaerobic respiration, using nitrite (NO_2) as electron acceptor switch from aerobic respiration to anaerobic respiration, using nitrite (NO_2) as an electron acceptor. The key to denitrification is the availability of oxides of N ($NO_2\text{-}N^-$ or $NO_3\text{–}N)^-$. These N forms are formed during the autotrophic nitrification of ammonia N-(NH_3) derived from ammonium N-$(NH_4)^+$.

Other denitrification pathways include the release of N_2O during the nitrification process (nitrifier denitrification); denitrification by chemical decomposition of $NO_2\text{–}N$ in soils with low-pH, and non-biological (chemo-denitrification) linked with nitrification that it is often difficult to determine whether the nitric oxide (NO) and N_2O produced are formed through nitrification or chemo-denitrification. Denitrification is a major pathway that accounts for some of the mass balances of total inputs and outputs of N in CWs. However, a portion of N unaccounted for is attributed to the loss of gaseous N (Skiba 2008).

2.3.1.5 Nitrogen recycling in wetlands

The recycling of nitrogen occurs through a biogeochemical cycle involving numerous biotic/abiotic transformations. Nitrogen compounds are broadly categorised as inorganic and organic. Both organic and inorganic forms of nitrogen are essential for all biological life. The principal inorganic forms of N are nitrite (NO_2^-), nitrate (NO_3^-) and ammonium (NH_4^+). Moreover, N species like dinitrogen (N_2), nitrous oxide (N_2O), nitric oxide (NO_2 or N_2O_4) and NH_3 exist.

Although the composition of N in stormwater can vary with the catchment, investigations conducted in Melbourne (Australia) during both baseflows and storm events showed that nitrogen in urban stormwater was largely dissolved (80 %), with ammonia-N (11 %) the least-abundant (Taylor et al. 2005). Furthermore, nitrogen species were reported as not significantly variable between baseflow and storms. However, the proportion of nitrogen in particulate form was higher during storm events. While the composition of N in Melbourne stormwater was consistent with global data; dissolved inorganic N was higher (Taylor et al. 2005). Consequently, N removal in stormwater VFCWs is likely to be influenced by the variability of N species but not necessarily the flow conditions. Therefore, the design of VFCW for N removal must ensure that the treatment system can deal with the stochastic influent N, and with the ability to remove total dissolved nitrogen (TDN). Thus, to attain higher rates of N removal, the design of the wetland should favour N transformations and N removal pathways, notably volatilisation, ammonification, nitrification, nitrate-ammonification, denitrification, N_2 fixation, assimilation (plant and microbial uptake), ammonia adsorption, organic nitrogen burial and anammox (anaerobic ammonia oxidation).

In CWs, the process of denitrification removes about 60-70% of the total nitrogen (TN), of which between 20 - 30% of the TN removed through plant uptake (Spieles and Mitsch 1999; Taylor et al. 2006). Crucially, in stormwater CWs, the proportion of N removed is significantly lower (Taylor et al. 2006). Furthermore, the mass balance of nutrients indicates that 14 % is originated by physical treatment processes and 8.6 % by plant uptake; *i.e.*, the absorbed amount of N into the plant itself is small, but the absorbed N stimulates diverse ecological activities (Yang et al. 2007).

2.3.2 Phosphorus (P)

Phosphorus in the environment is contributed by both point and non-point sources. It is often found bound or adsorbed onto submerged particles. Phosphorus impacts the quality of water just like other bounded pollutants like organic compounds, and heavy metals do. Like nitrogen, phosphorus supports the growth of algae and other aquatic plants which may lead to eutrophication.

Phosphorus is mainly found in dissolved form, with only a small fraction existing in particulate form. The different forms of dissolved P in urban stormwater runoff include ortho-phosphorus, polyphosphate, organic phosphate, and inorganic orthophosphate (Barron et al. 2010). Orthophosphate will also adsorb to soils.

Phosphorus is often regarded as a problem nutrient because it is a significant contributor to the eutrophication of freshwaters with nitrate-N playing a lesser role. However, in marine environments, nitrate-N is the leading cause of eutrophication. Thus, salinity determines which nutrient is likely to cause eutrophication.

Significant work in the agriculture sector has found that in acidic soils the adsorption of P is primarily controlled by the content of iron and aluminium oxides in the soil (Davis et al. 2010). These minerals provide the surface and binding sites for P. Additionally, particulate P is mostly found in sediments and comprises of the animal/plant, and mineral phosphate adsorbed on iron oxyhydroxide surfaces. Therefore, the media in CWs can have variable phosphorus adsorption capacity due to previously-loaded phosphorus. Since freshwaters are sensitive to phosphorus concentrations, the P contained in effluents treated in CWs must be low to meet established regulatory water quality standards. Consequently, the ability of the media to adequately adsorb P would require regular maintenance such as biomass harvesting and filter washing to improve the media adsorption capacity.

2.3.3 Heavy metals

Heavy metals in stormwater runoff result from diffuse sources such as particles of combustion from motor vehicle emissions, leaked lubrication and brake oil, vehicle tyre wear and asphalt from roads surfaces. During a storm event, these contaminant particles are washed off roofs, roads and other impervious surfaces and become part of the pollutant load in stormwater runoff. The concentrations of heavy metals in stormwater vary with the catchment type, with the lowest concentrations coming from uncultivated and rural areas and higher concentrations from industrial areas. Rule et al. (2006) established that metal concentrations in runoff were higher in the light industrial estate samples than in the domestic samples for all the metals and exhibited highest levels in the 'first flush' samples, coincident with the initial flow of runoff containing the highest concentrations of suspended solids. In another study, (Davis et al. 2010) reported that heavy metals tend to bind strongly to soil media, and that adsorption is generally a function of pH, with increasing metal adsorption at higher pH, such as within the pH range of the soil media (6–7).

Consequently, metal pollutants in stormwater are present in both the particulate and dissolved forms; with strong correlations observed between TSS and iron (Fe) as well as with other parameters including electrical conductivity. Heavy metals in stormwater runoff are of concern due to their persistence in the environment at trace concentrations (10^1 – 10^2 μg/L) and their toxic effects on aquatic organisms.

2.3.3.1 Copper (Cu)

The principal sources of copper in the environment include corrosion of copper plumbing and vehicle parts and industrial water. Agriculture is the other source of copper in stormwater as copper is mostly used an algaecide. The environmental mobility and bioavailability of copper are dependent upon its concentration in solution. Urban stormwater contains about 20-40 % of copper in the soluble phase (Hares and Ward 1999).

2.3.3.2 Zinc (Zn)

Primary sources of Zinc include automobile tyres and industrial electroplating and galvanised operations. Galvanised roofs and gutters contribute 70-90 % of total Zn loads. Other sources of Zn are atmospheric deposition, road salt, mining, paint, and stains. Approximately 30-50 % of Zn in runoff is in the soluble phase (Liebens 2001).

2.3.3.3 Lead (Pb)

Vehicle exhaust emissions are the principal sources of lead in stormwater derived from atmospheric depositions. However, since unleaded petrol was introduced in 1973, atmospheric concentrations of lead have declined by over 90 %. However, during stormwater events, the mobilisation of pollutants exhibits the first-flush behaviour, with electrical conductivity correlating with stormwater intensity. Materials used for roof covering (copper, zinc), gutters, and pipes (aluminium, lead) release metals during corrosion enhanced by the low pH of rainwater.

Generally, screening heavy metals (dissolved or particulate) depends on the metal’s adsorption characteristics; while the adsorption behaviour of the solids affects the bioavailability of the adsorbed metals. Research into the adsorption/desorption behaviour of metals on urban roadsides shows that deposited solid particles contain significantly high amounts of vacant charge sites and hence have the potential to adsorb additional metal ions (Gunawardana et al. 2013).

Relatedly, investigations into variations in metal content for different particle sizes of solids associated with pollutant build-up on road surfaces established that heavy metal concentrations in stormwater are related to fine particulates (20-0.4 μm) and that the association is influenced by the nature of storm events and antecedent conditions (Gunawardana et al. 2014). The commonly reported metals in the runoff include lead, zinc, copper, cadmium, nickel, and chromium (Kayhanian et al. 2012), and that these metals mostly occur in the dissolved phase, while the same metals in highway runoff are mainly in the particulate phase. However, the bioavailability of metals is most significant in the soluble phase (Mitchell 2005; Mitchell and Diaper 2006; Eriksson et al. 2007).

Clearly, stormwater run-off is a significant source of environmental contaminants (Athayde et al. 1983; Davis and Birch 2010; Morgan et al. 2017), and that the accumulation of stormwater pollutants in receiving waterways can have adverse impacts on the water environment(Brown and Peake 2006). Thus, watercourses receiving urban stormwater or highway run-off must be protected to reduce the effects such as ecological-toxicity, bioaccumulation, bioconcentration and other influences on biodiversity, caused by the non-biodegradable metals (Birch and Taylor 2002; Gill et al. 2017).

2.3.4 Emerging organic compounds (EOCs)

Emerging micro-contaminants are the latest environmental pollutants of most significant concern. Micropollutants are a concern because of their potentially adverse effects on human health and ecosystems. Micropollutants enter aquatic environments via urban run-off, industrial and agricultural wastewater; or as wastewater effluents resulting from an ineffective treatment applied for removal of contaminants (Fatta-Kassinos et al. 2011; Rizzo et al. 2013). Additionally, variations in chemical properties affect the behaviour of other chemical contaminants during wastewater treatment (Richardson and Ternes 2005; Xie and Ebinghaus 2008). Thus, chemical properties of micro-pollutants like antibiotics vary due to the presence of non-polar parts associated with polar functional moiety.

2.4 Monitoring pollutants in urban stormwater

Water quality in the receiving watercourses deteriorates in response to the environmental degradation in the catchments. This is because pollutants mobilised in different parts of the catchment get transported in runoff aided by the hydraulic efficiency of the drainage networks (Charters 2016). Thus, the characteristics of the stormwater runoff depend on the nature of the surfaces with which it comes into contact, natural processes like atmospheric deposition and anthropogenic activities in the catchments (Eriksson et al. 2007). Consequently, stormwater run-off contains a variety of pollutants at different concentrations, making it unsafe for discharge into the water environment.

Priority pollutants selected for monitoring in the stormwater used in this study consist of heavy metals - selected based on speciation (dissolved and particulate-bound metals, the cationic and anionic species within the pH range of stormwater). Additionally, the metals were incorporated in the monitoring studies because the heavy metals are indicators of human activity, pollutant sources and toxicity. Furthermore, the pollutants found in stormwater but whose origins include domestic septic tanks irrigated agricultural lands, and industrial wastewaters were included due to the likelihood of infiltration and hence groundwater pollution. Additionally, water-borne pathogens and bacteria, the primary component in stormwater management were considered. Pathogenic bacteria found in stormwater are known to spread diseases and to influence environmental change (Pandey et al. 2014).

Moreover, stormwater contains suspended solids because the solids deposited on ground surfaces enter sewer systems by suspension in the runoff. Solids originate from sources like the erosion of pervious surfaces and dust, litter and other particles deposited on impervious surfaces from human activities and the atmosphere. The denser solids settle in the gully pots of the drainage systems, while the remaining suspended solids are carried by the flow and end up either in the combined sewers or separately as surface water outfall. Furthermore, solids often associate with particulates in run-off hence provide a medium for the accumulation, transport and storage of pollutants including nutrients and metals. High levels of solids increase turbidity, reduce the penetration of light at depth within the water column, and limit the growth of desirable aquatic plants.

2.4.1 Event mean concentration (EMC)

Stormwater is characterised by flow measurements, and usually many samples are collected. The sample parameters can be described using descriptive statistics like the mean or range of concentrations, maximum, minimum, and standard deviation. However, when characterising a storm event, the event mean concentration (EMC) is preferred. The EMC is the concentration of a specific pollutant contained in runoff coming from a land use type within a watershed. EMCs are reported as a mass of pollutant per unit volume (mg/L). The EMC is calculated for each rainfall event and represents the total mass of pollutant divided by the total volume discharged. The Site Mean/Median Concentration (SMC) is the mean or median of all the measured EMC (Hvitved-Jacobsen and Yousef, 1991). EMCs can also refer to the pollutant concentrations of a composite of multiple samples collected during a storm event.

In such cases, the EMC is a flow-weighted average concentration or the total pollutant mass divided by the total runoff volume for a storm event of duration t (Sansalone and Buchberger 1997; Ballo et al. 2009; Choi et al. 2016).

$$\mathrm{EMC} = \frac{\text{Total pollutant loading per event}}{\text{Total run-off volume per event}} = \frac{\sum_{i=1}^{n} V_i C_i}{V} \quad \text{.............................. 2-6}$$

where; EMC = event mean concentration (mg/L); V = total runoff volume per event (L); V_i = runoff volume proportional to the flow rate at time i (L); C_i = pollutant concentration at time i (mg/L); and n = total number of samples in one storm event. From Equation 2-6, the EMC calculated for each storm event is the pollutant concentration contained in the flow or volume. This approach can lead to over-estimates or under-estimates, especially when the EMCs are used to compute the arithmetic mean for the total number of storms (Erickson et al. 2010; Maniquiz et al. 2010). Thus, a storm with little rainfall yields a high EMC, while a large rainfall gives a smaller EMC because the EMC is an average of the entire storm event.

EMCs are often used to characterise stormwater loadings, and when combined with the runoff volume, pollutant mass discharge can be estimated (Corwin et al. 1997; Barrett et al. 1998; Ballo et al. 2009; Choi et al. 2016; Gill et al. 2017). Furthermore, pollutant characteristics and the relationships between pollutant loads and runoff, as well as the first flush effect of storm events have been investigated using the EMC (Lee and Bang 2000; Lee et al. 2002b; Vaze and Chiew 2002; Gill et al. 2014). The first flush is the concept that the initial portion of a rainfall-runoff event is more polluted than the later portions. Therefore, studies of the first flush can inform the design of stormwater CWs. This is because the design features of the treatment system will have incorporated the relationship between the nature of run-off pollutant loads concerning the hydrograph.

Many studies regarding the first flush phenomenon have been conducted, and the hydrographs and pollutographs obtained from the studies established that watersheds with combined sewers had peak pollutant concentrations preceding flow-rates in smaller watersheds (< 100 ha, 80 % imperviousness). However, in larger watersheds (>100 ha, 50 % imperviousness), peak pollutant concentration followed the peaks for the flow-rate (Lee and Bang 2000; Lee et al. 2002b).

Similarly, investigations into heavy metals contained in road runoff reveal that in first flush loads, heavy metals were found together with particulates (Barbosa and Hvitved-Jacobsen 1999; Wang et al. 2013; Gill et al. 2017). In another study, EMCs were applied in generating pollutant build-up and wash-off formulae for stormwater modelling (Charbeneau and Barrett 1998). The researchers relied on suspended solids data obtained from a single-land-use watershed to evaluate the practicality of the method. It was concluded that a single EMC for all urban land-use was a realistic estimate of the suspended solids loads, and that the increases in suspended solids loads from a new development were primarily a function of the increase in runoff volume, which in turn was related to the increase in imperviousness (Charbeneau and Barrett 1998). Although water quality data did not show a strong correlation between initial pollutant loads and the length of the antecedent dry period, the concentration of suspended solids in the stormwater runoff followed a simple wash-off model (Charbeneau and Barrett 1998).

More recently, field investigations were conducted for over 5 years to determine pollutant loads from paddy fields (Choi et al. 2016). The average annual pollutant losses from the study were based on the method of long-term average annual precipitation, pollutant EMCs and run-off ratio. However, when compared to annual pollutant losses derived from unit loads (determined by three different methods), similar results were obtained with the method using arithmetic mean run-off ratio and EMCs. The study concluded that the estimation of the unit load from long-term average annual precipitation, pollutant EMCs and run-off ratio was closer to the observed unit load of pollutants from paddy fields than that of the method using pollutant EMCs from log-normal and gamma distribution (Choi et al. 2016).

Although the first flush phenomenon has been severally investigated, there remains the debate on whether the first flush exists; which environmental factors influence the first flush, and how best to represent the first flush. Nevertheless, the first flush is a complex phenomenon and tends to be specific to site or location. Moreover, peak concentrations in first flushes have been shown to vary with different pollutants during the same storm event, or during different storm events in the same watershed (Gupta and Saul 1996). Thus, where the first flush can result in heavy pollution of receiving watercourses, effluent storage tanks should be installed to retain the effluent and later discharge the effluent in a controlled manner.

Additionally, the storage volume can be optimised, by predicting both the total pollutant load discharged and the temporal variation in pollutant concentration within an event. Predictions of the pollutant concentrations in a first flush could be achieved using QSIM and MOUSETRAP models. However, the application of QSIM and

MOUSETRAP requires extensive data, and this tended to limit the use of the two models to large and often environmentally sensitive schemes (Gupta and Saul 1996).

2.5 Constructed Wetlands (CWs)

Constructed wetlands are engineered systems designed to mimic natural processes in wetland vegetation, bed media, and microbiomes to treat wastewater (Brix and Arias 2005; Kadlec and Wallace 2009a; Vymazal and Kropfelova 2009). The application of CWs has evolved over the past decades, where various studies have demonstrated that CWs are a reliable, cost-effective and sustainable technology effective for treating different types of wastewaters. Wastewaters treated in CWs include municipal, industrial, agricultural, landfill leachate and stormwater runoff (Brix and Arias 2005; Kadlec and Wallace 2009a; Vymazal and Kropfelova 2009; Vymazal 2010; Matamoros et al. 2012).

CWs contribute to creation and restoration of habitats for wildlife, environmental and landscape enhancement (Kapellakis et al. 2012; Martín 2013; Avila et al. 2014; Wu et al. 2014a; Zhang et al. 2014). CWs are particularly suited for on-site wastewater treatment requiring basic design and high buffering capacity. Contaminants in CWs can be removed through a combination of biological, physical and chemical mechanisms which include: biodegradation, transformation and uptake of pollutants by micro-organisms and plants, predation and die-off of pathogens; sedimentation/gravitational settling of solids, straining and filtration; chemical precipitation, complexation, adsorption and; ion exchange on surfaces of wetland vegetation and the media.

2.5.1 Classification of constructed wetlands treatment systems

Constructed wetlands differ both in design characteristics and treatment processes that contribute to pollutant removal (Vymazal 2010). CWs are broadly categorised into two types: sub-surface flow and free water surface systems (Figure 2-3).

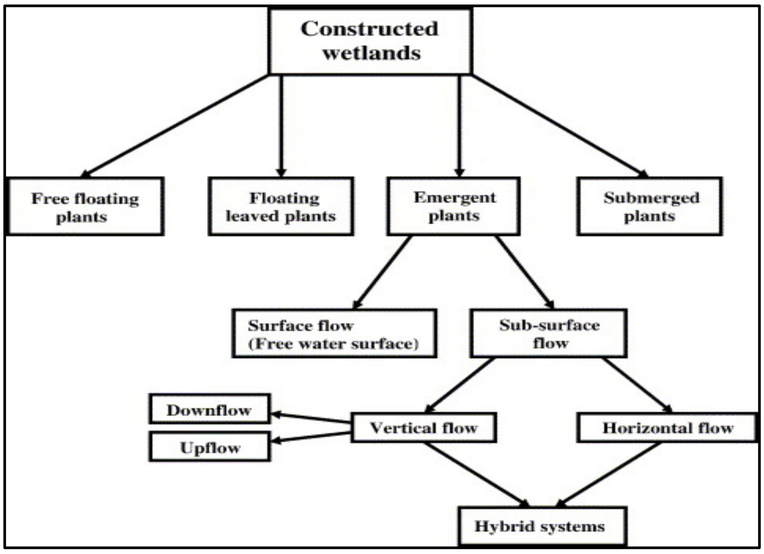


Figure 2-3 Classification of CWs for wastewater treatment (Vymazal 2001)

2.5.2 Free water surface constructed wetlands (FWS CW)

These are wetland systems where an area of the water surface is left exposed to the atmosphere. FWS CWs consist of basins or channels with soil or some other appropriate media that can support macrophyte vegetation (emergent plants, submerged plants, free-floating plants or floating-leaved plants (Vymazal and Kröpfelová, 2008). The macrophyte vegetation incorporated in the FWS CW acts as an area of biological activity, particularly in the upper layer of soil, and in the stems of macrophytes or the alternative media at the base of the wetland.

FWS CWs simulate natural wetlands, and as such, the water depths are shallow, with low flow velocity, and the presence of macrophyte plants tends to regulate water flow especially in long narrow channels hence plug flow conditions (Reed et al. 1995). As wastewater flows through the wetland system, pollutants are removed by sedimentation, filtration, oxidation, reduction, adsorption, and precipitation (EPA 2000). The trapped particulate matter enters the elemental biogeochemical cycles in the water column and wetland media. However, the resemblance of FWSCWs to natural wetlands attracts wildlife (fish, insects, birds and reptiles) (Kadlec and Knight 1996) making the FWSCWs breeding grounds for insects like mosquitoes. The interaction of wildlife and humans poses public health risks, making it essential to protect the public (Wu et al. 2014a).

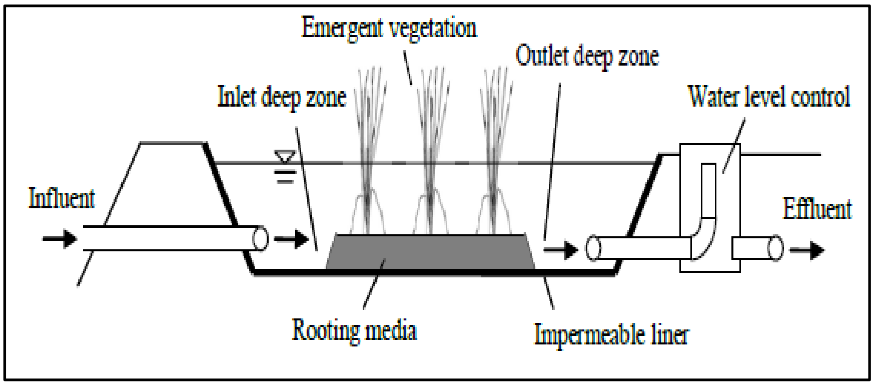


Figure 2-4 Typical set-up of an FWS CW adapted from (Kadlec and Wallace 2009a)

FWSCWs are multi-purpose systems due to the presence of emergent macrophytes as shown in Figure 2-4. The microphytes in FWS CWs reduce wind speeds thereby aiding sedimentation while preventing re-suspension. Furthermore, the macrophytes provide a suitable substrate for bacteria and periphyton to up-take nutrients (Vymazal 2013).

Since part of the FWSCW has high exposure to the atmosphere, the FSWCWs are efficient in pathogen removal, attributed to ultraviolet (UV) light. Furthermore, when implemented in carbon-constrained systems, FWSCWs can provide the carbon needed for denitrification (biomass decomposition). For these reasons, FWSCWs are mostly used for the secondary and tertiary treatment of wastewaters. Nonetheless, analysis of the sediments of FWSCWs showed that incomplete denitrification leads to the emission of the greenhouse gas, nitrous oxide (N_2O). Thus, the presence and type of vegetation were found to have correlated negatively to nitrate and nitrite reducers and positively to nitrite and nitrous oxide reducers; demonstrating that the potential for nitrous oxide emissions is higher in vegetated sediments (García-Lledó et al. 2011). However, the evaluation of the suitability of FWSCWs based on the water quality in Lake Manzala Engineered Wetlands Project in Egypt, concluded that presence of natural vegetation considerably increased the dissolved oxygen in the effluents (El-Sheikh et al. 2010).

2.5.3 Subsurface flow systems

These are designed to create subsurface flow through a permeable medium, keeping the treated wastewater below the surface. The benefit of keeping the water below is that development of odours and other associated problems is avoided. The media commonly used include soil, sand, gravel or crushed rock. The type of media used affects the hydraulics of the system. Subsurface flow systems are built with the horizontal flow. However, the increased demand for ammonia removal initiated a fast development and spread of vertical flow systems which are intermittently fed.

2.5.3.1 Horizontal subsurface-flow CWs (HFCWs)

This wetland type maintains water level below the surface of the media that forms a 1 % inclined bed. The major benefit of HF CW is the complete containment of wastewater with no surface exposure thus preventing humans from health risks. The macrophyte root zone is also known as the rhizosphere and constitutes the area of active reactions in this kind of wetlands. Macrophytes, therefore, provide a desirable place for attachment of microorganisms hence act as treatment sites due to limited oxygen transfer mainly to macrophyte roots as illustrated in Figure 2-5. Purification is done through biological, chemical, and physical processes as water flows through aerobic, anoxic and anaerobic zones (Cooper et al. 1996b). However, precise treatment mechanisms in these wetlands are not entirely understood.

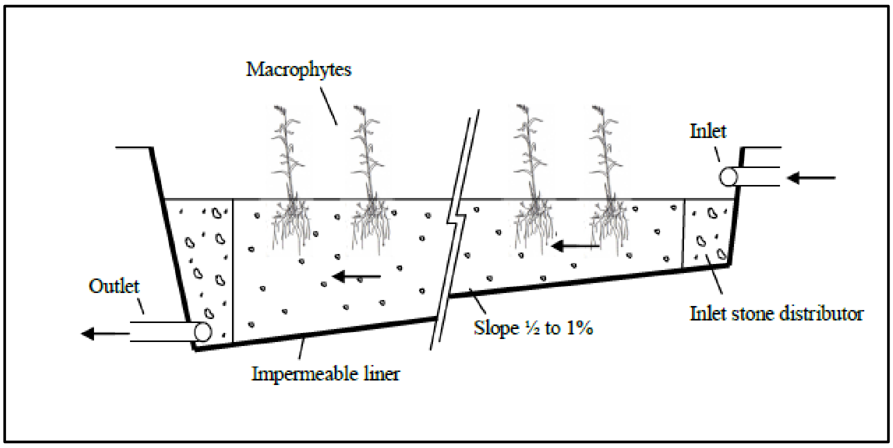


Figure 2-5 Arrangement of an HFCW system adapted from (Cooper et al. 1996b)

The major reason for performance-related failure in HF CWs is cited as negligence towards regular pumping (Davison et al. 2005) of the CW banks resulting into clogging of inlets which subsequently interrupts the surface flow.

2.5.3.2 Vertical flow sub-surface wetlands (VFCWs)

Constructed wetlands with the vertical flow were initially designed as pre-treatment units for wastewater treatment in flat flow beds (Seidel 1965). VFCW are usually wastewater treatment systems which contain wetland vegetation. The macrophytes are rooted in the bed media as shown in Figure 2-6. The media can be gravel or loamy sand compacted to a depth of between 0.6 -1.0 m.

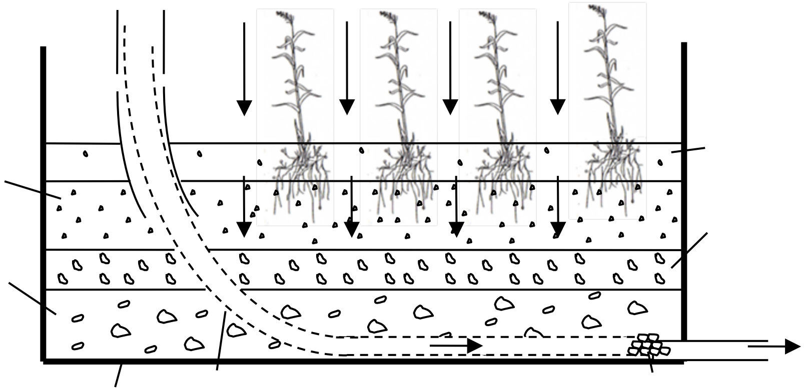


Figure 2-6 Typical plan of VFSSCW system (adapted from Cooper et al., 1996)

VFCW differ from HFCWs regarding feeding methods, water flow and substrate media are preferred to horizontal CWs because minimal land is required for construction of VFCW. Additionally, VFCWs are effective in secondary wastewater treatment. Apart from the few recent cases reviewed in (Langergraber et al. 2008), VFCW system is mostly intermittently dosed. The wastewater flows under gravity downwards and gradually through the biofilter media. This kind of feeding allows oxygen transfer from the atmosphere and hence the ability to nitrify (Cooper et al. 1996a). Furthermore, VFCWs have excellent removal rates of organics, suspended solids, and ammonia. However; VFCWs are not suited for denitrification; hence ammonia-N is mostly converted to nitrate-N. VFCWs are common in Austria, Denmark, France and the UK and are useful in removing stormwater pollutants.

VFCW are operated either as planted or unplanted. Some studies have reported about VFCW having enhanced performance due to the effects of plants maximising treatment efficiency (Taylor et al. 2011). High removal efficiencies are associated with the plants providing and maintaining a favourable environment that facilitates the rapid growth of microbial populations and oxygenating the system (Wang et al. 2012; Wu et al. 2015). Vegetation in SS CWs tends to reduce the demand for chemical oxygen, N and P from livestock wastewater and total suspended solids (Zhu et al. 2012). However, because VFCW has only recently gained importance, the operational conditions that affect this wetland type are not well understood.

2.5.3.3 Tidal-flow vertical subsurface-flow wetlands

Tidal flow is a recently developed technology used in constructed wetlands (Lavrova and Koumanova 2013). The characteristic feature of tidal flow systems is the dimensional movement of wastewater. The feeding stops as soon as the surface is fully submerged and flooded. The embedded bed serves to hold the wastewater until a set time is reached, and then it starts to drain in a downward direction. The treatment cycle is completed when effluents are fully drained from the filtration bed, and atmospheric air is drawn in and allowed to diffuse into voids in the biofilters (Bruch et al. 2014).

2.5.4 Hybrid constructed wetlands

Hybrid CWs are a distinct type of wetlands systems that result from combining different CW types to achieve high-performance, especially for nitrogen removal. Most hybrid systems comprise most frequently of vertical flow (VF) and horizontal flow (HF) systems arranged in a staged manner. In the 1990s and early 2000s, VF-HF systems were built in some European countries such as Slovenia (Urbanc-Berčič 1996); Norway (Mæhlum and Stålnacke 1999); Austria and Ireland (Mitterer-Bercic and Reichmann, 2002 and O'Hagan, 2003) respectively in Dunne et al. (2005).

In hybrid CWs, different cells are designed for specific reactions. Thus, recently, hybrid CWs comprise of FWs (example at Koo in Estonia which consists of two VF beds, followed by HF bed and two FWs wetlands (Mander *et al.,* 2003). In Italy, hybrid CWs have been successful in the treatment of concentrated winery wastewaters (Masi *et al.,* 2002).

2.6 Mechanisms of pollutant removal in constructed wetlands

Constructed wetlands treat a variety of wastewater types. Therefore, contaminant removal in CWs is a complex process that involves different treatment processes including the physical, chemical, and biological processes (Reed et al. 1995; Cooper et al. 1996b; Kadlec and Wallace 2009a). Contaminant removal in CWs will depend on the type of wetland, its design configuration, and other operational variables.

2.6.1 Physical mechanisms

Physical mechanisms of contaminant removal include sedimentation or gravitational settling, and filtration where particulates are mechanically filtered as water flows through the wetland bed media and the macrophytes roots. Other physical processes include volatilisation (ammonia) and adsorption based on intermolecular forces. Physical removal mechanisms are associated with decreasing flow velocities in the wetland, and thus make it possible for pollutants like heavy metal in highway run-off to be removed (Gill et al. 2014). Likewise, suspended solids, particulate P, and other particle-bound contaminants like PAHs are removed from runoff through filtration processes (Davis et al. 2010) while dissolved P and heavy metals fractions can be removed through sorption onto the media substrate (LeFevre et al. 2015). Equally, pathogens can be removed by filtration, exposure to sunlight and by any processes that promote natural die-off (Hunt et al. 2011).

2.6.2 Biological mechanisms

Nutrient removal by decomposition and plant uptake is attributed to biological mechanisms such as nitrification and denitrification; and biological transformation and degradation pathways (Kadlec and Wallace 2009a; LeFevre et al. 2015). Biological degradation of organic carbons in aerobic conditions often yields carbon dioxide. However, under anaerobic conditions, degradation leads to the formation of various gases including carbon monoxide and methane. Biological decomposition is affected by factors such as soil organisms, the physical environment and the quality of the organic matter (Brussaard and Van Faassen 1994). Other by-products of decomposition include energy, water, N, P and resynthesized organic compounds. Decomposition increases soil aggregation and aggregate stability; as well as the cation exchange capacity (ability to attract and retain nutrients).

Nutrients N and P can also be removed through plant uptake in vegetated practices (LeFevre et al., 2015). Similarly, bacterial metabolism is often associated with the removal of colloidal solids, and soluble organics by suspended, benthic and plant supported bacteria. Microbiological depredation of pathogenic micro-organisms is another biological mechanism involved in pollutant removal in CWs.

2.6.3 Sorption onto substrate media

Sorption is one of the major pollutant removal process in CWs. It is simultaneous absorption and adsorption. Features of the media that affect sorption include texture, organic matter content, ion exchange properties, electrolyte composition, pH, and the properties of pollutants. Thus, if the pollutant has acid-base properties, the determination of whether it is ionic or neutral occurs in the liquid compartment which subsequently affects the extent of sorption (Dordio et al. 2008).

2.6.4 Chemical oxidation

Microbial oxidation majorly takes place in wetlands and serves to transform soluble metals. Oxidisation of metals in the media results into sulphates or oxides.

Additionally, the process results in soluble BOD thus facilitates microbial growth in aerobic conditions (Ellis et al. 2003). Chemical decomposition produces altered and less stable compounds resulting from UV irradiation, oxidation and reduction.

2.6.5 Concluding remarks

Contaminant removal in constructed wetlands has been extensively investigated using several configurations of CWs to treat stormwater runoff and other types of wastewaters (Cheng et al. 2002; Walker and Hurl 2002; Bulc and Slak 2003; Revitt et al. 2004; Vymazal and Kropfelova 2009; Adhikari et al. 2011; Zhu et al. 2012). The studies demonstrate that CWs not only improve the water quality by removing pollutants including hydrocarbons, suspended solids and heavy metals but can also attenuate floods and reduce peak flow discharges. The efficiency of the removal of heavy metals (Cu, Zn Cd, Ni and Pb) in runoff is varied for the different metals. However, some reports indicated that efficiencies were as low as 6 %, while others reported metal reductions of higher than 90 %. Furthermore, the investigations showed that heavy metal removals were mostly by sedimentation and accumulation in sediments as compared to macrophyte uptake (Lung and Light 1996; Mays and Edwards 2001; Gill et al. 2014); Walker and Hurl, 2002). Nevertheless, the interactions of contaminants with the media, plant roots and micro-organisms in the rhizosphere requires more research (Williams 2002; Vangronsveld et al. 2009).

2.7 Design, operation and performance of constructed wetlands

2.7.1 Design parameters

CWs treat various wastewater types and in so doing, reduce the range of pollutants that reach water sources. Generally, the “black-box” procedure is used to design SSFCWs. Often, the wetland is designed to treat wastewater to a specified standard. Thus, the design aims to enhance the contact between wastewater and the various components of the wetland - the biofilms, macrophytes, and the media bed. Accordingly, the treatment efficiency of a CW is related to features such as water flow paths, which in turn is influenced by retention time (Torrens et al. 2009).

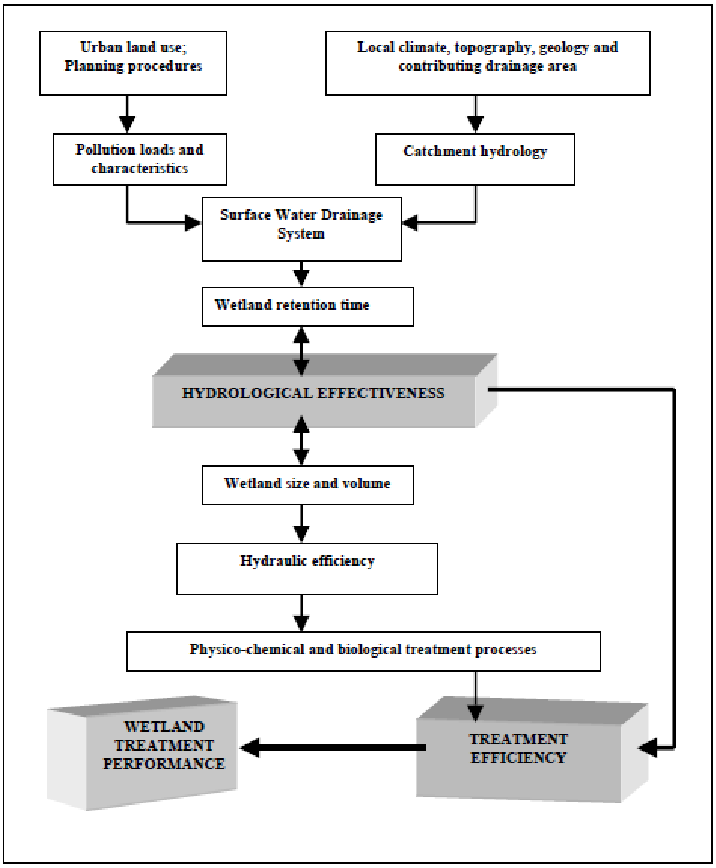


Figure 2-7 Linkages between wetland design elements (Ellis et al., 2003)

Presently, there are no standard design codes for CWs. Most designs are based on manuals and guidelines (Cooper et al. 1996b; Kadlec and Knight 1996; EPA 2000; Ellis et al. 2003; Stefanakis et al. 2014). A comprehensive review of the guidelines, manuals and technical reports (Ellis *et al.*, 2003) reveals that the rules for designing CWs are derived from experimental work. Thus, design process involves the analysis of catchment (land-use and hydrology), so that sizing of the CW is related to the pollutant mass load and consequently to the removal efficiency (Figure 2-7). Relatedly, the operational strategy (retention time and feeding mode) are determined so that the mechanisms involved in contaminant removal are linked to the treatment efficiency.

2.7.2 Media characteristics

The media bed constitutes the living system of CWs, and the media is commonly applied in CWs to support the growth of microbes and wetland macrophytes, as well as for the removal of pollutants by filtration and adsorption. However, the media is subject to variations such as the surface area of the biofilms. Furthermore, the process of media compaction, drying, channelling, and particle agglutination are properties that affect water flow and hence treatment.

Depending on availability, cost, and local practices, the media materials in everyday use include wood, charcoal, expanded forms of perlite, zeolite, gravel, loamy sand, industrial by-products such as blast furnace slag (BFS), and some specialised media forms that remove soluble pollutants through chemical processes (Singh et al. 2010; Akdeniz et al. 2011). Desirable features of the media include hydraulic conductivity (porosity), sedimentation, adsorptive properties, granular structure, air flow, and adaptability to weather changes (Andreasen et al. 2013).

The performance of the media depends on the grade, depth, and other factors such as the hydraulic loading rate and pollutant characteristics. Finer media can remove more pollutants but must operate at a low hydraulic loading rate to avoid premature clogging and excessive maintenance(Knowles et al. 2011). Media filters can for short durations, treat higher flows than they are designed for, but frequent maintenance requirements can be avoided by prioritising longevity at the design phase. However, unlike flow-through treatment practices, media filters tend to require a larger footprint due to the need to maintain lower hydraulic loading rates to enhance performance and longevity.

2.7.3 Sizing constructed wetlands

Numerous approaches have been proposed for sizing stormwater CWs in the UK. The most frequently applied design approach applied to stormwater CWs is the dynamic design method that utilises first-order reaction kinetics. The technique involves the application of Equation 2-7, to determine the CW size and the retention time required to reduce pollutant concentrations to a desired value (Ellis *et al.*, 2003). The equation is empirically derived and assumes plug flow in the CW:

$$A_S = \left(\frac{-k}{Q}\right) ln\left[\frac{(C_{out} - C^*)}{(C_{in} - C^*)}\right] \quad \text{2-7}$$

Where; A_S = CW surface area (m^2) , k = pollutant decay rate constant (m/day), Q = inflow rate (m^3/day), C_{in} = inflow pollutant concentration (mg/l) , C_{out} = targeted outflow pollutant concentration (mg/l), C^* = background concentration (mg/l).

The values for k and C^* are dependent on the pollutant and the type of the CW (i.e. sub-surface flow or surface flow), and recommended values are available in the literature by Kadlec and Wallace (2009). The k value represents the BOD_5 reaction rates. Since BOD_5 decay in CW occurs slowly, the dependency on BOD_5 k yields oversized dimensions of CWs. Consequently, BOD_5 k of low influent wastewater should not be compared to high strength wastewaters such as sewage.

Furthermore, stormwater CWs are mostly designed for the removal of suspended solids (SS) and heavy metals. Consequently, the design approach that assumes average flow rates and contaminant concentrations discounts the variability of the pollutant concentrations in stormwater inflows, as well as the various k values due to the distinct nature of CWs (Ellis *et al.*, 2003). Thus, although the approach involving Equation is useful for initial estimates, the limitations associated with the method stresses the need for more reliable sizing procedures.

Moreover, the stochastic nature of storm events dictates that the experimental design approach is applied for practical purposes. One such approach is to design the CW to a size suited to treat water volumes typical of a storm of a selected return period. The minimum duration recommended for the UK is a 10-year return period (Ellis *et al.*, 2003), while the Environment Agency (England) recommends designs of 1: 200-year return period in flood-prone catchments (Shutes et al. 2005). Additionally, the Environment Agency (England and Wales) and the Environmental Protection Agency (US EPA) recommend the Schueler (1992) guidelines that require the designed CWs to retain 90 % of the storm events (Schueler 1992).

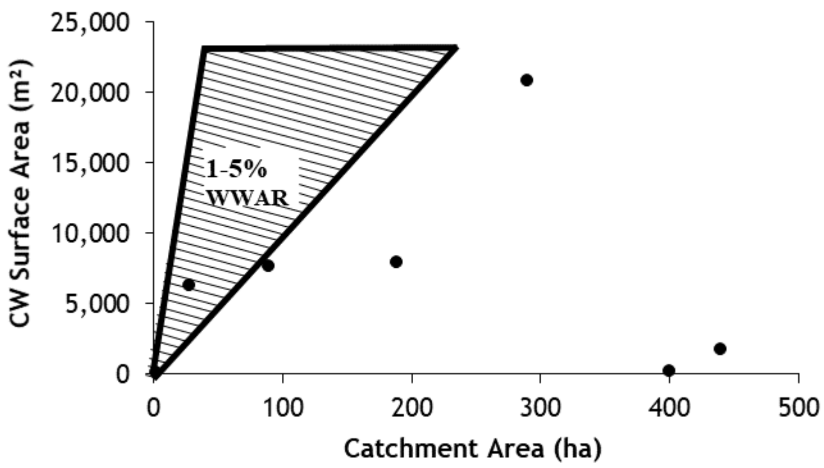


Figure 2-8 CW area vs catchment area for UK CWs (Lucas et al. 2015)

An alternative empirical approach to sizing CWs is to use values of the ratio of the wetland to the watershed as shown in Figure 2-8. The UK design guidelines recommend WWAR values of 1–5 % (Ellis *et al.*, 2003). The US guidelines recommend a minimum WWAR of 2 %, possibly because land is not a limitation in the USA.

2.7.4 Hydraulic loading and retention time

The hydraulic retention time (HRT) is a vital operational parameter in CWs because it determines the extent to which treatment processes occur. The HRT of a CW is selected depending on the pollutants and the major removal mechanism. Thus, for coarse solids, sedimentation is the main removal mechanism, for which an HRT of 3 to 5 hours is adequate. HRT greater than 24 hours is recommended for the removal of bacteria, degradable organics and toxic species embedded in finer solid fractions.

Similarly, longer HRTs of up to 14 days have been proposed for some UK treatment systems during the wet times of the year, but long HRTs are generally not required in the treatment of urban surface runoff. This is because the average nitrogen loads in UK urban runoff is under 9 Kg/impervious hectare/year, and therefore does not require full reduction (Shutes et al. 2005). Comparatively, in the USA the guidelines for a suitable HRT are not specific and are dependent on the needs and standards set by the regulator. Nonetheless, the US EPA recommends that shallow marsh treatment systems with dense vegetation and gradients should hold shallow depths of water for 18 - 24 hours. The recommended HRT of 18-24 hours would suggest that this HRT is appropriate for the treatment of stormwater CWs in the UK, where 24 hours is the recommended HRT for the treatment of bacteria, degradable organics and toxic species.

In Germany, investigations of CWs for combined sewer overflow (CSO) concluded that HRT should be restricted to a maximum of 48 hours since extended inundation creates anaerobic conditions which hinder degradation processes (Uhl and Dittmer, 2005). It was also reported that extended HRT could lead to clogging, due to increased biomass growth in the filter during the inundation period. However, unlike the influent CSO which contain sewerage, stormwater CWs would not be affected in the same way. Generally, the HRT is affected by the width to length ratio of the CW, the presence of vegetation, the porosity of the substrate media, water depth and the bed slope (Ellis *et al.*, 2003). Consequently, increasing the HRT would require larger wetland areas thereby limiting wastewater treatment by stormwater to the availability of large areas of land.

2.7.5 Wetland vegetation

The removal of some pollutants in CWs can be affected by the presence and type of wetland vegetation. Wetland plants remove pollutants through biological processes of nutrient uptake and mineralisation. Likewise, the presence of vegetation in CWs aids higher phosphorus removal rates compared to non-vegetated CWs, especially mesocosms constructed without vegetation (Menon and Holland 2014). In another study, vegetated CWs delayed the process of media clogging (Fu et al. 2013), and it was suggested that *Canna indica* was more effective than *Cyperus alternifolius*. Of the several factors causing clogging in CWs, fluvic acid and labile organic matter were considered prominent.

