Characterising and modelling pollutant dynamics in urban stormwater constructed wetlands.

THIS THESIS IS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY (PhD)

By

Mohammed A. B. Bosnina

B.Sc., M.Sc.

School of Engineering, Cardiff University

Cardiff, Wales, UK

2021

Abstract

Constructed wetlands (CWs) are a worldwide growing natural treatment technology for their effective treatment of various polluted waters, especially urban stormwater, to meet the requirements of authority legislations and for environmentally friendly and cost-effective application. Using a novel tidal flow vertical flow CW (VFCW) mainly overcomes the lack of flow distribution, oxygen supplementation, nitrate-nitrogen (NO3-N) reduction and land availability. Therefore, the aim was to understand and model of the various urban stormwater pollutants immobilisation in the long-term operation of novel pilot-scale VFCWs designed with different substrates configuration receiving different loading rates (catchment area sizes) and wet-dry operation conditions.

Generally, the results showed that VFCWs configurations of substrate type, pollutants loading, and wet-dry operation conditions affect the stormwater pollutants retention performance variably based on the mass balance analysis. From the experimental data of the first four VFCWs used loamy sand, gravel, and BFS as main substrates, significant changes in the chemical structure of the medias were noticed indicating chemical adsorption and calcium precipitation play a vital role in retaining heavy metals and nutrients causing the significant differences ($p \leq 0.01$) in the performance while total suspended solids (TSS) alongside with the metals in the particulate form were more likely removed via straining, settling, and interception mechanisms.

Six loamy sand VFCWs were experimentally and statistically evaluated to account the effect of three cases of both wetland to watershed area ration (WWAR) and wet-dry operation condition. Changing WWAR values influence significantly on the removal performance of TSS, iron (Fe), and phosphorus (P) while no significant impact on the removal performance of both total nitrogen (TN) and zinc (Zn) was accounted. The operation condition impact negatively on the removal of TSS as the condition changes from wet to partially and extended dry while these conditions did not influence statistically the VFCWs performance towards Fe, Zn, TN, and P retentions, which could be elicited to increase the substrate porosity as a result of shrinkage during the dry period and in the same enhance the diffusion of the pollutant into substrate's surface. All experimental data extracted from various operation conditions were gathered to build statistical predicting models using partial least square analysis (PLS). The resulted models were able with a high degree of accuracy to predict both the training and test data of Fe, Zn, TN, TP, and PO4-P at various operation conditions based on the pollutant loading rate and mass of substrate.

The internal N transformation dynamics were established theoretically and then with the experimentally measured data of stormwater VFCWs 1 and 2 were methodically modelled using STELLA software. The model produced a good agreement between the observed effluent data of organic-N, NH4-N, NO3-N, and TN and the predicted once for both model calibration and validation. The model revealed that N mostly removed via NH4-N adsorption (41%) while 19% and 9.55% of TN were removed via denitrification and plants uptake respectively.

Altogether, results showed that CW configuration has a great impact, not on stormwater pollutants removal but also the performance prediction. However, further research at field scale would be beneficial to understand practically more the underline processes of N transformation dynamics and also to enhance P adsorption.

DEDICATION

This thesis work is dedicated to my mama (Fatma) and my wife (Samira) for their unconditional love and continuous support, my family for their encouragement during the preparation of this research.

ACKNOWLEDGEMENTS

Foremost, I would like to express my sincere gratitude to my supervisors, Prof. Shunqi Pan and Dr Akintunde Babatunde who have helped me during my period at Cardiff University and have encouraged me to drive my PhD study.

I would like to thank the technical staff of Cardiff University, who supported me on my dissertation work, In particular, I would like to thank Jeffrey Rowlands for their laboratory activity with me, as well as supplying me with the needed equipment and setup of the tests. Equally, I would also like to thank the staff of the Research Office at the School of Engineering, who supported me during my thesis, providing office supplies, stationery, printing and photocopying, In specific, I would like to thank Aderyn Reid for her constant support.

I am uniquely grateful to Rhodri Lucas and Christopher Kiiza for helping with many aspects of my study, mostly with the set-up of the experiment and provided me with the tests' result data of two-year. I would also like to thank my colleagues who have worked together in the same laboratory for the past few years at Cardiff University for their encouragement and all the great moments we spent together: Chris, Alya, Talib, Abdulla, Mishari, and Y. To those whose names I have not mentioned, but who should also be here, I apologise.

Exclusive thanks go to my dearest and most precious mother, brothers, sisters and friends for their guidance, motivation, and affection. A huge thank you have to go to my wife Samira and my children. (Fatma, Huda, Ali, Takwa and Abdelsalam) who brighten each and every second of my life, and for their continues encouragement and devotion and love; my life has no sense without them, because they are the greatest part of it.

Finally, I pray to God to mercy and forgiveness to my father as well as to my friend and companion Hamad Ragrag, who has passed away on February 2020 and who was a big supporter and believed in me to continue for the PhD study at this advanced age.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Chapter 1: Introduction

1.1 Overview

Water is the element of life for humans, animals, plants, and all living creatures. Water is a vital natural resource found in the ecosystem in various forms. The current world population of 7.6 billion is expected to reach 9.8 billion in 2050 and 11.2 billion in 2100, according to a new United Nations report (United Nations/ Department of Economic and Social Affairs and Population Dynamics 2019). Over 55% of the world's population lives in urban areas, a proportion expected to rise to 68% by 2050, according to the United Nations. Combined with global population growth, this incremental change in human residence from rural to urban areas is expected to add another 2.5 billion people to urban areas by 2050, with approximately 90% of this rise taking place in Asia and Africa (United Nations/ Department of Economic and Social Affairs and Population Dynamics 2019). The main challenges facing climate change are water and food security, as both are highly vulnerable to continually changing climate patterns. Researchers have projected that the average global temperature may rise by 1.4–5.8° C, and by the end of the 21st century there would be a significant reduction in freshwater supplies and agricultural yield. Most freshwater supplies have already been exhausted, and there is a global decline in agricultural production with population and food demand escalation (Misra 2014). The relationship between urbanisation, population growth, climate change and high demand for water is complicated.

Rainfall and runoff are part of the hydrological cycle between water bodies, the atmosphere and the Earth. Industrial development and growth, climate change and an increasing population, together with the overuse and excessive use of resources, have increased rates of water pollution and its sources. Surface water can be polluted in many ways. This may be done by direct discharge from a drain or pipe into streams. Rivers and streams have been considered practical ways to dispose of all types of stormwater and wastewaters, including domestic and industrial waste. Without adequate treatment, industrial sources may discharge hazardous substances, organic matter and suspended solids. Surface water contamination can also result from runoff of stormwater, which can bring polluted materials into the water. Open defecation and the unregulated disposal of solid wastes are two potential causes of runoff pollution. For reasons explained earlier, groundwater is generally cleaner than surface water, but contamination of groundwater supplies has become a major problem worldwide. Groundwater has been contaminated by the leaching of human and industrial waste, chemicals and fertilisers from the soil and polluting groundwater sources into the aquifers.

It is important to understand how water moves through the ecosystem so we can understand how to successfully manage it. Stormwater runoff is created by rain and snowmelt events that flow over land or impermeable surfaces, while the land surface of urban and suburban areas is mostly covered by buildings and pavement that do not allow rain and snowmelt to soak into the ground. Alternatively, most urbanised areas rely on storm drains to carry large amounts of runoff to surrounding waterbodies from rooves and paved areas. There is a relationship between impervious cover and surface runoff. When the area of the covered area increases, the runoff increases, the percentage of pollutants that carries to waterways increases, and also the risk of flooding rises (see Figure 1.1). Therefore, runoff picks up contaminants such as garbage, chemicals, oils, and sediments that can damage our rivers, streams, reservoirs, and coastal waters.

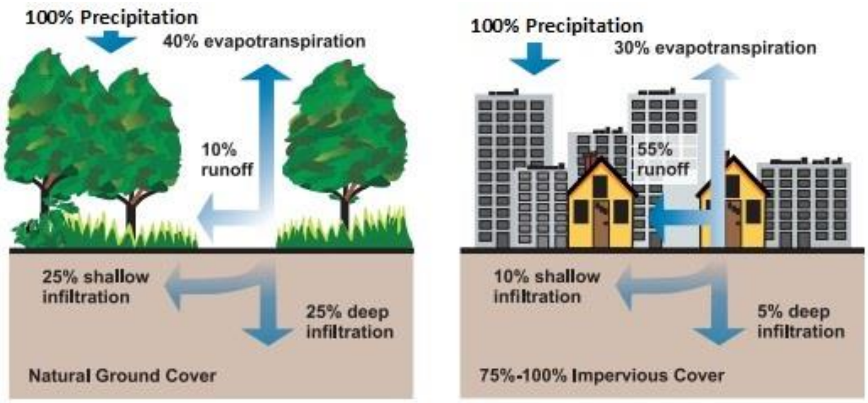


Figure 1.1 Relationship between impervious cover and surface runoff (Us Epa 2003).

The hydrological cycle changes (due to urbanisation) in the receiving watercourses lead to an increase in surface runoff and a deterioration of the water quality (Bagheri et al. 2015). The environment is directly affected by any urban development. Road or building construction significantly changes the hydraulic properties of a region through increasing the impervious covered areas and decreasing infiltration to result in increments in runoff. Therefore, to protect these resources, cities, construction companies, manufacturers, and others, stormwater management has been used, known as water management conditions or sustainable water approaches, although the policies are different from one country to another. For example, in the UK it is called sustainable urban drainage systems (SUDS). Development should be designed and built to minimise the increments in runoff to protect the quality of surface water and ground resources. Sustainable water resource management includes activities supporting water consumption minimisation, wastewater and stormwater treatment, water reuse, and water resource reclamation and safety. Whilst some policies and sustainable design have been planned to protect watercourses, there is still little scientific understanding of the effect of continuous increase in the quantity of urban stormwater and pollutants carried over. Thus, this study focuses on advancing understanding of the design and mechanism of pollutants removal by the environmentally friendly and cost-effective constructed wetlands (CWs) that have been used for treating stormwater and reducing runoff as part of a water management approach in wide use around the world.

1.2 Land use and water management

Urban stormwater management has become increasingly complicated throughout rece nt decades. As Wheater and Evans (2009) noted in their research on land use, water management, and future flood risk, human activities significantly impact land and hydrology, which “determines flood hazard, water resources (for human and environmental needs) and the transport and dilution of pollutants.” With the link between land and water management, there has been a greater understanding that the focus needs to be on designing urban land and water systems that can address current and future water issues (Wheater and Evans 2009). As recent research by the World Resources Institute (WRI) has noted, population growth and climate change are dramatically changing land and water systems in urban areas, creating a higher risk of future flooding and damage (Marshall 2015). For example, it noted that, in the UK, approximately 76,000 people each year could be at risk from increased flooding and the cost of damages would be very impactful (Marshall 2015). Despite this condition, until the 1990s, the solution to flood issues had been approached through a health services approach (Silveira 2002). Up to this time, flood issues have been addressed through the development of a rainwater drainage system designed to increase the capacity of the water flow by moving rainwater to another downstream body of water.

In the mid-1990s, in the face of this unsustainable environment, various nations, such as the United States, France, and Australia, proposed a set of new conditions for the qualitative and quantitative treatment of urban rainwater. The main thrust of the proposals offered for the management of stormwater in the urban area is the preservation of natural water flow mechanisms or the use of systems that aim to "imitate" any aspect of the natural hydrological cycle that has been changed.

Therefore, the main used approaches include the use of structures that aim to replicate the water infiltration potential of the soil lost due to impermeabilization. As a result, a lower amount of surface runoff is created and problems with flooding are minimised. In turn, this facilitates the recharging of underground aquifers and the enhancement of water quality.

Although the normal hydrological cycle is not completely restored by means of these approaches, there is a significant improvement in the urban environment. The sustainable urban drainage system (SUDS) is generally considered to be the set of best practices for water management in the urban environment.

SUDS are designed to allow either water to infiltrate the land or to be stored in devices to mimic the natural removal of surface water (Charlesworth 2017). Among the objectives of the SUDS are:

- Quantitative regulation of surface runoff
- Improvement in the quality of water from surface runoff
- Protection of the natural features of water bodies
- Management of hydrological variables in watersheds.

This system is supposed to mitigate the environmental risks arising from urban runoff and to lead to environmental change wherever possible. The SUDS goals are therefore to minimise the impact of growth on the quantity and quality of runoff and to optimise opportunities for amenity and biodiversity (Woods-Ballard et al. 2007). Long-term maintenance challenges and other operational considerations have hindered the widespread adoption of SUDS, but many local governments, environmental authorities and developers are keen to introduce this solution in addition to traditional urban drainage systems.

The Flood and Water Management Act, passed in the UK in 2010, called for a change in approach to flood control: strengthening flood risk management instead of constructing flood defences (Butler and Pidgeon 2011). Drainage systems now have to be licensed by authorities in new developments after consulting with any bodies likely to be affected by the discharge. The designer no longer has an automatic right to send the drainage to the local sewage system, and it is now necessary to use SUDS in new developments to control surface drainage (Flood and Water Management Act 2010).
Constructed wetlands (CWs) are considered as one of the SUDS tools.

1.3 Constructed wetland

A constructed wetland (CW) is a synthetical wetland designed to treat domestic, commercial, agricultural, and industrial wastewater or stormwater runoff. Constructed wetlands are engineering treatment systems that use natural processes involving wetland vegetation, soils, and their related microbial assemblages to improve water quality (Dotro et al. 2017). In general, CWs are a comprehensive wastewater treatment system. Current uses vary from single-family, municipal and industrial wastewater treatment to agricultural wastewater, mining and stormwater or combined sewer overflow (CSO) wastewater treatment. Two major structures are used for subsurface flow CWs, namely horizontal flow (HF) and vertical flow (VF). Constructed wetlands (CWs) are a fast-growing alternative to traditional intensive technological treatment systems for many reasons due to their simplicity of operation and treatment efficiency without the need for complicated technology and high investment costs (Pucher 2015).