Wetland plants also play a crucial role in surface-flow systems by reducing the flow velocity of water in the CWs. The reduction in flow velocity favours sedimentation, a major physical removal process in CWs. Additionally, in subsurface-flow systems, plants help to maintain the hydraulic conductivity of the wetland. Moreover, reduction of metals can be achieved through accumulation and storage in the rhizospheres of the wetland plants (Kadlec and Wallace, 2009). Therefore, the choice of plants could enhance removal of the nutrients, suspend solids and heavy metals from stormwater. The commonly used plants in the UK CWs are *Phragmites australis* and *Typha latifolia* (Ellis *et al*., 2003). Key features of wetland macrophytes are that the plants must be visually appealing, proliferate, and have high uptake of pollutants (Ellis *et al*., 2003). In the US, the wetland plants recommended by the US EPA are *Saggitaria latifolia*, *Scirpus americanus* and *Scirpus Validus*. These wetland plant species establish themselves and spread quickly, hence enhance biodiversity (US EPA, 2000), a biodiversity strategy that is comparable to the design of CSO in Italy(Meyer et al. 2015b)

2.7.6 Operational strategy: dosing and feeding regimes

Most HSSFCWs are operated on a continuous strategy while the VFCWs are mostly intermittently loaded. The feeding regimes influence the hydraulics of the media and oxygenation of the treatment matrix, as well the biomass growth thereby affecting the removal mechanisms and performance. Subsequently, the application of resting periods through intermittent feeding affects the performance of VFCWs depending on the number and quantity of doses loaded per day (Molle et al. 2008). However, the feeding and resting cycles reduce clogging and enhance the performance of HSSFCWs (Torrens et al. 2009; Blecken et al. 2010).

2.7.7 Performance: pollutant loads and pollutant removal

Pollutant removal in CWs is achieved through various processes including biological mechanisms. At low substrate concentration, most reactions are usually described as first-order due to the dependency of the reaction on substrate concentration. Thus, contaminant reduction by micro-organisms generally follows first-order kinetics (Benefield and Randall 1980). Accordingly, temporary changes in pollutant concentrations can easily impact the performance of CWs. This is especially so because the detention time between the loading of influents into the CW and the subsequent release of effluents involves a delay. Therefore, simple first-order models normally work well on a long-term mean basis, rather than on an instantaneous basis (Jing and Lin 2004). Consequently, monthly averages of the monitored parameters were determined and applied in the context of first-order plug flow concentration profiles represented in Equation 2-8 (Reed et al. 1995):

$$\ln\left(\frac{C_{out}}{C_{in}}\right) = -K_v\, t \quad \text{..........} \quad 2\text{-}8$$

Where: K_v = temperature-dependent volumetric rate constant (d-1); t = Vε/Q = hydraulic retention time in the wetland (d); ε = wetland porosity and V = volume of the wetland (m3), Cout = the mean pollutant concentration in the effluent (mg l−1); Cin = the mean pollutant concentration in influents (mg/L). More recently, removal rate constants based on a first-order degradation approach have been applied to evaluating the performance of CWs with regards to the removal of COD, BOD, TSS, TN and TP (Kadlec and Wallace 2009a; Abdelhakeem et al. 2016). The rate constants for the models were defined on either an areal (K_A) or a volumetric (K_V) basis. The areal rate constant (k_A) is calculated from Equation 2-9 (Kadlec and Wallace 2009a):

$$\ln\left(\frac{C_{out}}{C_{in}}\right) = {}^{-K_A}/_{q} \quad \text{..........} \quad 2\text{-}9$$

Where: q = Q/A = hydraulic loading rate (m/d); Q = flow rate through the wetland (m^3/d), A = area of the wetland (m^2) and K_A = areal removal rate constant (m/d). Since the removal constants K_A and K_v are related ($K_A = \frac{V}{A\, K_v}$), then either constant can be used where the variations in data are statistically insignificant (Abdelhakeem et al. 2016). Other methods for evaluating the performance of CWs include exceedance curve, effluent probability, regression of loads (ROL) and rainfall occurrence ratio (ROR), especially when assessing long-term performance of CWs.

EMCs are used to quantify the average pollutant load washed off during a storm event concerning the event run-off volume. The EMC is thus an important factor in predicting total pollutant load into receiving watercourses. Barbosa et al.,(2012) conducted literature reviews and observed that most models for stormwater run-off use build-up and wash-off equations, algorithms for sediment transport in the sewers, proportional relationships between the solids and their attached pollutants and pollutant decay or transformation equations. However, pollutant loading for a storm event and the removal efficiency of a stormwater treatment system can be calculated using several methods including event mean concentration efficiency (EMCE), efficiency ratio (ER) (defined in terms of the average pollutant removal efficiency for each storm event and summation of loadings (SOL) in equation 2-10:

$$\text{Removal (\%)} = \frac{\text{Average influent EMC} - \text{Average effluent EMC}}{\text{Average influent EMC}} \quad \dots\dots\dots\dots\dots\dots \text{2-10}$$

The summation of the load method is used to determine the average reduction of the pollutant mass or pollutant load. The sum of the influent and effluent mass loads can be calculated using Equation 2-11(applicable to any number of samples that correspond to discharge volume (V) and concentration measurements (C):

$$M = \sum_{i=1}^{n} V_i \, C_i \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{2-11}$$

where; M = total mass of pollutant, V_i = discharge amount corresponding to sample i, Ci = pollutant concentration in sample i, i = Sample number, and n = total number of samples collected. The treatment system's performance is then calculated from the sum of the influent and effluent loads using the summation of the loads method:

$$\text{Removal Efficiency} = \frac{\sum \text{Influent loadings} - \sum \text{Effluent loadings}}{\sum \text{Influent loadings}} \quad \dots\dots\dots\dots\dots \text{2-12}$$

Equation 2-12 can be re-written as:

$$\text{Removal Efficiency} = \left(1 - \frac{\text{ME}}{\text{MI}}\right) \text{x } 100 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots \text{2-13}$$

where; ME = Effluent mass load, and MI = Influent mass load, calculated from Equation 2-11 The results can be compared to other storm events for the same stormwater treatment practice; storm events for different treatment systems; other methods of analysis; or combined with storm event data for the same treatment system. Similarly, the mass removal rate, R (g m^{-2} d^{-1}), Equation 2-14 is often applied to assess the performance of wastewater treatment systems:

$$R = q\ (\text{Influent concentration} - \text{Effluent concentration}) \dots\dots\dots\dots\dots \text{2-14}$$

where; q = hydraulic loading rate (m/d), and influent/effluent loadings (mg/L).

2.8 Contaminant removal in constructed wetlands

Urbanisation has been linked to the quantity and quality of urban run-off and hence to the degradation of receiving waters attributed to the variety of pollutants carried in stormwater runoff. Consequently, stormwater management is a major concern not only for surface water quality but also for groundwater due to pollution associated with infiltration and seepage.

Among the innovative wastewater treatment technologies that are deployed to mitigate the effects of stormwater, CWs have emerged as a sustainable option, partly because treatment by CWs requires minimal energy. Additionally, CWs have low construction and maintenance costs. Equally, where large areas of land are required, VFCW designs can be used(Haberl et al. 2003). Moreover, contaminant removal in CWs occurs by numerous interrelated physico-chemical and biological processes. Thus, several methods have been proposed to assess the performance of CWs, the uncertainties associated with the performance indicators, and the use of the performance indicators as decision-aid tools (Charbeneau and Barrett 1998; Bertrand–Krajewski et al. 2002; Beck and Birch 2013). However, the various design of CWs makes it difficult to compare the performance of CW designs. Furthermore, operational variables like loading rates can affect the performance of the CWs.

Generally, the performance of CWs can be assessed by monitoring the influent and effluent concentrations. This method can be expensive, regarding analytical costs and time. Furthermore, the high variability in the quality of stormwater limits the possibility of applying representative mean concentrations. Additionally, the different designs of stormwater CWs yield different effluent quality. This suggests the need for models that can predict the variability of contaminant concentration in design and between other designs. Unfortunately, there are a few measured fundamental variables from which process-models could be built. This limitation has led to the development of statistical models, to make use of the accessible data.

Numerous literature reviews published highlight the modelling and simulation of the main biogeochemical processes in CWs. The models for these processes are either deterministic (simulate cause and effect relationships) or stochastic models (use statistical patterns in the data of a process to simulate that same process). However, some researchers argue that a deterministic model produces the same response to the same input, whereas a stochastic model can produce different responses to the same input, but with consistent statistical properties (Obropta and Kardos 2007). Accordingly, modelling wastewater treatment in CWs will require the selection of a suitable modelling approach and hence the model parameters to be monitored, and in some cases the sources of literature data for some parameters, notwithstanding that secondary data/assumed data increases the uncertainty already related to the data (David and Matos 2002; Barbosa et al. 2012).

2.8.1 Modelling pollutant removal in constructed wetlands

Modelling contaminant removal in CWs can be achieved using different methods, and therefore numerous models have been developed for different CWs. Generally, CW models are linked to the flow characteristics of the wetland system. Therefore, the CW is modelled as either saturated or unsaturated; vertical or horizontal flow, surface or subsurface flow; and many other practical combinations (Meyer et al. 2015a). Furthermore, the mechanistic models can simulate the treatment processes in CWs, the hydraulics, and nutrient biogeochemistry (P and N cycling) (Wynn and Liehr 2001; Lee et al. 2002b; Langergraber et al. 2008).

2.8.1.1 Regression models

Several investigations on wastewater treatment in CWs have concentrated on the input and output rather than on the internal process data (Kumar and Zhao 2011). However, regression analysis only reveals the vital relationships that exist between the influent and effluents of the wetlands. Therefore, regression equations tend to be useful tools for interpreting input/output. Stone et al. (2002) used the Regression Equation 2-15 to predict effluent concentrations from a swine lagoon:

$$C_{Out} = aC_{in}^{b}\, q^{c} \quad \text{2-15}$$

where, C_{in}= influent concentration; C_{Out} = effluent concentration; q = hydraulic loading rate HLR (m/d); and a, b, and c = regression coefficients.

Correspondingly, multivariate regression equations were used to predict effluent benzene concentration and benzene removal in VFCWs (Tang et al. 2009). Effluent benzene was set as a function of effluent dissolved oxygen, electrical conductivity, redox potential, pH and temperature of the treatment wetland. The regression equations provided useful information about the wetland performance, but the equations are only valid for the range of data used to develop the models. Therefore, the comparison of performance derived from the regression equations is limited to wetlands with comparable scales, wastewater strength, environmental conditions and plant species used as wetland vegetation (Stone et al., 2002).

2.8.1.2 First-order models

Most wetland processes including mass transport, volatilisation, sedimentation and sorption are considered to follow first-order kinetics represented in Equations 2-16 and 2-17 (Kadlec and Wallace, 2009). Consequently, first-order models are commonly applied in the design of treatment constructed wetlands.

$$\frac{C_{out}}{C_{in}} = e^{\frac{k_A}{q}} \quad \text{2-16}$$

where k_A is the areal decomposition constant (m/d)

$$\frac{C_{out}}{C_{in}} = e^{-k_v\, t} \quad \text{2-17}$$

where t is the HRT(days), k_v = volumetric decomposition constant (m/d).

Kumar and Zhao (2011) published an extensive review on the application of the first order models in designing CWs and for predicting effluent concentrations. Thus, a wetland of 5m wide and 20m long consisting of deep and shallow zones planted with *Typha Latifolia* and treating livestock wastewater produced a k_A of 0.026 m d^{-1} for the BOD_5, 0.011 m/d for TP, 0.018 m/d for total Kjeldahl nitrogen ; 0.019 m/d for $(N\text{-}NH_4)^+$, 0.005 m/d for $(N\text{-}NO_3)^-$N and 0.023 m/d for TSS. Furthermore, after the effluent concentrations were adjusted for dilution, the rate constants reduced by at least 0.005 m/d compared with the k_A values reported by Reed et al. (1995) and Kadlec and Knight (1996).

Similarly, Stone et al. (2004) registered lower k_A for marsh-pond-marsh wetlands. The discrepancies in the rate constants are attributed to differences in the hydraulic loading rates of the wetlands investigated. Despite the inadequacies of the first order model associated with fluctuations in influent concentrations, subsequent changes in internal storages, environmental and ecosystem factors (Kadlec 2000), the first order model remains a suitable design tool for contaminant removal in CWs (Kadlec and Wallace 2009a). Additionally, reviews of the first-order rate constants for HFCWs suggest that reaction rates could allow the harmonisation of the different design guidelines. Overall, the first-order model is adequate for calibration of wetland data and thus offers a realistic estimate of performance for a wide range of pollutants in wetlands (Knight et al., 1999).

2.8.1.3 Time-dependent retardation model

The first-order model has been extensively investigated and consequently modified to improve its accuracy. For example, a time-dependent retardation model has been introduced in the removal of chemical oxygen demand (COD) to replace the background concentration, C^*, with two parameters denoted by K_0 and b. The basis of the modification is that removal rates decrease with time due to the fact that easily biodegradable substances are removed first and fast, leaving a solution with lesser biodegradable contents and hence slower removal kinetics (Shepherd et al. 2001). Thus, the change in the composition of the solution is represented by a continuously varying volumetric first-order rate constant, K_v, in Equation 2-18.

$$K_v = \frac{Ko}{b_{\tau+1}} \qquad \text{2-18}$$

Where, K_0 = initial first-order volumetric rate constant (d^{-1}), b = time-based retardation coefficient (d^{-1}) and τ = retention time (d). This model allows for the steady decrease in COD (or any component) with increasing treatment time rather than a constant residual COD, C^* value.

2.8.1.4 Mechanistic models

Contaminant removal in SSF CWs was investigated using a compartmentally based model. The model considers cycles of nitrogen and carbon, growth and metabolism of autotrophic and heterotrophic bacteria, and water and oxygen balances (Wynn and Liehr 2001). Additionally, the model required air temperature, precipitation, flow rate, concentrations of biological oxygen demand (BOD), dissolved oxygen (DO), ammonium, nitrate and organic N, and a dataset containing several physical, microbiological, and biological processes. It was suggested that to improve the design of the CWs, biomass growth and nutrient uptake should be modelled with Monod Kinetics rather than simple nutrient cycles (Fuchs 2009).

A compartmental wetland model (WETLAND) to enhance the design and evaluation of constructed wetlands and to optimize nonpoint source (NPS) pollution control was developed by Lee et al. (2002a). WETLAND consists of modules for hydrologic, nitrogen, carbon, bacteria, DO, vegetation, phosphorus and sediment cycles, like the model of Wynn and Liehr (2001). A sensitivity analysis of WETLAND showed that the most important parameters are inputs that affect the bacteria and oxygen cycles. The authors assumed a uniform vegetation stand and constant transport of oxygen by roots to the wetland bottom. Vegetation was modelled using a linear growth rate at the beginning of the growing season, reaching a constant maximum through the growing season, and then a linear decrease to zero during senescence. The vegetation model did not account for root depth or plant species. WETLAND can be used to model nutrient removal in wetland design, but more data was needed to evaluate the model.

Similarly, Langergraber and Simunek (2005) combined a reactive transport model with the variably saturated flow model HYDRUS-2D to form CW-2D. HYDRUS-2D simulates water flow and solute transport through variably saturated porous media (Šimůnek et al. 1999) and can include water uptake by vegetation. HYDRUS-2D numerically solves the Richards equation for saturated-unsaturated flow and the convection-dispersion equation for heat and solute transport.

CW-2D modifies the HYDRUS-2D solute transport to include non-linear, coupled reactions for 9 processes relating 12 components. The components are coupled through hydrolysis, aerobic and anoxic growth of heterotrophs (including nitrate- and nitrite-based denitrification), the growth of autotrophs by two-step nitrification, and decay of microorganisms. Although HYDRUS-2D can simulate water and nutrient plant uptake in CWs treating domestic wastewater, neither the pilot-scale CWs nor the model of Langergraber and Šimùnek (2005) included vegetation.

Langergraber and Šimùnek identified the need to incorporate data on clogging, nutrient uptake by the plants, and full-scale operation of CWs. However, CW-2D restricts oxygen input to within the system, in a manner suitable for the activated sludge reactor but not for CWs (oxygen transfer occurs at the surface). Equally, ammonium was quickly oxidised in the aerobic section of the soil column, but denitrification did not occur. Additionally, no results were reported for the up-flow section of the CW, yet under saturated conditions and with the availability of organic matter, denitrification should be possible within the up-flow wetland, and so the CW-2D model should be able to simulate upflow treatment.

HYDRUS-2D/CW-2D was tested using data obtained from VFCWS treating combined sewer overflows (Henrichs et al. 2007). HYDRUS-2D/CW-2D was reported as sensitive to influent COD fractionation, adsorption of slowly biodegradable organic matter, and heterotrophic bacteria concentrations. Although single applications (6 hours - 6 days) of wastewater in lysimeters and field plots simulations agreed with the observations, the long-term simulations produced data in which the measured and simulated data did not match (Henrichs et al. 2007). Similarly, the modelling of organic matter degradation and nitrogen removal in a hybrid two-stage CW (HF followed by VF) using HYDRUS-2D/CW-2D, revealed that plant roots did not affect COD simulations. However, including the effects of plants overestimated N removal in VFCW (Toscano et al. 2009).

Wetland models have also been reviewed from other perspectives than contaminant removal. Thus, a review of first-order treatment models concluded that the first-order equations for solute transport could not accurately describe the effects of the flow path and spatial distribution of vegetation (Kadlec 2000). Similarly, model-based designs of horizontal SSF CWs compared the area required for a wetland based on rules of thumb, regression equations, first-order models, and the model of Wynn and Liehr (2001). Models built from the rules of thumb predicted the most consistent areal estimates, yielding higher areas than the other models (Rousseau et al. 2004). Generally, HYDRUS 2D/CW-2D is the best validated mechanistic model for describing dynamic or kinetic processes, transport, and variably saturated flow in CWs.

2.8.1.5 Artificial neural networks (ANNs)

The increase in water consumption, aquifer contamination, wastewater collection and treatment coupled with intensive agriculture, urbanisation and industrialisation has driven the demand for water of a desirable quality. Consequently, water quality modelling is a vital aspect of water resources management. Thus, monitoring tools are needed to evaluate the effectiveness of technological interventions like CWs.

Wetlands treat wastewater by a combination of physical, chemical and biological mechanisms. Therefore, several methods have been developed to evaluate the performance of CWs. The methods include the use of statistical models, mechanistic models or hybrid combinations of different types of models. Statistical models often determine the relationships between the variables based on historical data, while the mechanistic models simulate the underlying processes that affect the variable data relationships. Therefore, a combination of mechanistic and statistical models provides a significantly improved understanding of the biogeochemical processes affecting wastewater treatment in CWs. However, the scientific assumptions made about the treatment processes in various CWs are not definitive, especially regarding how these processes interact to influence the effluent quality.

Additionally, the data required to set the boundary conditions for the calibration of mechanistic models is generally difficult to obtain. Consequently, mechanistic models may not be appropriate when the treatment contributions made by the individual processes are not separately quantifiable. Thus, modelling techniques in which treatment processes can be integrated to predict the output are required.

Generally, wastewater treatment in CWs is monitored from influent-effluent data rather than on internal process data. Therefore, “black-box” modelling approaches such as neural networks could be suitable. Neural networks are a mathematical or computational modelling technique that simulates the structure and functional aspects of the neurons of the biological nervous system.

ANN models are currently applied in the fields of medicine, science and technology for pattern recognition, forecasting, and process control. However, the use of ANN depends on the nature of the problem and the data available. Moreover, unlike the other modelling methods, ANNs have the advantage that the neural networks do not need the mathematical form of the process under consideration (Nayak et al. 2006).

ANNs commonly used are the multi-layer perceptrons (MLP) and the radial basis function neural networks (RBF-NN). The RBF-NNs have a single hidden layer of radial units, with each unit modelling a Gaussian response surface (Akratos et al. 2008). RBF networks have some advantages over MLPs, including faster training and less danger to converge to local minima instead of the global minima. However, more units are often required for the hidden layer of RBF networks as compared to MLPs.

2.8.1.6 Structure of a multi-layer perceptron neural network

The multilayer perceptron consists of a system of simple interconnected neurons, or nodes (Figure 2-9) which is a model representing a nonlinear mapping between an input vector and an output vector. The nodes are connected by weights and output signals. Therefore, the output signal is a function of the sum of the inputs to the node modified by a simple nonlinear transfer/activation function.

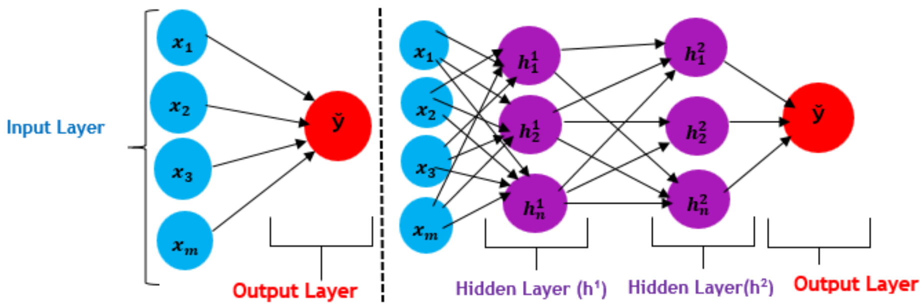


Figure 2-9 MLP networks with two hidden layers (Adapted from Knospe (2018)).

The superposition of several simple nonlinear transfer functions enables MLPs to estimate extremely non-linear functions. The multi-layer perceptron (MLP) can be trained to approximate virtually any smooth, measurable function. This is because, unlike other modelling techniques, the MLP makes no prior assumptions about the distribution of the data. Thus, MLPs can be trained to accurately generalise and model the non-linear functions when presented with unseen data. These features of the MLP make it an attractive alternative to numerical models, and when choosing between statistical approaches (Gardner and Dorling 1998). Training an ANN is a mathematical exercise that optimises all the network weights and threshold values, using a fraction of the test data. The optimisation routines determine the ideal number of units in the hidden layer and the nature of their transfer functions.

2.8.1.7 Applications of artificial neural networks

The application of ANN in environmental systems is separately reported in studies such as the assessement of water quality of riverine systems (Najah et al. 2013), seawater quality measurements (Hatzikos et al. 2009); surface water quality (Maier and Dandy 2000), prediction of rainfall-runoff (Hsu et al. 1995) and prediction of urban stormwater water quality (May and Sivakumar 2009). Additionally, ANNs were applied in the environmental flow assessments to provide evidence of ecological responses to different stormwater drainage systems based on hydrologic and hydraulic changes. Walsh et al. (2012) reported that the ANN modelling technique was successful in explaining the physical processes related to pollutant generation, mobilisation, and transport.

ANN models developed from specific conductance and dissolved oxygen as input data satisfactorily predicted water quality of Delaware River (Heydari et al. 2013). The model predictions were evaluated based on the mean absolute error (MAE), the root mean square error (RMSE), and correlation coefficients (R). Furthermore, the accuracy and precision of ANN model predictions were reported as varying with the optimisation technique.

In a study conducted to aid the classification process for predicting water quality, outputs of ANN models built using the cuckoo search (CS) optimisation algorithm were compared with outputs of models obtained using a genetic algorithm (GA) and particle swarm optimisation (PSO). The comparisons of performance involved analysis of accuracy, precision, recall, f-measure, Matthews correlation coefficient

(MCC) and Fowlkes-Mallows index (FM index) of the models. The simulated results revealed that cuckoo search optimisation was superior (Chatterjee et al. 2017).

Other applications of ANN involved the use of data mined from various sources. Thus, using data from 11 different canal sites, ANN models were built and used for classifying surface water quality. The study reported that the ANN models achieved high prediction accuracy with 96.5 % precision (Wechmongkhonkon et al. 2012).

Similarly, RBF-NN and MLP-ANN were used to derive parameters for water quality assessment. The RBF-NNs results were reported as precise, accurate and reliable compared to the results obtained from using MLPs. It was concluded that RBF-NN were preferred to MLP-NN for modelling data that is both non-linear and non-parametric (May et al. 2009).

Relatedly, the applicability of MLP-ANN, radial basis functions, and support vector machine (SVM) models to predict river flow time series has been an investigated. The study contrasted MLPs with support vector machine (SVM) and RBF to analyse the credibility of the models. It was established that RBF and MLP models produced better predictions as compared to the SVMs; and that the performance of the models could be improved by incorporating a time index (Ghorbani et al. 2016). However, the predictions of the monthly river flow revealed higher uncertainties associated with MLP and RBF compared with SVMs which had low uncertainties.

More recently, artificial neural networks were used for the prediction of stormwater quality (May et al. 2009); for the removal of ortho-phosphate (PO_4-P) and total phosphorus (TP) in HFCWs (Akratos et al. 2009); and for prediction of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) removal (Akratos et al. 2008). In the later investigations, the topologies of the successful neural network were suggested, and the neural network predictions validated against an extended dataset compiled from earlier published studies. The performance of the neural networks was reported as reasonably good for the design of CWs (Akratos et al. 2008). Additionally, a simple single-constant design equation was proposed as an alternative to the first-order model the prediction of BOD removal, presumably because the design equation was a hyperbolic mathematical approximation of the first-order model. The study also showed that COD removal in horizontal subsurface flow CWs was strongly correlated to the BOD removal. More importantly, ANN models were developed from experimental data obtained from monitoring five pilot-scale CWs, operated over two years, under four different hydraulic residence times (Akratos et al. 2008). Additionally, inputs for building the ANN model were selected using principal component analysis (PCA), with the study concluding that the main parameters affecting BOD removal are porosity, wastewater temperature, hydraulic residence time, and meteorological parameters (Akratos et al. 2008).

Similarly, the performance of HFCWs and free water surface flow (FWSF) CWs were compared using the ANN–back propagation modelling algorithm (Naz et al. 2009). The results showed that the R^2 values for predicting effluent total chemical oxygen demand (TCOD), soluble chemical oxygen demand (SCOD), and total biological oxygen demand (TBOD) of HF CW were 0.90, 090 and 0.94, respectively, whereas the R^2 values for FWSF CWs were 0.96, 0.74 and 0.84, respectively.

Furthermore, design and optimisation aimed at the cost-effective operation of CWs treating wastewater were implemeted using ANNs (Pastor et al. 2003). Similarly, a protocol for assessing the quality of ANNs developed for drinking water quality has been developed by Wu et al. (2014b). ANNs were applied in the determination of the appropriateness of field measurements for efficient nutrient removal using *Phragmites australis*, and to evaluate the removal capacity of light expanded clay aggregate in horizontal flow CWs (Ozengin 2016). The results indicated that the adopted Levenberg–Marquardt back-propagation algorithm yielded estimates with low mean squared error (MSE) values and that the CWs planted with *P. australis* may be a good option in mitigating pollution.

Generally, the published studies show that ANNs have a wide and varied application in the field of water management. Therefore, as a typically “black-box” modelling approach, neural networks can analyse process data to derive design and decision support tools (Akratos et al. 2008; May and Sivakumar 2009; Guepie et al. 2012).

2.8.2 Conclusion on modelling pollutant removal in CWs

The literature reviews have provided empirical evidence that urban stormwater run-off contains pollutants that degrade the water quality in receiving water sources. Furthermore, the review shows that CWs can treat wastewaters of various types making it safe for discharge into receiving watercourses. Although several modelling tools can simulate pollutant removal processes in CWs, the application of some computational models is at times limited by the operational strategy deployed to the CWs design. Thus, HYDRUS a robust modelling software with a CW module, cannot be applied to a tidal-flow system because HYDRUS cannot vary boundary conditions in a single modelling scenario. Therefore, there is a need to develop methods that can evaluate the effectiveness of CWs as a pollution control strategy. Subsequently, the evaluation could simplify the selection criteria of the optimal design of CW. This approach in part underlines the choice to apply ANNs in various investigations. The “black-box” nature of CW technology makes the application of neural networks suitable because ANNs can simulate the dynamics of pollutant removal to provide a satisfactory generalisation of the performance.

The ANNs are described as prospective data modelling tools for future research, including research in wastewater treatment and water resources management. However, the applicability and efficiency of ANNs depend so much on the selection of inputs, network architecture, data pre-processing, training and representation. Regrettably, the literature review shows little evidence of techniques that could improve the reliability and accuracy of ANNs. Nevertheless, with the current state of multi-disciplinary research, advanced optimisation algorithms will enhance neural network modelling and hence contribute to sustainable water management.

2.9 Summary

This chapter reviewed the literature on urbanisation and the effects of urbanisation on the environment. Chapter Two also contains an analysis of stormwater run-off and the impacts of stormwater pollution on water resources. Furthermore, the literature review examined the application of CWs in stormwater management; the different criteria for CW design; pollutant removal mechanisms in CWs, evaluation of the performance of CWs, and methods of modelling pollutant removal in CWs with specific emphasis on the application of artificial neural networks (ANNs).

The review shows that CWs reduce contaminants in various wastewaters, including stormwater. However, the uptake of CW technology in urbanised areas is low, partly due to land requirements, but also because of the lack of standard design codes. Although efforts to unify the current design guidelines is on-going, it is essential to improve our understanding of the effects of design and operational variables on the performance of CWs. Accordingly, the VFCWs requiring minimal space, and whose performance can be monitored over the long-term are selected for investigation. Furthermore, the review shows that several models, including HYDRUS, when used to predict contaminant removal in CWs have limitations in different contexts.

Thus, a 'Black box' modelling approach used by the neural networks could be suitable for both the dynamic processes of contaminant removal and for simulating the tidal-flow operational strategy. Consequently, an innovative approach that integrates principal components analysis (PCA) and artificial neural networks (ANNs) is applied in this research study to model pollutant removal in tidal flow VFCWs, as well as to assess the effects of design and operational variables on the long-term removal of contaminants.

Therefore, this study examines the hypothesis that different designs of tidal-flow vertical flow subsurface constructed wetlands (VFCWs) can treat stormwater to produce effluents that can safely be reused for non-potable purposes or be discharged into watercourses. The hypothesis was explored through experimental work and numerical modelling to address the following research questions.

2.10 Research questions and objectives

This study aims to address the following research questions:

a. What factors influence urbanisation and the quality of stormwater? Of what significance are these factors to water resources management?
b. Do key design variables like primary media, wetland area to watershed area ratio (WWAR) and operational strategies such as short dry and extended dry rest periods affect the pollutant removal in stormwater CWs?
c. What are the pollutant removal mechanisms in VFCWs? Are the removal mechanisms or performance affected by the design and operational factors?
d. How can the influences of design and operational variables on the long-term performance of stormwater VFCWs be evaluated?

The above research questions generated the specific objectives listed below:

a. To determine the factors that influence urbanisation, and to identify the links between urbanisation and water resources management.
b. To design novel configurations of VFCWs and to investigate the effects of design and operational variables on the long-term performance of VFCWs.
c. To identify the pollutant removal mechanisms in VFCWs and to evaluate the long-term performance of VFCWs towards a mechanistic understanding of design performance.
d. To develop data-driven models to predict the long-term performance of different designs of VFCWs treating stormwater.

Chapter 3 Materials and methods

In this study, experiments form a significant part of the work undertaken to address the research questions identified through literature review in Chapter 2; and to obtain data for developing ANN models in the later Chapters. In total, 8 pilot-scale physical models of VFCWs are designed and set-up on the Roof of the 3rd Floor of the South Buildings, School of Engineering (Cardiff University). The experimental samples collected were analysed in the Characterisation Laboratories for Environmental Engineering Research (CLEER), located on the ground floor of the South Buildings at Cardiff School of Engineering.

There are currently no standard codes for designing CWs. Therefore, the CWs investigated are designed based on the recommendations implemented worldwide and in the UK. The design process involved the catchment analysis of representative urban areas in the UK, with an emphasis on the land characteristics, land-use and meteorological changes over a period of 33 years. Meteorological data is used to size the VFCWs based on 1-5 % WWAR (wetland area to watershed area ratio).

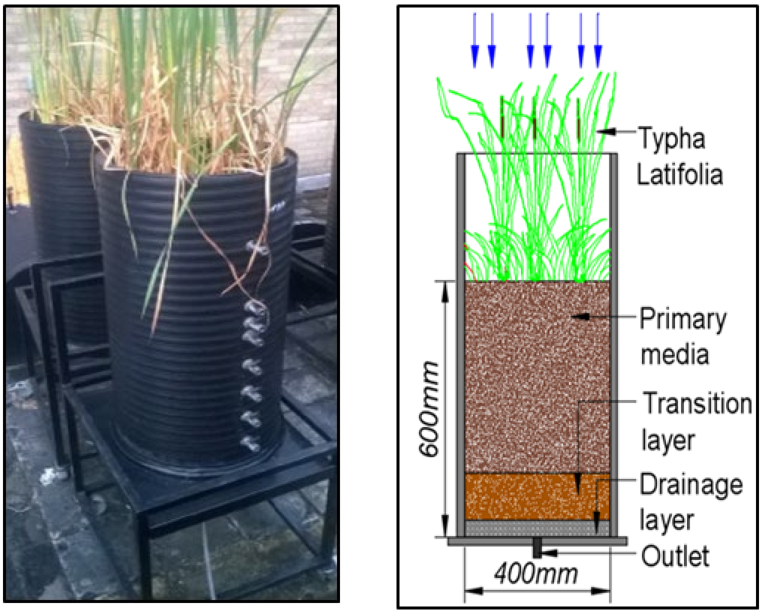
Moreover, the operational strategy simulated continuous wet and intermittent short dry and extended dry periods based on local patterns in the representative urban areas. The process of dosing influents into the CWs was by slow batch fill. Effluents were discharged by controlled draining using a tap at the bottom of each Unit. The tap was opened at the end of the retention time of 24 hours. The primary media were used based on the cost, local availability and sustainability.

Experimental work examining the influence of design and operational variables on the long-term performance of 8 pilot-scale VFCWs was conducted for 2 years. Performance indicators were the changes in the physical water qualities such as pH, electrical conductivity and temperature; measured in-situ using a multi-parameter probe. Similarly, the chemical water quality monitored are nitrite N-$(NO_2)^-$, Nitrate N-$(NO_3)^-$, N-$(NH_4)^-$, total nitrogen (TN), Orthophosphate P-$(PO_4)^-$, total phosphorus (TP), total iron (Fe), total copper (Cu), total Nickel (Ni), total Zinc (Zn), total Lead (Pb), total Cadmium (Cd) and total Chromium(Cr).

Total suspended solids (TSS), nitrogen and phosphorus species are determined by a spectrophotometer; while heavy metals are quantified using the inductive coupled plasma-optical emission spectrophotometer (ICP-OES). The data obtained are analysed using descriptive and inferential statistics, and innovative numerical modelling techniques involving the integration of principal components analysis (PCA) and artificial neural networks (ANNs).

3.1 Research design and experimental set-up

The effects of design on the long-term performance of VFCWs were investigated using 8 physical models of VFCWs. The VFCWs were designed and moulded from structured-wall high-density polyethene (HDPE) pipes, manufactured by Asset International Ltd. Each pipe was 1000 mm high and had an internal diameter of 400 mm as shown in Figure 3-1.



(a) **(b)**

Figure 3-1 (a) Typical test set up (b) Cross-section of a VFCW Unit

The CW Units were sealed off at the bottom with an HDPE plastic. The outlet tap was fitted at the centre of the sealed bottom end. The tap was used for controlling the collection of samples and for the discharge of the treated effluents. Although eight (8) outlet taps were fitted vertically (to collect various effluent samples), the logistical constraints restricted the effluent sample collection to the main outlet at the base of the VFCW models. Furthermore, all the VFCWs were placed outdoors on metallic frames (Figure 3-2) stationed on the roof of the 3rd Floor of the South Buildings at Cardiff School of Engineering.

Figure 3-2 Experimental set-up of the pilot-scale VFCWs

The internal flow in the CWs was predominantly vertical down-flow such that during filling, air trapped in the biofilter media bed escapes due to the rising influent run-off levels. Similarly, as effluents are discharged from the CW Units (drain phase), the receding effluents act as a passive pump, drawing air from the atmosphere into the CW media bed, thereby creating a cycle of “wet” and “dry” conditions in the wetland(Sun et al. 2005). Enhanced contaminant removal in tidal-flow operated CWs is attributed to the resultant maximum pollutant-biofilm contact and the increase in oxygen transfer rates during operation (Sun et al. 1999; Leonard et al. 2003).This operational strategy facilitates BOD_5 removal through aerobic decomposition; and the removal of ammoniacal-nitrogen N-$(NH_4)^+$ through nitrification-denitrification reactions. Thus, the dosing frequency and inflow volumes dosed into each CW Unit simulate the variables investigated.

3.1.1 Media configurations and macrophytes

Pollutant removal in CWs depends on the media matrix. The media bed provides the habitat for the important microbial communities. The media also acts as the source of ingredients required for bio-reactions (Saeed and Sun 2012). Additionally, the media can influence the environmental conditions such as the pH and the redox potential, particularly in the porous spaces of the CW. In this regard, pollutant removal in CWs is reliant on the media bed to regulate the co-existence of aerobic and anaerobic conditions which subsequently enhance nitrification, denitrification and removal of organics. Furthermore, the steady supply of internal carbon stored in the media ensures that denitrification metabolism is not limited to only the carbon available in influent wastewater. Thus, media types such as gravel do not provide carbon sources, and thus often tend to have limited denitrification and therefore low TN removal. Therefore, the effect of media on the performance of the designed VFCWs was studied using readily available and cost-effective media.

3.1.2 Media type and depth

Sand and gravel achieve good removals of priority pollutants such as heavy metals found in stormwater runoff (Hatt et al. 2007b; Li and Davis 2009). The other biofilter media used was blast furnace slag (BFS), an industrial by-product of iron production. VFCW in the UK is configured to a depth of between 0.5 m - 0.8 m. This range of depths provides adequate hydraulic residence time (HRT) and removal efficiency (Cooper et al. 1996b). Moreover, a similar media depth of 0.8 m was applied in the investigation of pilot-scale VFCWs (Scholz 2004; Blecken et al. 2009a; Blecken et al. 2010). Similarly, a gravel media depth of 0.5 m was described as suitable for removing sediment and heavy metals in stormwater infiltration systems (Hatt et al. 2007b; Feng et al. 2012). Therefore, the pilot-scale VFCW had a total media depth of 0.6 m (within the literature design range) to replicate the reported performances. The 0.6 m depth represents an increase of 0.1 m on the depth reported by Feng *et al.* (2012). The additional 0.1 m was created by adding 150 mm of a transition/drainage layer. The extra depth would be beneficial to ensuring that the media gains extra surface area for pollutant removal processes like adsorption.

Table 3-1 System media configurations in the 8 VFCW

CW Unit	1, 3, 4, 5, 6, 7	2	8
Vegetation	Typha latifolia		
Primary media	Loamy Sand	Fine gravel	Blast Furnace Slag
Transition media	Sharp sand	Medium gravel	Sharp sand
Drainage media	Fine gravel	Coarse gravel	Fine gravel

The media investigated in this study included loamy sand (LS), gravel (G) and blast furnace slags (BFS) and were configured as shown in Table 3-1. Thus, loamy sand media was selected in Units 1, 3, 4, 5, 6 and 7. Loamy sand media has multiple benefits which include: high permeability under compaction, high organic matter content for improved retention of water; and low nutrient content that favours vegetated beds (Blecken et al. 2009; FAWB 2009).

Similarly, gravel is cheap and available in most parts of the world. Besides, gravel media in CWs was reported as effective in removing suspended solids and heavy metals (Hatt et al. 2007b). Therefore, to evaluate the performance of gravel media, Unit 2 was configured from graded gravel (fine, medium and coarse gravel).

Equally, BFS consisted of silicates, aluminosilicates, calcium-alumina-silicates and absorbed sulphur adsorptive capacity for heavy metals and phosphorus (Taylor 2006). BFS is not only a cost-effective media option, but it also signifies sustainability in the treatment of wastewater. Thus, granulated BFS (diameter 4.0 – 12.5 mm) was placed in Unit 8 and separated from the drainage layer using gravel (Figure 3–2). Both the loamy sand and BFS CWs had fine gravel (6 mm diameter) as a drainage layer, and a transition layer of sharp sand meant to prevent the primary media from being washed out and subsequently clogging the drainage layer.

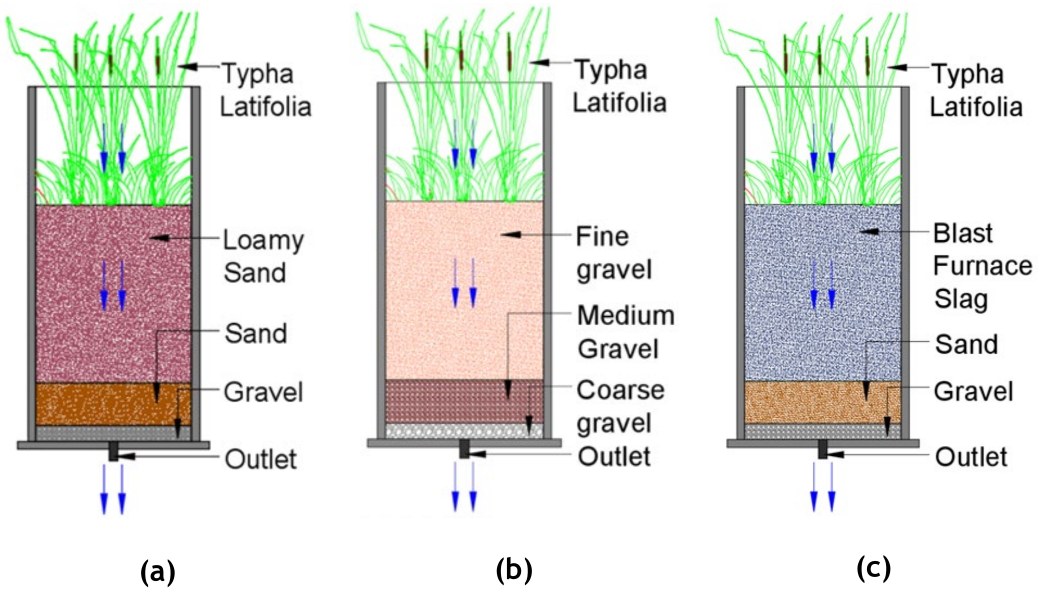


Figure 3-3 Cross-sections of the VFCWs : (a) Loamy sand (b) Graded gravel (c) BFS

Similarly, Unit 2 consisted of a transition layer of medium gravel (10 mm diameter), and a drainage layer of coarse gravel (20 mm diameter). The graded gravel layer configurations in Unit 2 is a characteristic feature of vertical downflow SS CWs (Cooper et al. 1996b). CW Unit 8 is based on recommendations by the FAWB (FAWB 2009), except that BFS replaces loamy sand. Accordingly, the effective biofilter depth in all the VFCW was 600 mm, of which 450 mm was primary media; 100 mm (transition layer); and 50 mm of drainage layer as illustrated in Figure 3-1. In addition to the media, each VFCW was planted with *Typha latifolia* plants. Each plant was about 20 cm long (stem and rhizome) and established in the bed at a density of 3 plants/m^2 (Ciria et al. 2005). *Typha* is readily available and is useful in removing metals thus suitable for treating stormwater (Ellis et al. 2003).

3.1.3 Media characteristics and elemental composition analysis

Typical characteristics of the media commonly used in the CWs are shown in Table 3-2. The elemental composition of the 3 primary media types (loamy sand and BFS media) was determined from samples taken from the media stock that was used to configure the 8 VFCWs.

Table 3-2 Properties of media commonly used in subsurface flow CWs

Media type	Effective size, D_{10} (mm)	Porosity, n (%)	Hydraulic conductivity, K_s ($m^3/m^2/day^{-1}$)
Coarse Sand	2	28 - 30	1000
Gravelly Sand	8	30 - 35	5000
Fine Sand	16	35 - 38	7500
Medium Gravel	32	36 - 40	10000
Corse Rock	128	38 - 45	100000

The digestion procedure involved separately weighing out finely crushed powdered samples (< 100 µm) of loamy sand (0.1053 g) and BFS (0.1011 g) to which 2 ml of hydrofluoric (HF) acid was added and the mixture left to stand overnight. Then 3 ml of aqua regia (50:50 ratio of HCl and HNO3) was added, and the digestion carried out using Anton-Paar Multiwave 3000 Microwave operated at 190 °C for 25 minutes. Complexation (neutralising the HF) was achieved by adding 12 ml of 4 % Boric acid solution before the final solution was made up to 50 ml with deionised water (Wilson et al. 1997; Pérez-Esteban et al. 2013). The resulting mixture was analysed for Ca, Al, Fe, Mg, Mn, Pb, Si and Zn using the inductive coupled plasma-optical emission spectrophotometer, ICP-OES 2100 DV (Perkin Elmer).

Table 3-3 Mass (mg) of elements in digested media samples

Media type	Mg	Ca	Fe	Al	Pb	Mn	Zn	Si
Loamy sand (LS)	0.49	28.736	1.186	1.545	0.007	0.039	0.01	6.04
% in LS	0.466	27.29	1.127	1.468	0.007	0.038	0.01	5.736
BFS	3.853	24.725	0.229	8.067	0.002	0.247	0.009	15.032
% in BFS	3.812	24.456	0.227	7.98	0.002	0.245	0.009	14.869

The experimental data in Table 3-3 and Figure 3-4 show that Ca was the main element in loamy sand (27.3 %) and BFS (24.5 %). Similarly, the presence of Al in BFS at 8 % was nearly 6 times higher than in loamy sand (1.5 %). Additionally, BFS media had 8 times more Mg (3.8 %) in comparison to the Mg in loamy sand (0.47 %).

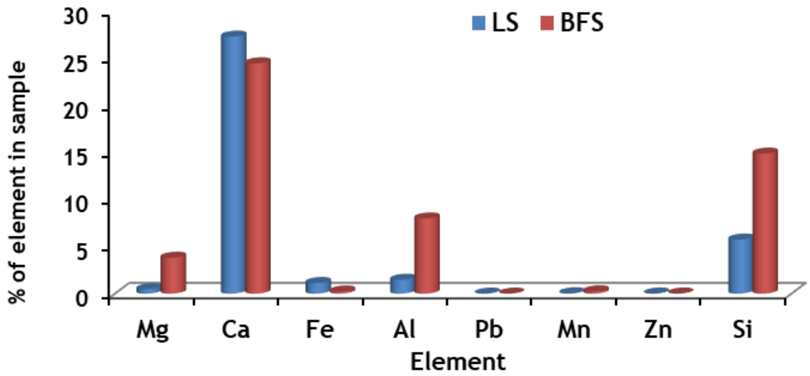


Figure 3-4 Elemental composition in loamy sand and BFS media

3.1.4 Sizing

Although the size of the CW would be determined by the catchment area or the number of people the wetland will serve, the design of a CW is mainly based on the ratio of the of the wetland area to that of the watershed (WWAR). The surface area is determined as a percentage of the size of the watershed area. However, because the design of CWs for stormwater treatment varies with the amount of rainfall received and the treatment requirements in different catchments, there is no general WWAR design specific codes. Standard guidelines and recommendations have typical values of the WWAR in the ranges of 1-5 % WWAR. For the UK, the WWAR of 2-3 % is recommended (Ellis et al. 2003). Nevertheless, any WWAR value that minimises land requirements without compromising on performance is ideal, particularly where retrofitting the system is planned.

In this study, the design process was reversed in that the uniform surface area of the VFCW (0.126 m^2) was determined from the diameter (400 mm) of the HDPE pipes. Therefore, instead of starting with a watershed area and calculating the size of the VFCW, the wetland area is known and the catchment area whose run-off is to be treated determined. This technique was applied in the design of pilot-scale stormwater VFCW investigated by Blecken et al., 2009.

Three separate WWAR values of 1.5 %, 2.5 % and 5.0 % were investigated to determine the performance of VFCW under different loading conditions. Thus, the

2.5 % WWAR was a system control value because it is within the recommended range of 2-3 % WWAR (Ellis et al. (2003). This WWAR was applied to VFCW Units 1, 2, 3, 4, 6 and 8. VFCW Unit 5 and Unit 7 had WWARs of 5.0 % and 1.5 % respectively. Both Unit 5 and Unit 7 were designed to investigate the effect of WWAR on treatment in relatively smaller and larger catchments respectively. The treatment performances obtained for the different WWARs could inform the choice of a suitable WWAR for tidal-flow operated VFCWs. Thus, the catchment areas were calculated as follows:

1.5 % WWAR: $0.126 \times \frac{100}{WWAR} = 0.126 \times \frac{100}{1.5} = 8.4\, m^2$ 3-1

2.5 % WWAR: $0.126 \times \frac{100}{WWAR} = 0.126 \times \frac{100}{2.5} = 5.04\, m^2$ 3-2

5.0 % WWAR: $0.126 \times \frac{100}{WWAR} = 0.126 \times \frac{100}{5} = 2.52\, m^2$ 3-3

Table 3-4 Variable matrix for the daily and weekly loading routine

CW Unit		1	4	2	3	5	6	7	8
Media depth (mm)	0 - 450	Loamy sand	Loamy sand	Fine gravel	Loamy sand	Loamy sand	Loamy sand	Loamy sand	Blast furnace slag
	450 - 550	Sand	Sand	Medium gravel	Sand	Sand	Sand	Sand	Sand
	550 - 600	Fine gravel	Fine gravel	Coarse gravel	Fine gravel	Fine gravel	Fine gravel	Fine gravel	Fine gravel
Variable		Control	Control	Media	short dry rest	5 % WWAR	Extended dry rest	1.5 % WWAR	Media
Influent load per wet day		22.5 L	22.5 L	22.5 L	22.5 L	11.3 L	22.5 L	37.6 L	22.5 L
Load frequency and total volume per week		Wet = 3 x 22.5 = 67.5 L	Wet = 3 x 22.5 = 67.5 L	Wet = 3 x 22.5 = 67.5 L	Alternating 1 week Wet 1 week Dry	Wet = 3 x 11.3 = 33.9 L	Alternating 1 week Wet, 4 weeks Dry	Wet = 3 x 37.6 = 112.8 L	Wet = 3 x 22.5 = 67.5 L

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

3.2 Pollutant loading

3.2.1 Semi-synthetic stormwater

Although fresh stormwater had been preferred, the logistics involved in obtaining large volumes of fresh stormwater with a constant inflow concentration were difficult. Similarly, the option of using synthetic stormwater with a consistent concentration was disregarded because the artificial composition of synthetic stormwater produces artifacts (Hatt et al. 2007a). Consequently, Semi-synthetic stormwater was used in the experiments. Influent concentrations were adjusted to within the ranges of the reported composition of run-off.

3.2.2 Preparation of semi-synthetic stormwater

The semi-synthetic stormwater was constituted by mixing natural stormwater sediment with dechlorinated tap water. The sediment was initially collected from a stormwater runoff pond in Nant y Briwnant (North of Cardiff) and later from gulley pots in the car park at Cardiff School of Engineering. The change of sediment source occurred after 3 months of operation because of the lack of access to the pond, especially following storms (floods made it challenging to collect the sediments). The sediments once collected were wet-sieved using a sieve (1 mm diameter) to obtain particle sizes typical of pre-treated stormwater runoff (FAWB, 2009). The product of wet-sieving was a slurry (a mixture of water and solids).

A sample of the slurry was analysed in the CLEER Labs at the Cardiff School of Engineering. Contaminant concentrations in the slurry were determined and are presented in Table 3-5. After that, Equation 3-4 was used to approximate the volume of slurry required to produce the desired composition of simulated stormwater. However, in some instances laboratory-grade chemicals were added to top-up pollutant concentrations to achieve the targeted stormwater concentrations.

$$\boldsymbol{V_S = \frac{TSS_T \times V_{ST}}{TSS_S}} \quad \text{3-4}$$

V_S = volume of slurry; TSS_T = targeted TSS concentration (mg/L); V_{ST} = volume of semi-synthetic stormwater (L) and TSS_S = slurry TSS concentration (mg/L). The volume, V_S, was added to 100 L of dechlorinated tap water. Dechlorination was achieved by adding about 0.1 g of Sodium thiosulphate to 100 L of standard tap water at 4 ppm chlorine content as recommended by FAWB (2009). The mixture was continuously stirred for 10 minutes to allow uniform distribution of the sediments in the water, adsorption of contaminants to the solids and oxygen to dissolve in the water.

3.2.3 Pollutant concentrations

Inflow pollutant concentrations were selected to reflect an urbanised catchment. Thus, priority stormwater pollutants reported in the UK and European cities were identified from the study of urban stormwater pollution (Duncan 1999; Pitt et al. 1999; Pitt et al. 2004) and others listed in the literature review (Table 2-1). The data represent common stormwater contaminants and their respective average concentrations in various catchments. The catchment type of interest in this experiment is the highly urbanised catchment. Therefore, the mean concentrations in the literature were adjusted per the objectives of this study. However, some pollutant groups reviewed were not selected for monitoring due to the analytical costs. The contaminants are listed in Table 3-5 alongside the influent concentrations, discharge limits of the respective influents and laboratory grade chemicals added to achieve the pollutant-specific concentration.

Table 3-5 Influent pollutant concentrations and discharge limits

Pollutant	Concentration (mg/l)	Reagents	Upper discharge limits (mg/L)
TSS	180.0	Sediment	717.5
TP	0.450	K_2HPO_4	0.230
PO_4-P	0.87	-	0.029
TN	3.00	NH_4Cl	0.207
NH_4-N	1.02	-	0.002
NO_2-N	0.005	-	0.098
NO_3-N	0.014	-	0.574
Pb	0.160	Pb $(NO_3)_2$	28.701
Zn	0.350	$ZnSO_4.7H_2O$	-
Cu	0.070	$CuCl_2.2H_2O$	9.184
Cd	0.005	1000 mg/l of Cd	-
Cr	0.025	Cr $(NO_3)_3$	-
Ni	0.040	$NiCl_2.6H_2O$	-
Fe	2.900	$FeCl_2.4H_2O$	1.148

3.2.4 Influent stormwater water quality

Influent water quality was determined for each dose treated in the VFCWs. Inconsistencies in the quality of the influent stormwater were minimised by adhering to a conservative approach for the preparation of slurry and mixing. This ensured that the prepared semi-synthetic stormwater contained pollutant concentrations within the ranges in literature. Consequently, inflow stormwater quality was largely stable.

It is worth noting that the quality of the natural sediment used to constitute the stormwater used in the experiments had marginally higher pollutant concentrations than that reported in the literature. However, some pollutants such as Cd, Cr, and Ni were below the 'standard' concentrations of urban stormwater. Thus, to achieve pollutant influent concentrations, pre-determined amounts of laboratory grade chemicals were added to top up the concentrations.

Similarly, the influent TSS concentration was less variable because pre-determined volumes of sediment slurry were added to fixed volumes of dechlorinated tap water. Dechlorination helped to minimise the reactions of chlorine with the contaminants, as well as restricted the effects of chlorine on the important microbial communities.

Some pollutant concentrations were indirectly determined from fixed volumes of slurry. This approach assumed that TSS in the simulated stormwater was proportional to the concentration of some pollutants. Interestingly, influents analysed during the first seven weeks of the study showed that heavy metals were predominantly particulate and as such were possibly bound to suspended solids. Thus, 9 % and 16 % of Zn and Ni respectively were dissolved, while dissolved Pb accounted for 2-3 % of total Pb (Lucas 2015). This relationship has implications for the removal of suspended solids and heavy metals.

3.2.5 Maximum allowable effluent discharge concentrations

Maximum allowable effluent concentrations for discharge were determined based on the lowest or strictest contaminant discharge limits. For example, the lowest upper limit for Zn in a watercourse of "good" ecological status is 0.008 mg/L. Thus, Zn discharge standards were complied with by ensuring that effluents from CWs do not increase Zn to more than 0.008 mg/L. Watercourses are different and as such flow rates were estimated at the lowest end. Firstly, a flow rate of 1000 m^3/d was selected. This flow was considered unlikely to dilute effluents from the CW. Secondly; it was assumed that the effluent volume from each CW would exit the treatment system within 15 minutes. Again, CW Unit 7 with a 1.5 % WWAR (37.6 L) of stormwater was selected. Maintaining discharge over 15 minutes produced an effluent flow rate of 3.61 m^3/d. The effluent flow rate and lower pollutant discharge limits were then fed into Equation 3-5 to determine the maximum allowable concentrations:

$$\mathrm{Q_w C_w + Q_{us} C_{us} = Q_{ds} C_{ds}} \quad \text{..} \quad 3\text{-}5$$

where; Q_w = discharge flow rate (m^3/d); C_w = discharge pollutant concentration (mg/L), Q_{us} = upstream flow rate (m^3/d); C_{us} = upstream pollutant concentration (mg/L); Q_{ds} = downstream flow rate (Q_w + Q_{us}) (m^3/d); and C_{ds} = downstream pollutant concentration (mg/L). Rearranging Equation 3.5 gives:

$$\mathrm{C_w} = \frac{\mathrm{Q_{ds} C_{ds} - Q_{us} C_{us}}}{\mathrm{Q_w}} \quad \text{...} \quad 3\text{-}6$$

The final assumption made was that the upstream concentration be 90 % of the upper limit for a "good" ecological status. Thus, for Zn:

$$\text{Zn } C_w = \frac{(1000+3.61)0.008-1000(0.9\times 0.008)}{3.61} = 0.230 \text{ mg} \quad \text{......................} \ 3\text{-}7$$

This method was applied to determine the maximum allowable concentrations of all the other pollutants namely Cu, Pb, Cd, Cr, Ni, Fe, TN, NH_4-N^+, TP and PO_4-P. However, for SS the standard of 25 mg/L was recommended by Natural Resources Wales (NRW) and consistent with the freshwater fish directive (European Union 2006). Some pollutant concentrations were based on UK TAG discharge limits.

The criteria for assessing performance of the 8 pilot-scale VFCWs involved monitoring variations in chemical and physical water quality parameters of the influents and effluents. Effluent data were examined based on guidelines by the UK Technical Advisory Group (UK TAG) and 2008 EU/UK Water Framework Directives. Although UK TAG standards do not specify discharge limits for effluents treated in CW, it was decided that the evaluation of the long-term performance of the 8 pilot VFCWs be based on the upper discharge limits specified for effluents released into “good” ecological watercourses (Table 3-5).

3.3 Hydraulic loading

The Hydraulic loading rate (HLR) is one of the factors that influence the performance of SSFCWs. The HLR is the flow applied to the surface of the filter per unit time. It is expressed in m/day or cm/day. The HLR varies inversely as the retention time for a specific SSFCW depth and is dependent on the configuration of the CW (Torrens et al. 2009; Saeed and Sun 2012). HRTs that were applied to the pilot-scale VFCW were determined from long-term meteorological data, specifically the annual rainfall received in the urban areas in the UK.

3.3.1 Average annual rainfall (AAR)

In the case of stormwater treatment, the hydraulic loading volume (HLV) was based on the rainfall patterns in the catchment. The main influential factors when determining the HLV are the catchment size and the amount of precipitation. Therefore, to derive the HLV, historical precipitation data of the selected catchments were analysed. The daily, monthly, and the annual rainfall data for selected catchments and stations were obtained from the Met Office. The data covered the period from 1978 – 2011(33 years). The AAR approach is used by the National Hydrological Monitoring Programme; the NERC Centre for Ecology and Hydrology (CEH), and the UK Met Office to provide information about the average outflow and rainfall for the UK. Similarly, the CEH derives important hydrological information from the daily and monthly rain gauge records based on the natural neighbour interpolation method combined with a normalisation step based on AAR (Keller et al. 2015).

Since the Met Office national database of rain gauge observations remains the most appropriate source of observation of the daily and monthly rainfall in the UK (Keller et al. 2015), it was considered that deriving the AAR from the UK Met Office data would be practically representative of the catchment. Furthermore, the period 1978-2011 was the longest available dataset for the selected stations. This period was considered satisfactorily long to include stochastic rainfall patterns and statistics typical of UK storm events, storm intensity, storm duration and frequency.

Figure 3-5 Locations of rainfall data stations (red markers)

The stations from which the data for the AAR and the subsequent hydraulic loadings into the 8 VFCWs was obtained included Armagh (Northern Ireland), Bradford, Cambridge, Durham, Heathrow, Oxford, and Sheffield (England); Cardiff (Wales) and Paisley (Scotland). The distribution of the stations is spread across the UK as shown on the map (**Figure 3-5**), with at least one station in each country providing rainfall data. The rainfall data (in mm) are provided for every month of each year at each site. These figures were summed up for each year to obtain the total annual rainfall. Subsequently, the AAR value was calculated for the period 1978 to 2011 (inclusive) and resultant AARs for each station were averaged to get the AAR for UK urban areas (Table 3-6).

The number of "rainy days" is counted as the number of days with >1 mm rainfall. The Met Office provides monthly and annual rainy days recorded in the meteorological districts of 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; and Northern Ireland. The AARs recorded at each station and the corresponding district values for average number of rainy days experienced per year (1978-2011) are shown in Table 3-6. The collated data gives an AAR value of 821 mm for UK urban areas, with a corresponding value of 147 rainy days for the period 1978 - 2011.

Table 3-6 UK urban rainfall data, 1978-2011 (Met Office)

Station	District	Average Annual Rainfall (mm)	Average annual wet days
Armagh	Northern Ireland	816	178
Bradford	North-West England and North Wales	873	166
Cambridge	East Anglia	561	115
Cardiff	South Wales and South West England	1143	156
Durham	East and North East England	663	131
Heathrow, London	SE and Central England	600	121
Oxford	Midlands	653	130
Paisley	West Scotland	1250	194
Sheffield	Midlands	833	130
UK wide average		**821.3**	**146.8**

3.3.2 Runoff entering the VFCW treatment system

The rainfall depth per event (1 rainy day) was calculated using 3-9:

$$\text{Rainfall depth} = \frac{\text{Average Annual Rainfall}}{\text{No of rainy days}} = \frac{821}{147} = 5.59 \text{ mm per day} \quad \ldots\ldots\ldots\ldots\ldots \text{ 3-8}$$

Representative sizing values were determined for 1.5 % WWAR, 2.5 % WWAR, and 5 % WWAR using equations 3-1, 3-2 and 3-3 respectively (section 3.2.3). An 80 % impervious catchment is assumed as per the guidance in the SUDs Manual (Woods-Ballard et al. 2007). Therefore, all the 8 VFCW were dosed as follows:

1.5 % WWAR: 5.59 L/m^2 x 8.4 m^2 x 0.8 = 37.6 L per event 3-9

2.5 % WWAR: 5.59 L/m^2 x 5.04 m^2 x 0.8 = 22.5 L per event.......... 3-10

5.0 % WWAR: 5.59 L/m^2 x 2.52 m^2 x 0.8 = 11.3 L per event.......... 3-11

Consequently, the number of storm events per week was calculated by dividing the total of rainy days in a year by 52 (weeks in a year):

Storm events per week = 147/52 = 2.83 = 3 3-12

Therefore, the weekly inflows were as follows:

1.5 % WWAR: 3 x 37.6 L = 112.8 L/week 3-13

2.5 % WWAR: 3 x 22.5 L = 67.5 L/week 3-14

5.0 % WWAR: 3 x 11.3 L = 33.9 L/week 3-15

There were five separate inflow regimes, as detailed in Table 3-7. The decision to keep regimes 1, 2 and 3 constants over the experimental period was based on the number of rainy days experienced per month in each of the Districts in the Met Office data selected (Table 3-6). Rainfall is distributed in each district relatively evenly throughout the year, thus inflow regimes 1, 2 and 3 were the same per week.

Table 3-7 Loading regimes

Loading regime	WWAR	Dosing patterns
1	2.5 %	3 batches (3 x 22.5) L = 67.5 L per week
2	5.0 %	3 batches (3 x 11.3) L = 33.9 L per week
3	1.5 %	3 batches (3 x 37.6) L = 112.8 L per week
4	2.5 %	3 batches (3 x 22.5) L = 67.5 L per week, 1 dry week rest
5	2.5 %	3 batches (3 x 22.5) L per week, 4 dry weeks rest

3.3.3 Wetting and drying periods

Inflow regimes consisted of intermittent wet (3 doses per week) and no dose during dry weeks. The pattern followed in dosing CW Unit 3 was: 1-week wet; 1-week dry; 1-week wet; 1-week dry. The purpose of this dosing regime was to replicate short dry weather spells and hence ascertain the impact of rest periods on the performance of the VFCWs. This strategy put into consideration the weather patterns in the UK, and the stochasticity of rainfall.

The inflow regime 5 (Table 3-7) applied to CW Unit 6 and consists of 1 wet week followed by a rest period of 4 dry weeks. This arrangement was investigated to assess the performance of the VFCWs subjected to periods of prolonged drought. The ratio of wet to dry weeks was based on the reduced rainfall experienced in East Anglia in Spring 2011. Thus, over a 3-month period, the region experienced 2.1 days of rain (> 1 mm) in March 2011; 1.8 days in

April; and 4 days in May or 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 (13 weeks) which, according to the pre-established dosing regime of 3 doses per week is equivalent to 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 ≈ 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 extended periods of drought. Between the "dry seasons" the CWs were dosed using regime 1.

3.3.4 Further considerations for deriving load volumes

The physical processes that convert rainfall to runoff are complex and highly variable and cannot be replicated with precise certainty. However, using simplifying assumptions and empirical data, some mathematical models and equations have been developed to simulate hydrological processes and to predict runoff volumes and rates. The selection of the appropriate model or equation depends upon factors such as the size of the drainage area and data availability. Thus, although loading volumes dosed into the VFCWs (3.3.2) were derived from rainfall data covering 33 years, variations in storm intensity, duration and frequency may not have been precisely simulated.

Table 3-8 Estimated runoff from the Cardiff (Wales) catchment

Catchment details		Design storm details			
M5-60 (mm)	19	Simulated area (m^2)	8.4	5.04	2.52
r Ratio	29	Storm duration (mins)	1	1	1
SAAR (mm)	1113	Return period (years)	30	30	30
WRAP SOIL	0.45	Climate Change Allowance	1.4	1.4	1.4
PIMP (%)	80	Maximum run-off (mm/hr)	207.6	207.7	207.8
Routing coefficient	1.3	Design Rainfall Intensity ($l/s/m^2$)	0.006	0.006	0.00677
		Percentage Runoff (%)	88.87	88.87	88.87
		Total design Runoff (l/s)	0.43	0.26	0.13

Thus, for comparison purposes the Wallingford Procedure (Wallingford 1983) was used to estimate stormwater run-off /loading volumes putting into consideration the variations in storm intensity, duration and frequency. Firstly, the minimum return period recommended for the UK is 10-years (Ellis *et al.*, 2003), while for flood-prone catchments, the Environment Agency in England and Wales recommends designs that can deal with a 1: 200-year flood (Shutes *et al.*, 2005). Additionally, both the Environment Agency (England/Wales) and the US Environmental Protection Agency recommend the Schueler (1992) guideline for CWs to retain 90 % of the storm events. Therefore, a storm event that consisted of a 1-minute duration and return period of 30 years (AAR was derived from 33 years of data) was selected for comparison, and the loading rates calculated are presented in Table 3-8.

It is noted from Table 3-8 that attenuation and storage of peak flows may be required to mitigate extra runoff that may result from new developments in the catchment so that the VFCWs can serve the additional role of reducing the volume and rate of stormwater runoff; ensuring that stormwater is suitably treated prior to discharge to the receiving watercourse; and that groundwater quality is protected.

Additionally, there are characteristics of both the rainfall event and the area upon which it falls that can influence the resulting runoff. For example, high intensity rainfall will generally produce a greater peak discharge than a rainfall that occurs over a longer period. Likewise, highly porous or permeable soils that can rapidly infiltrate rainfall will produce less runoff volume than soils with more restrictive infiltration. Furthermore, dense vegetation tends to intercept and help infiltrate rainfall, thereby reducing runoff volumes and rates. Conversely, impervious areas like roadways and rooftops prevent infiltration and increase runoff volumes and rates; while areas with shorter times of concentration will have higher peak runoff rates than those with longer times.

Therefore, if all these factors are considered, then CWs designed to treat the maximum peak flows or the loads would produce large and over-engineered systems. Consequently, effluent quality standards would have to be significantly lowered. Alternatively, flow volumes over the design maximum would have to be diverted or directly discharged into receiving waters after preliminary treatment. Similarly, pollution associated with the first flush accompanying long antecedent dry periods would lead to high polluted flows which could easily disturb and mobilise the contaminated media substrate as well as damage the wetland vegetation. Therefore, the design of a full-scale VFCW should put into consideration a suitable design storm return period, which in turn determines the wetland size and volume.

3.4 Systems operation and analysis

3.4.1 Systems operation

All the pilot-scale VFCWs were operated using a gentle-slow fill and drain approach. The influent stormwater was dosed in the VFCWs on 3 consecutive days of the same week as summarised in Table 3-7. Thus, influents were dosed into the VFCW on the Monday of each week and repeated on two consecutive days (i.e. Monday, Tuesday and Wednesday). However, on occasions when dosing was not done on a Monday, the routine was repeated on 3 successive days of the same week.

During feeding, the stormwater was carried from the mixing tank to each VFCW unit using a 10 L plastic bucket. During the filling phase, influent stormwater was slowly poured onto the top surface of the media in each CW unit. The slow feeding approach was used to minimise the impact of high flow on the structure of the biofilter media. Also, the presence of macrophytes in the CW units further reduced the effects of the influent stream on the media distribution. Additionally, a series of 3 passes (4 passes for Unit 7) was applied to all the units so that the semi-synthetic stormwater dosed in the VFCWs was of similar concentration. After that, the CWs were left to treat the stormwater for 24 hours. At the end of the retention period, effluent samples were collected from the outlet tap of each unit.

3.4.2 Influent and effluent sample collection

Weekly inflow and outflow samples were collected over the entire monitoring period. Although inflow sample collection and analyses were conducted three times per week, the outflow sample analyses were mostly done once each week due to time and analytical cost limitations. Furthermore, effluent samples were collected manually at the end of the set retention period. Outflow discharge measurements were taken from the volume collected and the time taken for complete drainage. Drainage was considered complete when over 98 % of the inflow volume dosed in each CW Unit had been collected. The in-situ water quality parameters like pH, EC and temperature were analysed on site using a HANNA Probe (Model HI 991301). The other water quality indicators were determined in the CLEER laboratories, using specific methods and instrumentations.

Briefly, before the feed cycle started, influent samples were taken from the feed tank, and the in-situ parameters recorded immediately. Similarly, at the end of the retention period (24 hours), the effluent water samples were taken from the outlet tap at the bottom of each VFCW. The outflow water sample was taken by mixed grab sampling. Mixed grab sampling was preferred because it did not require special equipment to be maintained on the roof where the experimental units had been set-up. Additionally, grab sampling had the primary advantage of reduced set-up and maintenance costs. Nevertheless, sample collection by manual sampling meant regular walks between the rooftop (experimental set-up) and the basement (CLEER laboratories) of the South Buildings of Cardiff School of Engineering.

A representative composite sample of 100 ml was collected from each VFCW. The approach used to obtain the 100 ml of the effluent sample was such that as soon as the drainage tap at the bottom was opened, 25 ml of effluent water were collected within the first 2 minutes, and a further 75 ml collected in equal volumes of 25 ml, after every 3-5 minutes. This ensured that the entire cross-section of the effluent water column was sampled. The time intervals between each grab sample were based on the time required for the maximum allowable limits of discharge discussed in section 3.2.5. This approach helped to minimise the effects of discharge flow velocity on the EMC of the grab sample. It is worth noting that in CWs that experienced short dry and extended dry periods (Units 3 and 6 respectively), samples were only collected during wet weeks.

3.4.3 Hydrological budget of the VFCWs

The net change in the influent and effluent water volumes was monitored using the dynamic water balance Equation 3-16. Consequently, the effects of precipitation and evapotranspiration were accounted for in the mass balance calculations.

$$D_s = Q_{in} + (P\text{-}ET\text{-}I) \times A - Q_{out} + Q_{Runoff} + GW_{in} \quad \text{3-16}$$

Where, D_s = net change in volume (m^3 day^{-1}), Q_{in} = Daily inflow to each unit (m^3 day^{-1}), P = daily precipitation rate (m day^{-1}), ET = evapotranspiration rate (m day^{-1}),I = infiltration rate (m day^{-1}), A = surface area of the CW (m^2), Q_{out} = daily outflow from the CW (m^3 day^{-1}), Q_{runoff} = catchment run-off (m^3 day^{-1}) and GW_{in} = groundwater inlet (m^3 day^{-1}) = 0. Thus, the daily precipitation (P) was equivalent to the Met Office record for Cardiff city, while water loss through evaporation was taken as negligible due to the small surface area of the CWs. Likewise, the evapotranspiration rate (ET) was derived from the literature values for the ratio (ET/E) of the wetland macrophyte investigated (Dong et al. 2011).

3.4.4 Hydraulics of the VFCWs

VFCWs were dosed by slow batch inflows and drained by through a control tap at the bottom of each CW Unit. The patterns were repeated 24 hours after the first batch. At the end of the retention period, the VFCWs were drained by opening the outlet tap at the base of each VFCW. The results obtained reflect the hydraulics of the 8 VFCWs (Table 3-9).

Effluent discharges were measured using a Gardena 8188-29 Digital Electronic Water Smart Flowmeter (8.5 mm internal diameter). The discharge velocities in all the VFCWs reduced with the time of discharge. Generally, all the CWs had velocities between 0.59 – 0.99 m/s, higher than the velocities reported in Torrens et al. (2009) probably because of the differences in hydraulic loading rates and the scale of the CW Units investigated.

The lowest velocity was in the loamy sand CW Unit 5. However, gravel and BFS media CW Units registered marginally higher velocities than all the loamy sand CWs (Figure 3-6). The difference in the outflow velocities is associated with the media grain sizes. Thus, the larger grain sized and hence more porous gravel and BFS had higher outflow velocity compared to the fine and small grains of loamy sand VFCWs.

Table 3-9 Inflow, outflow volumes and discharge velocity

Unit	Media	WWAR (%)	Inflow (L)	Outflow (L)	Threshold velocity (m/s)
1	LS	2.5	22.5	21.2	0.764
4	LS	2.5	22.5	20.8	0.822
3	LS	2.5	22.5	21.4	0.881
6	LS	2.5	22.5	21.6	0.852
5	LS	5.0	11.3	11.2	0.587
7	LS	1.5	37.6	34.4	0.939
2	Gravel	2.5	22.5	22.4	0.969
8	BFS	2.5	22.5	22.4	0.999

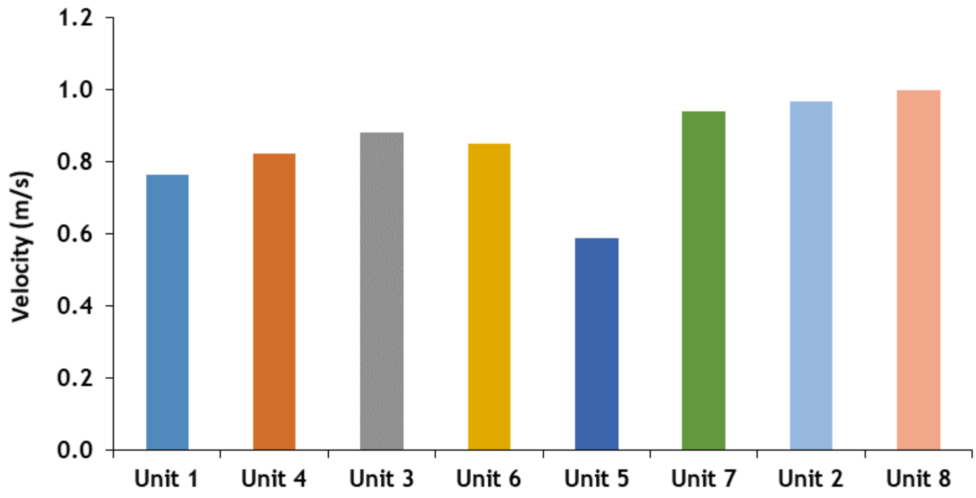


Figure 3-6 Threshold discharge velocities of the VFCWs

However, the loamy sand CW Unit 7 (1.5 % WWAR) developed discharge velocity like that of BFS and gravel units (2.5 % WWAR). The relatively high discharge velocity in Unit 7 may have resulted from the pressure caused by the drop in the large volume (37.6 L) of the stormwater treated in Unit 7. Both gravel and BFS media had the lowest infiltration capacities, while among the loamy sand VFCWs, Unit 7 retained the most stormwater. However, there was no clogging in all the CWs during the experimental period. This suggests that the biofilters were suitable for treatment of the influent loads. Additionally, the environmental conditions, loading regimes and the rest periods between inflows were adequate for drying and the mineralisation of removed contaminants.

3.4.5 Sample processing and laboratory analyses of samples

The parameters monitored included pH, temperature and electrical conductivity and were measured insitu using a multi-parameter HANNA Probe (Model HI 991301) immediately after the samples had been collected. Similarly, influent and effluent TSS were determined in the CLEER laboratory immediately after samples had been collected. Consequently, there were no storage requirements for parameters such as pH, temperature, EC and TSS.

All the other pollutant concentrations were measured in the CLEER laboratory using samples collected in acid rinsed polyethene bottles. Moreover, the chemistry of the stormwater consisted of a combination of natural stormwater sediment and top-up laboratory reagents added to achieve typical pollutant concentrations in stormwater. Hence, the pH buffering capacity of the simulated semi-synthetic stormwater was similar to that of fresh stomwater. Also, the VFCWs had a small surface area, so the amount of rainfall received was limited.

Water samples (40 mL) for analysis of heavy metals were acidified with 1 mL of 60 % HNO_3 solution and stored in a fridge at < 4°C. The analysis of metals was carried out using the inductively coupled plasma optical emission spectrometer (Optima 210 DV ICP - OES, Perkin Elmer), based on the standard methods (APHA, 2012).

Table 3-10 Pollutant lower detection limits (mg/L)

Parameter	ICP-OES	Parameter	Hach Lange DR3900
Fe	0.00987	TSS	5.0000
Zn	0.00139	TN	0.1000
Pb	0.00853	N-$(NH_4)^+$	0.0212
Cd	0.00051	N-$(NO_2)^-$	0.0020
Ni	0.00204	N-$(NO_3)^-$	0.0100
Cr	0.00054	P-$(PO_4)^-$	0.0500
Cu	0.00122	-	-
TP	0.04817	-	-

This involved internal calibrations of the instrument (Optima 210 ICP-OES) and subsequently, the determination of the method detection limits for each element monitored in the research study (Table 3-10). The detection limits were obtained by multiplying the standard deviations of the 20 blank replicates. The blanks were prepared using ultra-pure de-ionised water from a Milli-Q analytical reagent water purification system (Millipore). The blank samples were analysed against solutions prepared by successive dilution of a high purity ICP multi-element calibration standard. The lower calibration standard was set at 0.10 mg/L while the upper limit was 10 mg/L. Although variable, the results in Table 3-10 show that the detection limits of all the elements ranged from 0.001 mg/L to 0.005 mg/L.

Similarly, the lower detection limits for TN, N-$(NH_4)^+$, N-$(NO_2)^-$, N-$(NO_3)^-$, P-$(PO_4)^-$ and TSS were measured with a Hach Lange DR3900 benchtop spectrophotometer. The procedure used for $(N\text{-}NH_4)^+$ was the “Nessler” method, while N-$(NO_2)^-$ and N-$(NO_3)^-$ were determined using powder pillow reagents for diazotisation and cadmium reduction methods respectively. Likewise, detection limits for TN and P-$(PO_4)^-$ were measured using Hach Lange’s cuvette tests (analytical reagents and vessels are provided by the manufacturer, HACH). TN digestion procedure was carried out at 100°C using the Hach Lange LT-200 thermostat. Sample calibration curves for N and P species are shown in Figure 3-7.

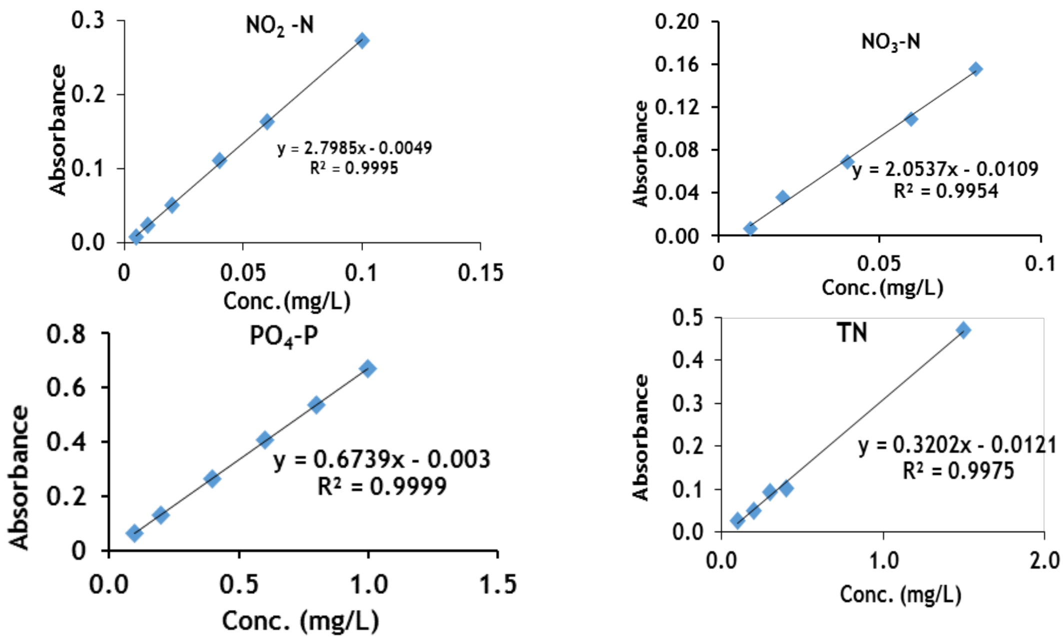


Figure 3-7 Calibration curves for NO_3-N, NO_2-N, PO_4-P and TN

3.4.6 Results of sample analyses and considerations for data analyses

The initial results obtained from the samples analysed showed that heavy metal removal efficiencies were generally high in all the 8 CW units. Specifically, the metal reductions achieved were comparable to results reported in studies with similar configurations (Blecken *et al.*, 2009b and Feng *et al.*, 2012). However, the effluent concentrations of Cu, Pb, Cd, Cr and Ni, were regularly low as shown in Table 3-11.

Table 3-11 Summary of samples with effluent concentrations reported as BDL

Format	Total number of samples	Zn	Fe	Pb	Cr	Cu	Cd	Ni
Discrete	183	-	-	164	175	176	183	183
Percentage	100 %	-	-	90	96	96	100	100

All Cd and Ni effluent concentrations were below their respective detection limits (Table 3-12). Effluent Cu and Cr concentrations were only detected at the beginning of the experiment in the gravel CW Unit 2. However, after 8 weeks Unit 2 produced effluents whose Cu and Cr concentrations were below the detection limits. The increase in Cu and Cr removal in Unit 2 is attributed to improved TSS removal resulting from the predominantly particulate heavy metals associating with TSS. Accordingly, pollutant concentrations below the analytical reporting limit were recorded as one half (1/2) the value of the lower detection limits (Avellaneda et al. 2009). The appropriateness of this approach was tested using ANOVA to determine whether there were significant differences between the effluents. Pb was selected because it was detected regularly than the other metals except for Fe and Zn. The ANOVA test established statistically significant variations in Pb removal between gravel and BFS, and between gravel and loamy sand. Thus, only Zn and Fe effluent concentrations were monitored and the data obtained used to assess the performance of the 8 VFCWs, and for comparisons with similar previous studies.

Chapter 4 Evaluation of the long-term performance of vertical flow subsurface constructed wetlands

A series of experiments were conducted to examine the long-term performance of VFCWs treating stormwater. The influents dosed into the 8 VFCWs were analysed to determine the water quality before treatment. Similarly, the effluents collected after the set retention time were analysed and the changes in the physico-chemical water quality used to assess the performance of each VFCW. Firstly, the data for the daily and weekly pollutant concentrations were processed into monthly averages. Monthly averages were considered a good indicator over the short-term because it took nearly 3 months for the CW units to attain treatment stability. Consequently, the initial experimental data were excluded.

4.1 Characterisation of influent and effluent stormwater

The physico-chemical water quality of the influent semi-synthetic stormwater dosed into the pilot-scale VFCWs was analysed and the data presented in Table 4-1. The descriptive statistics used include the maximum, minimum, mean and standard deviations. The influent concentrations for Cd and Cr were mostly below detection limits (bdl), while TSS, TN, TP, and metals like Pb and Fe had relatively high concentrations.

Table 4-1 Physico-chemical water quality of the influent stormwater

Parameters	Units	Max.	Min.	Mean	SD	dl	% bld	n
pH	-	8.08	6.78	7.5	0.31	-	-	183
Temperature	°C	25.6	6.80	16.4	4.00	-	-	183
EC	µS/cm	0.46	0.28	0.35	0.03	-	-	183
TSS	mg/L	290	79.0	167	31.00	-	-	183
PO_4-P	mg/L	1.18	0.517	0.829	0.134	-	-	183
TP	mg/L	1.70	0.748	1.042	0.141	-	-	183
N-$(NO_2)^-$	mg/L	0.15	-	0.005	0.02	0.01	-	183
N-$(NO_3)^-$	mg/L	0.42	-	0.014	0.046	0.0100	96	183
N-$(NH_4)^+$	mg/L	1.80	0.497	1.02	0.20	-	-	195
TN	mg/L	11.1	3.53	5.45	1.04	0.04817	-	183
Fe	mg/L	5.738	1.518	3.35	0.97	0.00987	-	234
Zn	mg/L	0.963	0.106	0.433	0.155	0.00139	-	234
Cu	mg/L	0.745	0.158	0.15	-	0.00122	-	156
Pb	mg/L	7.466	0.0004	0.599	-	0.00853	-	156
Cr	mg/L	0.054	-	0.03	-	0.00054	-	144
Cd	mg/L	0.026	-	0.004	-	0.00051	-	159
Ni	mg/L	1.021	0.01	0.097	-	0.00204	-	156

4.2 pH

Like the other influent parameters, the pH of the stormwater was mostly neutral, and this was achieved using conservative methods to prepare the semi-synthetic stormwater (Chapter 3, subsection 3.3.2). The pH data presented in **Table 4-2** and the temporal plots of pH in Figure 4-1 show that the pH of the influent stormwater averaged 7.5, while the effluent mean pHs ranged between 6.5 to 8.5.

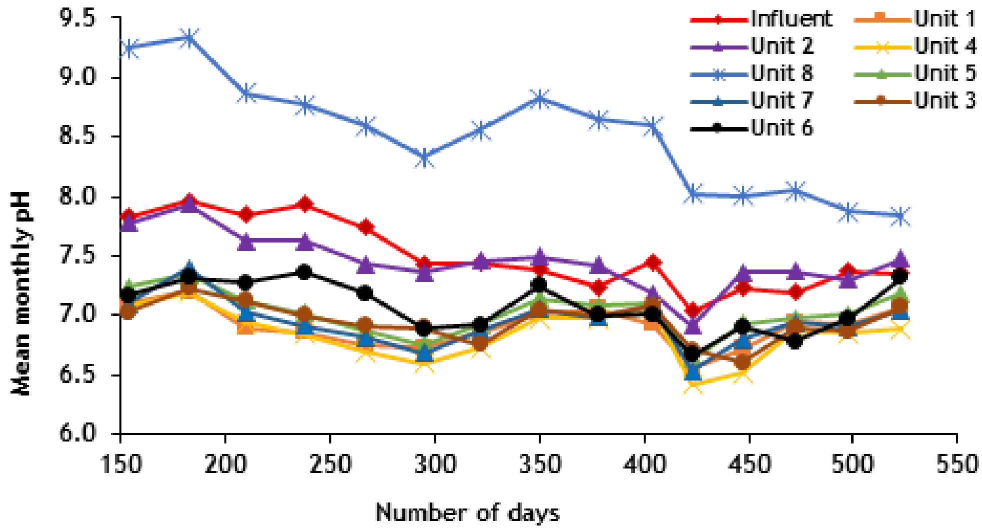


Figure 4-1 Variations of pH in the influent and effluent stormwater

While gravel media (Unit 2) maintained the mean influent pH at 7.5, all the loamy sand CWs lowered the influent pH to below 6.5. Comparatively, the effluent pH in the BFS (Unit 8) increased from 7.5 to 8.5. The data shows that effluent pH generally depended on the influent pH and the primary media. Thus, the graph in Figure 4-1 reveals that the significant pH variations were in the VFCWs containing different primary media. However, unlike the steady decrease in pH observed in the loamy sand CWs, the pH in the BFS Unit 8 initially increased but later gradually declined to level off at 8.5. The pH decline is attributed to the alkaline nature of BFS such that continuous dosing with influent stormwater diluted and washed away some of the chemical constituents of BFS.

Generally, all the VFCWs had the buffering capacity that maintained the pH within the circumneutral range of 6.5 - 7.5. Additionally, the pH conditions in the 8 VFCWs were appropriate for nitrification as well as for the solubilisation of ammonia, heavy metals and salts (EPA 2013). Furthermore, the effluent pH showed a minimal direct correlation with other analytes. However, because the precipitation of carbonate salts occurs at high pH, it is probable that the variations in the pH of CW Unit 8 might have influenced the removal dynamics of some metals and ammonia.

4.3 Temperature (˚C)

Temperature influences the physico-chemical properties of water. The temperature was monitored to establish whether the design and operational variables had any effect on some pollutant removal mechanisms that are temperature-dependent. The data shows that the influent stormwater temperatures averaged between 6.8 ˚C to 25.6 ˚C occurring in winter and the summer respectively. Correspondingly, the effluent temperatures were generally lower than the influent temperatures but within a range of 0.5˚C to 1.5 ˚C (Figure 4-2).

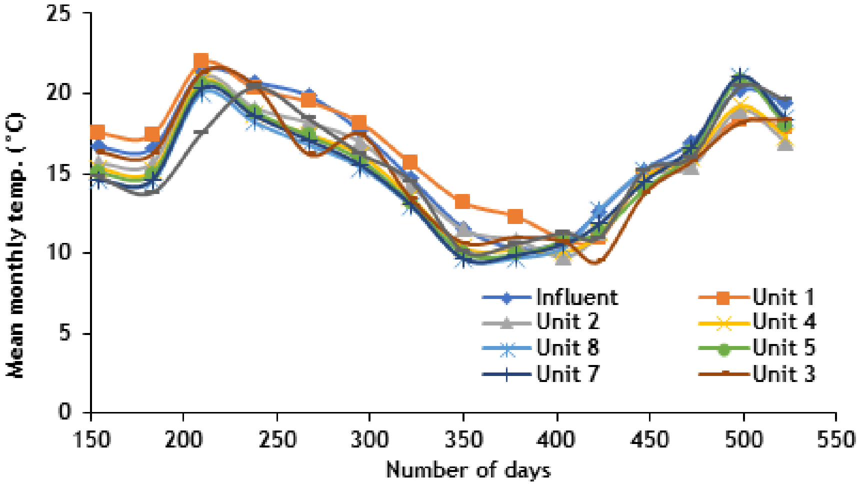


Figure 4-2 Influent and effluent temperature variations in VFCWs

The correlations between the effluent temperatures in the VFCWs were strong, ranging from 0.83 - 0.99; compared to 0.85 - 0.91 for influent and effluent temperatures. The correlation strengths decreased marginally from CW Unit 1 to 8, a pattern that is consistent with the positions of the VFCWs (Figure 3-2) hence the time of exposure to solar radiation. Thus, the VFCWs with the most extended exposure had comparatively high average temperatures indicating the influence of the external air conditions. Since temperature can influence the removal pathways of some pollutants such as nitrogen, the experimental set-up and other environmental conditions might have affected the performance of the VFCWs.