Several studies have confirmed that CWs are powerful in removing pollutants from different wastewaters (Saeed and Sun 2012). Nonetheless, CWs design and efficiency as an innovative technology remains a topic of debate, mainly because CWs have been built based on empirical results (Zhang et al. 2014). Hence, the performance of the various CW designs is difficult to compare. As several studies have shown variability in performance and a lack of pollutants retention, or uncompleted removal processes in CWs, the complex retention mechanisms to remove various stormwater pollutants in such passive treatment units are still unclear. The performance data from a CW design or operational method may therefore not be suitable in other contexts due to differences in operation and maintenance parameters associated with different wastewater treatments.

1.4 Stormwater constructed wetland

Recently, stormwater management is an area of study focus in several countries around the word. This is partly due to the continuous increase in the quantity of urban stormwater and carryover pollutants in addition to increased water demand, hence the need for a safe water supply. Therefore, stormwater treatment approaches have been developing to enhance water quality and thus facilitate efficient planning of water resources (Luzi 2010; Pittman et al. 2011). Such advances in science continue to develop and now include constructed wetlands, advanced treatment technologies such as chemicals and microbiological systems, and activated sludge, bio-filtration and bio-retention systems (Hatt et al. 2007a; Bratieres et al. 2008). However, very little is known about the design and performance with an increase in the variability of both urban stormwater and carryover pollutants. Moreover, most of the studies have focused on CWs evaluation and the prediction of their performance based on simple calculations of relative changes in the pollutants’ concentration before and after the treatment. To develop evaluation and prediction criteria under the variability of both quality and quantity of urban stormwater, therefore, it has become essential to enhance CWs design and find new approaches to overcome the lack of knowledge in understanding the influence of the variability on performance.

1.5 Aims and objectives

The research aims are to develop an understanding of the dynamics of long-term pollutants immobilisation in constructed wetlands (CWs) operated under variable urban stormwater loadings (different catchment area sizes) and tidal-flow conditions. The results of this study, therefore, demonstrate the impact of the design and operational parameters on the pollutants retention capability of CWs.

The objectives to achieve these aims are:

- To conduct experiments of predesigned pilot-scale vertical flow constructed wetlands (VFCWs) to assess the key parameters of urban stormwater loading rate, physicochemical characteristics of the used substrates, wet-dry strategy, and the physical and chemical characteristics variability of influent urban stormwater.
- To investigate the long-term priority pollutants immobilisation from urban stormwater in VFCWs, which were packed with substrates having variable physicochemical properties and loaded equally with variable urban stormwater characteristics.
- To analyse experimentally and statistically the effect of different operation conditions of urban stormwater loading and wet-dry regime on the long-term priority pollutants immobilisation in VFCWs.
- To construct a mathematical-statistical model generalising the variable operation conditions of pollutants loading and wet-dry regime using partial least square analysis (PLS) which enables future application to predict the removal based on the mass balance analysis.
- To develop a dynamic model utilising STELLA software to simulate N forms transformation in tidal-flow urban stormwater VFCWs in order to understand and quantify the fate and dynamics of N forms (Ammonium, Nitrate, and organic-N).

1.6 Thesis structure

This study is divided into seven chapters, as illustrated below:

Chapter 1 gives an introduction about the water and stormwater with the importance of pollutants removal using constructed wetlands and listing the aim and objectives of the study.

Chapter 2 includes a literature review discussing globally the application of constructed wetland for stormwater management and treatment, the design and limitations, main pollutant removal mechanisms, and general pollutants removal models used in such passive treatment.

Chapter 3 includes the description of the designed materials and methods used to set up eight pilot-scale vertical downflow constructed wetlands and involves all procedures to investigate the treatment performance of CWs.

Chapter 4 explores, investigates, and compares the performance VFCWs under different design and operation conditions toward the removal of solids, heavy metals, and nutrients from semi-synthetic urban stormwater. Moreover, this chapter outlines the dynamics of these pollutants from the liquid phase (representing semi-synthesised stormwater) to the solid phase of different type substrates used in VFCWs and how operations regimes and physiochemical characteristics of the substrate impact on the long-term pollutants' immobilisation.

Chapter 5 demonstrates the impact of variable urban stormwater loading and wet-dry conditions on long-term priority pollutants immobilisation in urban stormwater VFCWs. Statistical analyses were used to reveal the significant differences in performance at multiple levels of operation conditions. Additionally, this chapter describes the construction steps of the statistical-mathematical model for gathering experimental data of two and a half years of operation period. Mass balance analysis for solids, heavy metals, and nutrients removal was implemented to reflect the variable applied operation conditions. Partial least squares (PLS) regression analysis has been used to build a generalised prediction model.

Chapter 6 explores the developing steps for mathematical models using STELLA software to investigate and understand the fate of N forms transformation dynamics in the five main processes of ammonification, nitrification, denitrification, plants uptake, and adsorption within the integrated treatment processes. Adsorption experiments and further supporting measurements were also included in this chapter.

Chapter 7 outlines the main conclusions of the research and recommendations for future work.

Chapter 2: Literature Review

2.1 Introduction

This chapter includes a literature review of work already conducted that applies to the use of CWs to treat urban stormwater. This review aims to provide a comprehensive evaluation of CW application to treat high-strength stormwater with a focus on design, efficiency, retrofit issues, and design guidelines. First, it reviews the characterisation of stormwater and its pollutants and explores the treatment processes and associated limitations. Furthermore, this chapter focuses on CW types with brief descriptions, classifying removal processes involved within the CW structure, key points for using CWs to treat polluted stormwater in the UK and around the world, nitrification and denitrification processes, heavy metals removal mechanisms, predictions of performance, sizing and lifespan predictions, and modelling.

Key aims of this review are:

- To deeply understand and review the development and state of the art of applying CWs for urban stormwater treatment.
- To collate data on the design, and performance challenges faced in the use of VFCWs for stormwater treatment to initiate research guidelines.
- Identifying gaps in knowledge, studies, and practise and to provide recommendations on how to move CWs for stormwater management forward.

The literature review is conducted primarily as a desk study, using the great value of the information provided by high-impact journals, and it also thoroughly explores written guidelines, government and industry studies, and university textbooks.

2.2 The evolution of urban drainage approaches

Urban drainage is a very old field, with a history going back to at least 3000 BC (Burian and Edwards 2002). Two types of fluids are described for urban drainage: wastewater and stormwater (Butler† and Davies†† 2000). Wastewater is water that needs to be treated and disposed of properly after being used for life support, industrial processes, or life enhancement to avoid hazardous and contaminated conditions from growing in urban areas. Urban drainage plays several important roles in maintaining public health and safety (Poleto and Tassi 2012).

Stormwater is runoff generated by precipitation. During the designing of urban drainage systems, both wastewater and stormwater must be addressed. Historically, both were either combined into one conduit (i.e. combined sewer system) or kept separate during collection and disposal (i.e. separate sewers system) (Burian and Edwards 2002). Not treating both contaminated wastewater and runoff collected from impermeable surfaces such as roads, rooves, and pavements before discharging them into watercourses would have significant harmful effects on the water environment.

Nevertheless, in recent decades urban drainage and related literature have seen several 'modern' words introduced and adopted that attempt to describe the transition towards a more holistic approach. Moreover, the use of modern approaches has seen rapid growth, in the case of urban drainage management (also known as urban stormwater management) the development and use of terms has taken place with different names in various areas of the world, such as SUDS in the United Kingdom; low impact development (LID) and best management practises (BMPs) in the United States and Canada; low impact urban design and development (LIUDD) in New Zealand; and water sensitive urban design (WSUD) in Australia. Irrespective of the name, the ideas and concepts of sustainable systems discussed are very similar and all relate to the equilibrium between the variables of the hydrological cycle and their effects on watersheds (Poleto and Tassi 2012).

The existence of urban drainage as a discipline has historically increasingly integrated as part of civil engineering, with an increasing emphasis on the ecology of receiving waters (and their drivers, such as water quality and flow regimes) and the provision of multiple benefits (USEPA 2000), see Figure 2.1. This broadening of viewpoints represents the involvement of a wider range of professions, such as architects, landscape architects, planners, ecologists and social scientists.

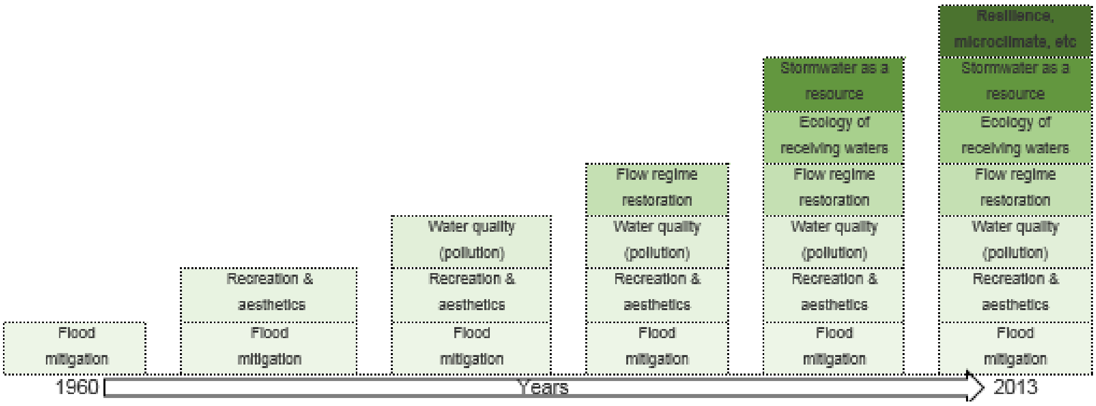


Figure 2.1 Growing the integration and sophistication of urban stormwater management since 1960s (Fletcher et al. 2015).

Sustainable systems of urban drainage treatment offer various advantages such as landscaping, environmental and economic benefits, reinforced by controlling not only peak flows but also the volume, frequency, duration and performance of runoff and drainage. Sustainable drainage covers a wide range of components, each with different approaches to the management of flows, volumes, water quality and advantages in terms of amenity and biodiversity. The following tools or techniques can be identified amongst the sustainable solutions being built and implemented (Poleto and Tassi 2012):

- Permeable pavement
- Semipermeable pavement
- Ponds and wetlands
- Infiltration gullies
- Micro-reservoirs
- Green roofing
- Grassed strips
- Swales and basins
- Detention and retention reservoirs
- Infiltration trenches and filter drains
- Infiltration wells
- Rooftop reservoirs
- Underground reservoirs

In the UK, with an increasing preference for SUDS, there have been major changes in the way surface water is supposed to be handled. For example, currently more than half of the local authorities include SUDS in their planning conditions (Woods-Ballard et al. 2007). Nevertheless, surface water is only one aspect of the water cycle and it is now possible to have a more comprehensive approach looking at the opportunities available from all areas of the water cycle. In the UK, SUDS consist of a variety of methods and techniques used to remove stormwater/surface water in a manner that is (arguably) more efficient than traditional methods. These are based on the concept of replicating the natural, pre-development drainage from a site as closely as possible, following the principles already stated behind LID. SUDS are usually designed as a sequence of stormwater activities and technologies that interact to create a management train.

SUDS are designed with three goals in mind (Environment Agency 2003):

- Controlling the amount of runoff from a development
- Enhancing the quality of runoff
- Improving the value of the site and its surroundings in terms of nature conservation, landscape, and amenity.

SUDS system selection would depend on several variables such as:

- The contaminants present in the runoff
- Size and drainage strategy for a catchment area
- The area’s hydrology and soil infiltration rate
- Groundwater source safety zones or contaminated land.

Large-scale ponds and wetlands are generally better suited to locations greater than five hectares. Trenches, swales, philtre strips, and porous pavements are suitable for large as well as small sites. A mix of mechanisms is often incorporated in the best drainage solution for a site.

The CIRIA design manual (CIRIA 2007) guides how to integrate SUDS devices, and how to choose them for a particular application. The combination of SUDS devices is an important concept in the guidance, and the product is called a 'surface water management train', sometimes called a 'treatment train'. The suggested sequence of options is given in Figure 2.2 with the devices suitable for each point. Having a drainage solution as close to the top of this diagram as practicable is optimal, but if all the drainage needs cannot be met at a particular stage, the designer must step further down the list. Bray (2001) describes a good example of the management train concept in practice, where drainage from various sections of a site for motorway services travels through separate trains of connected devices including swales, trenches, ponds and wetlands (Butler† and Davies†† 2000).

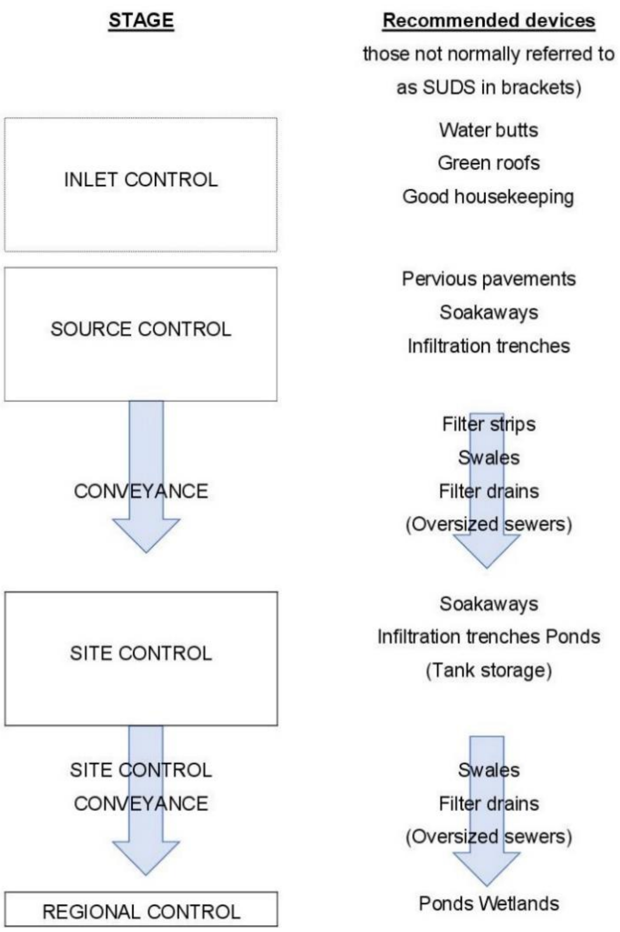


Figure 2.2 Surface water management train.

SUDS, however, provide a safe flooding solution. SUDS move from piped designed systems to activities and procedures using and improving natural processes (i.e. penetration, evapotranspiration, filtration, retention, and reuse). It offers drainage options by implementing alternatives to the direct channelling of stormwater runoff to nearby water bodies by pipes and sewers (Ghani et al. 2008). SUDS employ a range of conditions collectively referred to as the "Management Train" It requires four key steps: management of the source, pre-treatment, retention, and infiltration. The other aims of introducing SUDS are to reduce the pollution of surface water, increase water quality, and promote environmental amenity and biodiversity. SUDS decrease flow rates, transferring pollutants to the atmosphere and increasing the capacity for water storage to achieve the above objectives (Srishantha and Rathnayake 2017).

Over the last several decades, the urban drainage profession has made a significant change, moving from an approach focused largely on flood mitigation and health safety to one that considers a wide range of environmental, health, social and economic factors. Therefore, the profession has established and adopted new terminology for defining these new approaches and is likely to continue to do so as a transition to a more sustainable and integrated approach takes place. The studies have shown that terminology evolved in response to changes in the principle of urban drainage. However, also the converse is true; by working to set the vision into a more sustainable approach and involving participants from other professions and more generally from society, the terminology has played an important role in guiding and influencing this growth.

2.3 Urban stormwater quality

The impacts of urbanisation on the hydrological cycle are obvious. These impacts include variations in both the quantity and quality of stormwater (Goonetilleke et al. 2005). It is predicted that half the world's population will live in urban areas by 2050 (Aryal et al. 2011). Urbanisation results in the spread of impervious regions and diversification of land use, with great natural vegetated lands converted into impermeable zones such as rooves, roads and driveways, parking spaces and other paved zones. The increased percentage of impermeable surfaces leads towards more frequent high flow events and to an increase in the volume of stormwater runoff generated from urban catchments due to reduced infiltration of stormwater into the soil.

Stormwater quality is compromised in several ways during impervious overland flow. Deposited soils are mobilised, and particles are worn from buildings, vehicles and pavements. Likewise, heavy metals such as zinc, copper, and lead are mobilised as they are corroded and produced from building materials, industrial factories, and vehicles which often wear components such as exhaust emissions and brake pads. Gas and other engine spills, and surface precipitation lead to hydrocarbons. Excessive use of fertiliser in lawns and garden areas and atmospheric precipitation can add compounds of nitrogen and phosphorus. The chemical water quality composition of the urban stormwater runoff, taken cumulatively, can be quite low (Davis et al. 2010).

The climate of an area can have a considerable impact on the quantity and quality of the stormwater runoff. Variables such as the length of the preceding dry periods between storms, the average intensity of the rainfall, the duration of the storm, and the amount of snowmelt present can have a major impact on the characteristics of runoff from a region (O'Dell 2001).

The important source of contaminants in urban areas is non-point pollution. Throughout the wet weather cycles, a wide range of contaminants collected on urban catchment surfaces are transported with stormwater and eventually enter water receiving bodies. The main causes of these pollutants are human activities in urban and suburban regions. Thus, studies have focused on the numerous substances, including suspended solids, nutrients, heavy metals, hydrocarbons, and polycyclic aromatic. The stormwater quality present in drainage catchment can be determined by the types of land-use activities. Stormwater runoff treatment systems are available and are mainly natural treatment systems. Stormwater recycling treatment systems have been widely used in water and wastewater treatment and include fibre philtres, deep bed philtres, and biofilters. They can achieve a significantly higher percentage of pollutant removal required to treat stormwater without the need for a pre-treatment system.

2.3.1 The classification of urban stormwater pollutants

There are many forms to classify and group sources of stormwater pollution and the distinction between classes can be quite complicated, with the boundaries between origin categories seldom clearly established. Based on the classification methods employed, such sources of pollution may contribute to several categories of sources at different times or ambient conditions (Müller et al. 2020).

A large variation was identified in the concentration of pollutants. Heavy nutrients, hydrocarbons and polycyclic aromatic are present in dissolved form as well as in bound particulate form. The pollutant partition varies by region and based on the season as well. Almost all of the pollutants in particulate form are bound to the finer fractions, particularly those less than 100μm (Aryal et al. 2011). The major pollutants categories in urban stormwater can be classified as the following:

2.3.1.1 Sediment and total suspended solids

Solids are one of the most common pollutants present in urban stormwater. Suspended solids from stormwater are of environmental concern due to their effects on aquatic ecosystems and storm sewer systems (Newcombe and Macdonald 1991). According to the origin and form of urban runoff, the transported solids vary in size, basic gravity and chemical properties. Therefore, the effects of the solids from stormwater on the receiving waters depend on the origins and properties of the solids (Galfi 2014).

Such particulates derive predominantly from exhaust gas, traffic, asphalt/building degradation, dirt, sand, and silts transported by wind and other means, and consist of varying particle sizes. Urban runoff produces a wide range of particulate matter, from smaller than 1μm to more than 10,000μm in scale (Sansalone and Kim 2008). In Europe, TSS values for urban stormwater samples collected from separate sewer systems were in the range of 11 to 430 mg/l, and a 106 mg/l average value (Zgheib et al. 2012). While in the UK, the range is 21 to 2582 mg/l, and a 190 mg/l average value of TSS was recorded in separate sewer systems (Ellis 1991). In the USA the maximum concentration of sediments in urban catchments was 15,000-36,000 mg/l with average levels usually between 2,000 and 3,000 mg/l (Gower 1980).

2.3.1.2 Organic materials

Organic matter (OM) is the priority pollutants in the UK and European countries, especially in urban wastewater, expressed through the biodegradable component (biochemical oxygen demand (BOD5)) and the complete OM degradation (chemical oxygen demand (COD)) (Stefanakis et al. 2014f). Ellis (1991) reported the range and average values of BOD5 and COD for urban stormwater samples collected from separate sewer systems as (7 – 22), 11 mg/l and (20 – 365), 85 mg/l respectively. While a value range of 14 – 320 mg/l and mean value of 89 mg/l for COD urban stormwater in Europe was reported (Zgheib et al. 2012). These values represent approximately half the value of wastewater from combined sewer systems, indicating that the treatment requirements level for OM are less than that mixed with wastewater. The variability in the values reflects the pollutants carried over through various impervious surfaces.

2.3.1.3 Heavy metals

There are several different definitions of heavy metals. Some are calculated on density, some on atomic weight, whereas others are based on chemical properties and toxicity. For urban environments, heavy metals commonly refer to toxic metals that derive from human activism. Human and other living organisms involve these toxic elements in their biological functions, but only in trace quantities. Excessive amounts of these heavy metals can harm human health, and ecosystems. They are of particular concern in stormwater runoff because of their toxicity and the reality that they are not chemically easily converted and stay in the environment for a long time, affecting the ecosystem. The heavy metals of greatest environmental concern are chromium (Cr), nickel (Ni), zinc (Zn), copper (Cu), lead (Pb), vanadium (V), cobalt (Co), cadmium (Cd), and mercury (Hg). Pb, Cr, Zn, Ni, Cu and Cd seem to be the most common heavy metals of concern (Aryal et al. 2010). Heavy metal discharges into the environment system have been controlled by regulations and the rates of road and soil contaminants, river, lake and marine sediments, and industrial runoff has been investigated. The contribution of heavy metals from different sources has showed that approximately 75μg of Cu, 3μg of Pb and 89μg of Zn per km-vehicle were released from the brakes only (Davis et al. 2001). The reported brakes were an important source of Cu, while tyre wear was the main source of Zn. The main source of Cr is the body surface of vehicles covered with hexavalent Cr for the prevention of corrosion. Ellis and Revitt (1982) analysed many heavy metals in the sediment on the street surface as a result of grain size sediment. The measurement trend of Pb, Cd, Cu and Zn was linked to the level and type of traffic density. Their research found that concrete motor pathways had particles with less than 250μm, while other locations with asphalt surfaces displayed different degrees of wear, which produced a significant amount of free fine materials. Based on chemical analyses for sediment, heavy metals existed in urban stormwater within the ranges listed in Table 2.1.

Table 2.1 Heavy metals existing within the ranges.

Heavy metals		**Pb**	**Cd**	**Mn**	**Zn**	**Cu**	**Fe**
		μg/g					
Sediment	<250	040-1690	0.72-4.2	766-8550	119-2133	42.6-640	6780-22700
Size (μm)	>250	111-2296	01.3-6.8	694-1244	91.6-1760	27.2-212	4195-22850

Although the levels of heavy metals in stormwater are strongly linked to traffic density, other contaminants areas can impact on these levels. In the North London Borough, analysis carried out for heavy metal levels in road sediments revealed the maximum rates of Pb, Cu, Zn and Ni were respectively recorded to be 56 – 20.535 μg/g, 16 – 43.470 μg/g, 48 – 13.740 μg/g and 49 – 443 μg/g. Researchers concluded that the high levels were due to the presence of metal scrap yards. They assessed Pb in the background soil and noticed that the concentration was 407 μg/g (Harrop et al. 1990).

Bubb et al. (1991) analysed the concentration of heavy metals (Pb and Zn) in the Yare River, Norfolk, UK. Sediments within the Yare River were found to contain average concentrations of 180.5 mg/kg for Pb and 327.6 mg/kg for Zn. They also noticed that urban runoff containing coarse particles (250-1,000μm) appeared to be the main source of Pb contamination. Zn, on the other hand, showed a more widespread distribution. They also observed from low-volatile solids (< 5%) sediments, such as coarse sand and gravel deposits, that organic matter may have effectively controlled the aggregation of Pb and Zn, reducing the supply of active binding sites.

2.3.1.4 Nutrients

Nutrients (nitrogen and phosphorus) are important components of all aquatic environments. However, when these nutrients are noticed at significant levels, they can harm the aquatic ecosystems by encouraging the growth of algae and plants. Such nutrients are a tribute to the eutrophication of water bodies. Traditional sources of these nutrients are chemical fertilisers applied to agricultural land, lawns, parks, golf courses, and landscapes. Residential regions and grass areas are the biggest contributors of nutrients in urban stormwater (Garn 2002).

Nutrients can be found in many different forms. Phosphorus may be found in inorganic phosphate (phosphate, orthophosphates, polyphosphates) or organic bound phosphate. The inorganic and organic sources of nitrogen are also found. It is calculated as total nitrogen (TN), Kjeldahl nitrogen (TKN), nitrate (NO3-N), nitrite nitrogen (NO2-N), and ammonium (NH4-N). Based on the prementioned elements affecting nutrient content in the urban stormwater, Zgheib et al. (2012) found the range of both TKN and TP (total phosphorus) concentrations of 20 stormwater events ranged from < 2 –16 mg/l and 0.3 – 3.52 mg/l respectively, while Ellis (1991) reported that TN and TP concentration levels in UK urban stormwater ranged between 0.9 to 24.2 mg/l and 0.5 to 4.9 mg/l respectively.

2.3.1.5 Hydrocarbons / oil and grease

Petrochemical hydrocarbons involve oil and grease; the 'BTEX' compounds include benzene, toluene, ethylbenzene and xylene, and a variety of polynuclear aromatic hydrocarbons (PAHs). Petroleum hydrocarbon sources usually involve parking lots and roadways, spilling storage tanks, vehicle emissions and unsuitable waste oil disposal. Usually, petroleum hydrocarbons are distributed along the transport corridors (O'Dell 2001). Petrochemical hydrocarbons at low concentrations are well known for their acute toxicity (Schueler 1987).

2.3.1.6 Pathogens

Pathogens are disease-producing microorganisms which pose a significant threat to public health when present in contact water. Since stormwater runoff does not usually contact with household wastewater, and direct exposure to runoff is likely to be limited, there is typically little threat of stormwater runoff pathogens that pose a risk to public health. Furthermore, where runoff is discharged into recreational bodies of water such as beaches and lakes, or where runoff interacts with shellfish beds, there is a possible risk of pathogen contamination to the public health. There is a variety of indicator organisms that were used to determine the existence of harmful pathogens in stormwater runoff. Faecal coliform has been commonly used as an indicator for the existence of pathogenic organisms in household wastewater, and therefore research characterising stormwater runoff has also widely used this indicator. *Escherichia coli*, *streptococci* and *enterococci* have been used as other bacterial indicators to test the presence of harmful pathogens in stormwater runoff (O'Dell 2001).

2.3.2 Important sources of urban stormwater pollutants

The contaminants present in the water runoff of urban storms come from various sources. The main sources are residential and commercial pollution, manufacturing operations, development, vehicles, streets and car parks, and atmospheric deposition. The road runoff is likewise emitting most pollutant forms. Atmospheric debris also contributes significantly to stormwater runoff. Table 2.2 summarises pollutants typically found in the stormwater runoff and their likely sources (O'Dell 2001; Aryal et al. 2010).