4.4 Electrical conductivity (EC)

Conductivity is often an indirect measure of the dissolved electrolyte contents in water. High dissolved ions are mostly attributed to the presence of nitrates, phosphates and sodium, although significant increases in conductivity could indicate pollution of a watercourse or change in the geology of soils. Although conductivity is mostly reported in micro Siemens per centimetre (μS/cm), in this study the 'Milli' Siemens per centimetre (mS/cm) unit was chosen to match the range of the other analyte concentrations.

The monthly influent conductivities (InEC) varied from 0.28 - 0.46 mS/cm and had a mean of 0.35 mS/cm over the monitoring period (Table 4-1). Similarly, the effluent conductivities averaged between 0.37- 0.62 mS/cm depending on the type of media. Thus, the electrical conductivity in gravel media (Unit 2) was like the influent conductivity. However, moderate increases in conductivity were observed in BFS media in CW Unit 8; while the highest increase in effluent EC was registered in the loamy sand CW Units 1, 3, 4, 5, 6 and 7 (Figure 4-3).

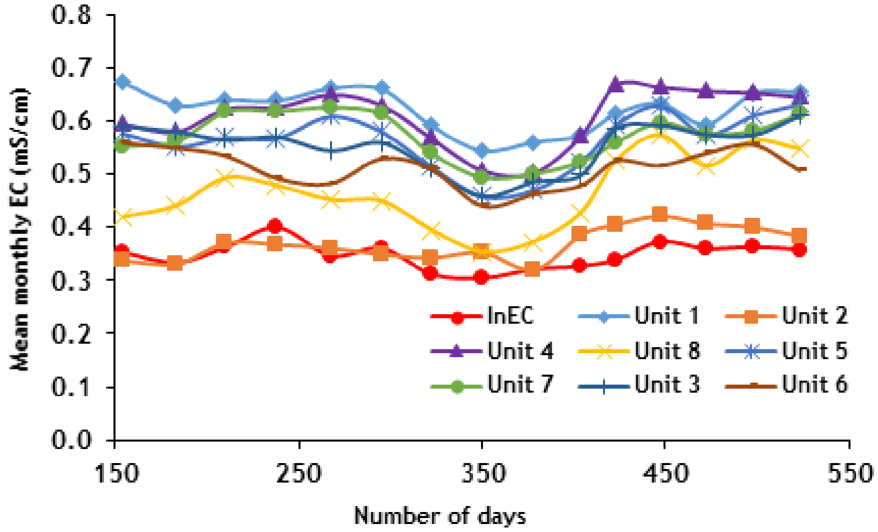


Figure 4-3 Variation in electrical conductivity in VFCWs

Furthermore, both the influent and effluent ECs followed seasonal patterns: highest in the summer; decreased in autumn and were lowest in the winter seasons. The seasonal fluctuations in the influent conductivity reflect the water quality of the influent stormwater. Thus, low conductivity of the influents during winter months suggests the stormwater consisted of mostly the less conducting pollutants (debris, leaves and decaying matter). Similarly, conductivity was highest in the summer possibly due to high concentrations of metals and other inorganic ions resulting from a combination of dry atmospheric deposition and ions released from the mineralisation of organic matter and the concentration effect associated with evapotranspiration.

Table 4-2 Effluent stormwater quality (Mean ± SD)

Parameters	Unit 1	Unit 4	Unit 2	Unit 8	Unit 5	Unit 7	n	Unit 3	Unit 6
pH	6.9 ± 0.2	6.8 ± 0.3	7.5 ± 0.3	8.5 ± 0.5	7.0 ± 0.2	6.9 ± 0.2	183	6.5 ± 0.3	7.0 ± 0.3
Temp. (^{o}C)	16.4 ± 3	15.2 ± 4	15.5 ± 3	15.0 ± 4	15.3 ± 4	15.2 ± 4	183	15.3 ± 4	15.0 ± 4
EC (mS/cm)	0.62 ± 0.04	0.61 ± 0.06	0.37 ± 0.04	0.47 ± 0.08	0.57 ± 0.06	0.57 ± 0.05	183	0.57 ± 0.05	0.55 ± 0.05
TSS (mg/L)	15 ± 11	7 ± 3	8 ± 3	9 ± 4	15 ± 9	11 ± 9	183	14 ± 10	12 ± 8
PO_4-P (mg/L)	0.11±0.06	0.11 ± 0.06	0.22 ± 0.05	0.23 ± 0.07	008 ± 0.04	0.16 ± 0.07	183	0.12 ± 0.05	0.12 ± 0.04
TP (mg/L)	0.22 ± 0.08	0.22 ± 0.09	0.35 ± 0.07	0.30 ± 0.07	0.16 ± 0.06	0.26 ± 0.11	183	0.27 ± 0.13	0.23 ± 0.10
N-NO_2^- (mg/L)	bdl	bdl	bdl	bdl	bdl	bdl	183	bdl	bdl
N-NO_3^- (mg/L)	0.24 ± 0.26	0.17 ± 0.16	0.72 ± 0.38	0.20 ± 0.2	0.2 ± 0.35	0.29 ± 0.23	195	0.20 ± 0.21	0.27 ± 0.24
N-NH_4^+ (mg/L)	0.12 ± 0.06	0.10 ± 0.04	0.07 ± 0.03	0.07 ± 0.03	0.12 ± 0.04	0.13 ± 0.08	195	0.19 ± 0.06	0.14 ± 0.09
TN (mg/L)	1.10 ± 0.62	1.09 ± 0.58	1.11 ± 0.63	1.18 ± 0.53	1.24 ± 1.00	1.59 ± 0.8	183	1.25 ± 0.58	1.73 ± 0.88
Fe (mg/L)	0.11 ± 0.08	0.039 ± 0.05	0.09 ± 0.09	0.043 ± 0.04	0.108 ± 0.10	0.06 ±0.07	234	0.38 ± 0.23	0.319 ± 0.28
Zn (mg/L)	0.11 ± 0.07	0.114 ± 0.08	0.02 ± 0.02	0.01 ± 0.02	0.10 ± 0.05	0.06 ± .05	234	0.06 ± 0.03	0.07 ± 0.03
Cu (mg/L)	bdl	bdl	bdl	bdl	bdl	bdl	156	bdl	bdl
Pb (mg/L)	0.005	0.001	0.11 ± 0.3	0.0003	0.0007	-	156	0.004	0.001
Cr (mg/L)	bdl	bdl	bdl	bdl	bdl	bdl	144	bdl	bdl
Cd (mg/L)	bdl	bdl	bdl	bdl	bdl	bdl	159	bdl	bdl
Ni (mg/L)	bdl	bdl	bdl	bdl	bdl	bdl	156	bdl	bdl

[1] n = 31 for CW Unit 3 and n = 26 for CW Unit 6; bdl = below detection limit.

4.5 Total suspended solids (TSS)

All the effluent TSS were parallel to the influent TSS concentrations, indicating that in VFCWs, the influent TSS load is related to TSS removal efficiency. Furthermore, the influent TSS concentrations were highly variable ranging from 79 - 290 mg/L with an average of 167 mg/L, much lower than the average of 4000 mg/L (Torrens et al. 2009) and 400-700 mg/L (Abdelhakeem et al. 2016). Similarly, the average effluent TSS ranged from 7-15 mg L^{-1} and were significantly lower than influent TSS, an indication that the all the 8 tidal-flow VFCWs achieved decent TSS removal.

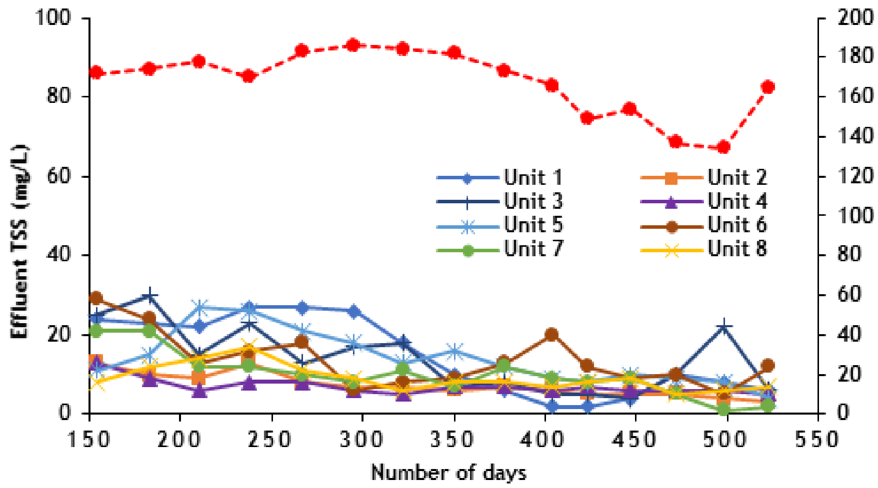


Figure 4-4 Variations of influent and effluent TSS in VFCWs

Furthermore, the cumulative mass TSS removal was greater than 90 % in all the VFCWs showing that the CW units had a excellent filtering capacity, as evidenced by the effluent TSS in Figure 4-4. Equally, the 24-hour HRT suited sedimentation processes for TSS removal. However, although Units 1 and 4 had similar design and operational strategy; TSS removal in Unit 1 was less efficient than in Unit 4. This discrepancy is attributed to the subtle variations in the media configurations. Thus, compaction of the media was inadvertently non-uniform resulting in different porosities, hydraulic conductivities and velocities of discharge (Section 3.4.4). Therefore, the water flow, sedimentation and filtration rates varied leading to minimal differences in TSS removal in the control units.

Generally, the variations in TSS removal trends are linked to the development of the microbial biofilms in the media bed. Since the growth of biofilms alters pore geometry and transport behaviour of active substances (Volk et al. 2016), the improved filtration of solids in all the VFCWs was in response to the change in the properties of the media hence the gradual increase in TSS removal (Figure 4-4) as each CW unit matured into an efficient treatment systems.

Table 4-3 Cumulative mass load reduction (%) and mass removal rate (g m^{-2} d^{-1})

Cumulative mass load reduction (%)							
Parameters	TSS	$P\text{-}PO_4^-$	TP	$N\text{-}(NH_4)^+$	TN	Fe	Zn
Unit 1	91.4	87.2	80.2	88.6	81.0	96.9	76.4
Unit 4	95.8	87.3	80.3	91.3	81.2	98.9	76.8
Unit 2	95.5	73.9	67.3	93.7	80.1	97.3	96.1
Unit 8	94.5	73.1	72.1	93.4	79.1	98.8	98.6
Unit 5	95.6	95.0	92.4	94.2	88.6	98.4	88.5
Unit 7	89.9	71.2	62.2	79.9	56.3	97.0	80.3
Unit 3	95.5	73.9	67.3	93.7	80.1	97.3	96.1
Unit 6	94.5	73.1	72.1	93.4	79.1	98.8	98.6
Contaminant mass removal rate r (g m^{-2} d^{-1})							
Parameters	TSS	$P\text{-}(PO_4)^-$	TP	$N\text{-}(NH_4)^+$	TN	Fe	Zn
Unit 1	2.823	0.014	0.016	0.017	0.082	0.06	0.007
Unit 4	2.957	0.014	0.016	0.018	0.082	0.06	0.007
Unit 2	2.947	0.012	0.013	0.018	0.081	0.06	0.008
Unit 8	2.917	0.012	0.014	0.018	0.062	0.08	0.008
Unit 5	2.952	0.015	0.018	0.018	0.090	0.06	0.008
Unit 7	2.776	0.011	0.012	0.015	0.057	0.06	0.007
Unit 3	3.044	0.015	0.018	0.018	0.100	0.06	0.004
Unit 6	3.056	0.015	0.019	0.018	0.096	0.06	0.008

4.5.1 TSS variations in the different media types

The three different media types were all operated at 2.5 % WWAR. However, each primary media type had distinct properties with regards to pH, porosity and hydraulic conductivity(Table 3-2). Because media properties can influence some of the contaminant removal pathways, the effect of the media on TSS removal was assessed from the cumulative mass load reductions, mass removal rate, and volumetric rate constants presented in Table 4-3 and Table 4-4.

BFS and gravel had comparable grain sizes which perhaps explains the comparable cumulative mass load reductions of TSS achieved in CW Units 8 and 2 (Table 4-3). However, TSS removal in Unit 2 was generally stable while TSS removal in Unit 8 exhibited a gradually decreasing trend related to pH declines in Figure 4-1. It is suggested that TSS removal in Unit 2 was achieved through sedimentation and filtration. However, in Unit 8 some solids may have undergone adsorption due to the chemical properties of BFS.

Table 4-4 Effect of design on the volumetric rate constant, K_V (d^{-1})

Variable	TSS	P-(PO_4)$^-$	TP	N-(NH_4)$^+$	TN	Fe	Zn
Unit 1	2.75	2.09	1.55	2.23	1.73	3.65	1.54
Unit 4	3.19	2.16	1.55	2.41	1.77	4.81	1.47
Unit 2 (Gravel)	3.21	1.33	1.09	2.78	1.73	3.91	3.56
Unit 8 (BFS)	2.97	1.30	1.24	2.70	1.63	4.83	3.73
Unit 7 (1.5 %)	3.02	1.74	1.46	2.11	1.36	4.23	1.79
Unit 5 (5.0 %)	2.58	2.41	1.93	2.18	1.68	3.57	2.21
Unit 3 (SDR)	2.68	0.015	1.39	2.34	1.52	2.24	1.92
Unit 6 (EDR)	2.62	0.015	1.54	2.10	1.34	2.37	1.92

Relatedly, the mass load reduction of TSS in the loamy sand VFCWs 1 and 4 is 91 % and 96 %, equivalent to mass removal rates of 2.82 and 2.96 g m^{-2} d^{-1} respectively. In the gravel CW, the mean TSS removal was 96 % or 2.95 g m^{-2} d^{-1}, while in the BFS media, TSS reduction was 94 % or 2.92 g m^{-2} d^{-1} shown in Table 4-3 and Table 4-4.

Similarly, the volumetric removal constants (K_v) in Table 4-4 showed that the loamy sand CWs 1 and 4 had their average K_v at 2.75 and 3.19 d^{-1} respectively; while gravel and BFS produced K_v of 3.21 d^{-1} and 2.97 d^{-1} respectively. It is observed that gravel media produced a slightly higher K_v than that of the loamy sand, Unit 4, which had had the highest TSS reduction. Consequently, the ANOVA revealed no significant differences in TSS removal between the gravel and loamy sand media ($p = 0.06$). This result compares well with that of Abdelhakeem et al. (2016) in which the different media were reported as having no significant effect on the Kv of TSS. However, the magnitude of the p-value suggests that there were subtle variations in the different media which likely influenced TSS first-order degradation kinetics. Vymazal and Kröpfelová (2008) concluded that total suspended solids are mainly removed through physical processes of sedimentation, straining and filtration; and that the processes occur by impaction of solid particles onto the roots and stems of the wetland macrophytes, and on the media bed. Consequently, influent dosing by fill and drain possibly resulted into variable sedimentation rates of suspended solids in gravel and loamy sand media beds hence the observed differences.

Besides, after feeding the VFCWs with stormwater, the water was held for a fixed retention time of 24 hours before the effluents were released. During these 24 hours, the suspended solids get trapped in the pore spaces of the media, resulting in TSS retention. Therefore, among the loamy sand CWs, Unit 4 had the highest TSS removal reductions possibly because the loamy sand supported the growth of macrophytes roots which possibly enhanced TSS removal through an increase in the surface area of the media bed. Moreover, the roots of the macrophytes likely reduced stormwater flow velocities thereby reinforcing settling and filtration in the root network. However, there were no statistically significant differences in the TSS volumetric rate constants between the media types, an indication that TSS removal was similar regardless of the removal processes involved.

4.5.2 TSS removal variations in the different WWARs

The different WWARs show contrasting TSS removal in the loamy sand VFCWs. TSS reduction at 2.5 % WWAR averaged 93.6 % (Units 1 and 4); 5.0 % WWAR reached 95.6 % (Unit 5) while the 1.5 % WWAR achieved lower TSS removal of 90 %. However, the TSS volumetric rate constants at 2.5 % and 1.5 % WWAR were generally higher as shown in Figure 4-5. It is that the high influent loads dosed in the 2.5 % and 1.5 % WWARs resulted in more TSS being trapped and hence effective filtration. However, the low influent loads at 5.0 % WWAR meant the TSS removal in Unit 5 was initially low because of the low influent loads, thus filtration was limited to the media bed. However, as after 250 days of monitoring, the 5.0 % WWAR had improved TSS reduction because more solids were trapped and hence improved filtration. However, the best overall TSS removal was in the 1.5 % WWAR due to the high influent volumes treated in the 1.5 % CW Unit. Blecken *et al.* (2010) theorised that repeated loadings lead to “repacking and settling” of the media bed which subsequently decreases the media pore sizes and hence improves solids retention. As more solids are retained, media resuspension is reduced, and the aggregated solids serve as adhesive surfaces on which more incoming solids may be deposited (Hatt *et al.*, 2007c). The larger inflow volumes in the 1.5 % WWAR CW may have increased this effect hence the observed TSS removal.

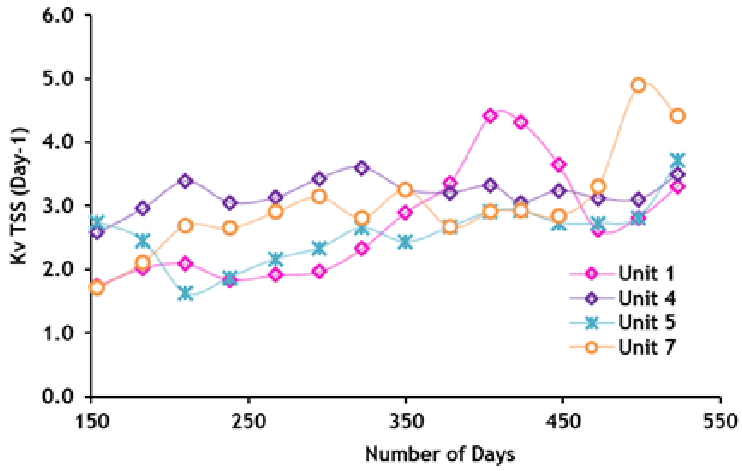


Figure 4-5 Volumetric removal constants at different WWARs

4.5.3 TSS variations in short dry and extended dry rest periods

The variation in the volumetric removal constants under short and extended dry rest periods is shown in Figure 4-6. Although Unit 3 recorded slightly higher TSS removal than Unit 6 (Table 4-3). However, no significant differences in TSS removal were found between the short dry and extended dry rest regimes ($p = 0.986$).

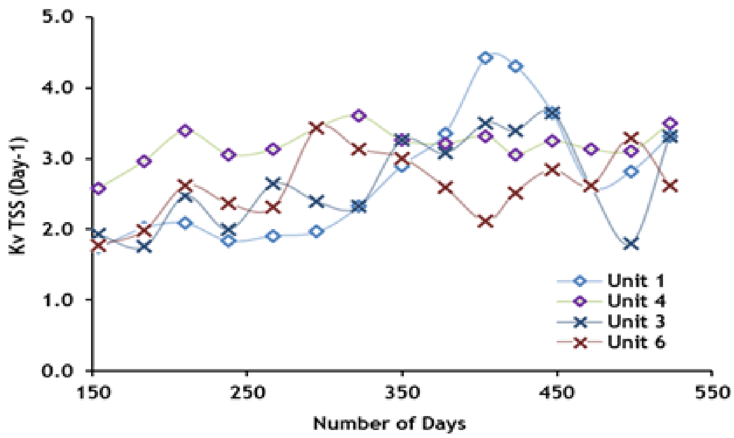


Figure 4-6 TSS volumetric rate constants under dry rest conditions

4.5.4 Conclusions on TSS removal in the different VFCWs

TSS removal improved in all the CWs conceivably because the CWs matured both in structure and function over the monitoring period. Consequently, the mean TSS removals (Table 4-3) show that the 8 CWs attained high TSS removals ranging from 90 % to 96 %, with Units 4 and 8 registering the highest TSS removals, attributable to media specific influences. Thus, the fine loamy sand in Unit 4 was adequate for straining, sedimentation and adsorption of the suspended solids.

Additionally, the presence of macrophytes in Unit 4 likely supported microbial growth, which in turn enhanced TSS removal by both impaction and biodegradation. Similarly, Unit 8 contained BFS media which consists of CaO, SiO_2, Al_2O_3, and MgO. The elemental compositions of BFS have adsorbent properties which possibly contributed to chemisorption and sorption processes and hence elevated TSS removals. Evidence for this proposition is inferred from the TSS removal trends: high TSS removal at the start of monitoring; and the subsequent decline in TSS removal as the pH of Unit 8 declined. Therefore, the variations in TSS reduction in Units 4 and 8 are indicative of the TSS removal mechanisms in each of these units. Although Unit 4 consisted of fine sand particles; the process of sedimentation and subsequent straining and filtration were effective in Unit 4. However, adsorption is known to influence removal of smaller particles, TSS removal by adsorption in CW Unit 4 was likely insignificant.

Furthermore, TSS removal of 90 - 96 % obtained in this study were consistent with TSS removal reported in previous studies (Garcia et al. 2010; Blecken et al. 2011; Malaviya and Singh 2012; Schmitt et al. 2015). However, the removal rates obtained for all the 8 VFCWs in this study were less than 5 g m^{-2} d^{-1} and therefore lower than the 18 g m^{-2} d^{-1} reported for VFCWs (Abdelhakeem et al. 2016). The discrepancies in TSS removal in this and earlier researches could be attributed to the differences in the influent pollutant loads (wastewater quality) and the hydraulic loading rates. Overall, TSS removal performances achieved in all the 8 VFCWs is satisfactory over the 2-year monitoring period. This is because the effluent TSS concentrations were below the 20 mg/L standard for clear water (MDEQ. n.d). Thus, the 8 VFCWs could be used in the treatment of stormwater to meet requirements for effluent discharge into “good” ecological status watercourses under the UK TAG, Water Framework Directive (2008); water reuse in Egypt (Abdelhakeem et al. 2016), Michigan (MDEQ. n.d) and Australia (Malaviya and Singh 2012).

4.6 Heavy Metals

Although several heavy metals were monitored, most metal species had effluent concentrations below their respective limits of detection, except Fe and Zn.

4.6.1 Iron (Fe)

The average influent and effluent Fe concentrations are presented in Table 4-1 and **Table 4-2** respectively. The average concentration of Fe in the influents was 3.35 mg/L an indication that influent Fe was generally particulate. However, Fe in the effluents varied between 0.039 - 0.379 mg/L, the least Fe concentrations of 0.039 mg/L (99 % Fe reduction) and 0.11 mg/L (97 % Fe removal) occurred in the loamy sand CWs 4 and 1 respectively. The discrepancies in Fe between CWs 1 and 4 are attributed to inconsistencies in media compaction.

The mean effluent Fe in the gravel media was 0.092 mg/L hence 97 % Fe removal, while effluent Fe in BFS was 0.043 mg/L representing a 99 % Fe removal. These results compare well with effluent Fe concentrations of between 0.25 - 1.2 mg/L and Fe removal of 81- 97 % for VFCWs reported by Feng et al. (2012).

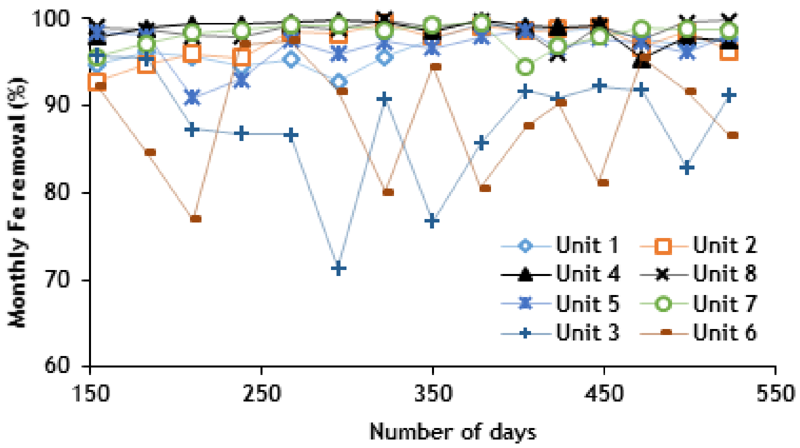


Figure 4-7 Fe removal in stormwater VFCWs

The design and operational regimes investigated show that Fe concentrations in the influents were reduced to below the theoretical upper discharge limit of 28.7 mg/L. Additionally, Figure 4-7 shows that although Fe removal was highest in the loamy sand (Unit 4), but generally comparable to the Fe reductions in BFS and gravel CWs. Additionally, in all the media types, Fe removal exceeded 95 %. Because influent Fe was mostly in particulate form, it is possible that Fe and TSS removal trends were related. The relationship is evidenced through strong correlations between effluent TSS and Fe in Unit 1 (0.82), Unit 2 (0.88), Unit 4 (0.96) and Unit 8 (0.74).

Although high Fe removals were registered in all the CW designs, the ANOVA established that there were significant differences between the volumetric rate constants for Fe in the different VFCWs. A Tukey post hoc test revealed that Fe removal was significantly different between the regularly wet and intermittently dry rested VFCWs (p= 0.000); between the loamy sand and BFS media (p = 0.01); as well as between the gravel and BFS media (p = 0.029). However, there were no significant differences in Fe removal between the loamy sand and gravel (p = 0.964).

Likewise, the effect of operating the CWs at variable WWAR had no statistical significance on the volumetric removal constant for Fe.

4.6.2 Zinc (Zn)

Effluent Zn varied between 0.0064 to 0.12 mg/L in the first year, and 0.007 to 0.11 mg/L in the second year (Figure 4-8). From Table 4-2, BFS media (Unit 8) registered the least mean effluent Zn (0.006 mg/L) and hence the highest Zn removal of 99 %. Comparatively, the highest effluent Zn was in CW Units 1 (0.109 mg/L) and 4 (0.114 mg/L) and the lowest Zn removals of 76 % and 77 % respectively (Figure 4-8).

In the gravel media (Unit 2), effluent Zn averaged 0.018 mg/L, representing 96 % Zn reduction. Therefore, Zn removal in the gravel media was higher than that in the loamy sand CW Units 1 and 4. More importantly, Zn removal in Unit 2 steadily improved initially from 91 % to the final average Zn reduction of 96 %.

Despite treating the highest pollutant loads, CW Unit 7 (1.5 % WWAR) attained 80 % Zn removal, higher than both CW Units 1 and 4 (2.5 % WWAR). Similarly, Zn removal in Unit 5 was 89 %, higher than at 2.5 % WWAR probably due to the low pollutant loads treated at 5.0 % WWAR. Likewise, Units 3 and 6 registered the lowest effluent Zn concentrations of 0.062 mg/L and 0.065 mg/L, corresponding to Zn reductions of 96 % and 99 % respectively.

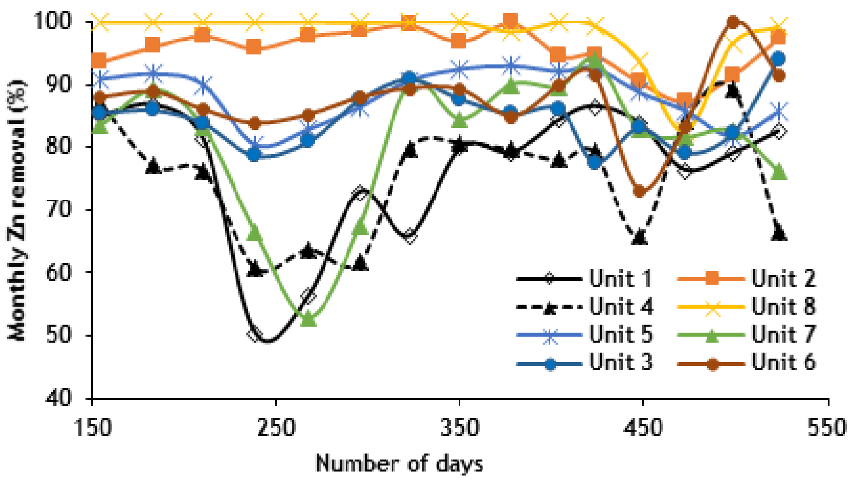


Figure 4-8 Zinc removal in VFCWs treating stormwater

Although the overall per cent Zn reductions were comparable in the different CWs, there were statistically significant differences in the volumetric removal constants for Zn between the media types as determined by ANOVA ($p = .001$). The Tukey post hoc test revealed that the K_v for Zn was significantly lower in loamy sand compared to gravel (3.56 d^{-1}) and BFS (3.73 d^{-1}) as shown in Table 4-4. However, no significant differences in Kv were found between gravel and BFS ($p = 0.995$).

Furthermore, there were statistically significant differences in the volumetric removal constants of Zn between the different WWARs as determined by the one-way ANOVA ($p = 0.001$). The Tukey post hoc test showed that Zn removal was statistically significantly lower at 2.5 % WWAR (1.54 d^{-1}) and 1.5 % WWAR (1.79 d^{-1}) compared to the 5.0 % WWAR (2.21 d^{-1}). There were no statistically significant differences between the 2.5 % and 1.5 % WWARs ($p = 0.263$). Likewise, statistically significant differences were found between the volumetric removal constants for Zn between the CW Units operated on the short dry and extended dry rest regimes as determined by ANOVA ($p =.013$).

Overall, Zn removal was most successful in BFS Unit 8, hence most effluent Zn concentrations below the limit of detection of Zn, especially before 250 days of monitoring. Zn removal in Unit 8 is likely related to TSS because Zn was mainly particulate in the influents. Thus, the successful TSS removal and Unit 8 may have enhanced the removal of Zn hence the higher K_v for Zn removal in CW Unit 8.

Moreover, Zn removal performance of CW Unit 8 could be linked to the pH variations of BFS (Figure 4-9). It is suggested that the alkaline pH of BFS media was ideal for Zn removal by precipitation (Rieuwerts et al. 1998). Furthermore, Rieuwerts et al. (1998) reported that cation adsorption is proportional to pH such that at higher pH, Zn adsorption is readily achieved. Similarly, the elemental composition analysis of the media revealed that BFS contained 24 % Ca and 4 % Mg. Both Mg and Ca are active adsorbents for metal ions in neutral and alkaline conditions (Kim et al. 2008). Besides, the existence of sulphur in BFS (1%) perhaps favoured Zn removal in Unit 8 by forming precipitates of ZnS, removed as part of the TSS load (Arroyo et al. 2010).

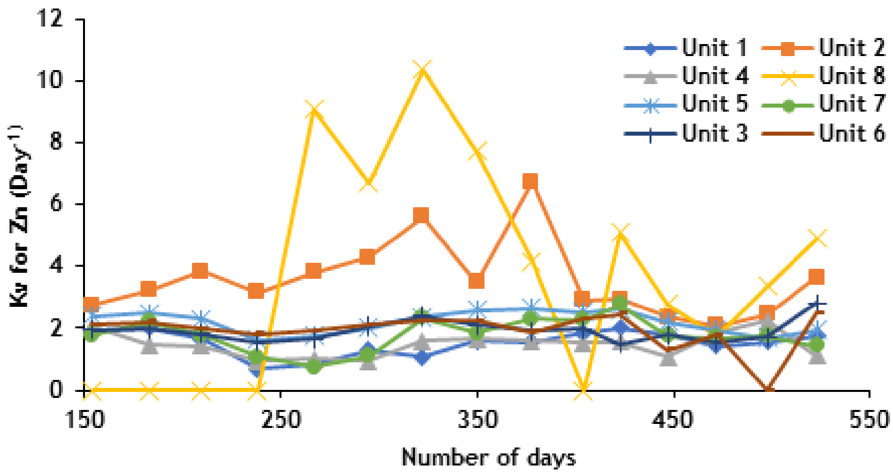


Figure 4-9 Variations in Zn volumetric rate constants in the different VFCWs

However, there were two notable declines in Zn removal among the loamy sand CW Units (1, 3, 4, 5, 6 and 7). The first decline occurred between the summer and early autumn (200–300 days); while the second decline occurred in all the CW units between the spring and summer (450 - 550 days). It is likely that these declines represented Zn remobilisation due to decaying DOM from macrophyte growth following the favourable summer conditions. Therefore, the high effluent Zn in loamy sand CWs was a mixture of influent Zn and the possibly the earlier adsorbed Zn released from on the media. Consequently, the Zn removal mechanisms in this study likely involved the physical processes of filtration, sedimentation, adsorption, and straining (Blecken et al. 2009) and (Blecken et al. 2011). However, other possible processes include the removal of dissolved Zn through microbial uptake in soils and organic matter, plant uptake, precipitation and complexation in the media (Blecken et al. 2009; Feng et al. 2012) and . It is probable that the different combinations of removal mechanisms enabled the 8 VFCWs to reduce particulate and dissolved Zn to concentrations below the upper discharge limits (0.23 mg/L) computed for this study.

4.6.3 Conclusions on Zn removal

Zn removal in all the investigated VFCWs averaged between 76 to 98 %. Previous laboratory-scale experiments reported performances of up to 90 % (Hatt et al. 2007c, b), similar to experiments by (Blecken et al. 2009a, 2009b; Blecken et al. 2011) and (Feng et al. 2012). The differences between the Zn removals obtained in this study and that reported in the previous studies is attributed to the variations in influent strengths, hydraulic loadings and the period of monitoring.

Although the Zn removal trends for the intermittently dosed Units 3 and 6 are comparable to the Zn removal in Units 2 and 8, this comparison could not be associated with the media nor the WWAR. It is recommended that future studies investigate Zn removal in gravel and BFS at 1.5 % and 5.0 % WWARs. Similarly, investigations into the effect of short and extended dry rest periods on Zn removal in gravel and BFS could help highlight the impact of WWAR on Zn removal under short dry and extended dry conditions.

4.7 Total inorganic and total organic nitrogen

Nitrogen (TN) was monitored in both the influents and effluents to understand the critical nitrogen transformations (nitrification, denitrification, volatilisation, and plant uptake) relevant to TN removal. Crucially, influences of environmental conditions, design and operational timespans on TN removal were evaluated. TN comprises of total organic nitrogen (TON) and total inorganic nitrogen (TIN). TIN consists of free-ammonia ($NH_3/NH_4\text{-}N^+$), nitrite (NO_2-N) and nitrate (NO_3-N).

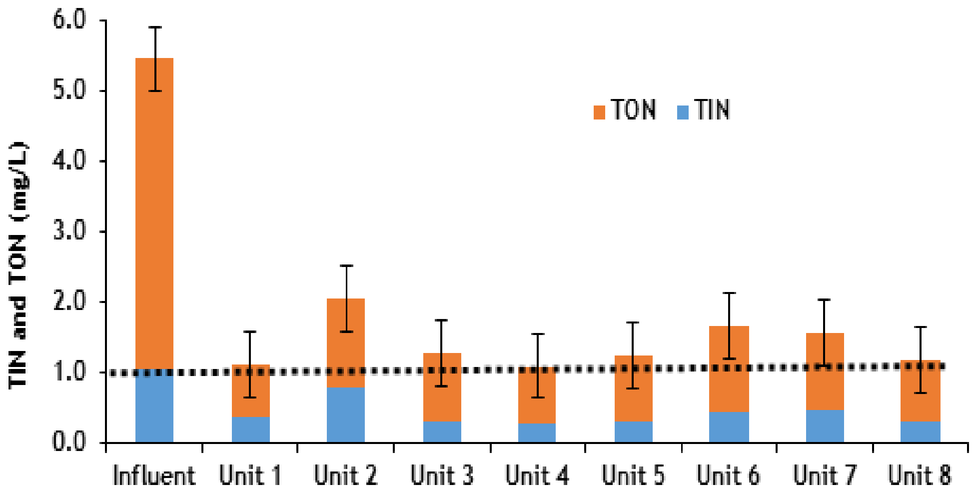


Figure 4-10 Composition of TN in influents and effluents

The mean concentrations of TN compositions (Figure 4-10) show that TON was higher than TIN in both the influents and effluents. The variation in TON and TIN suggests that both the influent and effluent TN were mainly organic N (decaying plant and animal forms). However, TIN and TON decreased significantly in all the 8 VFCWs, an indication that the VFCW designs were suitable for TIN and TON removal.

Furthermore, the data for TIN was most indicative of free-ammonia nitrogen (NH_3-N/NH_4-N) because the oxidised forms of N (NO_2-N and NO_3-N) were regularly below their respective detection limits. Overall, all the VFCWs reduced the dominant TON in the influent from 4.5 mg/L to below 1.0 mg/L (Figure 4-10).

The reduction in TON and TIN shows that the different media developed contrasting removal patterns. Thus, gravel media registered the highest effluent TIN and TON, attaining the least TIN and TON removal among the 8 VFCWs. By contrast, loamy sand Units 1 and 4 removed the most TIN and TON (Figure 4-10), while the BFS Unit 8 had comparable TIN and TON effluent concentrations to that from loamy sand.

The variations in TIN and TON in the different media could be related to the properties of the media. Thus, loamy sand which has a lower porosity (32 %) possibly favoured both aerobic and anaerobic N transformation hence the low TIN and TON.

Likewise, high TIN and TON in gravel media suggest that the removal of dissolved N was less effective probably due to the relatively large size of gravel grains and hence high porosity (40 %). Thus, Unit 2 likely developed aerobic conditions, thereby limiting the anaerobic N transformation. Similarly, although BFS and gravel have comparable grain sizes, the effluent TIN and TON in the BFS Unit were comparatively low. This suggests that BFS achieved TIN and TON removal by different mechanisms. The high alkaline pH of BFS media (8.5 - 9.5) suggests denitrification and volatilisation of N-NH_3 were viable pathways.

Relatedly, TIN and TON in effluents of CW Units 5 (5.0 % WWAR) and Unit 7 (1.5 % WWAR) varied. Both TIN and TON were higher at 5.0 % WWAR than at 1.5 % WWAR suggesting that N removal was less effective at 5.0 % than at 1.5 % WWAR, due to the high pollutant loads treated by Unit 7.

Similarly, the TIN and TON removal in CW Units 3 and 6 was mainly influenced by the effect of drying conditions on the development of the biological communities, such that more extended dry periods decreased the influent supply of organic material and hence limited the growth rate of important microbial communities. Consequently, in Unit 6, there is less ammonification and denitrification (low TIN removal) compared to Unit 3 which experienced more dosing events.

Generally, some influent TIN and TON will have been retained as sludge in the media bed, while N uptake by plants is variously reported as insignificant in VFCWs. Thus, the biological mechanisms of N removal were supported by the aerobic and anaerobic conditions that developed in the different media beds. Moreover, the tidal-flow operation enhanced aeration by convection during and after batch feeding as well as exposed the internal biofilms to atmospheric oxygen required for the oxidation of organic matter and ammonium-N.

4.7.1 Nitrate-nitrogen (NO_3-N)

Generally, pollutant removal and microbial activity in CWs is heavily reliant on carbon, nitrogen and sulphur cycling. Nitrates account for about two-thirds of TN loading to surface waters (Beutel et al. 2009). This makes nitrates a key contributor to the proliferation of algal blooms in freshwater ecosystems (Chang et al. 2013).

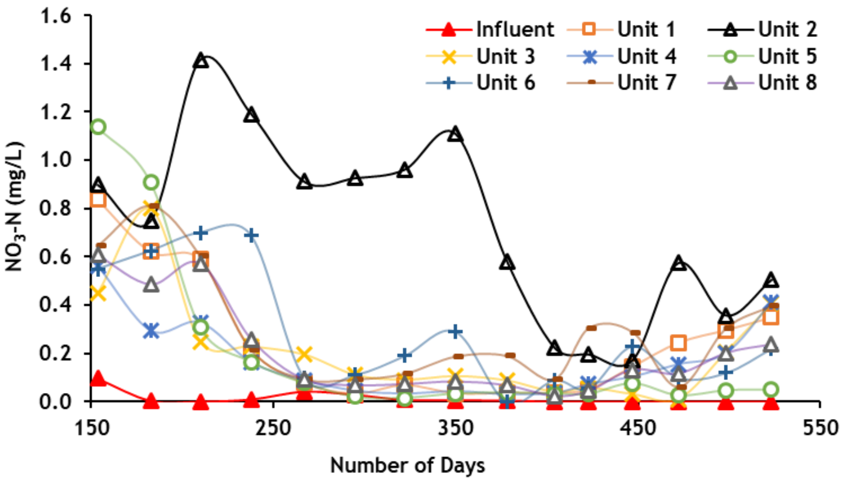


Figure 4-11 Nitrate N-(NO_3)$^-$ variations in VFCWs

Evidence for nitrification in the investigated CW units is inferred from the high effluent NO_3-N (Figure 4-11). A tidal flow system enables atmospheric oxygen to enter the VFCWs between treatments. The media become saturated with oxygen which leads to oxidation of NH_4-N^+ to NO_3-N.

Although N-(NO_2)$^-$ was monitored over the study period, the N-(NO_2)$^-$ in the effluents was mostly below the detection limit (Table 4-2). Similarly, the effluents registered no N-(NO_2)$^-$, indicating that nitration was effective during the 24 hours retention period. This time was adequate for nitrification agents (AOB and NOB) to convert N-(NH_4)$^+$ to N-(NO_3)$^-$. The initial nitrification rates were high in all the CWs except Unit 2 probably because gravel media lacked the conditions to sustain the microbial communities involved in nitrification. However, as the CWs matured, nitrification in Unit 2 improved across the seasons. Conversely, both the loamy sand and BFS units experienced gradual declines in nitrification. The reduction in nitrification was fastest in BFS than in loamy sand. The trends in nitrification in the various CWs are consistent with the N transformation reactions in the Equations 4-1 to 4-4:

NH_3 (aq) + O_2 (g) + 2H+ (aq) + 2e- → NH_2OH (aq) + H_2O (l) 4-1

NH_2OH (aq) + H_2O (l) → 5H+ (aq) + NO_2− (aq) + 4e-....................... 4-2

½O_2 (g) + 2H+ (aq) + 2e- → H_2O (l).................................... 4-3

Combining Equations 4-1, 4-2 and 4-3 gives Equation 4-4 below:

NH_3 (aq) + 1.5O_2 (g) → H+ (aq) + NO_2− (aq) + H_2O (l).................... 4-4

Equation 4-4 shows that nitrification leads to consumption of approximately 4.3 mg/L of O_2 per mg N oxidised (EPA 2002). This could explain the high nitrification in CW Unit 2: gravel drew in more atmospheric oxygen than loamy sand and BFS.

However, it has been reported that as CWs mature, there is an increase in the microbial community, number and complexity (Kadlec and Wallace 2009b) with time. Perhaps it is the evolution in microbial structure and function coupled with good aeration in CW Unit 2 that provided favourable conditions for AOB to reduce N-$(NH_4)^+$ to N-$(NO_3)^-$ in the gravel media. Furthermore, gravel media maintained a neutral pH, indicating that acidification due to nitrification reactions had minimal effect on pH changes in Unit 2. The reduction in nitrification in Unit 2 in the later stages is linked to microbial self-inhibitions that accompany the high biological activity. As microbes increase, competition for oxygen is initiated. Under these conditions, the resilient forms of anaerobic bacteria emerge, switching N removal from aerobic to anaerobic pathways, hence the decline in N removal in Unit 2.

Similarly, CW Unit 8 initially had high nitrification rates possibly due to a combination of atmospheric aeration and alkaline pH (porous and alkaline pH of 8.5). The pH ranges of between pH 7.0 and 8.0 are known to favour *Nitrosomonas spp*, whose optimum pH is 7.5 to 8.0 (EPA 2002). Furthermore, the viability of nitrifying bacteria depends on pH levels between 6.6 to 9.7 (Lee H.Odell et al. 1996). Thus, unlike loamy sand CWs that experienced declining nitrification; the alkaline BFS favoured ammonia reduction by *Nitrosomonas spp* and *Nitrobacter spp*.

However, as the pH in the BFS Unit 8 declined (acidification and biofilter washing), nitrification rates declined consistently with pH. Phylogenetic analyses of biological removal of N-$(NH_4)^+$ revealed that microbial compositions and structure tend to shift within the media bed and that *Nitrosomonas spp* becomes the major AOB (Jun and Wenfeng 2009). Thus, the differences in nitrification rates in the VFCWs could be attributed to variations in microbial species and succession in response to pH.

4.7.2 Free ammonia nitrogen (N-NH_3 and N-$(NH_4)^+$

Experimental results in **Table 4-2** reveal that the effluent N-$(NH_4)^+$ in the VFCWs (0.07- 0.19) mg/L were lower than the influent mean concentration of 1.02 mg/L. The reduction in the N-$(NH_4)^+$ suggests that VFCWs nitrified the stormwater influents to form nitrate-N. The high N-$(NO_3)^-$ in the effluents relative to the influents further demonstrates that a combination of the long-fixed retention time, batch dosing and tidal-flow operational strategy can draw oxygen into the VFCWs.

Although Units 1 and 4 were similar, Unit 4 had effluent NH_4-N^+ like that in CW Units 2 and 8. However, the variation of NH_4-N in both gravel (Unit 2) and BFS (Unit 8) was similar in that both gravel and BFS registered the lowest average effluent NH_4-N^+ of 0.07 mg/L. The experimental data for NH_4-N^+ removal in Figure 4-14 show that Units 2, 4 and 8 reduced N-$(NH_4)^+$ by more than 85 %. Consequently, N-$(NH_4)^+$ reduction was marginally higher in gravel (94 %) and BFS (93 %) than in loamy sand (90 %) perhaps because the media grain sizes of gravel and BFS is larger than that of loamy sand, hence high porosity favoured aeration of the gravel and BFS beds.