The contaminants from road runoff are listed in Table 2.2. The table shows that there are different sources for most contaminants. Major sources likewise emit most pollutant forms. Atmospheric debris also contributes significantly to stormwater runoff.

2.4 Constructed wetlands

Chinese and Egyptian civilizations are the oldest users of wetlands for water pollution control throughout history (Brix 1994). Natural wetlands were used as suitable wastewater disposal sites so long as wastewater was collected. Wetlands constructed to treat water originated from research carried out at the Max Planck Institute in West Germany, starting in 1952 (Kadlec and Wallace 2009a) and during the 1970s in the Western Hemisphere. Since 1985, the implementation of wetland technology has accelerated around the world, primarily because, while mechanically simple, treatment wetlands are biologically complex systems able to achieve significant levels of treatment.

In addition, constructed wetlands can be built using national materials and national labour, which is a big advantage in developing countries.

Table 2.2 Pollutants sources in urban stormwater.

Pollutants	Pollutants Sources
Sediment and Total Suspended Solids (TSS)	Soil erosions, vehicles, streets, gardens, driveways, roads, human/animal waste, construction activities, atmospheric deposition, drainage channel erosion.
Organic Materials	Parks, residential lawns, suburban lawns, commercial and industrial landscaping, animal waste.
Heavy Metals	Soil erosions, vehicles, bridges, atmospheric deposition, industrial areas, metal surfaces which corrode, combustion processes.
Oil and Grease / Hydrocarbons	Vehicles, household chemical, industrial processes, paints and preservatives, roads, driveways, car parks, maintenance areas for vehicles, gas stations, illegal dumping into storm drains.
Nutrients ‘’Nitrogen and Phosphorus’’	Fertilisers, agricultures, erosions, human/animal waste, household chemicals, industrial processes, atmospheric pollution, emissions from vehicles, detergents.
Pesticides and Herbicides	Residential lawns and parks, farming, roadsides, right-of-way infrastructure, commercial and industrial landscaped zones, infiltration through soil.
Pathogenic ‘’Bacteria and Viruses’’	Lawns, highways, leaky sewerage pipes, cross-connections with sanitary sewers, medical waste, industrial processes, animal waste, septic systems.

Constructed wetlands (CWs) imitate the properties of natural wetland systems for water purification. It uses the same plants, soils and microorganisms as natural wetlands to eliminate water contaminants, nutrients and solids. Commonly, constructed wetlands are man-made and are built in a manner like natural wetland operations. A popular description of these systems states that constructed wetlands are 'man-made systems of a saturated media, emerging and submerged vegetation, animal life and water simulating natural wetlands for human use and benefits’ (Stefanakis et al. 2014b).

Positive effects from constructed wetlands involve, among others, the provision of wildlife and habitat biodiversity, recreational activities (e.g. bird watching), water storage and aesthetic enhancement of the surrounding environment (urban or rural) (Knight et al. 2001). The wetland values can be divided into three main types: ecological, sociocultural, and economic. All of this together describes the wetlands. Total value each category of value has its own set of criteria and units of value (Groot et al. 2012).

2.5 Constructed wetlands classification

Constructed wetlands (CWs) are classified by function and purpose within three key application areas (Stefanakis et al. 2014a) as follows:

- Constructed wetlands for habitat development: Wetlands built primarily for the development of wildlife habitat are known as constructed habitat wetlands (Sundaravadivel and Vigneswaran 2001).
- Constructed wetlands for flood control: These wetland systems are designed to accommodate flood runoff events (Stefanakis et al. 2014a).
- Constructed wetlands for wastewater treatment.

Classification of constructed wetlands (CWs) can be further divided into other groups, based on two criteria of the vegetation type or water flow regime path through the system (Figure 2.3). According to the water flow direction, there are two main types:

a) Free water surface constructed wetlands (FWS CWs), and
b) Subsurface flow constructed wetlands (SF CWs).

Further classification may be made based on the vegetation's growth properties. So one can differentiate between (Langergraber and Haberl 2001).

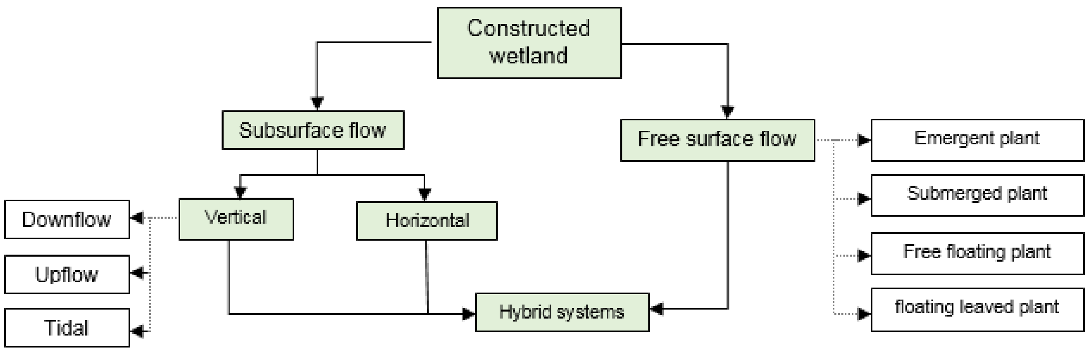


Figure 2.3 Classification of constructed wetlands.

There are three types of macrophytes used for the creation of constructed wetlands (Mahmood et al. 2013):

1) Floating macrophytes;
2) Emergent macrophyte; and
3) Submerged macrophytes.

Constructed wetland systems are usually planted with rooted emergent species of macrophytes (Stefanakis et al. 2014a).

2.5.1 Free water surface constructed wetlands

Free water surface (FWS) wetlands have open water areas and are similar in structure to natural marshes (Kadlec and Wallace 2009a). Water depths are typically shallow, and this, along with the presence of plants, helps to regulate the flow through the CW to create plug-flow conditions (Reed et al. 1998). Plug-flow conditions help to improve the interaction between the wastewater and the biological surfaces where reactions to the disposal of contaminants occur. Typical free water surface wetland (FWS CW) with emerging macrophytes is a shallow basin comprising 20–30 cm of rooting soil with a water depth of 20–40 cm. There are no specific guidelines for soil quality: the main role of soil is to promote plant growth. When wastewater flows through the wetland, sedimentation, filtration, degradation, absorption, adsorption and precipitation processes are treated.

Free water surface wetlands are suitable in all climates. FWS CW systems are more commonly used in North America (Kadlec and Wallace 2009a). A cross sectional diagram for FWS wetland is presented in Figure 2.4.

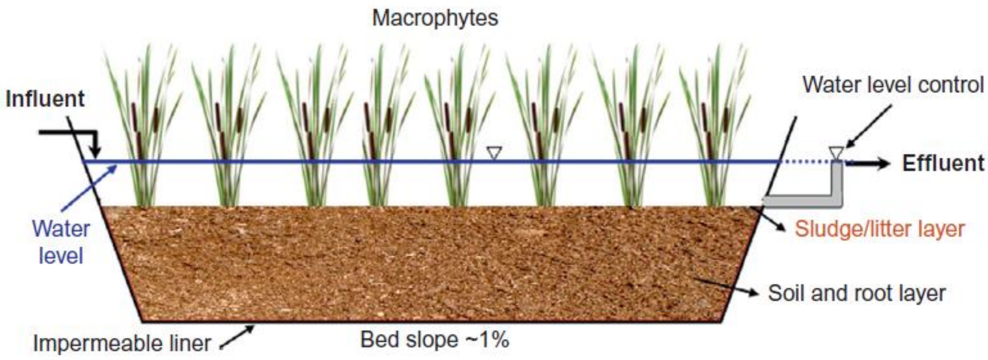


Figure 2.4 Free water surface (FWS) wetlands.

2.5.2 Horizontal subsurface flow constructed wetlands

Horizontal subsurface flow (HSSF) wetlands usually use a gravel bed cultivated with wetland vegetation, see Figure 2.5. The water that is held below the bed surface and its flow path, moves horizontally through the pores of the porous media and the plant roots from the inlet to the outlet (Kadlec and Wallace 2009a). In the UK, these HSSF systems are also known as reedbed treatment systems (RBTS) as the most commonly used plant is the common reed (*Phragmites Australis*) (Ellis et al. 2003a).

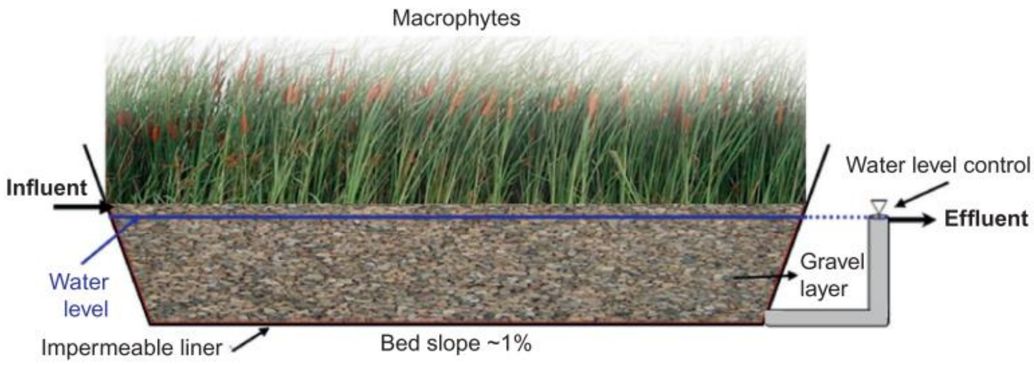


Figure 2.5 Horizontal subsurface flow (HSSF).

2.5.3 Vertical subsurface flow constructed wetlands

Initial development of vertical subsurface flow constructed wetlands (VFCWs) was carried out by Seidel (1965) as a middle stage after the anaerobic septic tank and the HSF (Langergraber and Haberl 2001). VFCWs have primarily been used for urban, industrial, and domestic wastewater treatment. According to their improved nitrification ability, they have also been used for the treatment of other forms of wastewater, particularly those with a high concentration of ammonia nitrogen, e.g. dairy wastewater, landfill leachate, agriculture wastewater and food wastewater, among others (Kadlec and Wallace 2009a).

Vertical flow wetlands scatter water across the surface of a sand or gravel bed cultivated with wetland vegetation. Water is processed as it filters down through the root zone of the plant. Biosolids wetland dewatering can be thought of as a form of VF wetland system (Kadlec and Wallace 2009a). VFCWs typically consist of sand and gravel layers, with wetland vegetation planted in the sand at the top of the system (Nathan and Scobell 2012). The flow direction in VFCWs could be downflow, upflow or tidal, but the downflow prevalent flow direction is normally used because the material deposited is easily removed (Fitch 2014). In most VFCWs, the influent wastewater is loaded at the top of the system, flooding the surface and then travelling through the substrate media before it is collected from the gravel drainage layer at the bottom of the system. Figure 2.6 shows a typical VFCW.

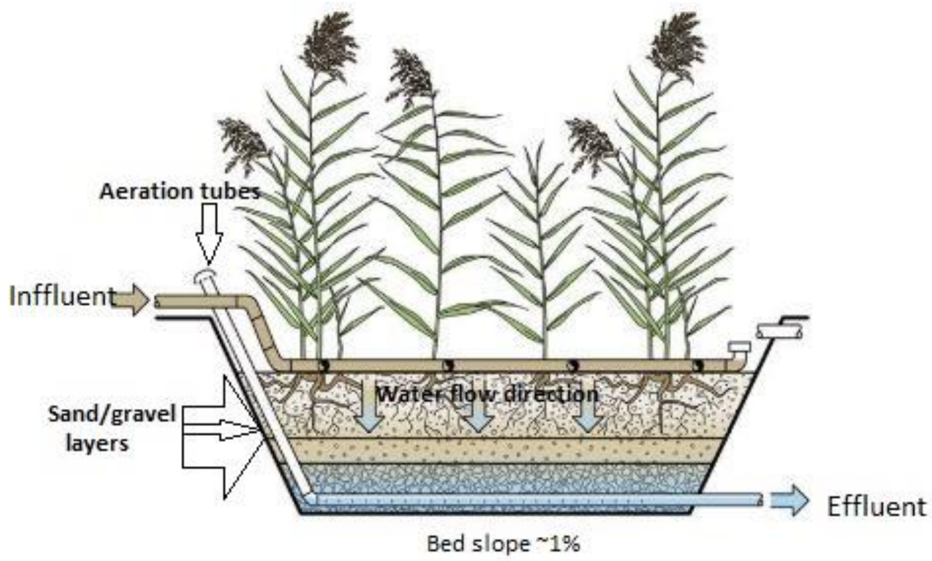


Figure 2.6 Vertical flow (VF) constructed wetlands (adopted from IWA, 2017).

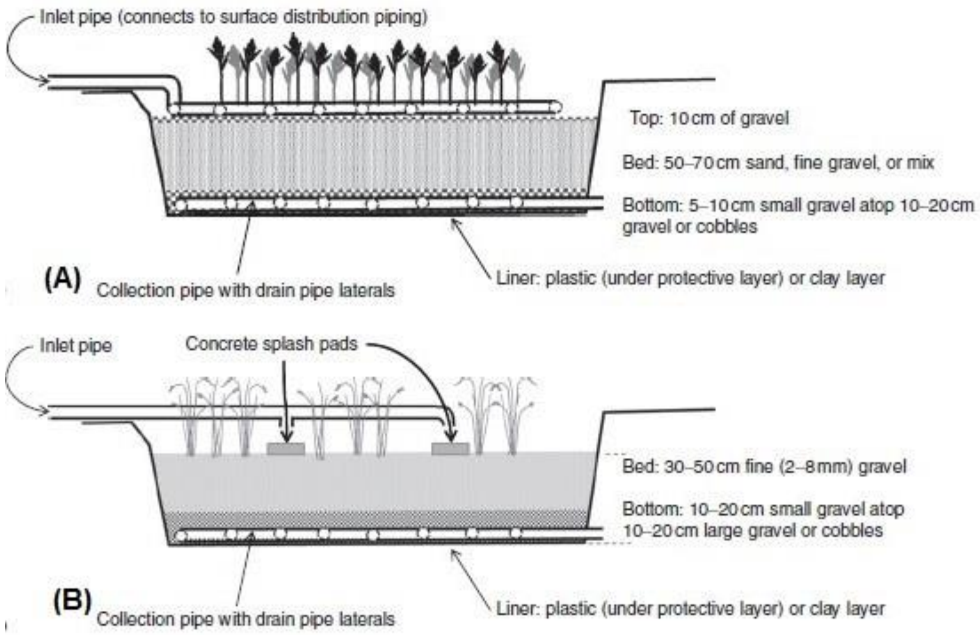


Figure 2.7(a) Vertical SSF, surface fed, common in Germany. The view is a section along the bed length. (b) Vertical SSF, surface fed, common in France. The view is a section along the bed length (Fitch 2014).