Also, N-$(NH_4)^+$ removal in BFS Unit 8 declined with the decline in effluent pH. It was earlier stated (section 4.3) that although correlations for TSS removal and effluent pH were weakly negative, the similarity in the decline in pH and TSS removal patterns pointed to other factors possibly influencing TSS-pH relationships in Unit 8. Therefore, the trends of N-$(NH_4)^+$ removal suggests that N-$(NH_4)^+$ could have contributed to the decline in the effluent pH in Unit 8. The decline in pH could be attributed to the reactions leading to the formation of H^+ (Equations 4-1 to 4-4).

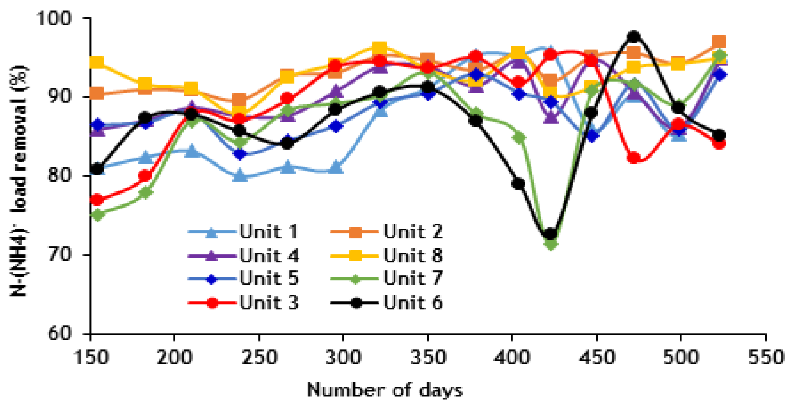


Figure 4-12 Monthly mean removal of N-$(NH_4)^+$ in VFCWs

However, the removal relationships between pH, N-$(NH4)^+$ and TSS seem to be non-linear because no strong direct correlations were found. Relatedly, N-$(NH_4)^+$

removal by volatilisation is likely to have depended on the pH of each VFSSCW. Thus, Units 2 and 8 with mean pHs of 7.5 and 8.5 respectively registered the highest N-$(NH_4)^+$ removal. At the start of the experiments, the pH of Unit 8 was 9, and this attained the initial highest N-$(NH_4)^+$ removal. However, N-$(NH_4)^+$ reduction decreased gradually with the declining pH of BFS. This suggests that volatilisation which depends on pH (9.3 and above) was a key removal mechanism in Unit 8. High alkalinity in the CWs favours the conversion of N-$(NH_4)^+$ to NH_3-N with the release of ammonia gas (Cooper et al. 1996b). However, below pH 7.5 the volatilisation of NH_3 in subsurface flow wetlands is negligible (Saeed and Sun 2012). It is likely that the relatively large grain size of gravel and BFS favoured the volatilisation of NH_3 gas thereby contributing to the observed high removal rates.

Correspondingly, the regularly dosed loamy sand CWs had N-$(NH_4)^+$ with an average of 0.12 mg/L, while the short dry and extended dry loamy sand Units 3 and 6 both recorded the highest mean N-$(NH_4)^+$ of 0.19 mg/L and 0.14 mg/L respectively. The relatively high effluent N-$(NH_4)^+$ in Units 3 and 6 suggests that nitrification was less efficient in the rest units than in the regularly dosed CW Units 1 and 4. This observation could be attributed to inefficient growth of the microbial communities.

Likewise, the 5.0 % CW Unit 5 and the 1.5 % CW Unit 7 produced 0.12 mg/L and 0.13 mg/L respectively of N-$(NH_4)^+$. The differences in N-$(NH_4)^+$ suggest that the removal of N-$(NH_4)^+$ was influenced by the media type, WWAR and dosing regime. Thus, to examine the differences in the performances of the various designs, the volumetric rate constant for N-$(NH_4)^+$ were computed (Table 4-4). All the 8 VFCWs attained mean volumetric rate constants (K_v) for N-$(NH_4)^+$ between 2.1 to 2.78 d^{-1}. However, the mass removal rates were minimal and ranged from 0.015 - 0.018 g m^{-2} d^{-1}. Consequently, the ANOVA (p = 0.002) found statistically significant differences in N-$(NH_4)^+$ removal between the different CWs. Additionally, a posthoc test identified that K_v for N-$(NH_4)^+$ was significantly lower in loamy sand and BFS as compared to gravel, but no significant differences were found between BFS and gravel (p = .867).

Similarly, there were significant differences in N-$(NH_4)^+$ removal between the different WWARs (p = 0.000). The Tukey test revealing that N-$(NH_4)^+$ removal was significantly lower at 1.5 % (2.11 d^{-1}, p = 0.000) and at 5.0 % (2.18, p = 0.041) as compared to the 2.5 % WWAR (2.23 d^{-1}, p= 0.015). However, no significant differences were found between the volumetric rate constants for N-$(NH_4)^+$ between the 2.5 % and 5.0 % (p = 0.319) ; and between the short dry and extended dry units.

4.7.3 Conclusions on variations in N-$(NH_4)^+$ removal in VFCWs

All the 8 VFCWs were operated outdoors under variable environmental conditions but attained N-$(NH_4)^+$ mass load reductions of 80-94 %. Thus, all the units were successful at N-$(NH_4)^+$ reduction. However, the N-$(NH_4)^+$ removal in BFS compared favourably with the laboratory-scale biofilters that yielded N-$(NH_4)^+$ removals of up to 95 - 99 % (Jun and Wenfeng 2009). Correspondingly, the average removal rates of N-$(NH_4)^+$ in both sand and gravel of 0.018 g of N-$(NH_4)^+$ m^{-2} d^{-1} were lower than the 7 and 4 g m^{-2} d^{-1} of N-$(NH_4)^+$ in sand; 9 and 0 g m^{-2} d^{-} N-$(NH_4)^+$ in gravel (Bohórquez et al. 2017); and 1.2 g m^{-2} d^{-1} of N-$(NH_4)^+$ in gravel (Abdelhakeem et al. 2016). Although the N-$(NH_4)^+$ removal rates in this study are low, the corresponding per cent reductions of N-$(NH_4)^+$ (80-94 %) are higher than the 19 - 48 % (Abdelhakeem et al. 2016) and the 38.3 % (Torrens et al. 2009) for similar VFCWs. The differences in the results are likely due to the differences in the strength of pollutant loads, hydraulic loading rates, retention times and operational strategy.

4.7.4 Total nitrogen (TN)

The mean influent TN was 5.45 mg L^{-1}, while the average effluent TN ranged from 1.1 to 1.73 mg L^{-1}. The corresponding TN removal (TNR) efficiencies were 56 – 89 % (Table 4-3). The removal of TN in all the 8 VFCWs generally improved over the study period. However, the increase in TNR was variable and distinctive perhaps due to the difference s in design and operational variables. Thus, the mean TNR in the loamy sand Units 1 and 4 was 81 %; followed by Unit 2 (80 %) and BFS Unit 8 (79 %).

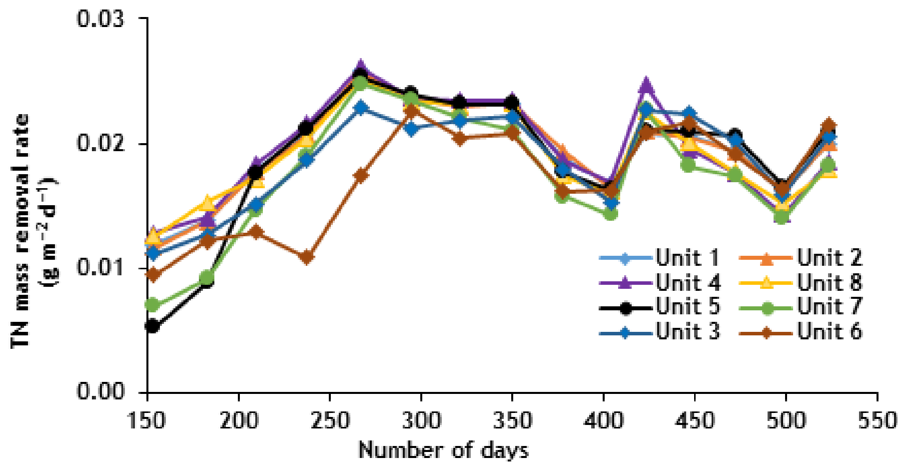


Figure 4-13 TN mass removal rates in different VFCWs

Likewise, TNR in the short dry and extended dry rested Units 3 and 6 averaged at 80 % and 79 % respectively. However, the TN mass removal rates (Figure 4-13) show that short dry and extended dry CWs lagged the continuously wet loamy sand units possibly because the microbial communities involved in transforming N matured slowly due to irregular disruptions in nutrient supplies.

Similarly, the mass removal rates of TN in loamy sand was higher than that of both gravel and BFS media. It is probable that the high organic matter associated with loamy sand media supported the growth of both aerobic and anaerobic microbes, which in turn facilitated TN reduction through nitrification and denitrification.

Equally, Figure 4-13 reveals that the TNR at 2.5 % WWAR (Units 1 and 4) was higher than at 5 % and 1.5 % WWARs respectively. However, the 1.5 % WWAR was commissioned later than the other CWs. Therefore, the low TNR is partly due to the high pollutant load (37.6 L) and a less developed microbial biome. Nevertheless, the TN mass removal of 0.06 g N m^{-2} d^{-1} achieved in Unit 7 is comparable to the 0.08 g N $m^{-}2$ d^{-1} for the best performing VFCWs (Table 4-3). Additionally, after 2 years of operations and monitoring, Unit 7 attained a TN volumetric removal constant of 1.36 d^{-1} which is comparable to the 1.68 d^{-1} in the 5.0 % WWAR (Table 4-3). More importantly, ANOVA revealed that there were no statistically significant differences in the TN removal rates between the different WWARs ($p=0.256$). This suggests that the media, WWARs and the intermittent short dry and extended dry rest regimes did not affect the mass removal rate and volumetric rate constants for TN.

Thus, the variations in the performances of the different VFCWs suggests that design and operation variables influence the extents to which mechanisms involved in TN removal interact. However, because TN removal increased in all the VFCWs at different rates, it shows that the environment could be an influencing factor. Thus, regarding media types, the theory is that gravel and BFS (high porosity) remove TN through nitrification facilitated by atmospheric aeration. Therefore, denitrification which tends to occur in anaerobic conditions was limited in Unit 2 thus restricting NO_3-N conversion to N_2 and NOx, hence the low TNR. Equally, Unit 8 had short but high nitrification rates which gradually decreased (Figure 4-11). Moreover, Unit 8 developed high alkaline pH suitable for TNR by denitrification and ammonia volatilisation. Therefore, TNR in Unit 8 was initially high and hence likely attained by nitrification, then later by denitrification resulting in high TN removal.

Loamy sand Units 1 and 4 on the other hand, registered the highest TN removals, and when compared with lower TNR in the more porous Units 2 and 8, it shows that loamy sand VFCWs developed appropriate aeration and microbial communities that favoured TN removal, hence the increase in TNR as the loamy sand units matured. Although both Units 2 and 8 had higher porosities, the organic content in gravel and BFS is lower than that in loamy sands, inferring that fewer microbial communities were supported in these units hence the relatively lower TN removal. The discrepancies in the results suggest that several factors determine TNR in VFCWs. Thus, TNR could be associated with the environmental conditions of pH, temperature and the availability of dissolved oxygen to support the microbial communities to conduct the vital nitrogen transformations.

4.7.5 Orthophosphophate (PO_4-P)

Influent and effluent orthophosphate data are summarised in Tables 4-1. Effluent EMCs show that all the CWs reduced the mean influent PO_4-P (0.829 mg/L) to 0.083 mg/L. Furthermore, loamy sand CWs recorded the lowest PO_4-P EMCs of 0.083 - 0.156 mg/L in Units 5 and 7 respectively. PO_4-P was reduced to 0.22 mg/L in gravel and 0.23 mg/L in BFS. The low variability suggests that PO_4-P reduction was stable perhaps due to the specific nature of P removal (Figure 4-14).

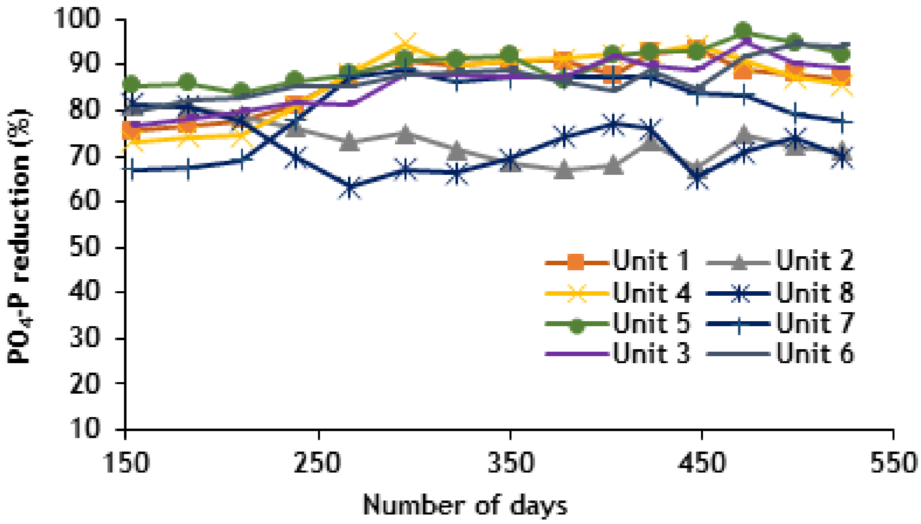


Figure 4-14 Monthly mean PO_4-P removals in VFCWs

PO_4-P removal in loamy sand VFCWs ranged between 67-97 % and averaged at 88 %. In gravel media, PO_4-P removal reached a mean value of 73 %; while in BFS media, PO_4-P reduction varied between 63 – 81 %, averaging at 72 % (Table 4-3).

Although both gravel and BFS media had comparable PO_4-P removal performances, BFS Unit 8 was the overall the least performing. Additionally, while all the loamy sand CWs show increasing PO_4-P removal, the trend for PO_4-P in gravel Unit 2 and the BFS Unit 8 declined over the monitoring period (Figure 4-14). It is suggested that loamy sand had better P adsorption capacity than both gravel and BFS media.

Generally, all the VFCWs initially attained low PO_4-P removals between 150 - 250 days (spring to summer) and after that, PO_4-P removal increased to over 90 % in the autumn. PO_4-P removal was stable in the autumn-winter months (300-450 days) but later decreased probably because the media adsorption capacity was saturated.

The ANOVA test revealed statistically significant differences in the volumetric rate constants of PO_4-P removal between the different media (p = .000). A Tukey posthoc test identified that PO_4-P removal was significantly lower in BFS (1.30 d^{-1}, p =.000) and gravel (1.33 d^{-1}, p =.000) as compared to loamy sand (2.1 d^{-1}, p = .000); while no significant differences in PO_4-P were found between gravel and BFS (p = 0.996).

Similarly, there were significant differences in the volumetric constants for PO_4-P removal between the WWARs as determined by ANOVA (p = 0.002). A Tukey posthoc test established that PO_4-P removal was significantly lower at 1.5 % (1.74 d^{-1}, p = 0.000) compared to the 2.5 % (2.1 d^{-1}) and 5.0 % (2.41 d^{-1}) respectively. No significant differences were found between the 2.5 % and 5.0 % (p = 0.223); as well as between 2.5 % and 1.5 % (p = 0.072).

Overall, PO_4-P removal was effective in all the VFCWs investigated. However, the different design variables influenced the extent to which PO_4-P removed in the CWs. Thus, PO_4-P removal was highest in loamy sand and least in BFS. With regards to WWAR, PO_4-P removal was highest at 5 % WWAR and least at 1.5 %. Likewise, the variation in PO_4-P removal in short dry and extended dry rest regimes was insignificant (p = 0.943).

4.7.6 Total phosphorus, TP

TP consisted of 86 % PO_4-P. However, the effluent TP ranged between 0.161 to 0.345 mg/L down from the mean influent TP of 1.03 mg/L (Table 4-2). The effluent TP reveals a 67 % reduction. As with PO_4-P, Units 2 and 8 recorded the highest TP effluent concentrations of 0.345 and 0.300 mg/L respectively.

Likewise, Units 3, 6 and 7 had comparable effluent TP, which suggests that the effects of dry rest periods and small WWAR on TP R were comparable. However, TP reduction was highest in loamy sand VFCWs. The larger 5.0 % WWAR of Unit 5 attained the highest TP reduction (92 %), while TP removal was lowest (62 %) in the smaller 1.5 % WWAR (Table 4-3). The variations in TP removal are consistent with the findings of Bratieres et al. (2008), who reported that larger WWARs produced better P removal. They proposed that because the influent volume through the larger surface area is smaller than the volume treated in the other units, a larger proportion of the water being washed through in any dose is made up of water that had been retained in the media bed from the previous dose. Subsequently, a more substantial proportion of the effluent will have been treated longer in comparison to the effluents of the other VFCWs, hence the observed variations in TPR.

The volumetric removal constants for TP were highest in the loamy sand VFCWs, while TP in gravel (Unit 2) and BFS (Unit 8) was generally steady over the monitoring period (Figure 4-15). However, TPR in all the 8 CWs exhibited variations which possibly reflects the influence of design and operational variables on TP removal.

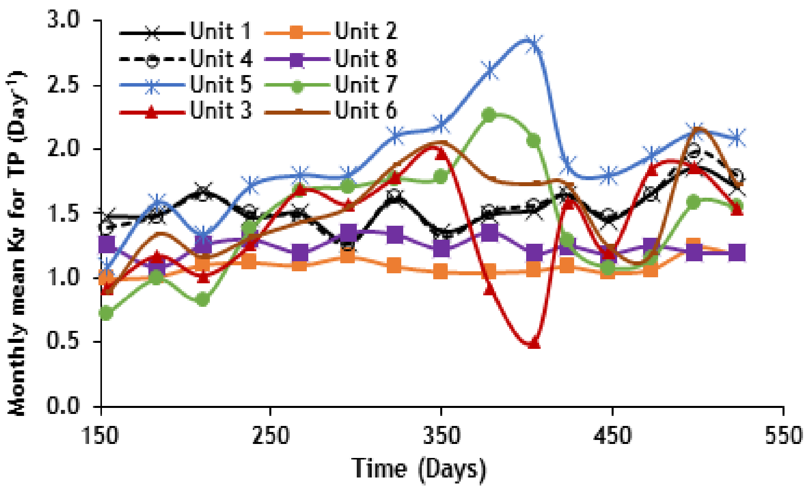


Figure 4-15 Volumetric rate constants for TP in VFCWs

ANOVA test found that there were significant differences ($p = .001$) between the volumetric rate constants for TP between the different VFCWs ($p = 0.001$). A Tukey post hoc test identified that TP removal was significantly lower at 1.5 % (1.46 d^{-1}) compared to 2.5 % (1.55 d^{-1}) and 5.0 % (1.93 d^{-1}) WWARs (Table 4-4).

Similarly, there were significant differences in the volumetric rate constants for TP between the different media ($p = 0.000$). A Tukey post hoc test revealed that TP reduction was significantly lower in gravel (1.09 d^{-1}) and BFS (1.24 d^{-1}) compared to loamy sand (1.55 d^{-1}). However, no significant differences in the volumetric rate constants for TP were found between the VFCWs operated on the intermittent short dry and extended dry rest strategy ($p = 0.18$).

Generally, TP reductions of 67– 92 % obtained from this study compared well with the literature values for both the laboratory and field-based studies of 86 % (Torrens et al. 2009) and 75–89 % (Huang et al. 2016) respectively. However, when compared with TP removal performances of 95-96 % (Žibienė et al. 2015), it shows that TP removal by media such as dolomite chippings is higher than when using loamy sand, gravel, and BFS media. Furthermore, it was reported that P could be stored long-term in VFCWs through soil adsorption and accumulation. Based on these assumptions, P stored long-term was estimated at 50 –78 g P m^{-2} $year^{-1}$. (Braskerud 2002) reported the estimated TP was within the range of particulate TP reductions of 26 –71 g TP m^{-2} $year^{-1}$ for CWs receiving non-point wastewater with a high content of soil particles. However, the P loads of 0.012 – 0.018 g TP m^{-2} day^{-1} obtained in this study were lower than the 0.34 - 0.52 g TP m^{-2} day^{-1} (Braskerud 2002) and 0.54-1.2 g TP m^{-2} day^{-1} (Abdelhakeem et al. 2016). According to Braskerud (2002), to achieve sustainable TP reduction, it is vital that P saturated sediments are regularly removed from treatment VFCWs. Additionally, Sierszen et al. (2012) suggested the annual harvest of wetland vegetation to maintain the TP reduction capacity of the different media. Accordingly, the high TP retention attained in this study could be sustained by periodically washing the media bed to remove the accumulated P; as well as harvesting the macrophytes in the VFCWs.

TP removal mechanisms were in some respects like those of PO_4-P removal possibly because TP was predominantly in the form of PO_4-P. Thus, the removal of TP might have occurred by mechanisms like sorption onto media, plant uptake, precipitation and microbial uptake (Vohla et al. 2011). Although microbial and plant uptake was not measured, both pathways are not thought to have significantly contributed to P removal in either the gravel or BFS CWs because the planted macrophytes did not survive the environmental conditions in the CW units (Lucas et al. 2015). Thus, the enhanced P removal in BFS suggests that P was removed by chemical precipitation and adsorption. Nonetheless, PO_4-P removal by adsorption was considered insignificant because the acidic conditions that favour this pathway (Reddy and D'Angelo 1997) were not prominent in all the 8 VFCWs.

Therefore, although Fe and Al were detected in the gravel media, the low compositions of both Fe and Al appear not to have influenced PO_4-P removal. Comparatively, loamy sand and BFS had Fe contents of 4 % and 2 % respectively. Additionally, BFS media contained 17 % Al, but the alkaline pH of BFS likely neutralised the acid products of Al hydrolysis, and hence inhibited PO_4-P removal.

Additionally, the different media beds had a varying particle size and specific surface area. The specific area of the media particles determines the area of the biofilm within which pollutant transformation takes place. Thus, when the particles of the media are coarse, the specific surface area of the particles decreases but the porosity increases hence lessening the clogging incidences (Žibienė et al. 2015). This could explain the variations in P removal in the different media. Furthermore, of the different media examined, materials which had average pH greater than 7 and high Ca (CaO) content attained higher P-removal. Additionally, the strong and positive correlation between P retention and Ca content of the media revealed a possibility of optimal hydraulic loading rates for P removal (Vohla et al. 2011). Thus,the presence of high Ca in loamy sand and BFS suggests that the PO_4-P removal mechanisms involved Ca in its elemental or compound forms. Furthermore, in calcareous CWs, P can be precipitated as Ca mineral-bound phosphorus (Richardson and Craft 1993). This suggests that the high Ca content found in the media samples aided precipitation of PO_4-P forming insoluble Ca-phosphates. Thus, chemical precipitation was the principal P removal mechanism in both loamy sand and BFS CWs. This proposition is consistent with the high mean effluent pH of 7.5 in gravel Unit 2 and 8.5 in BFS Unit 8. Additionally, the batch adsorption tests conducted to determine the adsorption characteristics of the media concluded that the rates of adsorption of all the metals to loamy sand and BFS took under 5 minutes. The reaction rates were described as consistent with a pseudo-second-order model, suggesting that chemisorption was a crucial in metal adsorption (Lucas 2015).

Overall, the different designs and operational variables of the VFCWs investigated in this study significantly reduced the influent P loads. Besides, the P loads retained in the VFCWs appears not to have substantially affected the retention capacity of P in the treatment systems over the study period.

4.8 Wetland design, suitability and removal mechanisms

A conceptual model was developed to relate the different design and operational aspects of the research (Figure 4-16) to the environmental challenges which informed the need for this research study. The aim was to propose the most suited stormwater management interventions based on the study outcomes. The model shows that a 1.5 % WWAR with loamy sand media offers enhanced TSS removal, mainly by physical mechanisms. However, a 2.5 % WWAR with loamy sand is best suited for biological removal of nutrients P and N, while the highest removal of heavy metals can be realised with BFS media operated at 2.5 % WWAR.

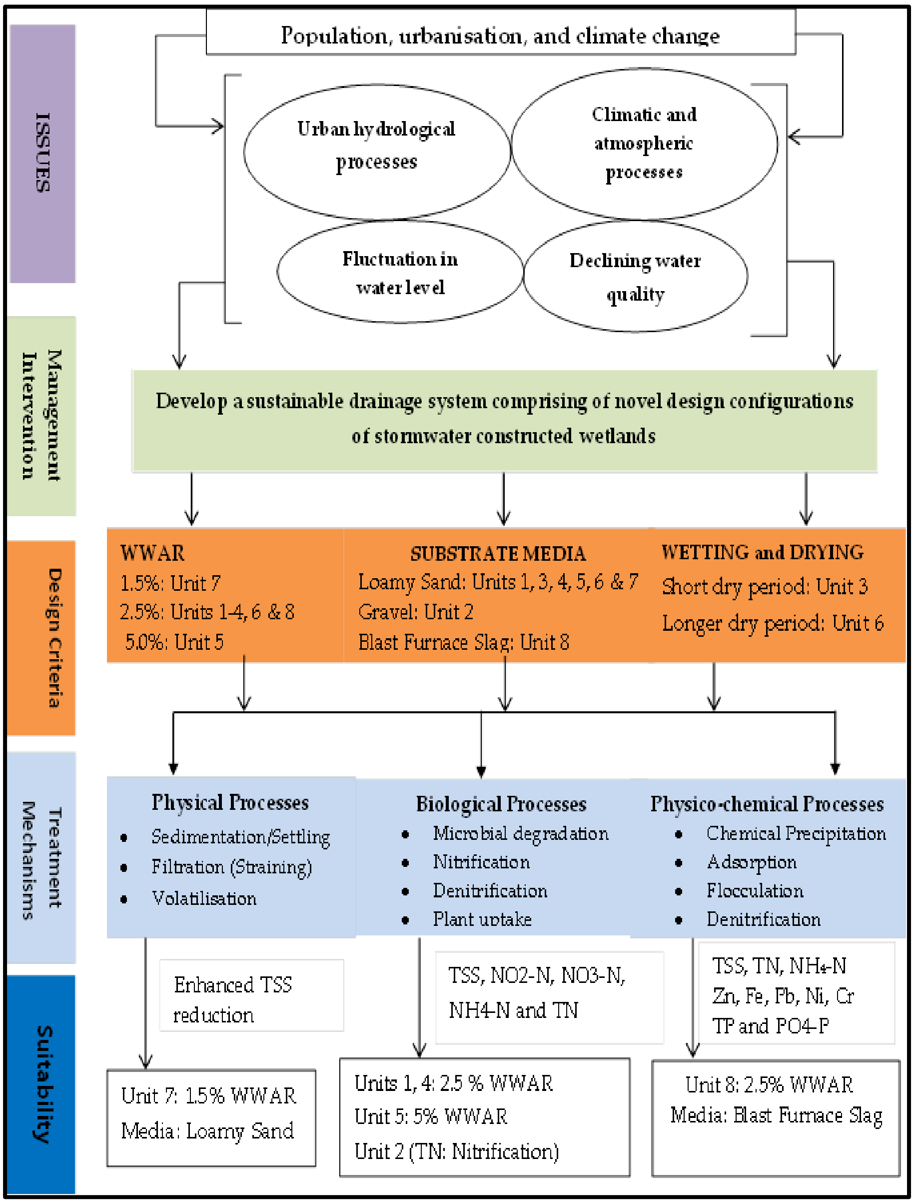


Figure 4-16 Conceptual model of wetland designs, removal mechanisms and suitability

Chapter 5 Influence of design and operational variables on the performance of vertical flow constructed wetlands

As shown in Chapter 4, the design and operational variables influenced the chemical and physical water qualities. WWAR influences the hydraulics of CWs by affecting water content, pressure heads, and the filtration capacity of the substrate media. Similarly, short dry and extended dry rest periods, and wet regimes affect the physico-chemical processes and the eco-structure of the wetland systems; the phase distribution of metals and soil structure and the porosity of the biofilter (Blecken et al., 2009). Therefore, to quantify the influence of each design variable, Chapter 5 implements inferential statistics to explore the significance of the effect on pollutant removal and hence the performance of the VFCWs. Thus, the analysis in this Chapter is focussed on the following:

a) To identify statistically significant variations caused by the design variables and to establish the effect of such variations on the treatment efficiency.
b) To determine the effect of design variables and other influencing factors on treatment performance.
c) To make recommendations of the design and operational strategy suitable for the optimal removal of pollutants

5.1 Criteria for analysis

The analysis criteria applied considered that influent quality varied within prescribed ranges on different days. Accordingly, effluent quality also varied. Thus, the first test was to separately establish if there were significant differences between the influent and effluent means of each variable. A paired samples t-test was conducted, with results showing that differences in means were not equal to zero at 95 % confidence interval. Therefore, to evaluate the effects of design and operational strategy on the performance of the VFCWs, a linear mixed effects model with repeated measures is executed, thus ANOVA with repeated measures. More importantly, since the data is clustered at the day level, it is likely that the repeated measurements in CW Unit may have led to a dependency between observations such that measurements taken on a future day might have depended on the previous days' measurements and conditions. This dependency is accounted for in a treatment effects model. Finally, the response variable applied across all the parameters is the change in the influent and effluents quality. For example, pHdiff is the difference between the influent and effluent pH in each CW Unit.

5.2 Influence of primary biofilter media

Substrate media filters applied in the pilot-scale stormwater CWs comprised of three distinct types namely: Loamy Sand (LS1 and LS4; 3 and 6; 5 and 7); gravel (Unit 2) and blast furnace slag (BFS) in Unit 8. Each biofilter media had different chemical and physical properties, which likely influenced the development and treatment functions of the CW Units.

Consequently, the same removal mechanisms in each CW changed partly in response to specific media properties. For example, media pH in each CW Unit is likely to have determined the growth in microbial community and structure, which in turn influenced biological processes of biodegradation and transformation of nitrogen in the VFCWs. Additionally, pH variations possibly altered key removal pathways through the physico-chemical interactions like precipitation and sorption.

Therefore, all the three media types namely: loamy sand (Units 1 and 4), gravel (Unit 2) and BFS (Unit 8) were compared on the basis that each had the same dosing (3 times weekly wetting) frequency and volume (22.5 L or 2.5 % WWAR).

5.2.1 Effect of primary media on pH

There were noticeable variations in pH in the different VFCWs (Figure 4-1). ANOVA established statistically significant differences in pH changes between the different primary media. Therefore, the null hypothesis that there is no change in pH between the different media is rejected. Furthermore, a Tukey *post hoc* test revealed that the change in pH was significantly lower in loamy sand (6.9, $p = 0.000$) and gravel (7.5, $p = .000$) as compared to BFS (8.5, $p =.000$) (Table 5-1). The differences in pH changes in CW Unit 1 and Unit 4 were minimal (0.006) probably due to higher nitrification rates in Unit 4 than Unit 1. Nitrification releases H^+ ions which can cause the acidification of the media (Section 4.6.1). Since pH in Units 1 and 4 declined, then it is possible that TNR in Unit 4 was higher than in Unit. Thus, Figure 5-1 suggests that the pH of loamy sand CW Units 1 and Unit 4 generally decreased possibly due to continuous nitrification.

Table 5-1 ANOVA results for media comparisons of pH changes (α = 0.05).

	NumDF	denDF	F-value	p-value
Intercept	1	547	2.7506	0.0978
Primary media	3	547	2506.3355	<0.0001
Media comparison				
	LS1: LS4		7.60845	0.006
	LS1: Gravel		469.6911	< 0.0001
	LS1 : BFS		1672.4266	< 0.0001
	Gravel : BFS		522.8951	< 0.0001

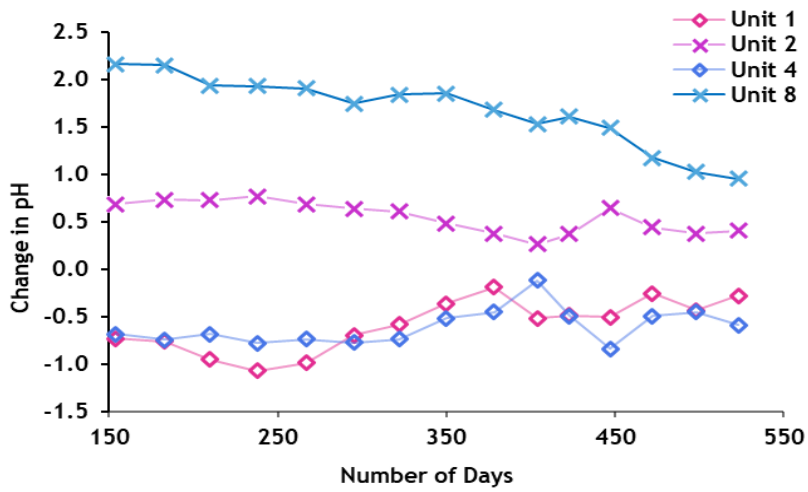


Figure 5-1 Variations in the mean monthly change in pH in the different media

Similarly, pH in the BFS media generally increased relative to the inflow pH. The decline in the chemical nature of BFS is the probable cause of the observed changes. Figure 5-1 shows that the change in the pH of BFS initially increased and peaked (150-250 days), and after that gradually declined in part due to continuous loading causing dilution. The other possible cause in decline in pH of BFS would include the H^+ ions from nitrification reactions neutralising the alkaline ions in BFS; and the complexation and precipitation reactions associated with P removal. Likewise, gravel media displayed insignificant pH changes, suggesting that the chemical properties of gravel media were the least affected by continuous loading and that the nitrification reactions were not effective in the gravel media bed.

5.2.2 Effect of primary media on electrical conductivity (EC)

All the VFCWs experienced changes in electrical conductivity (EC). Therefore, there were statistically significant differences in EC changes between the different media substrates as determined by ANOVA (p = 0.000). Thus, the null hypothesis that there are no significant differences in EC when different media are used is rejected. A Tukey p*osthoc* test produced outputs listed in Table 5-2.

Table 5-2 ANOVA for electrical conductivity in different media (α = 5%).

	NumDF	denDF	F-value	p-value
Intercept	1	547	4027.699	<0.0001
Primary media	3	547	1939.369	<0.0001
Media comparison				
LS1: LS4			4.466606	0.035244
LS1: Gravel			3177.850	<0.01
LS1: BFS			2152.306	<0.01
Gravel : BFS			414.0937	<0.01

Like the variations in pH discussed in section 5.3.1, the differences in EC between the different media were significantly highest in loamy sand (0.62 ± 0.04, $p = 0.000$) and in BFS (0.47 ± 0.08, $p = 0.000$) and least in gravel (0.37 ± 0.04, $p= 0.000$). Since the EC is a measure of the concentration of dissolved solids, differences in EC among the biofilters reflects the ability of each media to filter suspended solids.

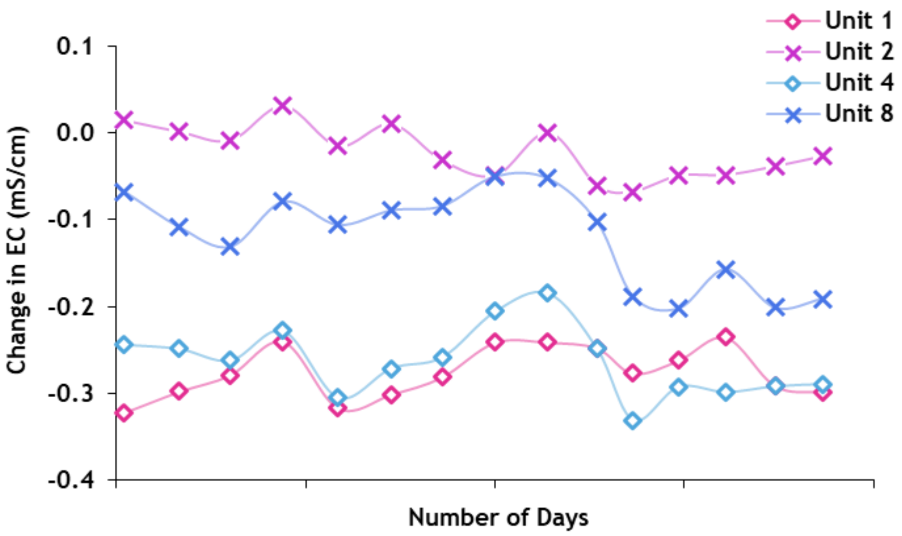


Figure 5-2 Mean monthly change in conductivity of VFCWs

EC in the gravel CW Unit 2 did not experience major fluctuations. When compared with loamy sand and BFS, the later show a sharp decline in EC (Figure 5-2). As discussed in Section 4.1.1, BFS alkalinity decreased over time hence the conducting ions in BFS were gradually diluted and washed out on subsequent treatments. Also, neutralisation reactions between the H^+ ions from denitrification and acid hydrolysis of Fe and Al likely produced lesser conducting products.

5.2.3 Effect of primary media on TSS removal

ANOVA and the Tukey posthoc results revealed statistically significant differences in TSS removal between the different media types ($F (3,547) = 94.2994$, $p = 0.000$). Consequently, the null hypothesis that there is no difference in the effect of primary media on TSS removal is rejected (Table 5-3).

Table 5-3 ANOVA for TSS removal in different media (α =0.05)

	NumDF	denDF	F-value	p-value
Intercept	1	547	744.8968	< 0.0001
Primary media	3	547	94.2994	< 0.0001
Media comparison				
LS1: Gravel			84.32956	< 0.0001
LS4: BFS			33.84427	< 0.0001
Gravel: BFS			24.92423	< 0.0001

The differences in TSS between the different media were significantly lower in loamy sand (7, p = 0.000) and gravel (8, p = 0.000) and highest in BFS (9, p= 0.000). The differences in TSS removal suggest that TSS removal in the different media was achieved through similar mechanisms such as filtration and sedimentation. Furthermore, it is probable that the rate at which the removal mechanisms developed varied due to the differences in size of the media particles, compaction, porosity, and media chemical properties. The graphs in Figure 5-3 show that loamy sand CWs (LS_4) and the gravel CWs exhibited comparable TSS removal. It is likely that the retention time of 24-hours enabled the processes of filtration and gravitational settling at to occur at similar rates in loamy sand and gravel.

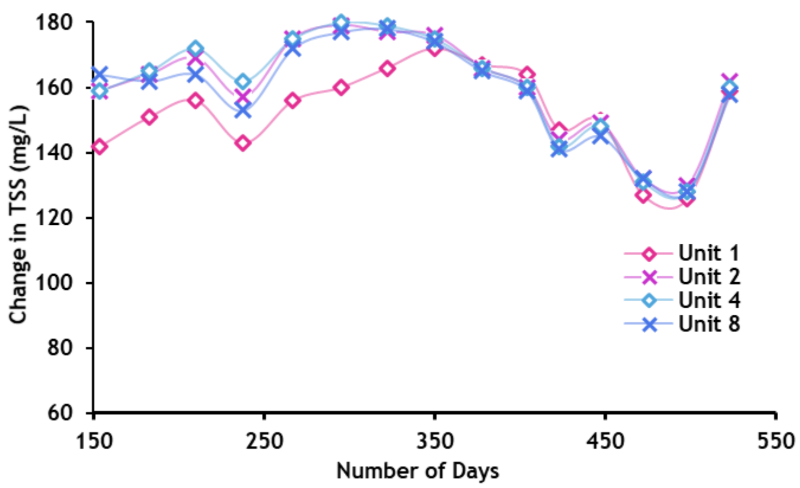


Figure 5-3 Changes in TSS removal in VFCWs containing different media

The similarities in TSS concentrations is attributed to several factors related to fully developed VFCWs. One theory is that repeated treatment cycles decrease the pore sizes which in turn improves the retention of solids (Blecken et al. 2010). Additionally, aggregation of solids inhibits the resuspension of sediments (Hatt et al. 2007c); while biofilm growth is thought to alter pore geometry and the transport behaviour of active substances (Volk et al. 2016). It is these factors that jointly determine TSS removal in CWs, and hence underline the statistical differences observed between the different biofilters. Overall, BFS media removed TSS most consistently probably because BFS constitutes few finer particles than loamy sand. Moreover, the sand transition layer in Unit 8 helped to filter smaller solids than the gravel drainage layer in the CW Unit 2.

5.2.4 Effect of primary media on Total Phosphorus (TP) removal

TP removal among the different media configurations revealed statistically significant differences as determined by ANOVA and the Tukey posthoc results ($F_{(3,547)} = 107.7241$, $p = 0.000$). Therefore, the null hypothesis that there is no difference in the effect of primary media on TP removal is rejected (Table 5-4). The observed posthoc differences show that TP removal was significantly lower in loamy sand CWs (0.219 ± 0.08, p = 0.000) and in BFG (0.300 ± 0.07, p = 0.000) as compared to gravel media (0.345 ± 0.07, p = 0.000).

Table 5-4 ANOVA results for media comparison of TP changes (α = 0.05)

	NumDF	denDF	F-value	p-value
Intercept	1	547	2689.1904	<0.0001
Primary media	3	547	107.7241	<0.0001

Media comparison	F-value	p-value
LS_1: LS_4	0.005122	0.942986
LS_1: Gravel	221.8875	< 0.0001
LS_4: BFS	99.59236	< 0.0001
Gravel: BFS	54.5229	< 0.0001

TP variations in the different media possibly reflect the way the removal mechanisms developed in the media applied in each stormwater CW. P removal pathways in CWs include processes such as adsorption on substrate media, chemical precipitation, bacterial immobilisation, algal and plant uptake, as well as incorporation into organic matter and sediments (Kadlec and Wallace 2009a; Ballantine and Tanner 2010). These processes require oxygen, suitable hydraulic conductivities, and microbial growth (Li et al. 2008).

Furthermore, the porosity and sorption characteristics of the media also determine the overall P-removal capacity of CWs (Cui et al. 2008). Thus, a combination of factors could explain variations in the observed TP removal. Thus, loamy sand CWs outperformed BFS which in turn performed better than gravel likely because loamy sand had high organic content that supported microbial growth, and the planted macrophytes in VFCWs 1 and 4. The macrophytes flourished and hence contributed to P removal by macrophyte biomass and microbial immobilisation. However, gravel and BFS media did not support macrophyte growth which possibly resulted in low P removal due to limited plant and microbial uptake. Also, loamy sand CWs had the finest media particles and hence higher P absorption to extents that the relatively bigger gravel and BFS particles could not achieve. Furthermore, while gravel maintained influent pH, loamy sand revealed a decline in influent pH, while BFS media showed an increase in pH (Figure 5-1, 5.3.1).

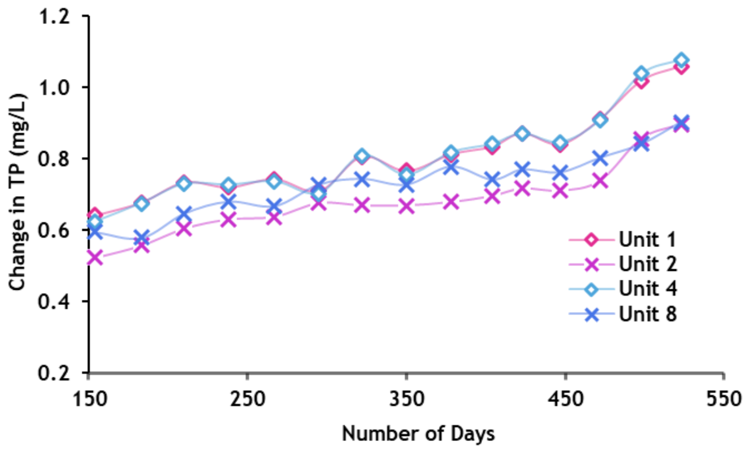


Figure 5-4 Change in TP in the different media

Since P adsorption decreases as pH increases (Zhou et al. 2005), then the high alkaline pH in Unit 8 initially inhibited P adsorption, while the declining pH in the loamy sand CWs (LS_1 and LS_4) contributed to the high P removal. Similarly, the high Ca, and Al content in BFS media favoured the precipitation of P.

Only loamy sand media had comparable Ca and Al hence the small difference in TP removal between loamy sand and BFS Units (Figure 5-4). Likewise, the decline in the alkalinity of BFS media allowed more precipitation and absorption of P hence the increasing trend in P removal. However, the change in P in gravel was minimal probably because P removal was limited to absorption and bacterial immobilisation.

5.2.5 Effect of primary media on Total Nitrogen (TN) removal

TN removal in all the CWs improved as the CW units matured. The highest increase was in the loamy sand CW Units 1 and 4, while the gravel-based Unit 2 had the least increase. TN removal in Unit 8 (BFS) showed steady increase, but like the loamy sand CW Units 1 and 4 , and gravel CW Unit 2, exhibited the similar TN removal patterns across the seasons (Figure 5-5). Consequently, ANOVA showed that overall, there were no significant differences in TN reduction (p = 0.3694) between the different media as shown in Table 5-5.

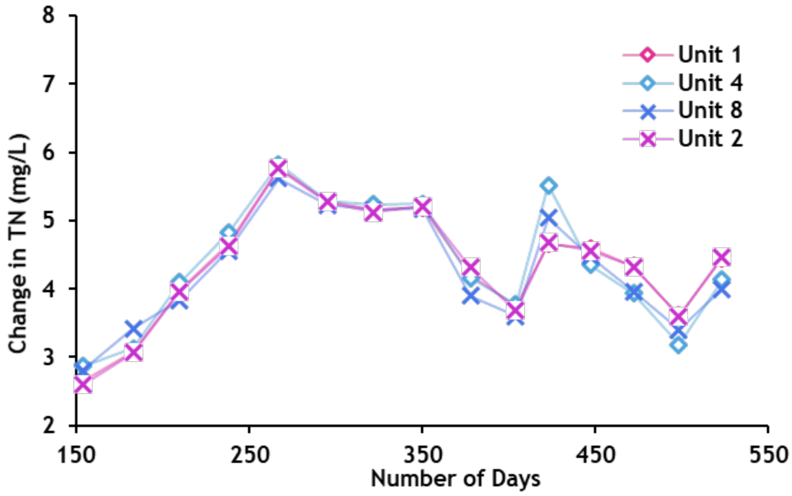


Figure 5-5 Change in TN after treatment in different media

Table 5-5 ANOVA for media comparison of TN removal (α = 0.05)

	NumDF	denDF	F-value	p-value
Intercept	1	547	2971.9193	<0.0001
Primary media	3	547	1.0512	0.3694
		Media comparison		
LS_1:LS_4			0.00389	0.9503
LS_1: Gravel			137.532	<0.0001
LS_4: BFS			2.0857	0.1495
Gravel: BFS			118.0996	<0.0001

However, a Tukey posthoc test identified that the differences were significantly lower in loamy sand and gravel compared to BFS. However, there were no statistically significant differences between loamy sand and BFS (p = 0.149).

These variations reflect the way the different TN removal mechanisms developed in each media. Thus, a combination of TN removal by nitrification, denitrification, plant and microbial assimilation were favoured in the loamy sand CWs hence the high TN removal. Similarly, the high porosity of gravel media possibly influenced atmospheric aeration and hence higher rates of nitrification-denitrification reactions. Additionally, remineralisation and annamox processes might have contributed to TN removal rates which compared well with TN removal in the loamy sand CW units. Moreover, the CW containing BFS media exhibited alkaline pH conditions. TN removal at high pH is thought to proceed by denitrification and ammonia volatilisation pathways. As NH_4-N is oxidised, the H^+ produced are neutralised in the alkaline conditions of BFS leading to more NH_4-N reduction. Other TN removal pathways might have included sorption and desorption on organic matter and minerals within the substrate media.

5.2.6 Effect of biofilter media on zinc removal

The mean concentration of Zn in effluents treated in the BFS CW was 0.007 mg/L (slightly higher than the detection limit for Zn of 0.0064 mg/L). BFS removed an average of 98 % of Zn; gravel managed 94 % Zn removal, while loamy sand CW Units 1 and 4 removed 76 % and 79 % of Zn respectively.

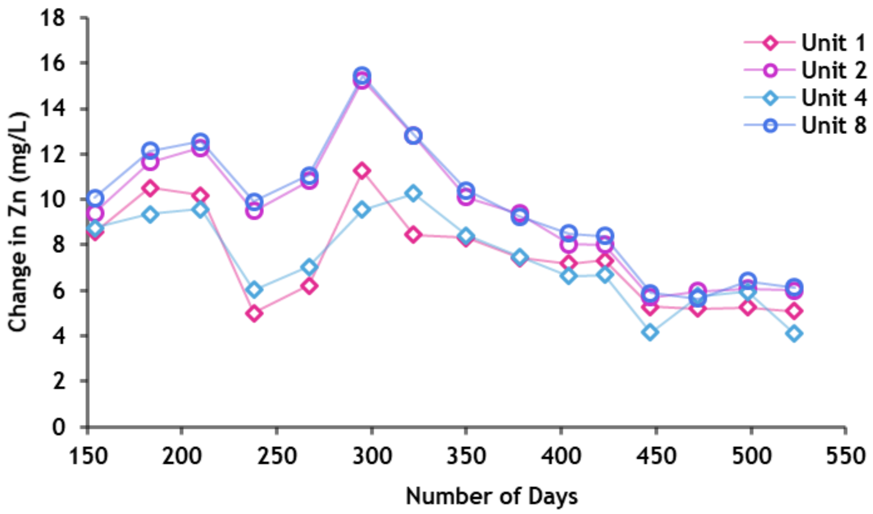


Figure 5-6 Change in Zn after treatment in different media

The changes in Zn concentration with time show that zinc removal was highest in BFS and lowest in loamy sand media (Figure 5-6). However, ANOVA and the Tukey posthoc results show that there were statistically significant differences in Zn removal among the three different biofilter media ($p = 0.0001$) as shown in Table 5-6. Therefore, the change in Zn was significantly lower in BFS (0.006, $p = 0.000$) than in gravel (0.018, $p = 0.000$) as compared to loamy sand (0.109, $p = 0.000$).

The differences in Zn removal between the CWs could be linked to variations in the effluent pH in the loamy sand, gravel and BFS CWs. This is because the gravel and BFS CWs mean pH values of 7.5 and 8.5 respectively, while the loamy sand CWs

(Unit 1 / Unit 4) had mean pH of 6.9 (good for Zn adsorption). Previous studies on Zn removal established that chemical precipitation and complexation of Zn are easily reached at neutral and alkaline pH (Rieuwerts et al. 1998; Rieuwerts et al. 2006)Therefore, Zn removal in the VFCWs produced results that are in agreement with the literature with regards to loamy sand and BFS CWs.

Table 5-6 ANOVA results for media comparison of Zn removal (α =0.05)

	NumDF	denDF	F-value	p-value
Intercept	1	547	1180.6426	<0.0001
Primary media	3	547	138.1357	<0.0001
Posthoc media comparisons				
LS_1: LS_4			0.1503	0.6984
LS_1: Gravel			284.182	<0.0001
LS_1: BFS			344.361	<0.0001
Gravel: BFS			13.8467	0.0002

The irregular increases in effluent Zn in LS_1 and LS_4 CWs might have resulted from plant growth. Plant roots slowly discharge organic substances which then initiate complex formation with metal ions thereby releasing adsorbed metals into solution (Rieuwerts et al. 1998). This probably explains the increase in Zn in effluents of loamy sand VFCWs. Additionally, during the summer months (temperatures increased to 20°C), which increases the biological activity of the macrophytes in the vegetated beds (Blecken et al. 2011). Consequently, there was high decomposition of organic matter and hence the release of dissolved organic matter (DOM) in effluents contributed Zn ions previously adsorbed to the media. BFS and gravel CWs did not support macrophyte growth, and therefore could not produce enough DOM content in their media beds. Consequently, gravel and BFS CWs did not have significant amounts of decomposing organic matter hence the consistent declines in effluent Zn concentrations and hence higher Zn removal.

5.2.7 Conclusion - the effect of substrate media on heavy metal removal

Nearly all the heavy metals had concentrations below their respective detection limits, an indication that the VFCWs satisfactorily removed the heavy metals from the stormwater. Thus, concerning the effect of biofilter media, it was only possible to determine whether there were statistically significant differences in the removals of effluent heavy metal concentrations above the limits of detection. The heavy metals Zn and Fe met this criterion. Therefore, Fe did not show significant differences, while Zn removal exhibited significant differences between the media types. Even then, Zn removal was relatively low among loamy sand CWs, particularly during the first 5-6 months of the first year of operating the CWs. This exception is attributed to the high biological activity in loamy sand CWs, which subsequently led to increased DOM and high sorption of Zn. This significantly impacted Zn removal in loamy sand CWs.

5.3 Effect of the wetland-watershed area ratio

5.3.1 Effect of wetland-watershed area ratio on TSS

ANOVA results show that there were statistically significant differences in TSS removal between the different WWARs (p = 0.000). Hence, the null hypothesis that there is no change in TSS removal at different WWARs is rejected (Table 5-7). The posthoc Tukey test identified that the differences in TSS were significantly lower at 2.5 % WWAR of CW Unit 4 and 1.5 % WWAR CW Unit 7 as compared to the 5.0 % WWAR CW Unit 7. There were no significant differences between the 2.5 % WWAR of Unit CW Unit 1 and the 5.0 % WWAR as well as with the 1.5 % WWAR.

The changes in TSS removal for the different WWARs in **Figure 5-7** show that except for the 5.0 % WWAR in which the change in TSS initially decreased, both the 2.5 % WWAR and 1.5 % WWAR had an increase in TSS removal over the same period between150-250days. After that, the variations in TSS between the 4 CWs followed similar trends. The control CW Units run at the 2.5 % WWAR (1 and 4) attained contrasting TSS removals. The average TSS removal in CW Units 1 and 4 was 91 %. However, TSS removal improved and converged in all the 4 CWs after the second year of monitoring (Figure 5-7).

Table 5-7 ANOVA for effect of WWAR on TSS removal (α =0.05)

	NumDF	denDF	F-value	p-value
Intercept	1	547	4941.402	< 0.0001
WWAR	3	547	22.695	< 0.0001
Posthoc WWAR comparisons				
2.5 % WWAR CW1 : 2.5 % WWAR CW 4			90.40744	< 0.0001
2.5 % WWAR CW1 : 5.0 % WWAR CW 5			1.152071	0.2838
2.5 % WWAR CW4 : 5.0 % WWAR CW 5			92.90794	< 0.0001
2.5 % WWAR CW1 : 1.5 % WWAR CW 7			0.155261	0.6938
2.5 % WWAR CW4 : 1.5 % WWAR CW 7			14.02454	0.0002
1.5 % WWAR CW7 : 5.0 % WWAR CW 5			0.737705	0.39097

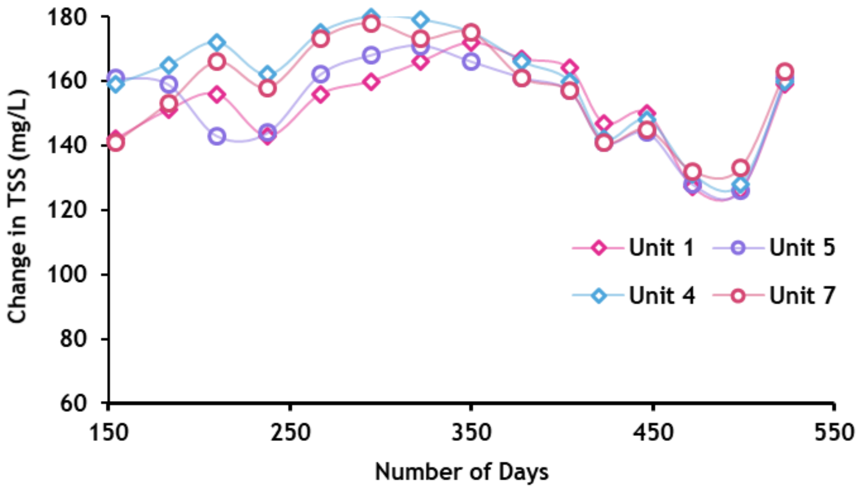


Figure 5-7 Mean monthly TSS variations at different WWAR

Nonetheless, the Tukey posthoc results show that variation in TSS removal efficiencies can be pronounced where subtle differences exist in the way the media is compacted, or influent loaded between CWs with the same design and operational configurations. Furthermore, the posthoc results suggest that the initial decline in TSS removal at 5.0 % WWAR had no major effect on TSS removal when compared with lower and higher WWARs of 1.5 % and 5.0 % respectively. However, the variations in TSS were significantly different between the 1.5 % and the 2.5 % WWAR of CW Unit 4 presumably because the physical processes of TSS removal such as filtration solids were influenced by the larger inflow volumes that the 1.5% WWAR receives. Thus, the greater loads of incoming TSS lead to the aggregation of more solids in a shorter period, thus reducing resuspension in the 1.5 % CW thereby providing adhesive surfaces on which incoming solids may be deposited (Hatt et al. 2007c). Similarly, the larger inflow volumes in the 1.5% WWAR CW may increase this effect of repeated loadings causing "repacking and settling" of the media and hence decreases pore sizes resulting into improved solids retention (Blecken et al. 2010). Overall, the changes in TSS suggest that the TSS removal mechanisms are stochastic even between VFCWs with the same media configuration and loading patterns.

5.3.2 Effect of wetland-watershed area ratio heavy metal removal

5.3.2.1 Effect of wetland-watershed area ratio on Zinc removal

ANOVA results summarised in **Table 5-8** found that there were significant differences in Zn removal between the various WWARs investigated (p = 0.000). Thus, the null hypothesis that there is no effect on the change in Zn removal between the different WWARs is rejected. The posthoc Tukey test revealed that the differences in Zn were significantly lower in the 1.5 % WWAR Unit (0.06, p = 0.000) and 5.0 %

WWAR (0.10, p = 0.000) compared to the 2.5 % WWAR (0.11, p = 0.000). No significant differences were found between the 2.5 % and 5.0 % WWAR.

Table 5-8 ANOVA results for WWAR comparison of Zn removal (α =0.05)

	NumDF	denDF	F-value	p-value
Intercept	1	547	1660.91	< 0.0001
WWAR	3	547	7.3512	< 0.0001
WWAR comparison				
2.5 % WWAR: 2.5 % WWAR (LS)			0.150344	0.698433
2.5 % WWAR: 5.0 % WWAR (LS)			0.020589	0.573205
2.5 % WWAR: 1.5 % WWAR (LS)			96.31543	< 0.0001
1.5 % WWAR: 5.0 % WWAR (LS)			114.13723	< 0.0001

At 1.5 % WWAR Zn removal was 87 % higher than the 76 % and 79 % reached by the 2.5 % WWAR of VFCW 1 and 4 respectively. CW Unit 5 (5.0 % WWAR) attained a mean Zn removal of 75 %. High Zn removal in the 1.5 % WWAR was attributed to the late operationalisation of Unit 5, and therefore the onset of the decomposition processes by the biological communities was late which in turn delayed the release of dissolved organic matter (DOM), hence the low Zn EMC in the effluents.

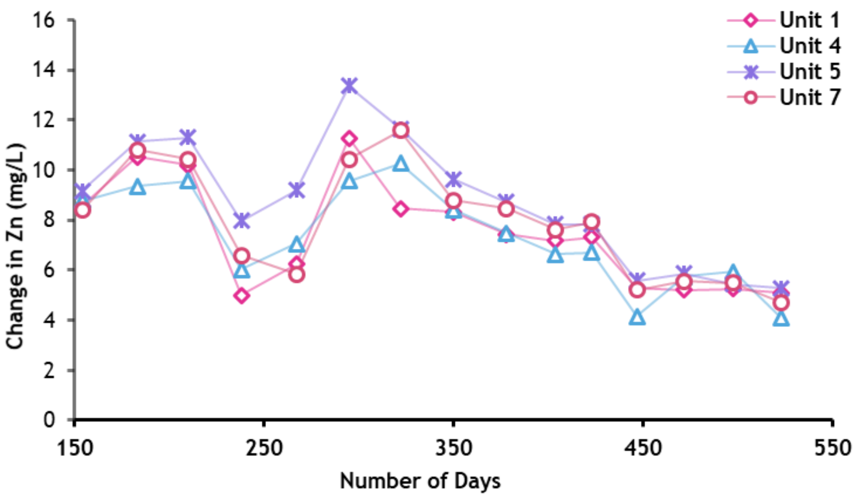


Figure 5-8 Mean monthly variations in Zn at different WWAR

However, after 2 years of monitoring, the 2.5 % WWAR (Unit 1) exhibited stable Zn removal; while Units 4 and 7 (2.5 % and 1.5 % WWAR respectively) experienced marginal increases in Zn removal. Additionally, Zn removal in the 5.0 % WWAR (Unit 5) declined (Figure 5-8). This suggests that in addition to DOM, other factors like pH could have influenced variations in Zn effluents and hence Zn removal.

5.3.2.2 Effect of wetland-watershed area ratio on Fe removal

ANOVA test results show that were statistically significant differences in the effect of WWAR on Fe removal (p = 0.000). Furthermore, the Tukey posthoc analyses established that the differences in Fe were between the VFCWs operated at 2.5 % WWAR (Units 1 and 4); between the 2.5 % and 1.5 % WWAR; as well as between the 2.5 % WWAR (Unit 4) and 5.0 % WWAR. Similarly, significant differences in Fe were found between the 5.0 % and 1.5 % WWAR (Table 5-9).

Table 5-9 ANOVA results for effects of WWAR on Fe removal (α = 5 %)

	NumDF	denDF	F-value	p-value
Intercept	1	547	2122.159	< 0.0001
WWAR	3	547	16.1818	< 0.0001
WWAR comparisons				
CW1: CW4 (2.5 %: 2.5 %)			93.71839	< 0.0001
CW1: CW 5 (2.5 %: 5.0 %)			0.102702	0.748795
CW4: CW 7 (2.5 %: 1.5 %)			12.64027	0.00043
CW5: CW 7 (5.0 %: 1.5 %)			23.07921	< 0.0001

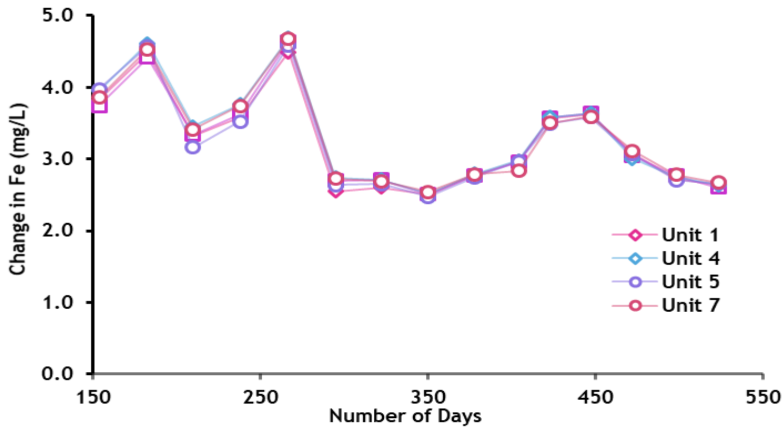


Figure 5-9 Mean monthly variations in Fe at different WWAR

However, Fe removal between the 2.5 % WWAR (Unit 1) and 5.0 % WWAR (Unit 5) was not significant, while at the same 2.5 % WWAR, there were significant differences in Fe removal between Unit 4 and Unit 5 (5.0 % WWAR). Generally, Unit 7 (1.5 % WWAR) had the highest Fe removal of 98 % ; 2.5 % WWAR (97.7 %) while Unit 5 attained 96.6 %. The relatively insignificant differences in Fe removal can be seen in Figure 5-9. This variation in Fe removal at various WWAR is like that observed in the effect of WWAR on TSS removal. It is probable that both TSS and Fe (mostly particulate) are removed through the same removal pathways which are similarly influenced by the WWAR. Besides, the discrepancies demonstrate that differences in the way the VFCWs are configured can result in significant variations in performance as observed between the control CW Units 1 and 4.

5.3.3 Conclusion – Effect of wetland-watershed area ratio on Zn removal

In general, as the results show, heavy metal removal was mostly impressive in all pilot-scale wetlands. Analyses of the effects of the different WWAR on Zn and Fe removal was possible because both Zn and Fe were frequently registered above their respective detection limits.

All selected WWAR values operated with loamy sand media proved effective with no significant influences on the performance of each design unit. It is also very likely that since a significant percentage of the metal fractions were particulate or bounded to suspended solids, then physical mechanisms like filtration, straining, and adsorption were primary removal mechanisms; along with minor pathways such as chemical precipitation, and microbial and plant uptake. Under these circumstances, factors such as pH of the media may have been key to the success of the minor heavy metal removal mechanisms.

5.3.4 Effect of wetland-watershed area ratio on nutrient removal

5.3.4.1 Nitrogen removal

TN removal in the VFCWs with different WWARs exhibited statistically significant differences as determined by ANOVA and the Tukey posthoc results ($p = 0.000$). Therefore, the null hypothesis that there is no difference in the effect of WWAR on TN removal is rejected (Table 5-10). The observed differences show that TN was significantly lower at 2.5 % WWAR (1.09 mg/L) and at (1.24 mg/L, $p = 0.000$) as compared to 1.5 % WWAR (1.59 mg/L). The posthoc Tukey test identified that the differences were statistically significant between the 2.5 % and 1.5 % WWARs, and between the 5.0 % and 1.5 % WWARs (Table 5-10).

Table 5-10 ANOVA results for the effect of WWAR on TN removal ($\alpha = 0.05$)

	NumDF	denDF	F-value	p-value
Intercept	1	547	5419.555	< 0.0001
WWAR	3	547	172.172	< 0.0001
WWAR comparison				
CW1: CW4 (2.5%: 2.5%)			0.0038	0.95030
CW4: CW 5 (2.5%: 5.0%)			3.0394	0.08211
CW1: CW 7 (2.5%: 1.5%)			33.915	< 0.0001
CW5: CW 7 (5.0%: 1.5%)			11.475	0.00078

Although TN removal generally improved in all VFCWs (Figure 5-10), the mean TN removal rates were variable at 79 % in CW Units 1 and 4 (2.5 % WWAR); 76.1 % at 5.0 % WWAR; and 70 % in CW Unit 7 (1.5 % WWAR). Overall, the 1.5% WWAR was 7.5

% below the TN removal rates reached by both the 2.5 % and 5.0 % WWARs. This result is less than the 10 % difference registered in the first year between these group of wetlands. This suggests variations in CWs increase to a point and after that begin to decline with time. These observations are in the context that first-year monitoring data revealed a 10 % difference in performance when the 1.5 % CW had been in operation for a shorter time than the 2.5 % and 5.0 % CW units.

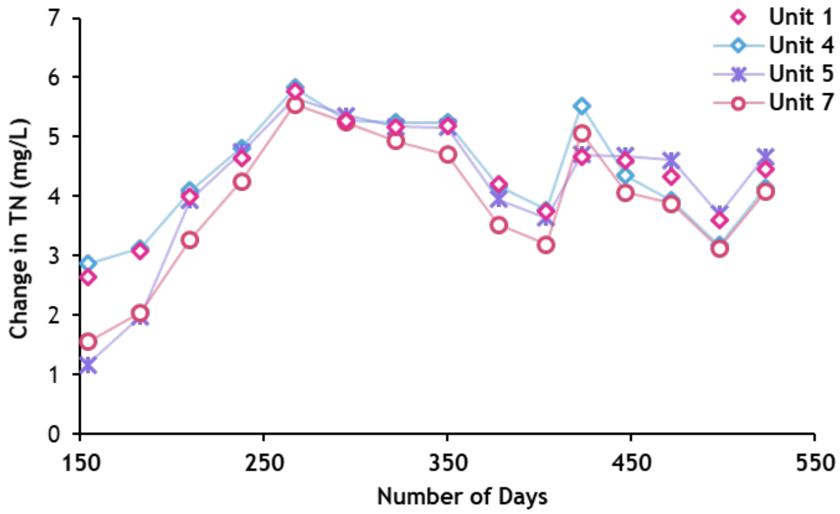


Figure 5-10 Mean monthly variations in TN at different WWAR

Thus, the proposition that the biological communities in the 1.5 % WWAR CW were not as developed as in the other VFCWs may have been valid in the first year of monitoring. However, after two years of operations, the 2.5 % WWARs had marginal differences in performance after the first and second years suggests that TN removal increases to a peak, and after that declines for all WWARs.

5.3.4.2 Total phosphorus removal (TPR)

ANOVA shows that the different WWARs produced significant differences on TPR. Thus, the null hypothesis that there is no difference in the effect of WWAR on TPR is rejected (Table 5-11). TPR in the VFCWs increased with time in the 1.5 % and 2.5 % WWARs, averaging at 75 % and 78 % respectively. Comparatively, TPR at 5.0 % WWAR was 86 %, the highest and most stable over the study period (Figure 5-11).

These findings are consistent with earlier studies that reported that TP removal in VFCWs was high at higher WWAR (Bratieres et al. 2008). Additionally, TP removal is a function of detention time than of hydraulic loading rate. Therefore, when inflow rates are high, resuspension of the settled solids occurs which compensates for the low hydraulic loadings and hence a decrease in particulate TP (Carleton et al. 2001).

Table 5-11 ANOVA comparisons of the effect of WWAR on TP removal (α = 0.05)

	NumDF	denDF	F-value	p-value
Intercept	1	547	5419.555	<0.0001
Primary media	3	547	172.172	<0.0001
Posthoc media comparisons				
CW1: CW4 (2.5%: 2.5%)			0.00512	0.94299
CW4: CW 5 (2.5%: 5.0%)			51.2988	<0.0001
CW4: CW 7 (2.5%: 1.5%)			16.1046	<0.0001
CW5: CW 7 (5.0%: 1.5%)			69.5699	<0.0001

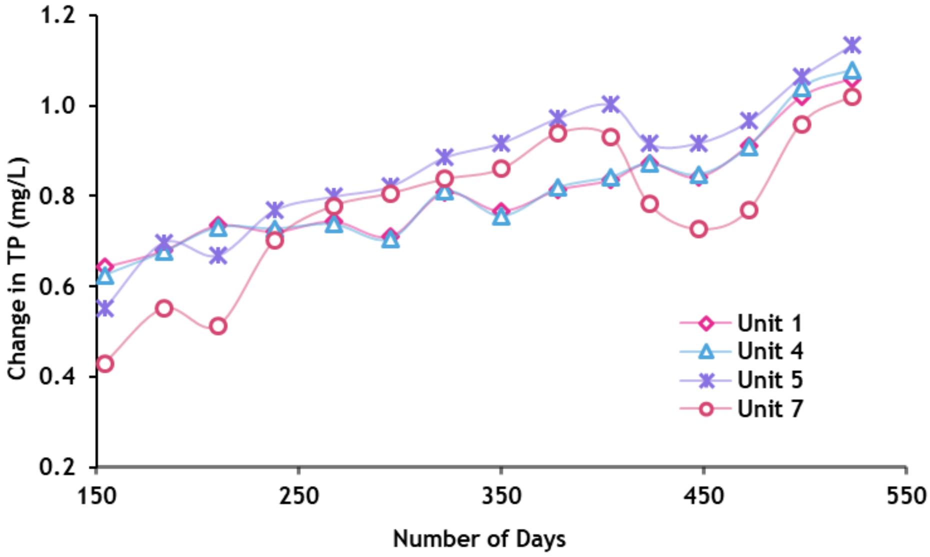


Figure 5-11 Changes in the mean monthly Fe at different WWAR

Thus, the 5 % WWAR VFCW (lowest influent volume) likely had a large proportion of the discharged effluent water comprising of water previously held in the CW's media. This water with a longer retention time had higher P adsorption potential and thus greater P removal. By contrast, effluents in the 1.5 % WWAR (high influent volume) were effectively flushed from the media bed thereby decreasing the fraction of previously held water (Bratieres et al. 2008).

5.3.4.3 Conclusion - Effect of WWAR on nutrients P and N removal

The results show that although both nutrients P and N were subjected to the same treatment, the effect of varying the WWAR on nutrient removal mainly impacted on P reduction. Thus, the 5% WWAR appear to have consistently improved and yielded higher P removal, while the long-term operations of the 1.5 % WWAR had marginal increases of the P removal. It seems that larger inflow volumes have an adverse effect on P removal, perhaps due to the low proportion of influent stormwater that is held in the CWs between doses. Furthermore, the results demonstrate that long-term contaminant removal in stormwater CWs can be predicted from the ratio of wetland area to the contributing watershed area.

5.4 Effect of short dry and extended dry rest periods

The effect of short dry rest periods (Unit 3) on pollutant removal involved dosing the VFCW Unit 3 on a 1 week wet, 1-week dry regime. The 2.5 % WWAR was used for this CW, and the primary media was loamy sand. Similarly, the effect of extended dry periods (Unit 6) on pollutant removal was investigated using CW Unit 6, operated at the 2.5 % WWAR and configured using loam sand media. To achieve extended dry periods, this VFCW was dosed once every after 4 weeks (1 week wet, 4 weeks dry).

5.4.1 Effect of short and extended dry rest periods on TSS

ANOVA results show that we cannot reject the null hypothesis that there is no difference in effect of drying regime on TSS (Table 5-12).

Table 5-12 ANOVA results for drying regime comparison on TSS removal (α = 0.05)

	NumDF	denDF	F-value	p-value
Intercept	1	40	999.3667	< 0.0001
Dry	1	8	2.6727	0.1407

TSS removal in Units 3 and 6 averaged at 82.7 % and 90.1 % respectively. Both CW Units 3 and 6 exhibited declines in their TSS removal performances after the first-year (where TSS removal had averages of 86 % and 92 % respectively). However, TSS removal in these intermittently dosed CW units compared well with TSS removal in the continuously dosed (wet) CW Units 1 and 4 (Figure 5-12).

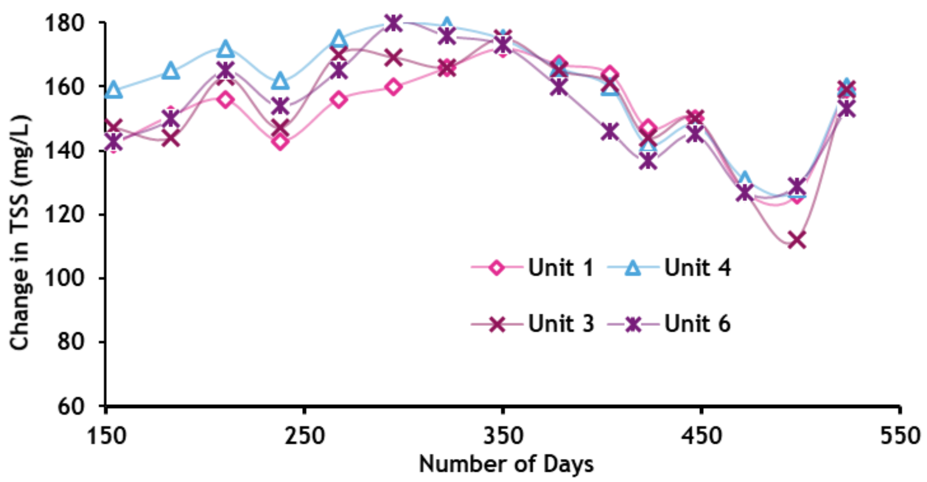


Figure 5-12 Mean TSS removal under short dry and extended dry rest conditions

TSS removal in stormwater CWs was not statistically significantly affected by either short or extended dry rest periods. However, because only loamy sand media was investigated, this conclusion cannot be extended to gravel or BFS media and the 1.5 % or 5.0 % WWARs. Equally, the relatively small data obtained for this strategy increases uncertainties and so limits the validity of these outcomes.

5.4.2 Heavy metal removal

Although several heavy metals were monitored, most metal species had their effluent concentration below their respective LODs namely: Ni (0.005 mg/L), Cu (0.001 mg/L), Pb (0.019 mg/L), Cd (0.0013 mg/L) and Cr (0.001 mg/L). therefore, only Zn and Fe are discussed in this section.

5.4.2.1 Zinc removal

ANOVA test results in **Table 5-13** show that there were no statistically significant differences in Zn removal between CWs operated as Unit 3. During the first year, CW Unit 6 attained Zn removal of up to 87 %, higher than the 85 % reached by Unit 3 (short dry rest regime). Similarly, at the end of the 2-year, the variations in the mean monthly Zn shows that the short dry Unit 3 and the extended dry Unit6 had better Zn removal of 83 % and 81 % respectively.

Table 5-13 ANOVA results for the effect of drying regimes on Zn removal (α = 0.05)

	NumDF	denDF	F-value	p-value
Intercept	1	40	204.35522	<0.0001
Dry	1	8	0.81332	0.3935

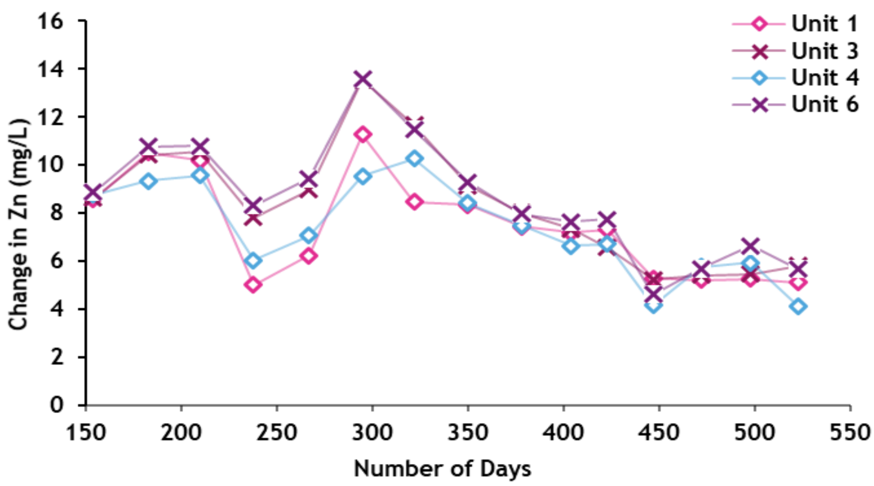


Figure 5-13 Monthly variations of Zn in short dry and extended dry conditions

These Zn removals were higher than those registered by Unit 1 (76 %) and Unit 4 (79 %). The trends are likely attributable to minimal biological activity in the short dry and extended dry VFCW Units 3 and 6 respectively. Thus, nutrient supply is limited hence reduced production and degradation of DOM. Consequently, minimal Zn is released into effluents.

5.4.2.2 Iron removal

ANOVA test results established that Fe removal was not statistically significantly affected by changes in the length of the dry weather conditions (Table 5-14).

Fe in the influent stormwater was mainly particulate. Unlike in the first year of monitoring where strong correlations between effluent Fe and TSS were found, the long-term data did not return consistently strong correlations between TSS and Fe in both CW Units 3 and 6.

Table 5-14 ANOVA for comparisons drying regime on Fe removal (α = 0.05)

	NumDF	denDF	F-value	p-value
Intercept	1	40	406.1826	<0.0001
Dry	1	8	1.0213	0.3418

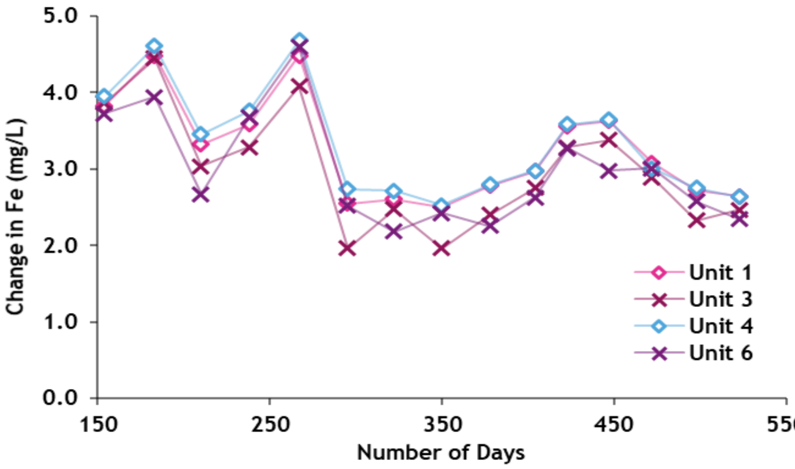


Figure 5-14 Changes in Fe under short and prolonged dry conditions

5.4.3 Conclusion – the effect of dry periods on heavy metals removal

Heavy metal removal in intermittently short dry and extended dry weather conditions can significantly affect the removal of metals such as Zn. Thus, when the drying regime is short (Unit 3), Zn removal is less efficient than when the drying regime is extended (Unit 6). Equally, the variations in both the short and extended dry CWs did not show declines in Zn removal. However, the weekly wetting strategy applied to loamy sand CWs (1, 4, 5 and 7) twice affected Zn removal in a cyclic pattern,while the same dosing plan in different media did not have any noticeable effect on Zn removal. Thus, if a reduction in treated stormwater volumes lowers biological activity (limited nutrient sources), then a decrease in DOM with sorbed Zn ought to be investigated.

5.4.4 Effect of short and extended dry periods on nutrient removal

5.4.4.1 Nitrogen

The ANOVA tests showed that there were no statistically significant differences in TNR when the periods of dry weather conditions are short or extended (Table 5-15).

Table 5-15 ANOVA for comparisons of drying regime on TN removal (α = 0.05)

	NumDF	denDF	F-value	p-value
Intercept	1	40	0.67535	<0.0001
Dry	1	8	0.0042367	0.948326

However, TN removal under short dry weather periods (Unit 3) and extended dry weather (Unit 6) generally increased. Initially, Unit 3 attained higher TN removal than Unit 6. However, towards the end of the first year of monitoring, TN removal in Unit 6 exceeded that in the Unit 3. After that, both Unit 3 and 6 experienced marginal gains and corresponding gradual declines in TN removal (Figure 5-15). Thus, the overall TN removal averaged at 76.4 % in Unit 3 and 68.1 % in Unit 6. The short and extended dry weather operated CWs (Units 3 and 6) had the highest mean NH_4-N values of 0.204 and 0.171 mg/l respectively. The data show that Units 3 and 6 VFCWs had nitrification rates that exceeded ammonification and denitrification hence the low TN removal observed in Units 3 and 6.

VFCWs are renown for aiding nitrification because ammonia adsorbed during dosing nitrifies during rest periods and later volatilises on subsequent dosing (Molle et al. 2008). Ammonification and denitrification are biologically mediated processes associated with the presence and activity of microbial communities in CWs. However, the growth and maintenance of these dynamic microbiomes for enhanced N transformation through ammonification and denitrification is subject to availability of oxygen, temperature, pH, carbon: nitrogen ratio (C/N), availability of nutrients and soil structure (Lee et al. 2009). Therefore, periods of dry weather will limit the amount of oxygen drawn into the CWs during dosing, as well as limit the sources of C and N. Consequently, the restricted supply of oxygen, carbon and nitrogen leads to growth of secondary microbial community structures which are less efficient at transforming nitrogen. Thus, the more extended the dry periods, the lower the TN removed hence the trends observed in Figure 5-15.

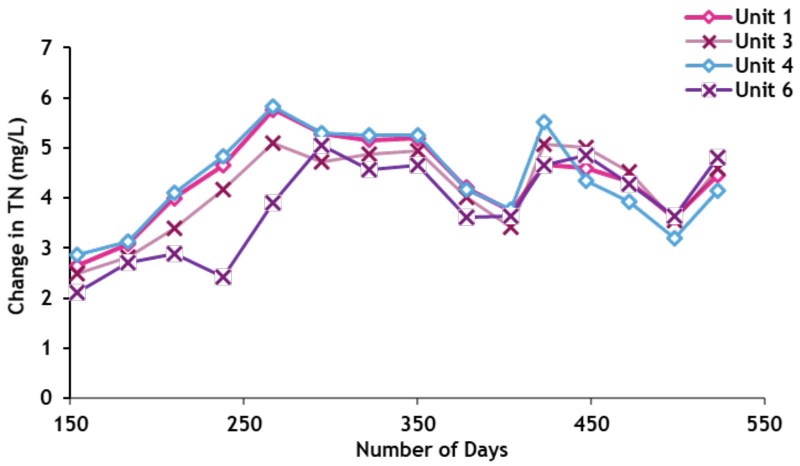


Figure 5-15 Variation of TN in short and prolonged dry conditions

5.4.4.2 Phosphorus

ANOVA test results (Table 5-16) reveal that there were no significant differences in TP removal attributable to short or extended dry rest periods.

Table 5-16 ANOVA results for drying regime comparisons on TP removal (α = 0.05)

	NumDF	denDF	F-value	p-value
Intercept	1	40	273.90694	<0.0001
Dry	1	8	0.90098	0.3703

Thus, the changes in the mean monthly TP in Units 3 and Unit 6 show cyclic patterns: a gradual increase in TP is followed by a decline. This could explain the convergence in TP at the end of the study period (**Figure 5-16**).

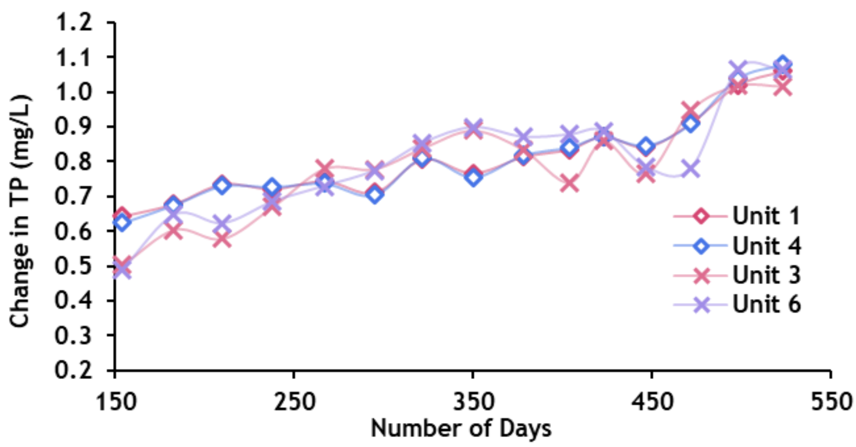


Figure 5-16 Changes in TP under short dry and prolonged dry rest periods

5.4.4.3 Conclusion – the effect of drying on nutrient removal

Generally, the effect of short and extended dry weather conditions (Unit 3 and 6 respectively) on the removal of TP and TN did not statistically significantly affect variations in P and N removal. This is because the operational strategies applied to the VFCWs Unit 3 and Unit 6 appear to have limited the nutrient and dissolved oxygen supplies. The limited nutrients and oxygen subsequently had a negative effect on the development of eco-treatment microbiomes. Consequently, microbial succession required to favour emergence of appropriate species was interrupted. Ultimately, TN transformations reliant on biological processes of ammonification and denitrification were not effective in CWs 3 and 6 hence the relatively low TNR observed in comparison to TNR rates in the regularly dosed VFCWs 1 and 4.

Chapter 6 Modelling contaminant removal in VFCWs: an integrated approach using principal components analysis and artificial neural networks

This chapter focuses on the development and application of multi-layer perceptron artificial neural network (MLP-ANN) models to explore the influence of design and operational variables on the long-term removal of pollutants in VFCWs. The neural network models are developed using a modified Broyden–Fletcher–Goldfarb–Shanno (BFGS) learning algorithm and are implemented in WinGamma Software.

The process of building the ANN models involved three major steps namely: data normalisation and partitioning (training, validation/prediction); the determination of Gamma and M-test statistics; the identification of cost-effective and reliable models for predicting TN and TP removals in the VFCWs. Furthermore, the variable inputs for building the ANN models were selected by data reductive exploratory analyses, principal component analysis (PCA), and local sensitivity analyses. The coefficient of determination (R^2) and Nash-Sutcliffe coefficient of model Efficiency (NSE) are used to evaluate the precision and reliability of the ANN models.

6.1 Exploratory data analysis of variables

The purpose of exploring the data was to establish trends and relationships in the data; as well as to evaluate data dependencies among the variables. One of the observations was that there were significant differences in the means of the various input variables (Section 5.2). Additionally, most variables exhibited non-normal distribution curves except for ISS, ETP and TPR, which suggests that not all the data were normally distributed. Similarly, some variable box-plots revealed outliers. Thus, PCA was used to determine which variables maximise the variance and hence contribute to the most variability within the data. Consequently, to avoid variables with significantly large means from dominating variables with smaller means, the entire data-set was normalised (Kokot et al. 1998). Normalisation was accomplished by re-scaling data features to achieve a standard normal distribution: mean of zero and standard deviation of one. This approach produces data components that appropriately explain the variance of each variable.

The PCA module in IBM SPSS Statistics 23, was applied to reduce the dimensionality of the 2-year experimental data. PCA simplified the extraction of the most significant input variables. The PCA methods used include the Kaiser-Meyer-Olkin measure of sampling adequacy and Bartlett's Test of Sphericity (BTS); Scree plot; extraction column of communalities, and the components matrix.

Although CW Unit 1 is selected to illustrate the process of data reduction by PCA, the same procedure was applied to all the 6 VFCWs for which ANN models were built. Furthermore, in addition to excluding input variables directly related to the output (e.g. ITN and ETN when predicting TNR), the output and derived variables were also removed from PCA so that all variable relationships obtained are independent of the output. This approach minimised the possibility of developing redundant models.

6.2 Principal component analysis (PCA)

The size, nature and type of the input variables or input data influence the performance and reliability of MLP-ANN models. Unlike mathematical models whose inputs are determined from empirical and analytical approaches, inputs in neural networks are selected using a combination of statistical analysis and a priori knowledge of causal links. However, the analysis of extensive data-sets with multiple variables requires techniques that can group similar data as well as identify the relationships among the variables. The multivariate method considered suitable for this study is PCA (Herngren et al. 2006; Gunawardana et al. 2014).

PCA describes the complete data matrix in a reduced number of principal components (PCs) by transforming the original variables to a new orthogonal set of PCs for defining the relationships among the variables. In PCA, the objects that exhibit similar variances have similar PCA scores hence form a cluster when plotted on a biplot. Additionally, correlated variables have the same orientation when plotted, whereas uncorrelated variables are orthogonal to each other.

6.2.1 Kaiser-Meyer-Olkin (KMO) and Bartlett's test of sphericity (BTS)

KMO test assesses the appropriateness of applying PCA to reduce a multiple dataset. KMO values vary between 0 and 1. A KMO tending towards 1 suggests that the sample data is adequate to conduct PCA. Several rules of thumb recommend a KMO minimum of 0.5 and a BTS p-value less than 0.05. The KMO and BTS test results for all the data of the 6 VFCW are presented in Table 6-1. The values of both the KMO and BTS reveal that PCA can be applied for reducing the dimensionality of the constituent datasets.

Table 6-1 KMO and Bartlett's Test for VFCWs

	Variable	Unit 1	Unit 2	Unit 4	Unit 5	Unit 7	Unit 8
	KMO	0.709	0.635	0.599	0.576	0.582	0.546
BTS	x^2	6738.468	5776.13	5913.89	6198.30	6258.67	6036.03
	df	378	378	378	378	378	378
	p-value	0.000	0.000	0.000	0.000	0.000	0.000

6.2.2 Scree plot

Eigenvalues are variances of the principal components, and therefore, the component with the most significant eigenvalue accounts for the most substantial variation within the data, then the component with the second most abundant variance accounts for the following most considerable variation in the data, and this applies for the serial component numbers. Therefore, a scree plot represents a plot of eigenvalues against variable numbers. The scree has a characteristic feature – a sudden break as the variable eigenvalues drop. The break on the scree plot (Figure 6-1) aids with the identification of components whose eigenvalues are higher than 1. As the curve elbows, the successive eigenvalues with values below 1 begin to level off suggesting that these components account for minimal variation in the data analysed. Based on CW Unit 1 data, 8 principal components with a threshold eigenvalue (variance of 1) were extracted.