The vertical flow wetlands are popular in Europe, used for the removal of nitrogen by the intermittent flow. The storage or accumulation of water at the bottom of the wetland is a problem, either upstream or downstream. The uneven distribution of water will minimise the efficiency of treatment by channelling and short-circuiting into one section of the wetland. Therefore, a layer of stone is used as a horizontal wetland, and the water is dispersed or stored within that layer by the length of the drainpipe, see Figures 2.7(a) and (b) (Fitch 2014).

Since pressure can be applied without relation to overland flow, a greater flow (hydraulic loading) than a horizontal flow system can be achieved, resulting in a lower total wetland volume requirement. Nevertheless, greater speed also means greater opportunities for channelling to develop (Fitch 2014).

2.5.3.1 Tidal-vertical subsurface flow constructed wetlands

Tidal vertical flow wetlands are operated in batch sequencing mode, while others receive continuous flow. In batch sequencing mode, the wetland is filled and then allowed to drain completely to refill again. Such a filling and draining process allows for more oxygen to the environment than is the case with horizontal SSF wetlands and thus allows for an anoxic/anaerobic (filled) period followed by an anaerobic (drained) time. This process contributes to the mineralisation of contaminants, especially for the treatment of ammonia (Fitch 2014).

Furthermore, in the mid-dose, CW is depleted, and oxygen can then enter the system, supplying aerobic treatment for the next batch of wastewater. Therefore, VFCWs are also chosen for their nitrification capabilities. The oxygen supplied by the roots of plants in VFCWs is negligible compared to that retained in the system between doses, and the main reason for plant inclusion is to maintain the hydraulic conductivity of the system. BOD5 and COD removal efficiency is high, but denitrification is limited due to the high aerobic content found in VFCWs (Nathan and Scobell 2012).

2.5.4 Hybrid constructed wetlands

Hybrid systems are a specific category of wetland system mixes of different CW types, primarily VFCWs and HSF CWs, with the target of achieving high performance particularly in nitrogen removal (Vymazal et al. 2006). The idea is to leverage the benefits of one type to counterbalance the drawbacks of the other. Therefore, the reality that HSF systems have a lower nitrification potential due to limited oxygen transfer capacity (OTC) can be balanced against VFCWs that are more successful in nitrification (higher OTC) (Vymazal et al. 1998). On the other hand, HSF CWs have perfect conditions for denitrification, in comparison to VFCWs. The first attempt to merge various CW types was made by Seidel (1965), who developed a two-stage system: linear VFCWs followed by HSF CWs in series (Seidel 1965). Throughout the 1990s and early 2000s, VF-HF CWs were used in some European countries, such as Norway (Mæhlum and Stalnacke 1999); Slovenia in 1996 (Urbanc-Bercic 1996); Ireland, and Austria (Vymazal et al. 2006).

There are typically two common forms of hybrid systems; Figure 2.8 (a) shows a phase with VF units followed by HSF units in series, and (b) an HSF phase followed by VF units (Cooper 1996) (Cooper et al. 1999).

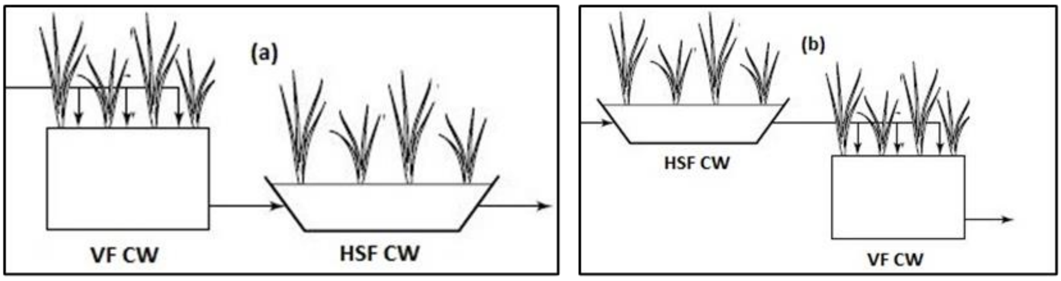


Figure 2.8 Hybrid Constructed Wetlands configurations: (a) VF-HSF, (b) HSF-VF (Stefanakis et al. 2014a).

The first hybrid CW configuration (Figure 2.8a) is the most commonly used hybrid system (Kadlec and Wallace 2009a). Meanwhile the VF-HSF configuration (Figure 2.8b) involves VF systems first installed to eliminate OM and SS, as well as strong oxidative conditions (Nitrification: NH4-N transfer to NO3-N). The oxidised nitrogen form is further transformed by denitrification in the subsequent HSF method, while further removal of organic matter (OM) and suspended solids occurs (O'Hogain 2003) (Vymazal 2001). The first two stages, according to the Seidel model, comprise multiple parallel operating VF units followed by the third stage of two or three HSF units (Vymazal 2005). Various adjustments of this form were tested with various stages, different beds per stage, different filtration media, and various types of wastewater (O'Hogain 2003).

2.6 Application of constructed wetlands

Wastewater from human settlements and activities has been a primary target of many treatment systems. Many early applications were for domestic and municipal wastewater, and that technology sector in many places continues to grow at a rapid pace. Furthermore, there are increasing numbers of applications concerned with municipal and industrial wastewaters, urban and agricultural stormwater, animal and mine waters, groundwater remediation, and other purposes (Kadlec and Wallace 2009a).

- **Municipality wastewater treatment:** HF developed wetlands are typically used as secondary and tertiary treatment stages for municipal and domestic wastewater (single house or cluster of houses) (Vymazal 2009).
- **Animal wastewater treatment:** Constructed wetlands for the treatment are consistent with traditional farm and ranch activities. Forms of livestock wastewater that are treated by developed wetlands include milk manure and milk

plant wash water, concentrated cattle farming runoff, poultry fertiliser, swine manure, and catfish pond water (Kadlec and Wallace 2009a). According to database (LWDB) in North America in 1998, livestock wastewater treatment covered 68 sites, with a total of 135 separate systems (Knight et al. 2000).

- **Mine water treatment:** Many constructed wetlands were developed in the 1980s in the United States to treat acid mine wastewater (Wieder 1989) and (Kleinmann 1990). In 1989, more than 300 locations in the United States used developed wetlands to raise pH and minimise iron and/or manganese concentrations at coal mine sites (Kleinmann 1990).
- **Industrial wastewater treatment:** Industrial companies distinguished by their participation in food processing, produce highly biodegradable organic and nitrogen-rich wastewaters. Such wastewaters are usually very solid, and some sort of preliminary treatment is routinely undertaken**.** Nevertheless, nutrient and organic decreases to regulatory standards are gradually being achieved by constructed wetlands. Project areas also cover wetlands supporting the manufacturing sectors for wheat, wine, olive oil, sugar, starch, alcohol and poultry. Constructed wetland treatment systems were used for advanced secondary or tertiary treatment in pulp and paper mills (Hubbe et al. 2016), also to provide advanced secondary and tertiary treatment of cycle water and stormwater in an increasing number of oil refineries (Knight et al. 1999).
- **Leachate and remediation:** The treatment and management of liquid leachates are one of the most difficult issues related to the use of sanitary landfill sites for solid waste processing. The use of CWs to manage landfill leachates is a fast-growing technology, with both surface wetlands and subsurface flow wetlands (Mohammed 2017; Mulamoottil et al. 1998).
- **Urban stormwater treatment:** FWS constructed wetlands are mostly used for the treatment of urban stormwater runoff (Vymazal and Kröpfelová 2008). However, there several examples of the use of wetlands to treat stormwater. Geary et al. (2003) discussed the use of HF wetland constructed in Blue Haven, Australia, to handle stormwater from an urban 21ha catchment. Shutes et al. (2004) identified the use of HF CW for the treatment of highway runoff along the A34 Newbury bypass in the UK. The project of 17km of highway in Villesse-Gorizia, Italy includes a total of 60 constructed wetlands for runoff treatment (Vymazal 2009).

2.7 Limitations of constructed wetlands

Like any other biological wastewater treatment system, the performance depends on various environmental variables, such as temperature, pH, availability of oxygen, hydraulic and pollutant charges (DLWC 1998). Specifically, the chemical and biological processes are vulnerable to changes in environmental factors. There are restrictions relating to the use of constructed wetlands, the most important of them is summarised in the following (USEPA 1995; DLWC 1998; Ellis et al. 2003b):

- Typically, they require larger areas of land than standard wastewater treatment systems. Wetland treatment may be economic only where land is available and affordable compared to other alternatives.
- Constant baseflow (i.e. minimum water level) for productive wetlands: to survive they require a minimum amount of water level. While wetlands can withstand temporary drawdowns, they cannot resist full drying.
- The efficiency may be poorer than that in conventional treatment. In response to changing environmental conditions, including rainfall and drought, efficiencies in the treatment of wetlands can differ seasonally.
- The biological components are susceptible to toxic chemical substances, such as ammonia and pesticides.
- Management of sediments is crucial to maintaining long-term wetland efficiency
- Pollutant flushes or spikes in water flow can temporarily reduce the effectiveness of treatment.
- Monitoring and management of vegetations.
- Makes possible breeding environment for mosquitoes.

2.8 Constructed wetland design criteria

Although there is a massive amount of research and published literature, the optimum design of constructed wetlands has not yet been determined for various applications. Several techniques are employed to design stormwater CWs, each design varying in the volume of permanent water and the volume of dry detention above the permanent water level in the wetland (Jayaratne et al. 2010). The performance has varied and the influences of the various factors effecting performance, such as location, type of wastewater, stormwater or drainage, wetland design, climate, environment, disturbance, and regular or seasonal fluctuations, have been difficult to quantify. The treatment performance of a constructed wetland benefits from the cumulative effect of the hydrological efficacy and efficiency of the procedure (Ellis et al. 2003b). Figure 2.9 shows the linkages between wetland design elements and interactions.

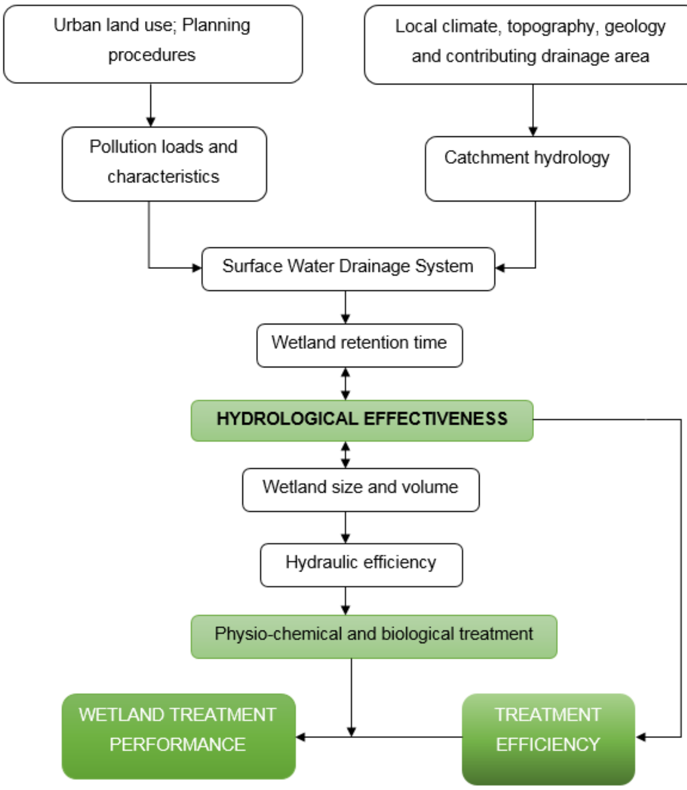


Figure 2.9 Linkages between Wetland Design Elements and Interactions (Ellis et al. 2003b).

Currently, there are no standard design codes in place for CWs. Designs are mostly built on the base of the guidelines and manuals (Cooper 1996; Kadlec and Knight 1996; Ellis et al. 2003b; Stefanakis et al. 2014c).

2.8.1 Sizing

Compared to other treatment systems wetlands have a higher demand on the area but less external power and operation and maintenance requirements. If the environment permits, wetlands can be managed without pumps and therefore without any external power supply. Like all comprehensive systems, wetlands are strong and adaptive of fluctuating influent flow and concentration. Treatment wetlands are therefore particularly suitable for use as small, decentralised treatment systems. Table 2.2 shows the requirement area for listed wastewater treatment technologies for secondary treatment (Dotro et al. 2017).

Table 2.3 The requirement area for secondary treatment of wastewater treatment systems (Dotro et al. 2017).