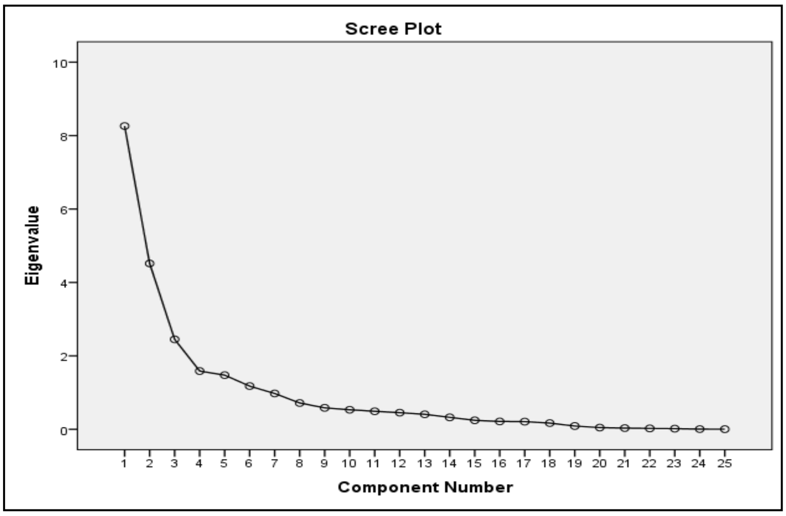


Figure 6-1 Scree plot for CW Unit 1

6.2.3 Cumulative proportion of variance and eigenvalue

Here two different PCA techniques are combined to extract variables. Firstly, all variables contributing to 95 % of the variance are extracted (Hair et al. 2009). From the 95 % contributing variables, further reductions are made by extracting variables with eigenvalues greater than 1 (the scree plot). Thus, although components 1-15 explain 97 % of the total variance (Table 6-2), only principal components 1 to 6 with eigenvalues exceeding 1 were extracted. Furthermore, variables that are strongly correlated with components 1 and 2 were different from those between components 1 and 3. This further validates the observed cumulative percentage of variance. Because identifying relationship strengths among the variables is key to building robust models, the components matrix was applied (Table 6-3).

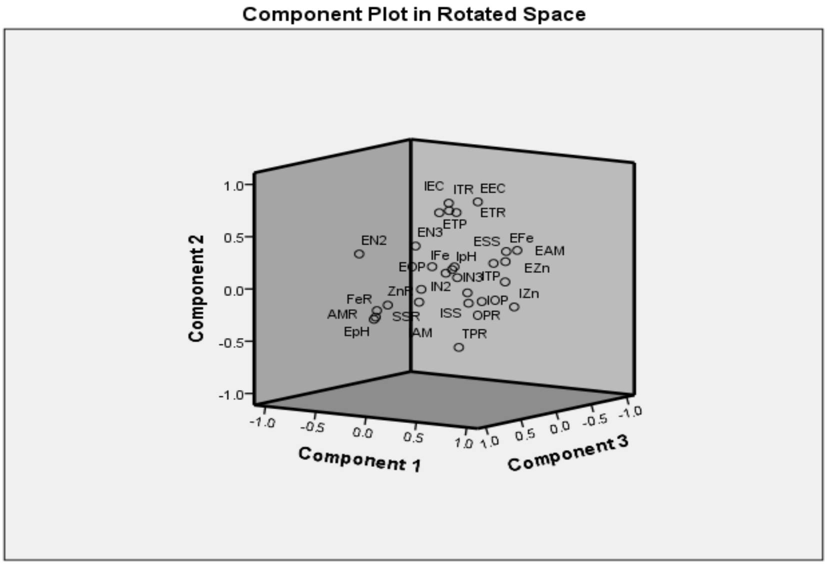


Figure 6-2 Component plot in rotated space of CW Unit 1

PCA outputs for CW Unit 1 data show that components 1, 2 and 3 account for 33.97 %, 16.23 % and 10.16 % respectively (50 % of total variance). This proportion is considered low (Pett et al. 2003) and is an indication that all 24 variables analysed independently contribute to the observed correlations. Besides, a low cumulative variance suggests that the relationships are likely non-linear. The two assumptions are based on the cumulative percentage of mean-variance. Therefore, not all the components extracted by PCA are needed for developing models. The component plot in rotated space obtained for Unit 1 reveals strong relationships between components 1, 2 and 3 (Figure 6-2).

Table 6-2 Total eigenvalue and cumulative percentage of total variance for Unit 1

	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
Component	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	8.155	33.978	33.978	8.155	33.978	33.978	5.739	23.914	23.914
2	3.896	16.232	50.210	3.896	16.232	50.210	3.510	14.627	38.541
3	2.438	10.159	60.369	2.438	10.159	60.369	3.256	13.567	52.109
4	1.555	6.480	66.849	1.555	6.480	66.849	2.858	11.910	64.019
5	1.468	6.119	72.968	1.468	6.119	72.968	1.787	7.447	71.466
6	1.144	4.766	77.733	1.144	4.766	77.733	1.504	6.268	77.733
7	.966	4.024	81.758						
8	.700	2.915	84.673						
9	.584	2.434	87.106						
10	.492	2.048	89.154						
11	.486	2.026	91.181						
12	.449	1.870	93.051						
13	.365	1.519	94.570						
14	.325	1.353	95.923						
15	.243	1.012	96.935						
16	.208	.867	97.802						
17	.198	.824	98.627						
18	.168	.701	99.328						
19	.077	.323	99.650						
20	.034	.140	99.790						
21	.024	.099	99.890						
22	.017	.072	99.962						
23	.006	.024	99.986						
24	.003	.014	100.000						

Extraction method: principal component analysis (PCA).

6.2.4 Components matrix

The component matrix includes the component loadings or correlations between the components and the variables. A threshold correlation of 0.3 is set so that the missing component loading is an automatic implication that their correlation is less than 0.3. The correlation matrix was selected because the variables analysed had different scales, variances that differ significantly and therefore required standardisation. While correlations greater than ± 0.3 are suitable for reduction, in this study only relationship strengths greater than ± 0.5 were selected to further reduce the multiple variables (Table 6-3).

Table 6-3 Component Matrix for TNR in CW Unit 1

Variable	Component						
	1	2	3	4	5	6	7
IpH	.790						
ITR	.672		-.421			.303	
IEC	.359		-.518				
ISS		.440	.514	.448			.334
IOP	.350	.574	.407				
ITP		.513		.416	-.460		
IN2				.416	.451		-.497
IN3				.449		-.302	-.576
IAM			.537	.609			
IFe	.386				.594	-.455	.304
IZn	.412	.477	.355				
EpH		-.333	.594			.465	
ETR	.814					.314	
EEC	.637		-.389				
ESS	.913						
EOP	.769		.439				
ETP	.593	-.574					
EN2	-.444	-.437				.449	
EN3	.571	-.636					
EAM	.865						
EFe	.912						
EZn	.482	.713					

It is noticed that some influent and effluent variables were eliminated as these did not strongly influence other variables and hence the output. Furthermore, the extraction of input variables for the development of models were based on the highest correlation extracted from the component matrix. Additionally, since PCA outputs for CW Unit 1 data pointed to non-linear relationships among the variables, regression models were considered inadequate for developing predictive models. Hence, the MLP- ANN models were preferred. MLP-ANN have been used in studies in which pattern recognition is key to understanding complex relationships.

6.2.5 Discussion of principal component analysis

Principal component analysis (PCA) enables the identification of small uncorrelated variables (principal components) within a large data-set. As the number of variables is reduced, multicollinearity is avoided, making it possible to develop models from many predictors relative to the number of observations (Minitab 2014). Of the PCA reduction methods discussed above, the components correlation matrix was the most effective in extracting significant relationships among the variables of each

CW unit. The components matrices created a simplified data-set while retaining substantial information contributed by all the variable predictors.

Generally, effluents and derived variables (per cent reductions) showed strong relationships, while influent variables revealed few and mostly weak relationships with the other variables. The weak relationship strengths could be attributed the nearly constant influent semi-synthetic stormwater concentrations that were applied. The strong relationships among the inputs in each VFCW were varied and thus indicative of the distinctive ways the different designs treated the stormwater.

Moreover, the pollutants commonly targeted for removal in CWs are TN, $N\text{-}NH_4^+\text{-}N$, and $PO_4\text{-}P$. However, the removal mechanisms of these contaminants are influenced by other environmental conditions like the pH and temperature (for nitrification and precipitation reactions). Therefore, it was proposed that to reduce the cost of monitoring; ANN models are built from the relatively cheap to monitor parameters (electrical conductivity, pH, and temperature), and then subsequently apply the models to predict the removal rates of costlier parameters (TN and TP). However, the data analysis by PCA revealed that the different VFCWs produced effluents of variable water quality. Furthermore, the data of some nutrient species (TN, $N\text{-}(NH_4)^+$, and $P\text{-}(PO_4)^-$ were not collected from inception (to attain stability). Accordingly, it was not possible to directly compare the physico-chemical data at inception with the pollutant removal collected later. Additionally, although pH and temperature formed strong relationships with other variables, these relationships could not adequately describe the treatment processes that control pollutant removal in VFCWs. Thus, all the physico-chemical data were treated as inputs.

Similarly, the influent and effluent concentrations directly related to the output variable were not included in PCA. This procedure was intended to minimise the possibility of building models whose inputs are directly related to the output variables. Consequently, the ANN models were mostly developed from the influents and effluent variables not related to the outputs.

6.3 ANNs for predicting pollutant removal in VFCWs

While investigating the influence of design on pollutant removal in Chapter 5, it was reported that there were multiple non-linear combinations among the variables suggesting non-linearity in the data. Likewise, the multiple variables monitored (27, including derived variables) were an indicator of an exponential number of patterns within the data signalling pattern complexity. These two factors were enough to validate the application of ANNs as an appropriate modelling technique adopted in this study for predicting the long-term pollutant removal in tidal-flow VFCWs. Additionally, pollutant removal in CWs is a combination of biological, chemical and physical processes (Wynn and Liehr 2001; Lee et al. 2002b; Langergraber et al. 2008). Modelling such multifaceted processes is complicated thus requires specific methods (Langergraber 2007). Under such circumstances, computational models are often valuable tools (Steven 1997). Some researchers have simulated pollutant removal in CWs; the hydraulics of CWs, and nutrient biogeochemistry in CWs using various tools (Wynn and Liehr 2001; Lee et al. 2002b; Langergraber et al. 2008). Likewise, to simulate ecological behaviour in polluted water bodies, a modelling approach that utilises hydro-informatics software was used to collate physical, chemical and biological interactions that underpinned the processes under investigation (Binliang et al. 2006). Recent research studies about stormwater treatment deployed mechanistic models like AQUASIM, HYDRUS and STELLA to describe adsorption phenomenon in CWs (Mburu et al. 2012; Mburu et al. 2014). It was concluded that obtaining boundary conditions to represent constructed wetland systems as well as describe treatment processes is vastly challenging. Specifically, HYDRUS software could not simulate tidal-flow dosing because Hydrus cannot vary boundary conditions in a single modelling scenario. Nonetheless, HYDRUS successfully predicted biologically influenced removal processes for ammonia $(N\text{-}NH_4)^+$, but the same technique could not model orthophosphate $(P\text{-}PO_4)^-$ removal (Lucas 2015).

However, in earlier modelling studies, neural networks were developed to predict the biochemical oxygen demand (BOD) and suspended solids (SS) concentrations in the effluent of a wastewater treatment plant (Hamed et al. 2004); prediction of BOD and chemical oxygen demand (COD) removal in HFCW (Akratos et al. 2008); to predict stormwater quality (May et al. 2009); for prediction of the removal of ortho-phosphate (PO_4-P) and total phosphorus (TP) in HFCWs Akratos et al., (2009). In the latter publication, the topologies of the successful ANNs were proposed, and the ANN model predictions described as reasonably good for the design of CWs (Akratos et al. 2008). By contrast to neural networks, the application of mechanistic models is at times limited by several factors including the operational strategy deployed to the treatment system and the measurement of the definitive boundary conditions. Therefore, there is a need to develop simple yet effective models for evaluating the overall performance of any pollution control strategy. This approach underlines the application of ANNs in various investigations. More specifically, the “black-box” nature of CWs technology makes the use of neural networks appropriate for predicting pollutant removal. The performance of ANNs, however, depends so much on the selection of input variables and the network architecture.

6.4 Network architecture and optimisation algorithm

ANN is a form of artificial intelligence technique which imitates the neurology of the brain. ANNs are a highly interconnected web of nodes or neurons (processing elements (PE)) that perform progressive, complex computations on a specific set of inputs in order to produce a set of outputs. ANNs are composed of layers (containing neurons) that include, a single input layer, a hidden layer (which can be multiple) and a single output layer. Each input variable is relayed to the proceeding neuron having a unique bias via a connection with a specific weight.

ANNs are categorised into two major groups: perceptrons and sigmoid (Figure 6-3). The perceptron activates an output of either 0 or 1 if the computed difference between the weighted sum of the inputs is less or greater than a predefined threshold value respectively as shown in Equation 6-1. The condition $\sum_i^n \boldsymbol{w_i x_i} \leq \boldsymbol{threshold}$ is simplified by introducing a dot product i.e. $\boldsymbol{w} \cdot \boldsymbol{x} \equiv \sum_i^n \boldsymbol{w_i x_i}$, and the threshold is replaced by the bias, i.e. for MLP's the new rule is written as:

$$\begin{cases} \mathbf{0}\ \boldsymbol{if}\ \boldsymbol{w} \cdot \boldsymbol{x} + \boldsymbol{b} \leq \mathbf{0} \\ \mathbf{1}\ \boldsymbol{if}\ \boldsymbol{w} \cdot \boldsymbol{x} + \boldsymbol{b} > \mathbf{0} \end{cases} \quad \text{......} \quad 6\text{-}1$$

Inputs into a sigmoid neuron are not necessarily 0 or 1. Similarly, the outputs can fall anywhere between 0 or 1 defined by $\boldsymbol{f(x)} = \boldsymbol{\sigma}\ (\boldsymbol{w} \cdot \boldsymbol{x} + \boldsymbol{b})$ **or**

$$\boldsymbol{f(x)} = \frac{\mathbf{1}}{(\mathbf{1} + \boldsymbol{e^{-x}})} = \frac{\mathbf{1}}{(\mathbf{1} + \mathbf{exp}(\boldsymbol{w} \cdot \boldsymbol{x} + \boldsymbol{b}))}$$ 6-2The sigmoid is a modified perceptron that activate outputs in the range of 0 to 1 by applying a sigmoid function to the weighted sum of inputs as shown in Equation6-2. The perceptrons output is represented in Equation 6-3:

$$\begin{cases} 0 \text{ if } \sum_i^n w_i x_i \leq \text{threshold} \\ 1 \text{ if } \sum_i^n w_i x_i > \text{threshold} \end{cases} \quad \text{......} \quad 6\text{-}3$$

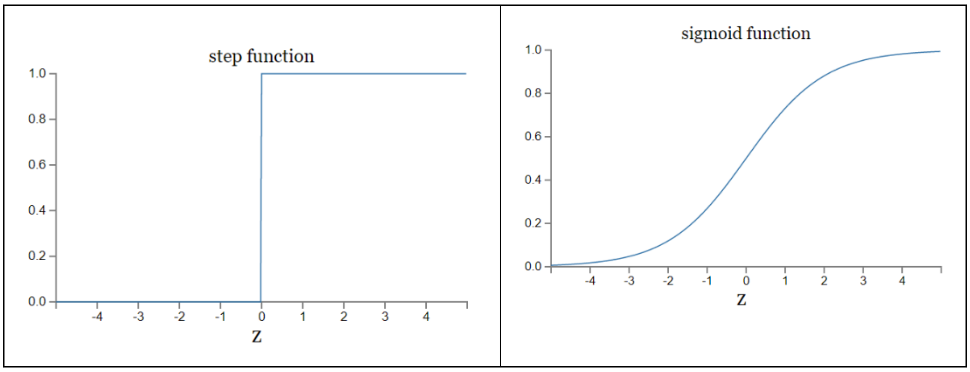


Figure 6-3 Illustrating the Step and Sigmoid functions of MLPs

Although the perceptron output does not precisely reflect the real-world decision making, it does show how evidence is used to make decisions. A larger perceptron containing more nodes and more layers is often called a multi-layered perceptron.

In this research study, a feed-forward network structure was used. Feedforward is a multilayer perceptron (MLP) in which information is fed forward and never backward. The signal flows through from one layer to the next in a unidirectional manner. The network uses the sigmoid function shown in Equation to perform non-linear interpolations on inputs to derive an output, a process known as training.

During training, the neural network learns the input-output relationship from training data based on a particular optimisation algorithm with the aim of improving the performance of the network. The optimization algorithm employed in this study is called modified Broyden–Fletcher–Goldfarb–Shanno (BFGS). It is considered the most efficient in WinGamma. BFGS algorithm uses hybrid annealing-genetic algorithms with second differences, a technique dependent on matching input and output patterns. When training, the BFGS algorithm adjusts network weights and thresholds so that errors made on predictions are minimised. Network learning begins in the input layer, where the input variables are processed into signals and distributed to the hidden layer per Equation 6-4:

$\mathrm{Net}_{pj}^{h} = \theta_j^h + \sum_{i=1}^{N} W_{ji}^{h} X_{pi}$ 6-4where: Net_{pj}^{h} = sum of the input signal to the hidden layer neurons (j), W_{ji}^{h} = connection weights from the input layer (i) to the hidden layer neurons, h = quantity in the hidden layer, θ_j^h= weight bias term in the input layer, X_{pi}= input variable; n = input dimensionality vector.

Signal transmission from the hidden to output layer is represented by Equation 6-5:

$$\mathrm{Net}_{pj}^{o} = \theta_k^o + \sum_{j=1}^{L} W_{pj}^{o} \quad \text{...} \quad 6\text{-}5$$

where, W_{ji}^{h} = connection weights from neurons in the hidden layer neurons to the output layer, 0 = output layer, θ_k^o = weight bias term in the output layer; and L = number of nodes in the output layer.

The signal in the output layer neuron (j) takes the form of Equation 6-6:

$$O_{pk} = f_k^o\left(Net_{pk}^o\right) \quad \text{6-6}$$

Equations 6-2, 6-3 and 6-4 represent the feed-forward phase of training. Feedforward is followed by backward training to minimise the error on the training set. The procedure is the same as the feed-forward training except that it begins from the output layer and makes a change of ΔW_{ji}^{h} on the connection weight (W_{ji}^{h}) such that:

$$\Delta W_{ji}^{h} = \eta\, \delta_j O_i \quad \text{6-7}$$

where, η = learning rate, O_i = Output of the ith unit and; δ_j = Local error gradients. The local error gradient is dependent on whether the unit into which the weights feed is in the output layer or in the hidden layer. I the local gradients are in the output neurons, then the gradients are products of the derivatives of the network's error function and the unit's activation function shown in Equation 6-8:

$$\delta_j = \left(\frac{\partial f}{\partial Net_j}\right)\left(O_{pk}^{(t)} - O_{pk}\right) \quad \text{6-8}$$

On the other hand, local error gradients in the hidden layers/neurons are the sum of the units of outgoing weights and local gradients of the units to which these weights connect. The term $O_{pk}^{(t)}$ defines the target output for the output neuron j and is non-existent in hidden layers/neurons as these have no target outputs. This term is corrected for by the sum of the $\boldsymbol{\delta_q}$ terms already obtained for neurons q that connect to output j in Equation 6-9

$$\boldsymbol{\delta_j = \left(\frac{\partial f}{\partial Net_j}\right)\sum_q W_{qi}\, \delta_q} \quad \text{6-9}$$

ANN modelling in this study utilised on-line supervision shown in equation 6-10:

$$\boldsymbol{\Delta W_{ji}(t+1) = \eta\, \delta_j O_i + \alpha \Delta W_{ji}(t)} \quad \text{6-10}$$

where: t = Epoch number; $\boldsymbol{\alpha} =$ Momentum coefficient; $\Delta W_{ji}(t+1)$ and; $\Delta W_{ji}(t)$ = weight change in epochs (t+1) and (t) respectively. Once trained, an ANN can simulate the unknown function from the input-output relations to make predictions.

6.5 WinGamma

WinGamma is a novel data analysis tool developed by researchers at Cardiff School of Computing and Informatics, Cardiff University. The application of WinGamma software to this research study was premised on the ability of WinGamma to determine patterns within data, even where the underlying function is unknown. WinGamma estimates the least mean squared error (MSError) that any smooth model can achieve on data without over-training. The application of WinGamma software to this research study was premised on the ability of WinGamma to determine patterns within data, even where the underlying function is unknown.

However, where describing the ongoing phenomenon is not of concern, other modelling approaches can be applied. For example, WinGamma software can be an excellent tool for comparing two or more similar systems and their behaviour under different conditions. Furthermore, WinGamma can be useful at developing predictive models for evaluating system performance, optimising design and making design recommendations. Equally, WinGamma can create models that can answer 'What if' queries, in this case, whether certain pollutant concentrations can be treated in the CWs.

WinGamma assumes that non-determinism in a smooth model from inputs to outputs is due to the presence of statistical noise on outputs. WinGamma hence determines whether a steady model can be built by analysing noise levels of the data. Thus, WinGamma software is designed to produce near-optimal smooth functions from inputs data. Inputs and outputs should be continuous real variables from some limited range; while the unknown function is presumed to be smooth (bounded first and second derivatives). If the function has regions of high curvature, it will be much harder to produce an accurate predictive model (Jones et al. 2000).

WinGamma also assumes that the noise variance on outputs is bounded and independent of input values. Thus, if the independence condition is false, the Gamma test will return an average noise variance over the whole input space. Therefore, subject to these circumstances WinGamma can be applied to a wide range of non-linear problems. WinGamma software simulates non-linear processes by computing statistical noise or gamma statistic, r, of the data. The Gamma statistic is related to the unknown function through Equation 6-11:

$$y = f\ (x) + r \qquad \text{6-11}$$

where; f (x) = smooth unknown function, and r = stochastic/noise variable (Evans and Jones 2002). Gamma statistic measures noise variance, r, which is dependent on sample size such that as the data size increases, the Gamma statistic converges in probability to an asymptotic value characteristically equal to the variance of the noise on the output. The converged probability values are used to select variables, with priority given to those variables with a tendency to minimise the asymptotic value of the Gamma statistic.

The Gamma test is useful because it directly works out whether there is enough data to form a smooth non-linear model and how good that model could be. Thus, a Gamma statistic close to zero suggests that the prospects of finding a stable model are high, subject to the number of available data-points. Data-points and stability of the gamma statistic are established by the M-Test (variance of Gamma statistic).

6.6 Development of ANNs models for TNR and TPR in VFCWs

CWs are among the most cost-effective wastewater treatment technologies worldwide. However, changes in land-use, weather and climatic conditions, make it difficult to control the non-point pollutants carried in stormwater. Therefore, this study investigated the effects of design and operational variables on the long-term performance of VFCWs treating urban stormwater. The investigations were carried out using an experimental monitoring program consisting of 8 VFCWs.

ANNs can model environmental systems in which the key processes are challenging to quantify. Thus, in contrast to mechanistic models whose application reduces as data dimensions increase, the predictive power of ANNs improves with an increase in data. Nonetheless, careful selection of variables is essential to reducing data dimensions. While some studies applied rule-based systems (Kotti et al. 2013), fuzzy-logic based systems (Blauw et al. 2010), and cellular automata (Chen and Mynett 2006) to develop ANN models, this research study uses an approach that integrates PCA (George and Mallery 2016) and WinGamma software (Jones et al. 2000). The reason this approach is used is that the processes involved in wastewater treatment by CWs are highly variable and exhibit non-linear characteristics.

Although neural networks can be implemented by different network architectures, the multi-layer perceptron artificial neural network (MLP-ANNs) and radial basis function neural works (RBF-NN) are the most common (Binliang et al. 2006; Binliang Lin et al. 2008; Abyaneh 2014; Bagheri et al. 2015; Li et al. 2015). Furthermore, the 'Black-box' nature of the experimental data, coupled with the budget constraint associated with other modelling options, building ANN models was the practical option, particularly when accomplished with WinGamma software.

MLPs consist of three distinct layers: input, hidden and output layers. The input and output layers can operate with any number of variables such that neurons in both the input and hidden layers assess output responses concerning the weighted sum of inputs based on the activation function (Dawson et al. 2006). In this research study, the focus was on the application of MLP-ANNs for predicting long-term pollutant removal in stormwater CWs. The variables fed to the input layer were selected from the variable relationships identified by PCA. The input variables data were normalised for compatibility as well as for each variable to have an equal chance to contribute towards predicting the output. The ANN network in this study comprised of 5 nodes in both the input and hidden layers (Figure 6-4).

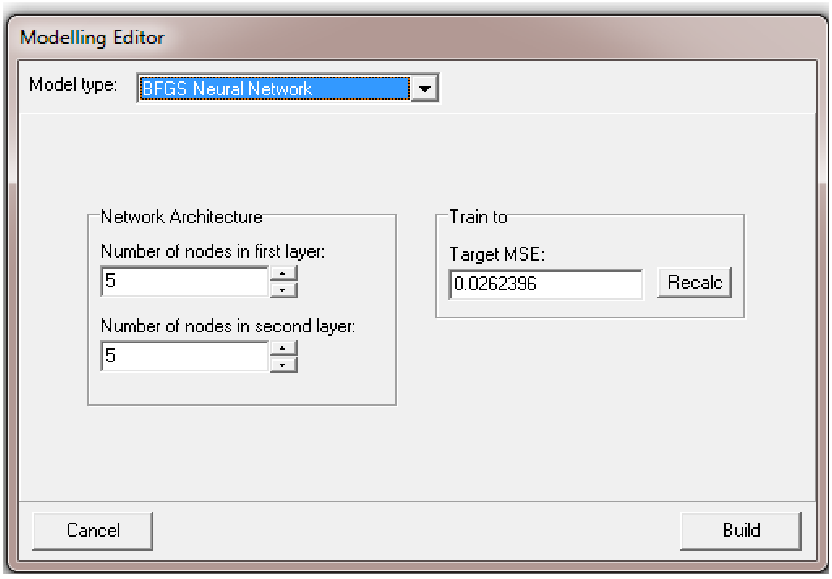


Figure 6-4 Neural network architecture in WinGamma

PCA extracted predictor variables for TNR and TPR from a set of inputs which had no relationship with the outputs. Additionally, to enhance the reliability of the models created, derived inputs (per cent reductions) were removed from PCA. Finally, to evaluate the performance of the ANN models in the different VFCWs, a 'standard model' denoted as Model 1 was created from all the principal components identified. This approach provided a basis for conducting sensitivity analyses on subsequent models in each VFCW. Equally, to ensure a uniform modelling process, the data for all the VFCWs were randomised so that each data point had an equal chance to influence the training and validation processes. Similarly, input data were standardised and partitioned into training (70 %) and validation (30 %), thus reduced the possibility of underfitting or over-fitting the model.

6.6.1 ANN models for TNR in CW Unit 1

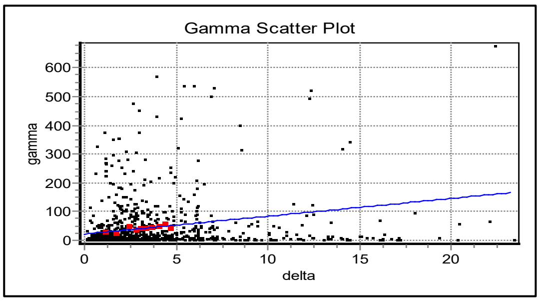
ANN models for predicting total nitrogen removal (TNR) were selected from the PCA extracted input variables (most significant principal components). The variable inputs directly related to the output were excluded from PCA. Therefore, the predictors of TNR in CW Unit 1 consisted of suspended solids (ISS), zinc (Zn), pH, ammonia (IAM), iron (IFe), nitrate (IN3), and nitrite (IN2). However, to improve the robustness of the ANN models, the principal components were reduced further by simulating various combinations (weights decrease from left to right in (Table 6-4).

Table 6-4 ANN models for predicting TNR in CW Unit 1

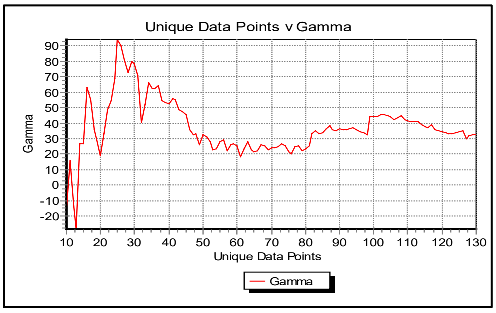
Model	Network Inputs	TRMSE	VRMSE	R^2	NSE
1	ISS, EZn, EpH, IAM, IFe, IN3, IN2	0.042	0.059	0.81	0.79
2	ISS, EZn, EpH, IAM, IFe, IN3	0.066	0.068	0.74	0.65
3	ISS, EZn, EpH, IAM, IFe, IN2	0.046	0.101	0.50	0.39
4	ISS, EZn, EpH, IAM, IN3	0.049	0.077	0.69	0.65
5	ISS, EpH, IAM, IN3	0.060	0.083	0.65	0.59
6	ISS, EZn, EpH, IN3	0.048	0.173	0.20	0.06
7	ISS, EZn, EpH, IAM	0.048	0.136	0.30	0.20

Several input scenarios were simulated to identify the combination with the lowest input variables and thus least monitoring costs. Subsequently, a local sensitivity analysis was used to determine the effect of any input variable on the output. Thus, although Models 1 and 2 had comparable low training root mean square errors (TRMSE) and validation root mean square errors (VRMSE), masking the input IN2 from Model 1 resulted in a decline of 10 % in R^2 and 17 % in the NSE of Model 2.

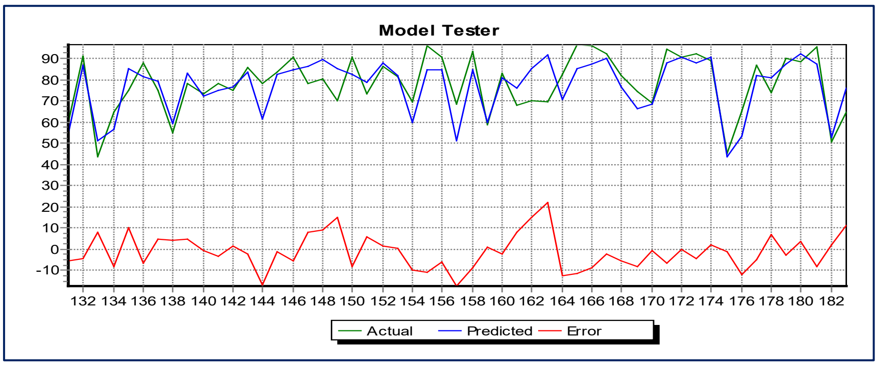
Similarly, further reductions of input variables in Models 3 to 7 did not improve the performance in the resultant models. Noticeably, Models 2 and 4 attained similar predictions during training and validation; and produced comparable R^2 and NSE. This shows that IFe and IN2 are not critical predictors of TNR in Unit 1. Additionally, Model 3, 6 and 7, had low precisions, which can be attributed to the absence of the influent Nitrate-N (IN3). Thus, although all the 7 principal components extracted were relevant to predicting TNR, it appears that nitrate-N (IN3) plays a key role in TNR. Accordingly, the best fit model for predicting TNR in CW Unit 1 was Model 5, because it had fewer inputs; the least TRMSE and VRMSE; and good R^2 and NSE. The results of the gamma statistic, M-test and TNR predictions are shown in Figure 6-5.



(a)



(b)



(c)

Figure 6-5 (a) Gamma plot (b) M-test (c) Model 5 TNR predictions in CW Unit 1

6.6.2 ANN standard models for TNR in CW Units 1, 2, 4, 5, 7 and 8

Standard models for predicting TNR in the different VFCWs are presented in Table 6-5. All the models produced low TRMSE and high VRMSE except Units 1 and 7. Correspondingly, TNR models from Units 1 and 7 attained good predictions with strong R^2 and NSE Table 6-5. Although Units 1 and 4 had similar configurations and treatment conditions, the input variables identified through PCA were different for each unit. Therefore, the variations in the model predictions in Units 1 and 4 could be due to the influence of the different input variables.

Overall, CW Unit 1 and Unit 7 data returned the best performing standard models. However, the standard model for Unit 1 had more input predictors. The probable explanation for the observed variations in the models predicting TNR among the different CW Units could be the difference in the media type and WWAR. Thus, TNR models derived from loamy sand CW Units produced outputs whose relationship to the experimental data was generally strong (Units 1, 5, and 7), while Unit 2 (gravel) and BFS Unit 8 returned outputs weakly related to observed data Table 6-5.

Table 6-5 Standard models for TNR in VFCWs 1, 2, 4, 5, 7 and 8

CW Unit	Network inputs	TRMSE	VRMSE	R^2	NSE
1	ESS, EZn, EpH, IAM, IFe, IN3, IN2	0.042	0.059	0.81	0.79
2	IpH, EOP, ETR, IAM, EN2, EN3, ETP, EpH	0.028	0.133	0.47	0.25
4	EOP, IOP, EEC, IFe, IN3, ITP, IZn, ISS	0.024	0.154	0.43	0.40
5	ESS, EEC, EN3, ISS, IAM, EpH, IN2, IFe	0.043	0.149	0.68	0.63
7	ITR, ISS, EAM, IAM, IFe, IN2	0.048	0.053	0.79	0.77
8	IOP, ESS, ETR, EN3, EFe, EZn, IN2	0.042	0.174	0.25	0.21

Generally, the standard models for the loamy sand VFCWs performed better than the gravel (Unit 2) and BFS (Unit 8). Likewise, the outputs of the standard models demonstrate that TNR in Units 2 and 8 frequently fluctuated, an indication that the cumulative mechanisms involved in TN removal appear highly variable and inconsistent in Units 2 and 8. It is likely that PCA was ineffective in extracting the most important predictor variables from both the gravel and BFS VFCWs.

6.6.3 ANN models for predicting TNR in CW Unit 2, 4, 5, 7 and 8

Similarly, ANN models for TNR in CW Unit 2, 4, 5, 7 and 8 were developed using the same approach applied to CW Unit 1. The most significant PCA extracted input v VFCWs treated stormwater to varying extents related to the design specification and operational strategy. In cases where the design was replicated (Units 1 and 4), the performances of the models were subtly different as shown in Table 6-6.

Table 6-6 ANN models for predicting TNR in CW Units 2, 4, 5, 7 and 8

Output	Unit	Model	Input variables	TRMSE	VRMSE
TNR	1	5	ISS, EpH, IAM, IN3	0.060	0.083
	2	5	IpH, ETR, IAM	0.073	0.091
	4	8	EOP, IOP, EEC	0.056	0.071
	5	4	ESS, EEC, EN3, ISS, IN2, IFe	0.065	0.148
	7	7	EOP, ISS, IZn	0.083	0.078
	8	6	IOP, ESS, ETR	0.068	0.072

Thus, Unit 1 and 4 required 4 and 3 input variables respectively to predict TNR. However, to determine the model that best fits the data, numerous input variable combinations were simulated, and the subsequent models compared. Details of the outputs from each simulation are listed in the Appendix. Training and validating the models produced RMSE which were considerably low and ranging from 0.05 to 0.08 and 0.07 to 0.15 as shown in Table 6-4 and Figure 6-6.

Figure 6-6 TRMSE and VRMSE of ANN models for TNR in VFCWs

All the representative models in all the VFCWs had comparable TRMSE. However, CW Unit 5 produced the model with the highest validation errors, which is perhaps attributed to the many input variables in the model. The best fit models for TNR selected from each VFCW are presented in Table 6-7, along with other parameters like the R^2, NSE, mean experimental TNR, predicated TNR and prediction errors.

Table 6-7 Performance of ANN models predicting TNR in VFCWs

Unit	Model	Experimental (%)	Predicted (%)	Mean Error (%)	R^2	NSE
1	5	78.14	76.97	-1.16	0.65	0.59
2	5	61.87	61.70	-0.17	0.70	0.60
4	8	80.06	78.49	-1.57	0.73	0.54
5	4	73.07	71.41	-1.66	0.71	0.69
7	7	73.03	72.04	-0.98	0.73	0.61
8	6	78.95	77.42	-1.53	0.68	0.44

The predictions of TNR returned R^2 values higher than 0.65, indicating a strong correlation between the experimental and the predicted data. However, the reliability of the models was variable with the NSE values ranging from 0.44 to 0.79. Based on the R^2 and NSE values in Table 6-7, Model 4 from CW Unit 5 appears to be the best performing model. However, despite containing many input variables, validation error and prediction mean error margins of model 4 were higher than the errors of all the other models. Model 5 (Unit 2) had fewer input variables comprising of IpH, ETR, and IAM; produced the least prediction errors; and attained moderate R^2 and NSE as shown in Figure 6-7.

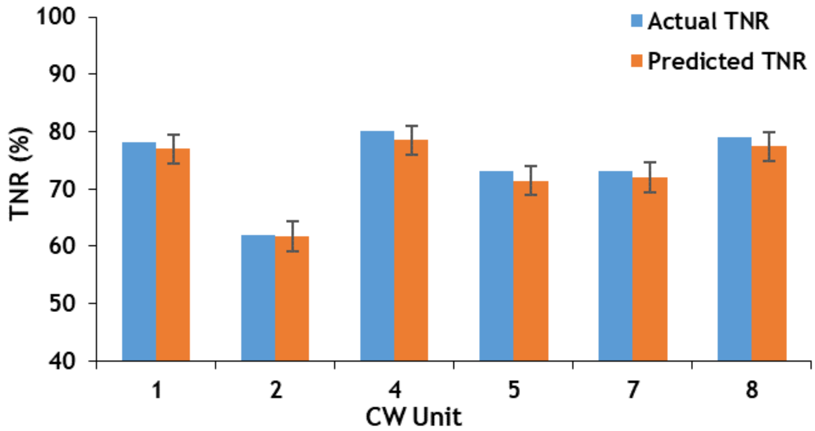


Figure 6-7 Comparisons of the actual and predicted TNR in VFCWs

The performance of the ANN models in Units 1 and 5 are linked to the predictor variables in both models. Similarly, the TNR models for Units 2,4,7 and 8 had fewer predictors, hence the low R^2 and NSE values. TNR predictions with a low NSE of 0.44 in Unit 8 could have resulted from changes in TN removal mechanisms in BFS media.

Similarly, in gravel media Unit 2; influent pH, effluent temperature and influent ammonia (IpH, ETR, and IAM) were identified. However, in loamy sand CW Units, the relationship between TNR and other variables is variable even between the control Units 1 and 4. Similarly, in BFS media, the variables with the most robust relationship with TNR were IOP, ESS, ETR. However, unlike gravel, the reliability of the model formed from BFS media is very low.

Generally, the data obtained from the VFCWs produced ANN models with fewer input variables relative to the standard models of each VFCW. This suggests that TNR can be monitored indirectly through the analysis of less costly input. Moreover, all the VFCWs produced ANN model which predict TNR with a mean prediction error of less than 2 % across the 6 VFCW designs. Thus, the generalisations derived by ANNs are satisfactory regarding TNR in tidal-flow VFCWs. Nonetheless, better models could be developed by using non-linear data reduction techniques than PCA.

6.7 Development of ANN models for predicting TPR in **VFCWs**

6.7.1 ANN models for predicting TPR in CW Unit 1

Models for predicting total phosphorus removal in CW Unit 1 were developed based on the input variables listed in Model 1, the 'standard model' for predicting TPR. Subsequent variations in input combinations are also listed in Table 6-8. PCA extracted the variables listed in Model 1 by following the same procedure illustrated using data for CW Unit 1. A critical feature of TPR in the VFCW Unit 1 is that masking the input ETN affected the predictions of Model 6, hence the low R^2 and NSE. Equally, nitrogen-related inputs namely IAM, EN2, and IN3 constituted the most TPR predictors. Correspondingly, ISS and Fe as co-predictor variables of TP reinforces the theory that TP and suspended solids removal occur by similar mechanisms of sedimentation and filtration. Nonetheless, ANN models created from the different inputs had outputs such as in Models 4 and 8, as well as Models 5 and 7 (Table 6-8).

Except Model 6, the rest of the ANN models had low TRMSE and VRMSE for training and validation phases respectively. Additionally, in all the network scenarios, variations in the predictions of TPR were related to the masked inputs, with ETN the most influential contributor to the precision and reliability of the models. Unfortunately, no remarkable improvements in the precision and reliability of the ANN models as the number of input variables were reduced. Consequently, Model 2 is the best fit for TPR in CW Unit 1. The variations in the Gamma scatter plot, the M-test and TPR predictions produced by Model 2 are shown in Figure 6-8.

Table 6-8 ANN models for predicting TPR in CW Unit 1

Model	Network Inputs	TRMSE	VRMSE	R^2	NSE
1	ESS, ETN, ISS, IAM, EN2, IFe, IN3	0.038	0.043	0.76	0.75
2	ESS, ETN, ISS, IAM, EN2	0.038	0.047	0.74	0.73
3	ESS, ETN, ISS, IAM, EN2, IN3	0.047	0.042	0.75	0.69
4	ESS, ETN, ISS, IAM, EN2	0.033	0.062	0.66	0.65
5	ESS, ETN, ISS, IAM, IFe, IN3	0.033	0.073	0.58	0.56
6	ESS, ISS, IAM, EN2, IFe, IN3	0.029	0.110	0.20	0.13
7	ETN, ISS, IAM, EN2, IFe, IN3	0.039	0.086	0.57	0.52
8	ESS, ETN, ISS, EN2, IFe, IN3	0.044	0.048	0.69	0.64

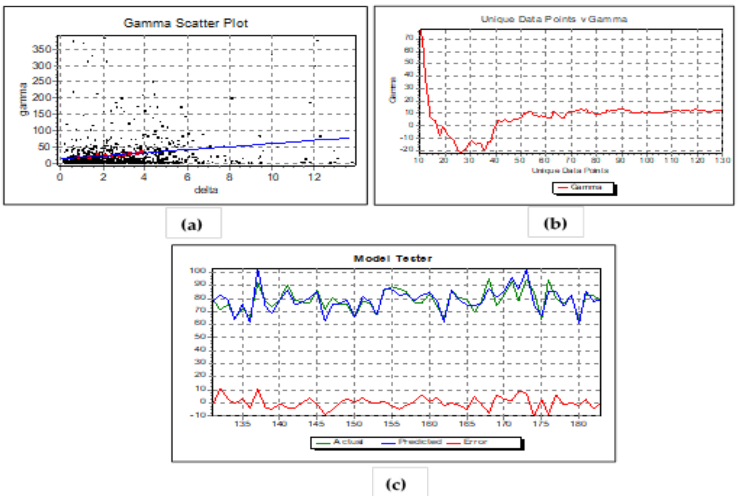


Figure 6-8 (a) Gamma plot (b) M-test (c) Model 2 predictions of TPR in CW Unit 1.

6.7.2 Standard models for TPR in Units 1, 2, 4, 5, 7 and 8

All the standard models for TPR produced low TRMSE and VRMSE as shown in Table 6-9. However, the data obtained from CWs 2 and 8 returned meaningless models.

Table 6-9 ANN standard models for TPR in CW Units 1, 4, 5, and 7

Unit	Network Inputs	TRMSE	VRMSE	R^2	NSE
1	ESS, ETN, ISS, IAM, EN2, IFe, IN3	0.038	0.043	0.76	0.75
4	IpH, EZn, EEC, ESS, IN3, EFe, IFe, IZn	0.038	0.056	0.72	0.49
5	ESS, EN3, ETN, ISS, EpH, ITN, IN2, IFe	0.017	0.056	0.18	0.11
7	ETN, ITR, ISS, EAM, IAM, IFe, ITN, IN2	0.049	0.053	0.79	0.77

Thus, the predicted outputs from all the possible input combinations in CW Unit 2 and 8 are not included in Table 6-8 because the models from the respective CWs produced TPR predictions that are weakly correlated to the experimental TPR. It is suggested that the weak correlations between ANN predictions and experimental data indicate that PCA and ANNs were not suitable for modelling TP removal in CW Units 2 and 8. Therefore, no representative models for TPR were selected for CW Units 2 and 8. However, data from CWs Units 1 and 7 produced models whose predicted TPR compared well with the experimental data. Likewise, although CW Units 1 and 4 were control units; only Unit 1 data produced a model with modest generalisation. Overall, Unit 5 produced the weakest TPR predictions despite containing many input variables. A comparison of TRMSE and VRSME shows that model training and validation were achieved with relatively low errors (Figure 6-9).

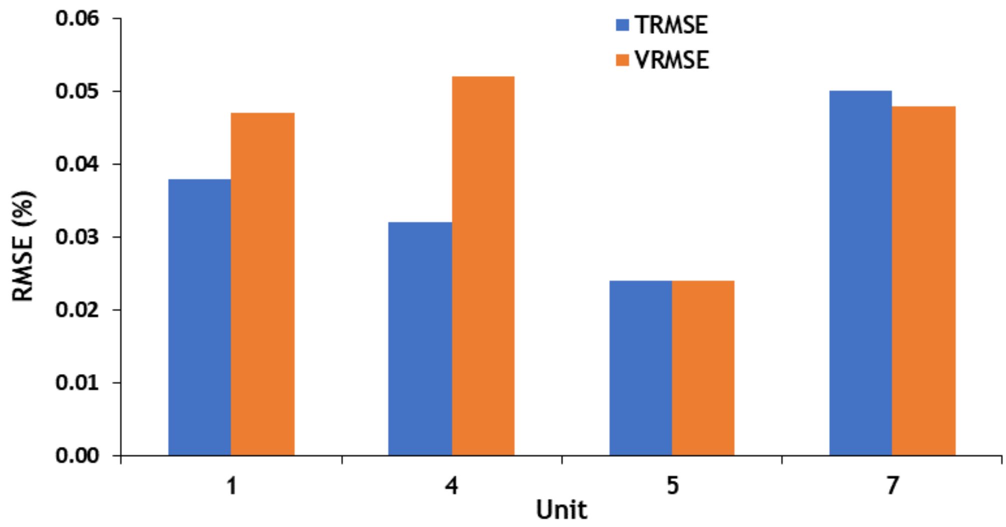


Figure 6-9 TRMSE and VRMSE of ANN models for TPR in VFCWs

6.7.3 Representative models for TPR in Units 1, 4, 5 and 7

Representative TPR models were built starting from the standard models of VFCWs. As with TNR, numerous input combinations were modelled, and the outputs presented in Table 6-10. All the models exhibited robust generalisations. TPR outputs from Units 5 and 7 and had the lowest TRMSE and VRMSE (Table 6-10) and hence returned the best predictions of TPR. Additionally, apart from Model 3 of Unit 4, the representative models of all the VFCWs were developed from fewer inputs relative to their respective standard models. Thus, regarding the media types, loamy sand CWs 1, 4, 5, and 7 produced good models; while both BFS and gravel CWs produced weak models.

Table 6-10 Comparisons of selected TPR models for CW Units 1, 4, 5 and 7

Output	Unit	Model	Network Inputs	TRMSE	VRMSE	R2	NSE
TPR	1	2	ESS, ETN, ISS, IAM, EN2	0.038	0.047	0.74	0.73
	4	3	IpH, EZn, EEC, ESS, IN3, EFe	0.032	0.052	0.73	0.62
	5	5	ESS, EN3, ETN, ISS, EpH	0.024	0.024	0.83	0.80
	7	5	ETN, ITR, ISS, EAM, IAM	0.050	0.048	0.83	0.81

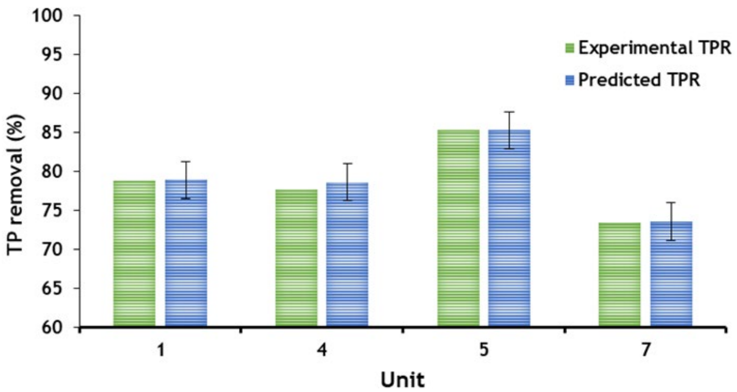


Figure 6-10 Comparisons of the actual and predicted TPR in VFCWs

Among the loamy sand VFCWs, the differences in performance could be attributed to variations in WWARs. At 2.5 % WWAR (Units 1 and 4) the TPR models performed well but did not reach the removal consistencies attained by the 5.0 % and 1.5 % WWARs in Units 5 and 7 respectively (Figure 6-10). The cumulative TP mass reductions were highest in the 5.0 % WWAR (92 %), followed by the 2.5 % WWAR (80 %) and least at 1.5 % WWAR (62 %). Similarly, the differences in TP volumetric constants among the different VFCWs were found to be significant. Furthermore, the Tukey post hoc test revealed that TPR was significantly lower at 1.5 % WWAR (1.46) compared to the 2.5 % WWAR (1.55) and 5.0 % WWAR (1.93). Thus, the ANN models predicting TPR reflect these variations and suggest that low TP removal occurs by specific removal mechanisms hence the consistency observed, while higher TPR could suggest the involvement of several factors and removal processes.

6.8 Comparison of TNR and TPR model performances

The extracted principal components revealed that although all the 6 VFCWs treated the same influent stormwater, each VFCW Unit produced data specific to its design. Consequently, the ANN models developed had varying generalisations. Additionally, the principal components extracted to predict TNR and TPR differed within the and between the different VFCWs. This suggests that the relationships between input and the outputs variables are dependent on other factors such as air temperature, design, and operational variables.

6.9 General discussion of ANN model predictions

This chapter aimed at developing MLP-ANN models for predicting contaminant removal in stormwater VFCWs. The initial objective was to develop ANN models to predict the removal of time-consuming and costlier to monitor pollutants (heavy metals, TP and TN) using the relatively cheaper to monitor parameters namely pH, temperature, and conductivity. However, the exploratory data analysis revealed significant differences between the means of the input variables. Moreover, most of the variables exhibited non-normal distribution.

Additionally, temperature, pH, and EC had weak relationship strengths with the target outputs (TNR and TPR). This was perhaps an indication that the physical water quality parameters cannot reasonably represent the complex dynamics of N and P removal in VFCWs. Thus, PCA was applied to reduce that dimension of the data, and subsequently to identify the most significant predictor variables for building ANN models that could predict TNR and TPR.

Although VFCWs configured using loamy sand media yielded reliable model performances for TNR and strong models for TPR, the data from the gravel and BFS exhibited non-linear patterns which likely influenced the quality of the ANN models.

Although 8 CWs Units were monitored, only 6 provided enough data for developing MLP-ANN data-driven models. Thus, loamy sand CW Units 3 and Unit 6 operated (short and extended dry weather strategies) and 2.5 % WWAR would require more extended periods of monitoring to obtain data for model training and validation.

This section compares the ANN model outputs for each CW Unit. Initial comparisons will focus on the performance of standard models (containing all PCA identified inputs). Also, the best performing models for each Unit are compared to assess the influence of design variables on nutrient N and P removal in stormwater CWs.

Most of the CW Units investigated produced MLP-ANN models with satisfactory generalisations. The training and validation error margins associated with the ANN models for TNR were considerably low. Furthermore, predictions of TNR gave R^2 values greater than 0.65, an indication of strong correlation between the predicted and experimental data.

Except Units 1 and 5, the ANN models for predicting TN removal in Units 2,4,7 and 8 were developed from few variable inputs. However, ANN model predictions of TNR were least reliable in Unit 8, perhaps due to the various TN removal mechanisms involved.

It is concluded that the long-term monitoring of the performance of VFCW regarding nitrogen removal (TNR) can be achieved with ANNs. Similarly, it is possible that more reliable ANN models for predicting TNR in VFCW could be developed by using non-linear reduction methods instead of PCA to identify significant input variables.

ANN models for predicting TPR in VFCW contained more input variables than the variables in TNR models. This suggests that TP removal in the VFCW is more complicated than TN removal. Additionally, no reliable models were developed for Units 2 and 8. Unsurprisingly, Units 2 and 8 contained gravel and BFS media respectively. Thus, the three media developed different P removal mechanisms, of which only loamy sand CWs had consistent and predictable TP removal.

However, the ANN model predictions revealed variations in TP reduction in the loamy sand CWs. The differences in P removal could be attributed to changes in WWARs. Thus, the ANN models for TPR in the 2.5 % WWAR (Units 1 and 4) models performed well but were less reliable when compared to the models for the 5.0 % WWAR (Unit 5) and 1.5 % WWAR (Unit 7). Thus, the ANN models for TP removal suggest that P removal is consistent at higher WWAR (influent water is held longest due to the larger surface area available to small inflow volumes). In contrast, at lower WWARs (1.5 % WWAR), less water is withheld for a shorter treatment time resulting in consistent but low P reduction. However, at 2.5 % WWAR, the factors that influence P removal at 1.5 % and 5.0 % WWARs produce the observed inconsistencies in P removal and model reliability.

Although different media yielded different TN and TP removal performances, gravel and BFS media exhibited high nonlinearity, which perhaps influenced the quality of the MLP-ANN models generated. Similarly, among the loamy sand VFCW, only Units 1 and 4 did not significantly differ in their TN and TP reductions. Therefore, the long-term removal of pollutants in the VFCWs is likely influenced by the media and WWAR configurations. Additionally, the differences in the performance of loamy sand VFCWs is related to WWAR, but this relation was not studied for gravel or BFS.

Although 8 CW Units were monitored, only 6 CWs had enough data for developing MLP-ANN models. Thus, loamy sand Units 3 and Unit 6 (short dry and extended dry rest periods regimes respectively) would require longer monitoring times to obtain enough data necessary for training and validation of the MLP-ANN model.

Similarly, VFCW in which gravel and BFS are the primary media were operated only at 2.5 % WWAR. Thus, the performance of both gravel and BFS at both 1.5 % and 5% WWAR; as well as intermittent short dry and extended dry rest periods ought to be investigated for these media types. Such studies could help determine the influences of 1.5 % and 5.0 % WWARs, and intermittent dry rest periods and the media on TN, TP, and metal removal. Outcomes from such research could inform the options for optimal configurations of more designs.

Furthermore, implementing nonlinear reduction techniques could yield better ANN models, reduce simulation times as well as reduce input-output data requirements. Moreover, future research should implement other ANN optimisation strategies like radial basis function and machine learning.

Chapter 7 Conclusions and recommendations

Urbanisation, hydrology, and stormwater runoff are linked to population growth and an increase in economic activity. The relationship is complex but using the food-water-energy nexus can help to understand the dynamics of urbanisation and its effects on the natural environment. Stormwater contains a variety of pollutants that can have adverse effects on the water environment and public health. Therefore, new sustainable approaches such as the treatment of stormwater run-off using CWs can help reduce water demand. Additionally, CWs can mitigate floods and improve aesthetics of urban landscapes. Therefore, the uptake of CWs could be increased if CW designs with minimal land requirements are developed.

This research study examined the influence of design and operational variables on the long-term performance of tidal-flow VFCWs in treating stormwater. The rationale of the research was that tidal-flow draws atmospheric oxygen into VFCWs thereby increasing the concentrations of dissolved oxygen in the wetland system. Moreover, a combination of high dissolved oxygen and the fixed long hydraulic retention time of 24 hours enhances the removal of nutrients N and P. Therefore; this research was conducted in two major parts. The first part was focused on laboratory experiments, which were designed and carried out using 8 pilot-scale VFCWs over a continuous period of 2 years at the School of Engineering, Cardiff University. The VFCWs were configured from a series of media compositions and were fed with various loads of simulated stormwater to be treated over 24 hours. The performance of the VFCWs regarding the removal of solids, nutrients (N and P), and heavy metals was monitored throughout the experimental period. The data obtained were analysed using descriptive and inferential statistics. The second part of the research focused on using the experimental data for the development of ANN models to predict the performance of the VFCWs. Thus, exploratory data analyses using PCA aided the identification of the most significant input variables, and hence reduced the dimensionality of the dataset. The results show the influence of design and operational variables on the removal of pollutants in VFCWs; and provided practical guidance of optimising ANN models for predicting the long-term removal of contaminants in VFCWs. The research can be concluded as follows.

7.1 Conclusions

The performance of VFCWs based on the fixed retention time of 24 hours was investigated through experiments and numerical modelling. The experimental design and set-up were developed to replicate local conditions. Additionally, the stormwater used in the experiments was prepared from a mixture of natural sediments (filtered through a 1 mm diameter sieve); and laboratory reagents added to reach concentrations typical of stormwater. Moreover, the VFCWs were configured from locally available materials; while the energy requirements for operation and maintenance were minimal. Therefore, VFCWs are cost-effective and sustainable technology for wastewater treatment.

Contaminant removal in the 8 VFCWs was evaluated based on the per cent mass load reduction, mass removal rate, and volumetric rate constants. Both per cent mass load reductions and volumetric rate constants exhibited high variability for the different pollutants, while the mass removal rates for Fe reduction were mostly similar under different treatment conditions (Table 4-3). Thus, the application of mass removal rates may not be suitable for evaluating Fe removal in VFCWs treating low pollutant loads.

The experimental results show that VFCWs optimised at the design phase can significantly reduce the pollutants carried in stormwater and thus decrease the impact of urban stormwater pollution on water resources and aquatic life. Furthermore, the patterns of pollutant removal in the VFCW designs differed, demonstrating that the treatment conditions influenced the performance of the VFCWs. Accordingly, ANOVA established that VFCWs operating under similar treatment conditions develop pollutant-specific volumetric rate constants (Kv). Likewise, similar pollutants develop different volumetric rate constants. Thus, both TP and TN had lower K_v than their soluble forms of P-$(PO_4)^-$ and N-$(NH_4)^+$ respectively, indicating that VFCWs reduce TN and TP by removing their soluble forms. Additionally, the volumetric rate constant for the VFCWs shows that BFS media effectively reduced more pollutants than loamy sand and gravel media.

The first order dynamic model used in the design of CWs does not fully account for the pollutant removal in the different VFCWs. Thus, 5.0 % WWAR performed better than the 2.5 % and 1.5 % WWAR regarding Zn, TP, and P-(PO_4)- removals. Likewise, the short dry and extended dry rested VFCWs had higher Zn removals than the wet CWs. However, the high Zn removals are related to the low pollutant loads (5.0 %

WWAR or 11.3L) and lower load frequency, respectively, but these variations are not accounted for in the dynamic model.

All the tidal flow VFCWs had adequate hydraulic performances characterised by regular flow patterns throughout the monitoring period. Only BFS Unit 8 showed minor signs of clogging probably due to the accumulation of suspended solids, precipitates and sludges of the removed pollutants. Moreover, TSS removal was high at 1.5 % WWAR, demonstrating that VFCW could reduce particulate pollutant loads at high flow, such as during extreme storm events.

Nitrate-N or N-$(NO_3)^-$ were frequently detected in effluents, with gravel media reaching the highest nitrification and NH_3 / N-$(NH_4)^+$ reduction. This reinforces the theory that tidal-flow operation enhances dissolved oxygen in CWs, making VFCWs effective nitrification systems and thus suitable for ammonium removal.

Heavy metal removal is the highest among the contaminants studied, with some metals like Cd, Cu, Cr, and Pb reduced to below detection limits. Equally, high removals of Fe in association with suspended solids was registered in the VFCWs.

The reduction of suspended solids (TSS) in the VFCWs is mostly by sedimentation and filtration, straining and adsorption onto media. Likewise, N reduction is by the biological processes of nitrification and denitrification. However, low anoxic conditions limit the denitrification resulting in low TN removal. Similarly, TP removal in the loamy sand and BFS units was likely attained through chemical precipitation, evidenced by substantial Ca in both media types. The presence of Ca augments the theory that P-$(PO_4)^-$ is removed by chemical precipitation. Furthermore, the amount of Mg in BFS exhibited the potential of BFS to adsorb the metal ions. The high Mg in BFS is consistent with the findings that chemisorption is an essential process in adsorption; and that the adsorption rates of the metals to loamy sand and BFS followed a pseudo-second-order model (Lucas 2015).

Exploratory data analysis techniques were reasonably successful in analysing the experimental data. Thus, ANOVA revealed significant differences in the means of all the variables suggesting that the different designs distinctly influence the removal of pollutants in VFCWs.

Subsequently, PCA reduced the dimension of the large datasets, and thus helped to extract the most significant variable inputs. Consequently, fewer network scenarios were modelled, and the resultant ANN models had few inputs. Thus, only relevant variables can be monitored to reduce analytical costs and time.

ANN-based models were built and optimised using a modified Broyden–Fletcher–Goldfarb–Shanno (BFGS) learning algorithm executed in WinGamma Software. The ANN models produced satisfactory generalisations of TNR and TPR, showing good agreement between the predicted and experimental data. Therefore, ANN is a useful tool for modelling pollutant removal in VFCWs.

7.2 Recommendations for future research

The experimental design, materials, and methods generated data that demonstrates that tidal-flow VFCWs are cost-effective for stormwater treatment. However, the results of these pilot-scale investigations may be challenging to scale up, because the actual physical processes that convert rainfall to runoff are complex and highly variable and could not be replicated with precise certainty. However, simplifying assumptions were made to make it possible to conduct the experiments.

Consequently, the hydraulic loading volumes were based on the average annual rainfall rather than on the rainfall intensity. Additionally, the retention time of 24 hours applied in this study did not consider situations where rainfall could last longer than a day. However, design storm events would yield a retention time based on flow conditions, such that storm events more extensive than the design event would have a shorter retention time, while smaller storm events would have a longer retention time. Therefore, field studies must be conducted to supplement the findings of this study. Nonetheless, this study has highlighted the effect of fixed long retention time on pollutant removal in tidal flow VFCWs.

Furthermore, research continues to demonstrate the feasibility and effectiveness of using CWs in wastewater treatment. Thus, although traditionally, CWs were built to serve small populations, there appears to be a gradual shift to the use of CWs in large-scale wastewater treatment. Therefore, as more experiments and numerical modelling investigations demonstrate the success of CWs in wastewater treatment, it is probable that CWs will challenge other wastewater treatment technologies. However, more research studies such as monitoring the growth in microbial biomass and microbial composition analyses are needed to understand better and hence enhance the nutrient and other contaminant removal pathways in VFCWs.

Additionally, the VFCW investigated in this study operated a fixed retention time of 24 hours, so changes in anoxic conditions with dissolved oxygen and redox potentials were not monitored. Therefore, the limited ability of VFCWs to achieve satisfactory denitrification requires more investigations. Ultimately, cost-effective designs of VFCW could contribute to sustainable water management.

Models developed for TPR in loamy sand VFCWs produced robust and reliable predictions. However, the ANN models for predicting TPR in BFS and gravel VFCWs generated meaningless and unreliable predictions. Therefore, although PCA was adopted for data reduction, it appears ineffective in analysing highly non-linear data. Accordingly, future research should explore the use of non-linear data dimension reduction methods, as well as neural networks such as radial basis function and machine learning for developing predictive models. Additionally, the relatively small size of the dataset was a limitation in the modelling process. Thus, more data ought to be collected if neural networks are the technique of choice.

Finally, hydro-informatics continues to gain credibility in modelling environmental systems. Consequently, fuzzy logic models, genetic algorithms, and neural networks have succeeded in modeling a variety of environmental phenomenon. In this study, the suitability of neural networks for predicting the long-term performance of various designs of tidal-flow VFCWs is satisfactorily demonstrated. Therefore, this research shows the potential of neural networks to model contaminant removal and hence evaluate the performance of water treatment systems for which obtaining definitive calibration data is still a challenge.

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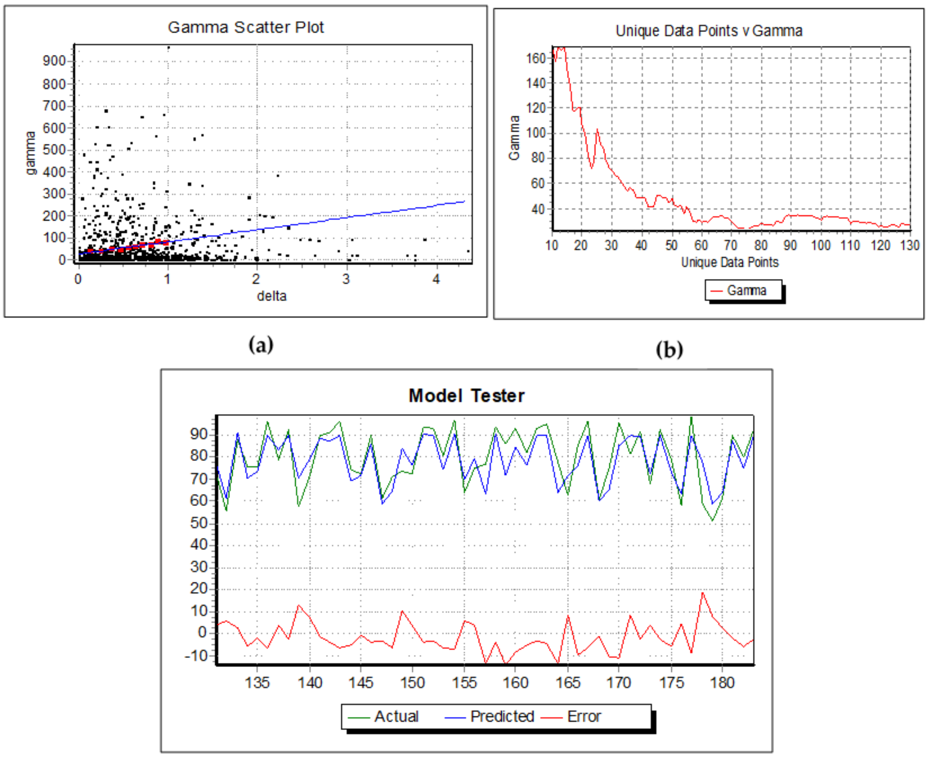
Appendix 1 ANN Models for predicting TNR in VFCWs

Table 7-1 Simulations of TNR in CW Unit 2

Model	Network Inputs	TRMSE	VRMSE	R^2	NSE
1	IpH, EOP, ETR, IAM, EN2, EN3, ETP, EpH	0.028	0.133	0.47	0.25
2	IpH, EOP, ETR, IAM, EN2, EN3	0.040	0.133	0.74	0.65
3	IpH, EOP, ETR, IAM, EN2	0.048	0.092	0.69	0.53
4	IpH, EOP, ETR, IAM	0.063	0.109	0.61	0.51
5	**IpH, ETR, IAM**	**0.073**	**0.091**	**0.70**	**0.60**
6	IpH, ETR, IAM, EN2, EN3	0.028	0.116	0.57	0.51



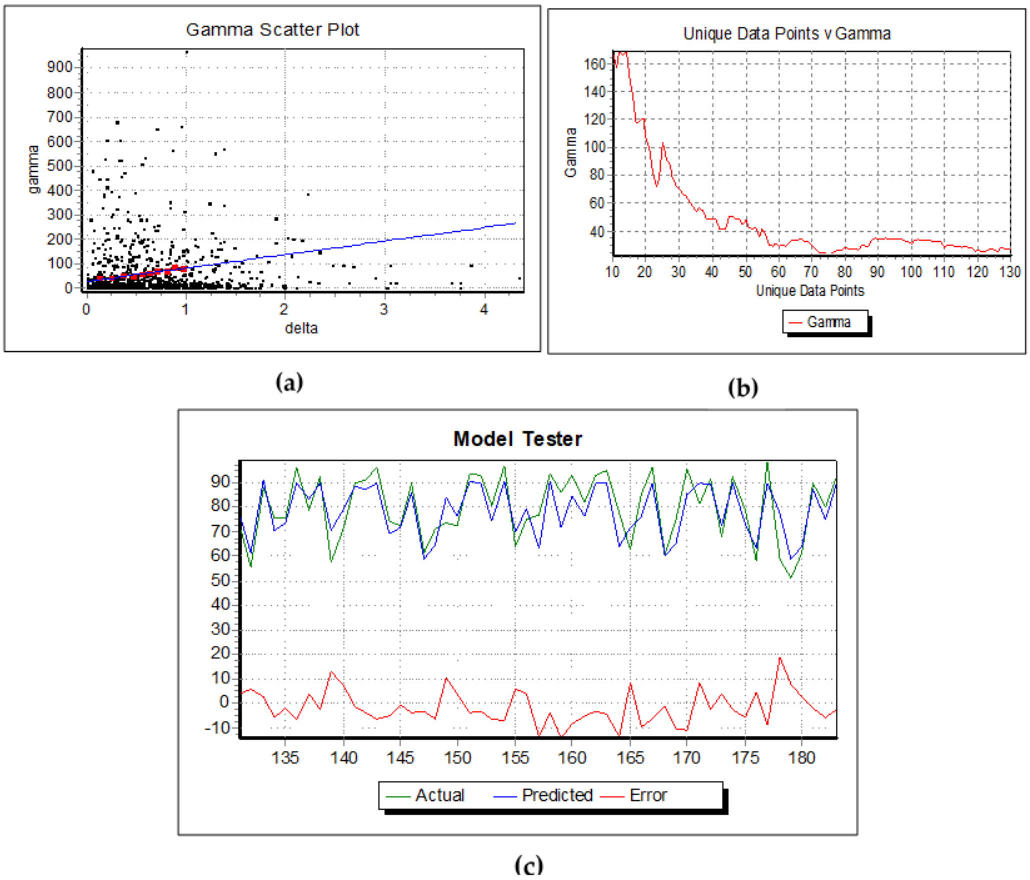
(a) (b)

(c)

Figure 7-1 (a) Gamma scatter (b) M-test and (c) Model 5 TNR predictions in CW Unit 2

Table 7-2 ANN models for predicting TNR in CW Unit 4

Model	Network Inputs	TRMSE	VRMSE	R^2	NSE
1	EOP, IOP, EEC, IFe, IN3, ITP, IZn, ISS	0.024	0.154	0.43	0.40
2	EOP, IOP, EEC, IFe, IN3, ITP, IZn	0.033	0.121	0.47	0.45
3	EOP, IOP, EEC, IFe, IN3, ITP	0.033	0.081	0.62	0.49
4	EOP, IOP, EEC, IFe, IN3	0.071	0.089	0.55	-0.03
5	EOP, IOP, EEC, IFe, ITP	0.041	0.096	0.53	0.41
7	EOP, IOP, EEC, IFe	0.037	0.082	0.64	0.59
8	**EOP, IOP, EEC**	**0.056**	**0.071**	**0.73**	**0.54**
9	EOP, IOP, IFe	0.081	0.071	0.62	0.39



(a) (b) (c)

Figure 7-2 (a) Gamma plot (b) M-test (c) Model 8 predictions of TNR in CW Unit 4.

Table 7-3 ANN models for predicting TNR in CW Unit 5

Model	Network Inputs	TRMSE	VRMSE	R^2	NSE
1	ESS, EEC, EN3, ISS, IAM, EpH, IN2, IFe	0.043	0.149	0.68	0.63
2	ESS, EEC, EN3, ISS, IAM, EpH, IN2	0.044	0.270	0.44	0.43
3	ESS, EEC, EN3, ISS, IAM, IN2, IFe	0.048	0.194	0.56	0.56
4	**ESS, EEC, EN3, ISS, IN2, IFe**	**0.065**	**0.148**	**0.71**	**0.69**
5	ESS, EEC, ISS, IN2, IFe	0.092	0.151	0.69	0.66
6	ESS, ISS, IN2, IFe	0.116	0.135	0.67	0.59

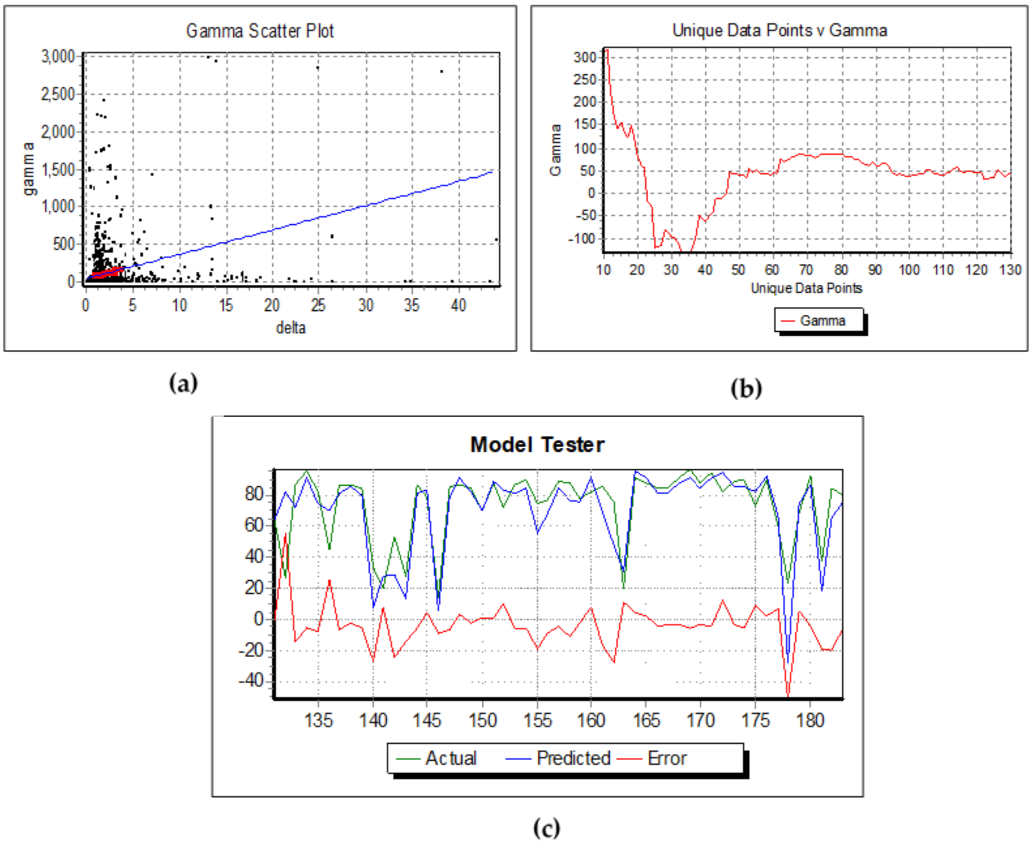
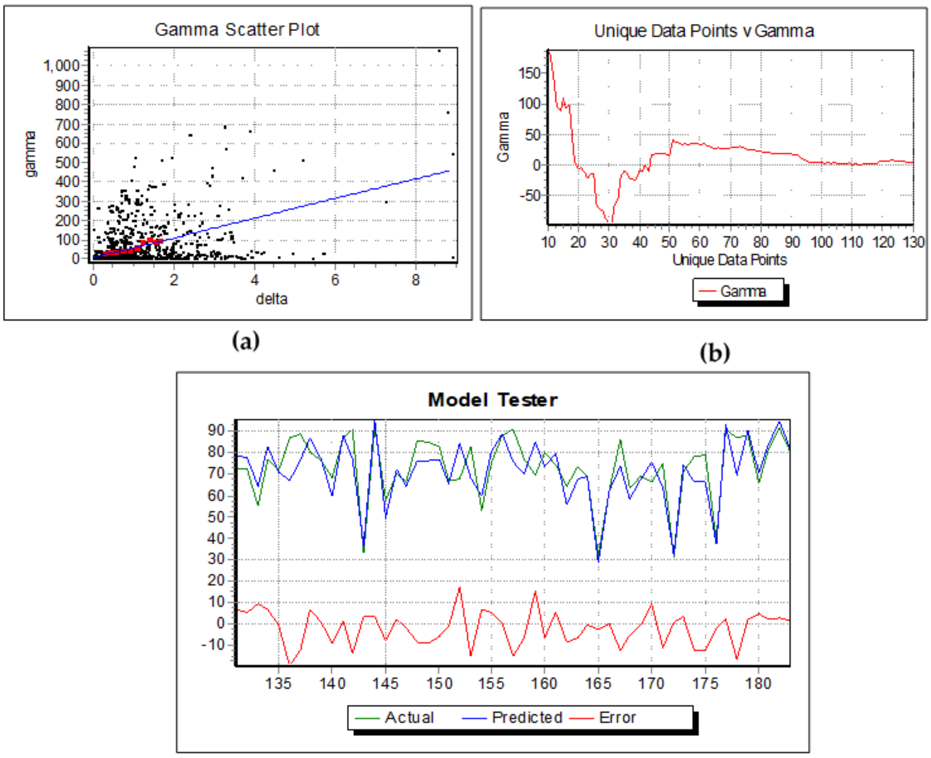


Figure 7-3(a) Gamma scatter plot (b) M-test (c) Model 4 TNR predictions in CW Unit 5

Table 7-4 ANN models for predicting TNR in CW Unit 7

Model	Network Inputs	TRMSE	VRMSE	R^2	NSE
1	EOP, ITR, ISS, EAM, ITP, IZn, IFe, IN2	0.034	0.078	0.74	0.69
2	EOP, ITR, ISS, EAM, ITP, IZn, IFe	0.019	0.124	0.43	0.24
3	EOP, ITR, ISS, EAM, ITP, IZn	0.033	0.105	0.69	0.69
4	EOP, ITR, ISS, EAM, ITP	0.059	0.100	0.62	0.55
5	EOP, ITR, ISS, EAM, IZn	0.041	0.081	0.73	0.70
6	**EOP, ITR, ISS, IZn**	**0.029**	**0.084**	**0.72**	**0.67**
7	EOP, ISS, IZn	0.083	0.078	0.73	0.61
8	EOP, ISS, EAM, IZn	0.060	0.127	0.53	0.50

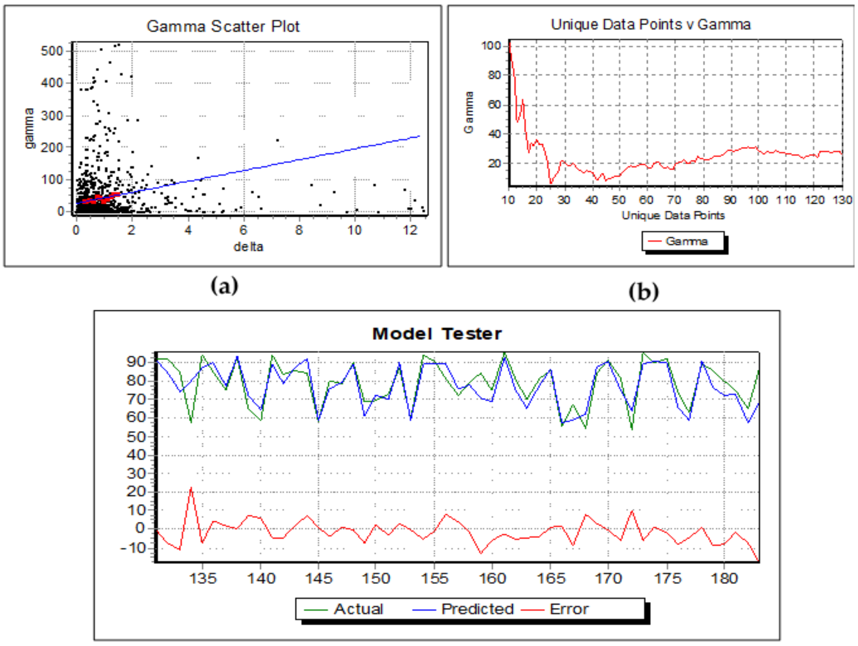


(a) (b) (c)

Figure 7-4 (a) Gamma scatter (b) M-test c) Model 6 predictions of TNR in CW Unit 7.

Table 7-5 ANN models for predicting TNR in CW Unit 8

Model	Network Inputs	TRMSE	VRMSE	R^2	NSE
1	IOP, ESS, ETR, EN3, EFe, ITP, EZn, IN2	0.042	0.174	0.25	0.21
2	IOP, ESS, ETR, EN3, EFe, ITP, EZn	0.042	0.086	0.53	0.40
3	IOP, ESS, ETR, EN3, EFe, ITP	0.039	0.099	0.54	0.51
4	IOP, ESS, ETR, EFe, ITP	0.050	0.074	0.67	0.63
5	**IOP, ESS, ETR, EFe**	**0.053**	**0.068**	**0.71**	**0.65**
6	IOP, ESS, ETR	0.068	0.072	0.68	0.44



(a) (b) (c)

Figure 7-5 (a) Gamma plot (b) M-test (c) Model 5 predictions of TNR in CW Unit 8.

Appendix 2 ANN models for predicting TPR in VFCWs

Table 7-6 ANN models for predicting TPR in CW Unit 2

Model	Network Inputs	TRMSE	VRMSE	R^2	NSE
1	EFe, IZn, ETR, IAM, ITN, EN2, EZn	0.038	0.064	0.19	-0.31
2	EFe, IZn, ETR, IAM, ITN, EN2	0.037	0.069	0.24	0.04
3	EFe, IZn, ETR, IAM, ITN	0.036	0.061	0.22	-0.33
4	EFe, IZn, ETR, IAM	0.038	0.103	0.15	0.07

Table 7-7 ANN models for predicting TPR in CW Unit 4

Model	Network inputs	TRMSE	VRMSE	R^2	NSE
1	IpH, EZn, EEC, ESS, IN3, EFe, IFe, IZn	0.038	0.056	0.72	0.49
2	IpH, EZn, EEC, ESS, IN3, EFe, IFe	0.026	0.053	0.75	0.58
3	**IpH, EZn, EEC, ESS, IN3, EFe**	**0.032**	**0.052**	**0.73**	**0.62**
4	IpH, EZn, EEC, ESS, IN3	0.035	0.076	0.48	0.33
5	IpH, EZn, EEC, ESS, EFe	0.032	0.054	0.73	0.58
6	IpH, EEC, ESS, EFe	0.051	0.082	0.44	0.26

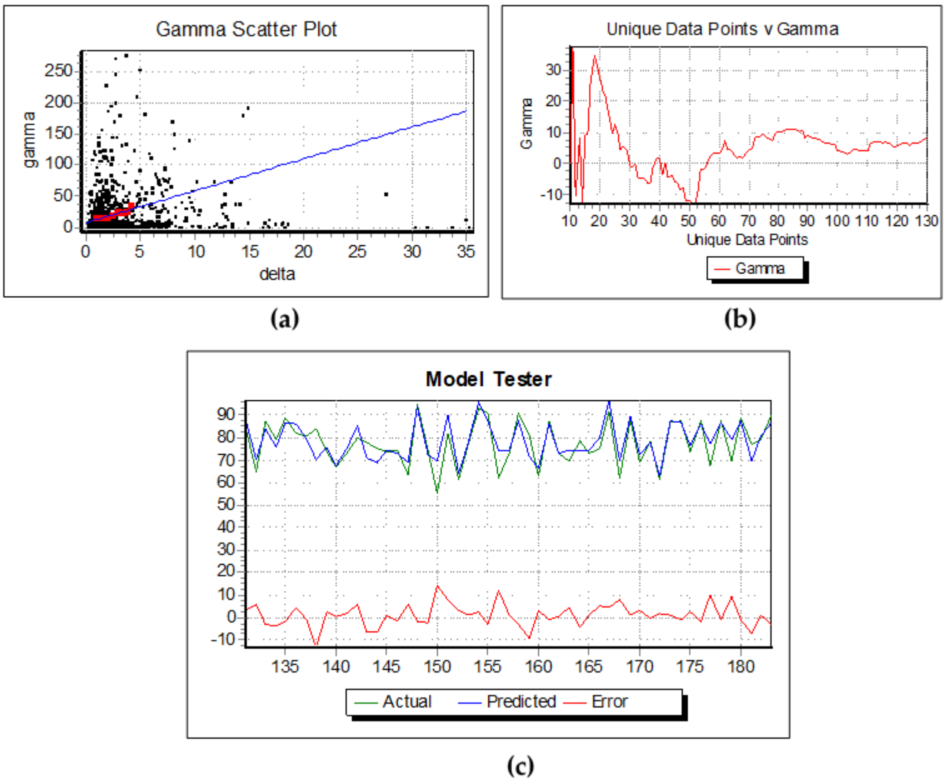


Figure 7-6 (a) Gamma plot (b) M-test (c) Model 3 predictions of TPR in CW Unit 4.

Table 7-8 ANN models for predicting TPR in CW Unit 5

	Network Inputs	TRMSE	VRMSE	R^2	NSE
1	ESS, EN3, ETN, ISS, EpH, ITN, IN2, IFe	0.017	0.056	0.18	0.11
2	ESS, EN3, ETN, ISS, EpH, ITN, IN2	0.017	0.046	0.49	0.39
3	ESS, EN3, ETN, ISS, EpH, ITN	0.04	0.04	0.55	-0.38
4	ESS, EN3, ETN, ISS, EpH	0.027	0.033	0.70	0.39
5	ESS, EN3, ETN, ISS	0.024	0.024	0.83	0.80
6	ESS, EN3, ISS	0.045	0.048	0.36	-0.60
7	ESS, ETN, ISS	0.040	0.051	0.25	-0.80

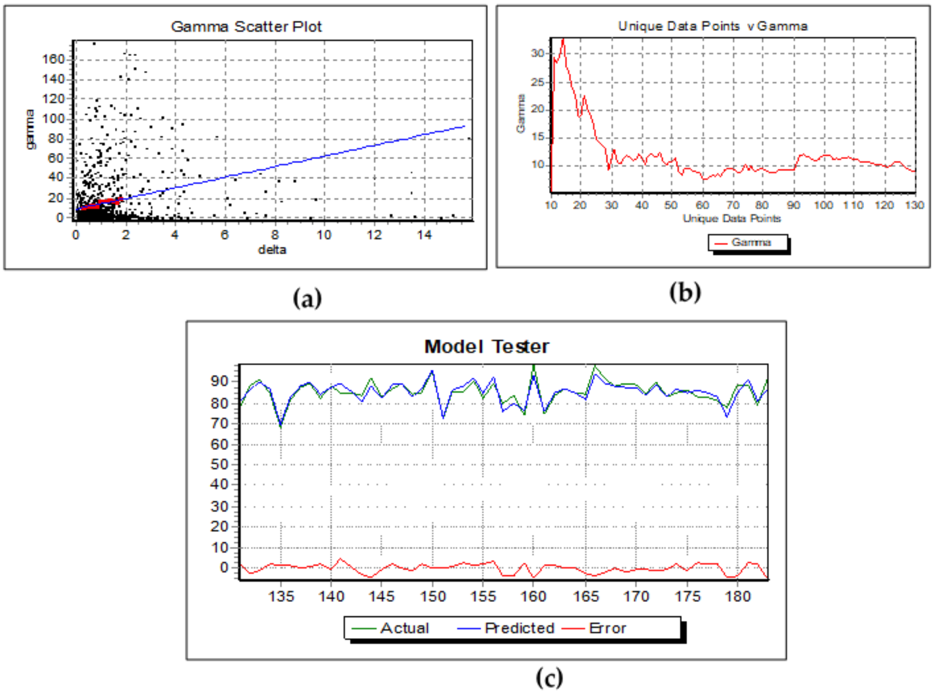


Figure 7-7 (a) Gamma plot (b) M-test (c) Model 10 predictions of TPR in CW Unit 5.

Table 7-9 ANN models for predicting TPR in CW Unit 7

Model	Network Inputs	TRMSE	VRMSE	R^2	NSE
1	ETN, ITR, ISS, EAM, IAM, IFe, ITN, IN2	0.049	0.053	0.79	0.77
2	ETN, ITR, ISS, EAM, IAM, IFe, ITN	0.070	0.071	0.62	0.37
3	ETN, ITR, ISS, EAM, IAM, IFe, IN2	0.048	0.107	0.40	0.35
4	ETN, ITR, ISS, EAM, IAM, ITN, IN2	0.035	0.102	0.54	0.51
5	**ETN, ITR, ISS, EAM, IAM**	**0.050**	**0.048**	**0.83**	**0.81**
6	ETN, ITR, ISS, EAM	0.063	0.061	0.73	0.68
7	ETN, ITR, ISS, IAM	0.050	0.145	0.21	0.11
8	ETN, ITR, EAM, IAM	0.048	0.066	0.72	0.70
9	ETN, ISS, EAM, IAM	0.049	0.127	0.38	0.37
10	ITR, ISS, EAM, IAM	0.064	0.081	0.55	0.45

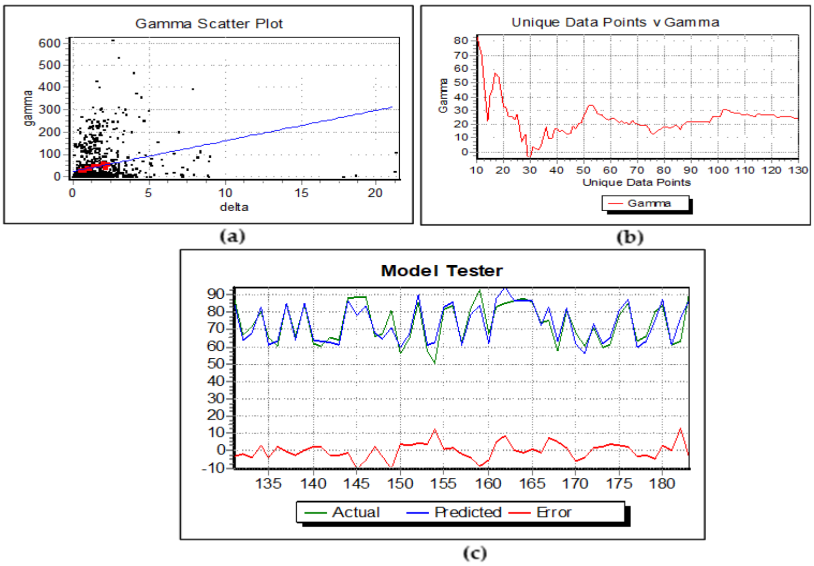


Figure 7-8 (a) Gamma plot (b) M-test (c) Model 5 predictions of TPR in CW Unit 7.

Table 7-10 ANN models for predicting TPR in CW Unit 8

Model	Network Inputs	TMSE	VMSE	R^2	NSE
1	ETN, IpH, EOP, EFe, IAM, EZn, EAM, IN2	0.018	0.070	0.17	-0.22
2	ETN, IpH, EOP, EFe, IAM, EZn, EAM	0.02	0.057	0.38	0.26
3	ETN, IpH, EOP, EFe, IAM, EZn	0.028	0.054	0.33	0.07
4	ETN, IpH, EOP, EFe, IAM, EAM	0.024	0.054	0.29	-0.19
5	IpH, EOP, EFe, IAM, EZn, EAM	0.026	0.078	0.08	-0.30
6	ETN, EFe, IAM, EZn, EAM, IN2	0.047	0.049	0.35	-0.96