Treatment technology	Treatment area requirement (m^2/PE)
Facultative pond	2.0 – 6.0
Anaerobic + facultative pond	1.2 – 3.0
UASB reactor	0.03 – 0.10
Activated sludge, SBR	0.12 – 0.30
Trickling filter	0.15 – 0.40
HF CW	3.0 – 10.0
VF CW	1.2 – 5.0

There are many proposed ways in the UK to determine the required area for stormwater CWs. Many general CW design techniques, such as kinetic design frameworks based on first-order reaction rates, are used and applied to stormwater CWs. Here the CW size and retention time needed to effectively reduce different concentrations of contaminants are determined in equations such as Equation 2.1, taken from the UK guidelines (Ellis et al. 2003b). Equation 2.1 was empirically established, considering the CW plug-flow (Lucas 2015).

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

where: A_s = CW surface area (m^2)

k = pollutant rate

Q = inflow rate (m^3/day)

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

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

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

The above equation has been scientifically developed, assuming values for and depending on the pollutant and CW form (e.g. surface flow or sub-surface flow), and suggested values are available in the literature (Kadlec and Wallace 2009a). The value often used is that which reflects BOD5 reaction levels. In the CW, BOD5 decays very gradually, resulting in conservative CW measurements when using a BOD5. It can also lead to oversizing of CWs, particularly for urban stormwater CWs, as the influent includes very low concentrations of BOD5 opposed to CWs that handle other forms of wastewater, such as sewage. Stormwater CWs aim to treat the priority pollutants such as SS, nutrients, and heavy metals. Another problem with using a design concept like this is the use of average flow rate and concentration values of contaminants, as this does not truly reflect the stochastic existence of stormwater inflows and variable received concentrations of pollutants. K values also vary considerably from one CW to another (Ellis et al. 2003a). While this method is therefore useful as an initial estimate of the sizes of a CW, it should not be depended on for the sizing process.

Empirical stormwater CW design techniques are popular because storm occurrences are stochastic. Another example is designing the CW to a size able to withstand the volumes of water that accumulate throughout a storm with a specified return period. Practical suggestions from the UK state that urban stormwater CW should be capable of creating storms with a minimum return period of 10 years (Ellis et al. 2003a), and in flood-prone areas, the EA recommends that the flood return period be 1:200 years (Shutes et al. 2005). An additional analytical technique proposed in UK guidelines is to size a CW as a percentage of catchment area size applying proven wetland to watershed area ratio (WWAR) values. UK guidelines recommend a 1–5% WWAR (Ellis et al. 2003b). US guidelines say a 2% higher minimum WWAR, a sign of land availableness (US EPA, 2000a). Figure 2.10 is a plot that shows available information for catchment area versus CW surface area of several UK stormwater CWs.

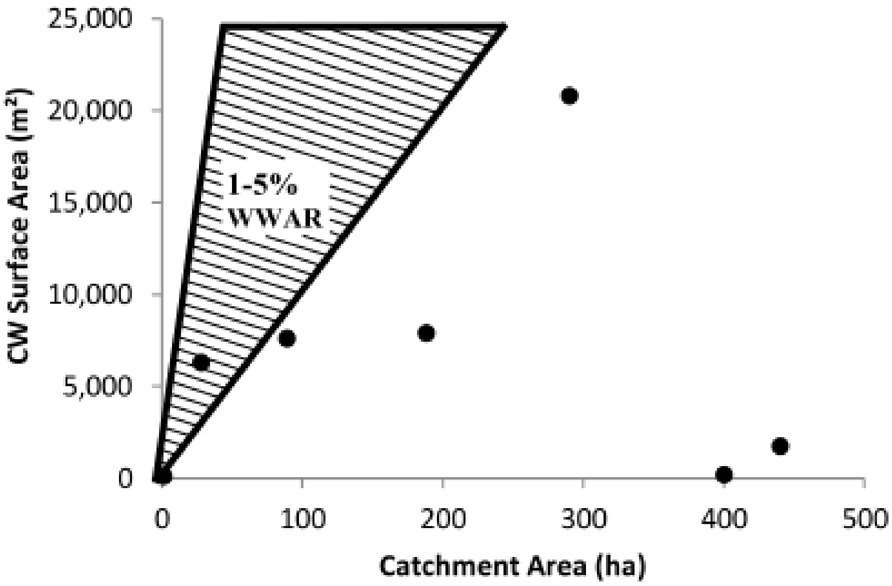


Figure 2.10 CW surface area vs. drained catchment area for UK stormwater systems adopted (Lucas 2015).

Figure 2.10 shows that most of the CWs researched have less than 1% of the WWAR. One CW comfortably has a WWAR within the suggested 1 to 5% range. These CWs' average WWAR is 0.71%. A report of US stormwater CWs, by contrast, shows that the average WWAR was 4.26% (John Bryan Ellis, R. Brian E. Shutes, et al. 2003). This is a significantly larger WWAR and may indicate the increased availability of land in the USA.

2.8.2 Substrate structure

The selection of substrates is one of the most significant choices in the design stage for a stormwater CW project. Preferably, the material should also be available locally and widely to facilitate their adoption and need to be able to feed the vegetation. Wetland substrates support the ecosystem of wetlands, provide biochemical and chemical processing sites, and provide storage sites for extracted contaminants. Substrates include products from soil sand, gravel and organic matter.

Hydraulic conductivity of 100-300 mm/hr is suggested for subsurface-flow systems in a temperate climate like that of the UK, and the substrates should also include some organic material to increase water retention (Lucas 2015). Under drainage, the material should achieve a higher permeability and should not be hydrophobic (FAWB 2009). Sand, gravel and loam are typical stormwater CW media choices (Hatt et al. 2007b; Adeola et al. 2009) and they are available UK-wide. USA recommendations simply state that topsoil or mulch should be used to support "vigorous" plant growth (New Jersey Department of Environmental Protection 2004). In general, the American guidelines have a very prominent focus on the encouragement of biodiversity in stormwater CWs.

The substrates in CWs are usually three layers (FAWB 2009) and (USEPA 1995) as the following:

1. **Primary or filter layer:** It could be from soil, sand, gravel or organic material. Most soils are ideal for CWs. Soil characteristics that should be included in soil selection include organic matter, cation exchange capacity (CEC), pH, electrical conductivity (EC), and texture. Soil pH influences the production and preservation of nutrients and heavy metals. The pH of soil should be around 6.5 to 8.5. A soil's EC impacts the capability of microbes and plants to absorb the waste material that flows into a constructed wetland. Soils with an EC of less than 4 mm ho/cm are suitable as a medium of production (USEPA 1995).

   The soil's redox potential is an important factor in reducing nitrogen and phosphorus. To enhance the removal of nitrate and ammonia reduction a substrate must be provided. Mine water-extracting iron and manganese often requires a reduced atmosphere.

The texture of the soil impacts root growth and pollutant retention. Sandy, coarse-textured soils have low pollutant retention potential and almost no root growth limits. Such soils keep plants and seem to have a low nutrient content. Addition of organic matter to coarse-textured soils over the first few years has been shown to enhance plant survival and development while the organic litter is starting to build up throughout the wetland. Medium textured or loamy soils are a good option because these soils have strong pollutant retention and little plant growth restriction. Loamy soils are particularly good since they are soft and friable, allowing easy penetration of the rhizomes and root. It is important to avoid dense soils, such as clay and shale, as they can prevent root penetration, unavailability of nutrients, and have low hydraulic conductivity.

Soils with a high level of clay help in phosphorous retention but their low nutrient content may restrict growth and progress, although such soils may be ideal for wetlands used for nutrient-rich wastewater, such as farming and domestic wastewater. Organic modifications are needed. Soils with greater extractable aluminium have a better potential for assimilation of phosphorous than organic soils, rendering them better suited for the treatment of domestic wastewater. Strongly organic soils promote sulphate reduction and ionic adsorption and are a good fit for wetlands that drain from mines (USEPA 1995).

Constructed wetlands receiving nutrient-rich water, such as domestic and agricultural wastewater may be constructed with gravel or sand. Sand is a cost-effective alternative to soil and provides the perfect texture for hand-planting. Gravel can be used as well. Most United States domestic sewage SSF wetlands have used media from medium gravel to coarse rock or dry sands and gravel.

In other hands, stabilised organic material has been used as organic substrates, such as discarded mushroom compost, sawdust, hay or straw bales, and chicken litter. Organic material provides a carbon source which supports the microbial activity. Organic material often absorbs oxygen and produces the anoxic conditions required for certain treatment procedures such as nitrate reduction and acidic mine drainage neutralisation.

2. **The transition layers:** It does not require philtre media to wash into the drainage layer. A healthy, well-graded sand material containing < 2% fines shall be the transition layer content. In order to avoid the movement of the philtre media into

the transfer layer, the particle size distribution of the sand should be measured to ensure that it follows bridging requirements, i.e. the smallest 15% of the sand particles bridge with the largest 15% of the philtre media particles (FAWB 2009).

3. **The drainage layer**: It gathers treated water at the system's bottom and transfers it to the underdrain tubes. Drainage layer substrate should be clean, fine gravel, such as screenings washed 2-5 mm. To prevent movement of the transition layer into the drainage layer, bridging requirements should be used (FAWB 2009).

It is not surprising since the habitats are so big that resources are available to handle large ecosystems. An alternate solution of engineered substrates may be used in an attempt to increase the removal efficiency for some pollutants, but the use of locally available materials is a priority in terms of widespread implementation.

2.8.3 Constructed wetland plants

Plants are among the key components of CW systems. Species of plants used in CWs are typically the same species found in natural wetlands. Wetland plants are principally vascular plants, also called macrophytes (Stefanakis et al. 2014g). In addition to biological processes, plants play an important role in surface-flow systems because they decrease the water flow velocity in the wetland to assist sedimentation, which is particularly important because sedimentation is a major disposal mechanism in wetland systems. Plants also help to maintain the wetland's hydraulic conductivity in subsurface flow systems, whereas heavy metal removal is performed by accumulation and storage in wetland plant rhizospheres (Kadlec and Wallace 2009a).

The most common classification categories of the plant (USEPA 1995; Kadlec, R.H. and Knight 1996; Vymazal et al. 1998) are:

- **Emergent:** These plants are grown in soils or pore substrates. A root system and shoots develop under the wetland's water surface, while the leaves and stems rise above the surface. They find the essential nutrient quantities in soil and water for growth (Cronk and Fennessy 2001). Common species in this category are Phragmites, *Typhaceae, Juncaceae, Scirpus, Glyceria, Iris, Zizania aquatica,* and *Cyperaceae*.
- **Submerged:** Such plants can also be planted in the bottom substrates, while rootless species float on the surface of the water too. Their photosynthetic sections are normally under the surface of the water (Cronk and Fennessy 2001). They are considered anaerobic, have a strong circadian effect and may be shaded by algae (USEPA 1988). This category includes species of *Callitrichaceae, Ceratophyllaceae, Haloragaceae, Potamogetonaceae,* and

Lentibulariaceae, whereas *Hydrocharitaceae* is the largest species (Cronk and Fennessy 2001).

- **Floating-leaved:** They are planted in the substrates, whereas the leaves float on the surface of the water. Petioles and/or stems link the underside with the leaves. This species shadows the water column and can, therefore, compete for the absorption of sunlight against submerged organisms. *Nymphaea, Nuphar, Nelumbo lutea* and *pennyworth* species are included in this group.
- **Floating:** Such species are also referred to as floating attached plants, floating on the surface of the water (Cronk and Fennessy 2001). Floating plants typically exhibit high rates of growth. It includes *crassipes, Eichhornia, stratiotes, Pistia* and *Lemna* species (Stefanakis et al. 2014g).

Not every wetlands species is useful for the treatment of wastewater since plants must be able to tolerate the combination of continuous flooding and exposure to wastewater or stormwater containing relatively high and often variable pollutant concentrations.

In the UK, the most used plants in stormwater constructed wetlands are *Typha latifolia* (reedmace) and *Phragmites australis* (common reed) (Ellis et al., 2003a).

2.8.4 Hydraulic conditions

The depth of water is an important element in deciding which plant types will be established (Ranieri et al. 2013), and it also impacts the biochemical reactions responsible for removing pollutants by modifying the redox status and the level of dissolved oxygen (DO) in CWs (Wu et al. 2015). Through comparing a 0.27 m water level of wetland with a 0.5 m water level of wetland, the results from a García et al. (2004) study showed that beds with a water level of 0.27 m reduced stronger COD, biochemical oxygen demand, ammonia, and dissolved reactive phosphorus and also showed that there are variations in pollutant transformation within systems of varying depth. However, experiments conducted by Aguirre et al. (2005) in order to investigate the impact of water depth on the efficiency of removal of organic matter in HFCWs concluded that the relative contribution of various metabolic pathways varied with the water level.

Hydrology is one of the main factors in regulating wetland functions, and flow rates should also be controlled to achieve satisfactory performance in treatment (Lee et al. 2009). A wetland system's treatment efficiency requires a balance between the pollutant hydraulic loading rate (HLR) and hydraulic retention time (HRT). Constructed wetlands typically have fairly steady HLR (and pollutant loading) for the treatment of effluent wastewater, with the most efficient retention period for the removal of suspended solids and nutrients in the Queensland pilot wetlands being around seven days (Phillips and

Greenway 1998). In comparison, stormwater runoff in hydraulic and pollutant loads is highly variable due to the unpredictable nature of both the intensity and duration of storm events (Greenway and Woolley 2001). Greater HLR facilitates faster wastewater passage through the media, thus minimising optimal contact time.

Hydraulic retention time (HRT) is among the few operating variables controllable in CWs. HRT is an indicator of the average length of time a soluble material is left in a CW. For instance, a crucial efficiency in removing BODs can be achieved at an HRT shorter than one day, while the efficiency of the system will be improved at an HRT of about seven days (Reed and Brown 1995). Depending on this, HRT is an important element influencing the performance of CW treatment, which designers typically focus on. Despite the benefit of improving treatment efficiency this can also be considered as the major disadvantage for large wetland areas, particularly when land availability is limited (Yan and Xu 2014). The concentrations of NH4-N and TN in treated effluent declined significantly, with increased HRT in a CW for domestic wastewater treatment (Huang et al. 2000). In CWs with 0.8-day HRT found positive removal of nitrogen compared to 0.3-day residence period outcomes (Toet et al. 2005). In addition, the impact of HRT can vary between CWs depending on the prevailing plant species and temperature, as those factors can affect wetland hydraulic efficiency in a long-term experiment (Wu et al. 2015).

There is a slight drop in the removal of NH4-N and TN from household wastewater in VFCWs when HLR increased from 7 to 21 cm/d. Consequently, the mean removal of NH4-N decreased from 65% to 60%, while TN decreased from 30% to 20% (Cui et al. 2010). Moreover, at a HLR of 7 cm/d, the TP percentage removal was 71% but was 61% at a HLR of 21 cm/d (Cui et al. 2010). Nonetheless, Stefanakis and Tsihrintzis (2012) published a long-term examination of fully matured VFCWs for treatment or synthetic wastewater, and they found that the highest nitrogen and organic removal was reached by the wetland systems as the HLR increased. The feasibility of hybrid CW systems used to extract emerging organic pollutants was also studied and the removal efficiency of most compounds was demonstrated to decrease as HLR increased (Ávila et al. 2014).

Feeding regime of influent is another important design parameter effecting the removal efficiency of CW treatments (D. Q. Zhang et al. 2012). The difference in feeding patterns (such as continuous, batch, and intermittent) can affect the conditions of oxidation reduction and oxygen transfer and diffusion in wetland processes and thus alter the efficiency of treatment. Generally, a batch feeding regime can achieve better performance than continuous operation by cultivating more oxidised conditions (Wu et al. 2015). An experiment with tropical SSF CWs found that the batch flow regime demonstrated significantly higher efficiencies in NH4-N removal (95.2%) compared to the continuously fed systems (80.4%) (D.Q. Zhang et al. 2012). Intermittent feeding regimes may be considered to improve the removal of organic matter and nitrogen in CWs (Saeed and Sun 2012). The effects of intermittent operation and a specific duration of drying period on removal efficiencies in VFCWs were also examined, and the intermittent operation encouraged a lower level of COD and TP removal compared with continuous operation in wetland systems (Jia et al. 2010). In addition, the intermittent method significantly increased the performance of NH4-N removal (more than 90%), which may be due to more oxidising conditions in wetlands. Likewise, Jia et al. (2011) examined the impacts of constant and intermittent feeding modes on the removal of nitrogen in FWS and SSF CWs.

2.8.5 Climates and weather

Since wetlands are exposed to the atmosphere as shallow bodies of water, they are strongly influenced by climate and weather. During project planning and site selection, the climate is critical, because it influences the type and size of the wetland to be used. The topography is the climate's most critical parameter, as it defines seasonal temperature ranges. Other important climatic factors that can all affect CW management and during project planning are rainfall, snowmelt, spring runoff, drought, freezing, temperature, evaporation, evapotranspiration, insolation, and wind speeds (Bendoricchio et al. 2000).

Throughout the coldest month of the year, the long-term average temperature was found to be a great estimator of the lowest water temperature which will be encountered in a wetland system (Kadlec, R.H. and Knight 1996). For areas where the monthly average minimum annual temperature is below zero, this can be assumed.

One concern regarding the UK's use of CWs is their ability to perform in cold climates. The UK may be sensitive to cold temperatures, with extreme circumstances in Scotland, England and Wales being below -25°C (Met office 2020). The main concerns of the cold conditions are ice formation, which in turn causes hydraulic problems, and the effect of low temperatures on CW processes of microbiological treatment (Wittgren and Mæhlum 1997). Nevertheless, in areas with more regularly cold climates or harsher winters than the UK, such as Norway (Mæhlum and Jenssen 2003) and Minnesota (Kadlec et al., 2003), CWs were shown to be fully operational and have negligible or no effect on performance (Lucas 2015).

2.9 Pollutant removal in constructed wetlands

Municipal wastewater, urban runoff, and agricultural and industrial processes contain various types of pollutants (sediment, suspended solids, metals, BODs, nutrients, hydrocarbons, pathogens) which can adversely affect aquatic species and ecosystem health. The CWs efficiency of improving water quality depends on a range of dynamic and interacting processes that can be loosely divided into three groups of physical, chemical, and biological. Table 2.4 summarises the process in wetlands to improve water quality.

2.9.1 Chemical processes

Chemical processes assist the adsorption and deportation of phosphorus and metals to and from particles in sediments. Oxygen diffusion from the roots of emerging macrophytes creates an oxidised surface layer of the sediment and a microenvironment around the root zone. This amends the redox outcomes of the sediments and facilitates aerobic microbial processes including nitrification. Chemical processes support the degradation of hydrocarbons related to photochemical oxidation and pathogen degradation due to natural causes of radiation from UV.

2.9.2 Biological processes

Plants and photosynthetic microorganisms, by direct uptake, remove heavy metals and soluble inorganic nutrients (NH4-N, NO2-N, NO3-N, PO4-P). Rooted macrophytes absorb such nutrients from the soil while floating and submerged macrophytes and algae (phytoplankton, periphyton and biofilms) extract the nutrients directly from the water column. Emerging macrophyte vegetation in FWS allows particle sedimentation by minimising water velocity due to viscous drag, particularly around plant stems, and by wind effects. Because of the sticky nature of biofilms, both submerged and emerging vegetation is especially effective in removing fine particles which will bind directly to the plant surface. The plant also spreads the flow and thereby reduces friction and enables particle settlement. The root structure binds and stabilises particles that have been accumulated. Re-suspension is limited by leaf litter and vegetation (Greenway 2004).

2.9.3 Physical processes

Physical contaminant removal processes involve sedimentation or gravitational deposition, and filtration where particulates are physically filtered as water goes through the bed substrate of wetlands and the roots of macrophytes. Certain physical processes involve intermolecular force-based volatilisation (ammonia (NH3-N)) and adsorption (Kiiza 2017).

Other particulate pollutants, such as polycyclic aromatic hydrocarbons (PAHs), are eliminated from the wastewater by filtration processes (Davis et al. 2010), while dissolved P and heavy metal fractions can be separated from the CW substrate through sorption (Le Fevre et al. 2015). Likewise, pathogens can be eliminated by filtration, sunlight exposure and any methods that facilitate natural die-off (Hunt et al. 2012).

Table 2.4 Processes of pollutant removal in constructed wetlands.

Pollutant	Removal Process		
	Physical	**Chemical**	**Biological**
Organic matter (as BOD5 and COD)	Filtration and settling (particulate OM)	Oxidation	Bacterial degradation (soluble OM), Microbial consumption
Suspended solids (as TSS)	Filtration, sedimentation	---	Bacterial decomposition
Nitrogen	Volatilisation	Ion exchange	Nitrification/denitrification, microbial consumption, plant uptake
Phosphorus	Filtration	Adsorption, precipitation	Plant uptake, microbial consumption
Heavy metals	Settling	precipitation	Biodegradation, phytodegradation, phytovolatilisation, plant uptake
Pathogens	Filtration	UV-degradation, adsorption	Predation, natural die-off

2.10 Mechanisms of organic matter removal in CWs

Mechanisms for removal of organic matter, both particulate and soluble organic matter, vary and depend on the design of the wetland treatment. Chemical oxygen demand (COD) is commonly used as the key analytical tool for calculating organic matter, but 5-day (carbonaceous) biochemical oxygen demand (BOD5) may be used as well. Microbial pathways are the main disposal mechanisms for soluble organic matter. While physical processes such as filtration and sedimentation mainly retain particulate organic matter which enters with the influential wastewater (Dotro et al. 2017). The dissolved (soluble/colloidal) portion of the OM is aerobically and anaerobically decomposed. Figure 2.11 illustrates the mechanisms of organic matter removal in CWs.

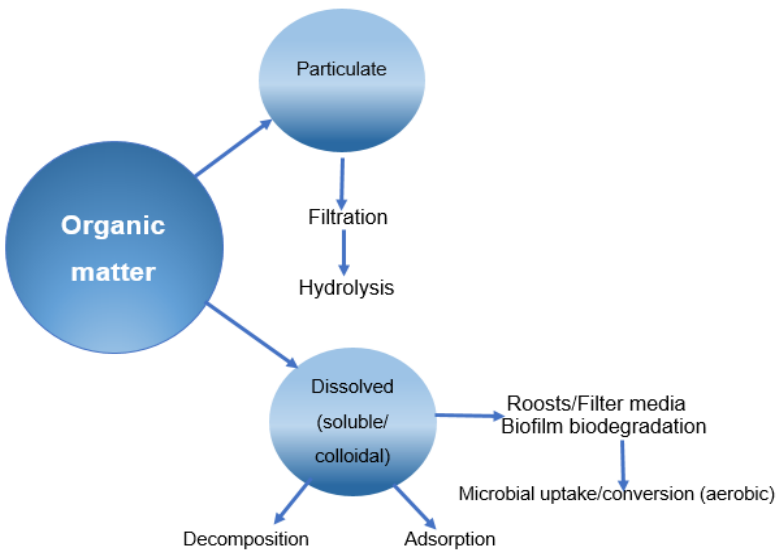


Figure 2.11 Mechanisms of organic matter removal in CWs (Stefanakis et al. 2014f).

2.11 Mechanisms of suspended solids removal in CWs

Physical processes will remove inorganic and suspended solids. Gravitational settling (sedimentation) and filtration are the main removal mechanism for total suspended solids (TSS) in CWs. They move through the media pores, and the water current velocity is reduced (Stefanakis et al. 2014f). The solids are either mechanically trapped within the pores or through adhesion (Kadlec and Wallace 2009a).

2.12 Mechanisms of nitrogen removal in CWs

Nitrogen (N) is a highly interesting pollutant for wastewater removal. Typical forms of N in wastewater are organic (urea, amino acids, uric acid, purine, and pyrimidines) and inorganic (ammonium, nitrate, nitrite, nitrous oxide, nitrogen gas, nitric oxide, and free ammonia) (Kadlec, R.H. and Knight 1996; Vymazal 2007; Kadlec and Wallace 2009a). The three major processes are physical, chemical, and biological treatment techniques to achieve the removal of nitrogen. Standard biological removal of nitrogen from water and wastewater, composed primarily of a mixture of aerobic nitrification and anaerobic denitrification, is generally considered to achieve optimal and economical treatment of nitrogen.

Ammonification, nitrification-denitrification, plant uptake, adsorption, and physicochemical methods such as sedimentation, ammonia stripping, breakpoint chlorination, and ion exchange are included in the nitrogen removal mechanisms of constructed wetlands (USEPA 1993; Saeed and Sun 2012; Stefanakis et al. 2014e). Figure 2.12 provides a schematic of nitrogen conversion for CWs.

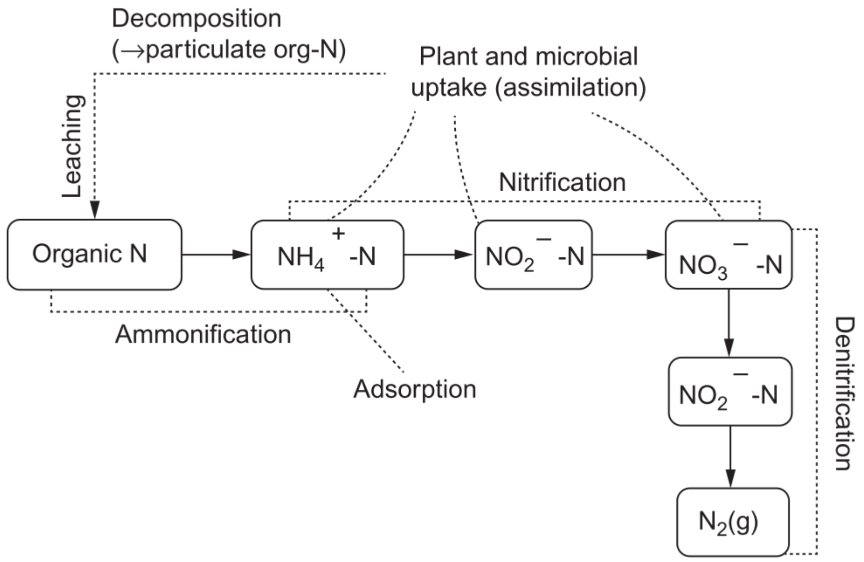


Figure 2.12 Removal processes and transformation Nitrogen in CWs (adapted from Stefanakis et al. 2014e).

2.12.1 Ammonification

Ammonification (mineralisation) refers to the degradation of organic nitrogen (organic-N) to ammonium (NH4-N) through enzymes excreted by microorganisms from extracellular activity (Vymazal 2007). This process occurs in both aerobic and anaerobic environments of the bed, but in the oxygen-rich layers it continues rapidly. Moreover, In terms of kinetics, it happens faster than nitrification (Vymazal 2007; Saeed and Sun 2012). Ammonification is considered an essential initial step towards the transition of nitrogen to nitrate and/or removal but is rarely a limiting step for subsequent removal of TN. A significant percentage of organic nitrogen (up to 100%) is readily transferred to NH4-N (Kadlec and Knight, 1996).

The ammonification cycle is basically an amino acid catabolism and probably involves multiple forms of deamination reactions. One can write the oxidative deamination as Equation 2.2 (Datta 1995) (De Datta 1995).

$$\textit{Amino acids} \rightarrow \textit{minoacids} \rightarrow \textit{Ketoacids} \rightarrow \textit{NH3} \qquad (2.2)$$

2.12.2 Nitrification

Generally, nitrification is described as the biological oxidation of ammonium to nitrate together with nitrite as an intermediate in the sequence of reactions (Vymazal 2007). It is the second step in the NH4-N chain of transformation (Figure 2.12). Biological nitrification by chemolithotrophic bacteria such as *Nitrosomonas, Nitrosococcus, Nitrosolobus,* and *Nitrosospira*, firstly, under aerobic conditions convert NH4-N to NO2-

N, then to NO3-N by *Nitrospira, Nitrospina, Nitrococcus,* and *Nitrobacter* bacteria (Vymazal 2007; Faulwetter et al. 2009; Kadlec and Wallace 2009a). Nitrification accompanied by denitrification, is assumed to be the key route for NH4-N removal in constructed wetlands.

2.12.3 Denitrification

Commonly, denitrification is described as the process by which NO3-N is transferred to dinitrogen via nitrite, nitric oxide and nitrous oxide intermediates (Vymazal 2007). It is the next step in the ammonia N chain of transformation by bacteria (Figure 2.12). From a biochemical perspective, denitrification is a bacterial mechanism in which nitrogen oxides (in ionic and gaseous forms) operate as terminal electron receptors for the transfer of respiratory electrons. Heterotrophs and Autotrophs are the two main species of bacteria responsible for denitrification.

2.12.4 Plant uptake

Plants lead to the elimination of nitrogen in CW systems both directly and indirectly. Plants uptake and use nutrients in wastewater (e.g. nitrogen and phosphorus) to assist their growth (as shown in Figure 2.12) (Stefanakis et al. 2014f). The uptake of NH4-N and NO3-N by plants converts inorganic nitrogen to organic compounds as essential elements to build cells and tissues (Vymazal 1995). The ability of rooted plants to utilise sediment nutrients illustrates their extensive crop compared to planktonic algae in several systems (Wetzel and Hill 1997). The degree of this plant uptake depends on different parameters, such as the bed size, the loading rate, the volume of wastewater, the type of plant and the climate (Lee et al. 2009). Plant uptake and storage of nutrients depends on the concentration of nutrients in their tissues, the density (species stands per meter square) and the height of plant biomass (Lee et al. 2009; Stefanakis et al. 2014e; Vymazal 1995).

2.12.5 Adsorption of ammonia

Ammonia N on the surface of the substrate material can be adsorbed (Figure 2.12) (Stefanakis et al. 2014e). Adsorbed ammonia is loosely bound to the substrates in CWs, and can be released easily as conditions of water chemistry alter (Lee et al. 2009). However, the movement of NH4-N ions depends on the properties of the porous substrate used. When nitrification reduces the NH4-N concentration in the water column, some NH4-N will be adsorbed to restore ecological balance with the new concentration. If the NH4-N concentration in the water column is increased, the adsorbed NH4-N will also increase (Vymazal 2007). If the substrates of wetlands are exposed to oxygen, adsorbed ammonium may be oxidised to nitrate through periodic drainage (Connolly et al. 2004; Sun et al. 2006).

Generally, ammonium ion is adsorbed on clays as an exchangeable ion, and adsorbed by humic substances, or fixed inside the clay lattice. Such reactions can tend to occur simultaneously. The rate and duration of these reactions are stated to be affected by several factors, such as nature and quantity of clays, alternative submergence and drying, nature and quantity of organic soil, submergence time and vegetation presence (Lee et al. 2009; Vymazal 2007).

2.12.6 Other nitrogen processes

There are other Nitrogen removal processes in constructed wetlands such as the following (Stefanakis et al. 2014f):

- **Ammonia volatilisation:** In this phase, unionised ammonia (NH3) is lost by diffusive and advective forces from the water surface into the atmosphere, i.e. ammonia N is in a balance between the gaseous and hydroxyl forms (Saeed and Sun 2012; Stefanakis et al. 2014f). The method is pH dependent and losses are important at pH values above 8.0, while the transfer of NH4-N to NH3 gas increases at pH>9.3 (Vymazal 2007; Stefanakis et al. 2014f).
- **N2 fixation:** Fixation method involves the synthesis of ammonia, amino acids and proteins from gaseous nitrogen by heterotrophic soil bacteria, cyanobacteria, and actinomycetes. Fixation is insignificant in wetlands with high influential nitrogen concentrations compared to other processes of nitrogen conversion, as it consumes high amounts of cellular energy (Kadlec, R.H. and Knight 1996; Stefanakis et al. 2014f).
- **ANAMMOX:** ANAMMOX (anaerobic ammonium oxidation) is a comparatively recently discovered N removal method that transforms NH4-N to gaseous N2 under anaerobic conditions (Faulwetter et al. 2009; Stefanakis et al. 2014f). The ANAMMOX process requires lower energy and oxygen compared to coupled nitrification/denitrification processes and does not need an external carbon source or external aeration (Saeed and Sun 2012; Lee et al. 2009).
- **CANON:** Completely autotrophic nitrogen removal over the nitrite cycle, a mixture of partial nitrification and ANAMMOX methods (Sun and Austin 2007).

2.13 Mechanisms of phosphorus removal in CWs

Eutrophication that causes water quality deterioration is typically the result of excessive production of dissolved and particulate nutrients. In freshwater, the limiting nutrient is often phosphorus (P) and elevated P concentrations have been identified in many types of non-point urban stormwater runoff discharges (USEPA 1993). It is found in different forms of wastewater. P is an extremely important macronutrient for all biological organisms. It's like nitrogen, it's a valuable plant nutrient that it uses to grow (Stefanakis et al. 2014f). To effectively control phosphorus loading in order to reduce eutrophication and improve the water quality remains a high priority and daunting challenge for wastewater and stormwater treatment management agencies. P is either particulate or dissolved in stormwater runoff. Particulate types can be part of organic materials or precipitate minerals (Ma et al. 2009).

Phosphorus (P) occurs in various organic and inorganic forms in wastewater. Free orthophosphate (PO4-P) is a common wastewater form and is present in ionic equilibrium (Vymazal 2001). Many transformations of P forms occur in wetlands; Figure 2.13 shows transformation of P in CWs (Stefanakis et al. 2014f).

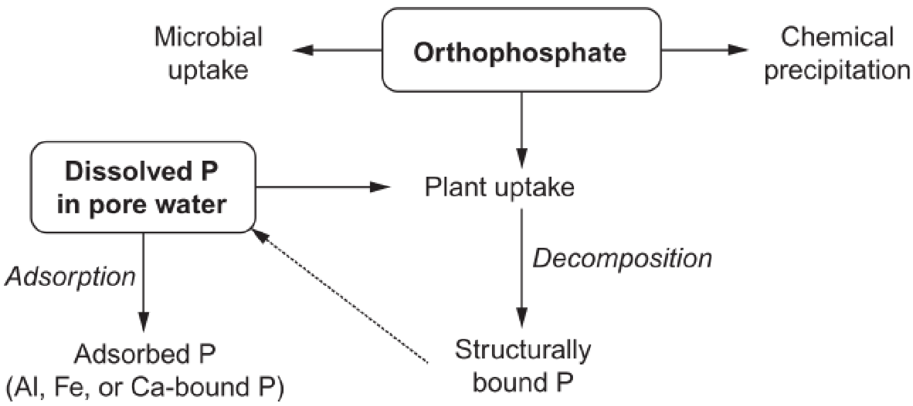


Figure 2.13 Removal processes and transformation of Phosphorus in CWs (adapted from Stefanakis et al. 2014f).

2.13.1 Adsorption and precipitation

It is likely that P adsorption on the substrate media plays the most significant role in eliminating P from wastewater in CWs (Vymazal 2007; Drizo et al. 1999). The substrate's physicochemical properties determine the adsorption potential and therefore the retention of P (Drizo et al. 1999; Kadlec, R.H. and Knight 1996). The high aluminium (Al), iron (Fe), and calcium (Ca) oxides content in the substrate media increases phosphorus (P) adsorption and precipitation reactions (Drizo et al. 1999; Stefanakis et al. 2014b).

Additionally, Studies indicate the feeding scheme and the loading frequency also impacts P removal. P elimination improved with HRT, as contact time increased (Tang et al. 2009; Stefanakis et al. 2014f). Also, certain parameters such as pH and Eh can also influence the adsorption cycle (Saeed and Sun 2012; Stefanakis and Tsihrintzis 2012).

2.13.2 Plant uptake

Plants use P in wastewater to meet their growing needs (Grandgirard et al. 2002; Greenway and Woolley 1999). In general, the quantity of P extracted by plants and subsequent processing of the aboveground plant biomass is marginal compared to the total quantity removed, even taking into account the fact that the main portion of the assimilated P is present in the belowground biomass (Kadlec and Wallace 2009a; Stefanakis et al. 2014f).

2.13.3 Microbial uptake

Microorganisms such as bacteria, algae and fungi can quickly assimilate and store P, a partly reversible mechanism (Vymazal et al. 1998). When they die off and decay, the initially assimilated amount of P by microorganisms is released back into the system. Microorganisms take organic P and convert it into inorganic P by catabolic action, while P is retained in microbial biomass during its development (Ready et al. 1999). In general, many studies do not investigate microbe absorption of P and there is limited information available on quantitative intake in VFCWs (Stefanakis et al. 2014f).

2.14 Mechanisms of heavy metals removal in CWs

In water/wastewater treatment, the major heavy metals (HM) of concern are iron (Fe), copper (Cu), lead (Pb), cadmium (Cd), zinc (Zn), nickel (Ni), chromium (Cr), mercury (Hg), and arsenic (As). The forms of HM in CWs are dissolved, colloidal or particulate, and free metal ions are essential for biological transformation (Cooper et al. 1996). The principal removal mechanisms are shown in Figure 2.14.

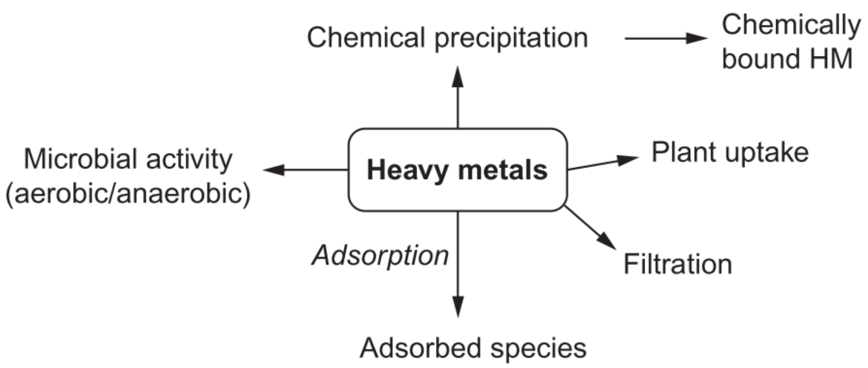


Figure 2.14 Removal processes and transformation of Heavy Metals in CWs (adapted from Stefanakis et al. 2014f).

2.14.1 Sorption

Sorption is the most important chemical removal process in wetland soils, resulting in short-term retention, or long-term immobilisation of several pollutant classes. Sorption is the shift of ions from water to the soil, i.e. from the stage of the solution to the solid stage. Sorption basically describes a series of processes which contains reactions to adsorption and precipitation (Sheoran and Sheoran 2006).

2.14.2 Adsorption and precipitation

Heavy metals in sediments are adsorbed by either cation exchange or chemisorption to the soil particles (Matagi et al. 1998). The heavy metals are adsorbed by electrostatic attraction to clay and organic matter (Matagi et al. 1998). Cation exchange includes the physical attachment by electrostatic attraction of cations (positively charged ions) to the clay and organic matter surfaces. Once heavy metals are adsorbed to heavy metals of humic or clay colloids they will remain as metal atoms, unlike organic contaminants which will gradually decompose. Over time their speciation can change as the organic molecules that bind them decompose, or as the conditions of the sediments change (Wiessner et al. 2005; Matagi et al. 1998).

Soil capacity for cation retention, expressed as cation exchange efficiency, tends to increase with some substrates with rising content of clay and organic matter. Chemisorption is a more robust and permanent form of bonding than the exchange of cations. The ability of adsorption by cation exchange or non-specific adsorption depends on the media's physio-chemical characteristics, the metals' properties, and the concentration and properties of other metals and soluble ligands (Matagi et al. 1998). In the wetland, 50% of the heavy metals can be easily adsorbed into particulate matter and thus separated by sedimentation from the water portion (Sheoran and Sheoran 2006). HM adsorption varies with pH fluctuation in the outflow water (Machemer and Wildeman 1992).

Iron, manganese and aluminium can create insoluble compounds that occur in wetlands through hydrolysis and/or oxidation. This results in the production of a number of oxides, hydroxides and oxyhydroxides (Batty et al. 2002; Ngwenya 2004). Removal of iron depends on pH, capacity for oxidation-reduction, and the presence of specific anions (ITRC 2003). Heavy metals may also create carbonates when the concentration of bicarbonate is high in water. While carbonates are less stable than sulphides, they can still play an important role in initial metal trapping. Sobolewski (1996) and Sobolewski (1999) identified significant quantities of accumulated copper and manganese carbonates in some natural wetlands. The precipitation of carbonate is particularly effective for removing lead and nickel (Sheoran and Sheoran 2006).

The removal of heavy metals by precipitation and co-precipitation is an important adsorptive mechanism in wetland sediments. The formation of insoluble precipitated heavy metals is one of many factors that limit the bioavailability of heavy metals to many aquatic environments. Precipitation depends on the metal solubility product K_{sp}, wetland pH, and concentration of metal ions, and relevant anions. When the cation and anion concentration values are such that their product exceeds K_{sp}, precipitation usually happens (Sheoran and Sheoran 2006).

2.14.3 Filtration and sedimentation

CWs often act as active HM philtres. As the wastewater flows through the philtre substrate pores and the thick and extensive plant root structure, HM is trapped and blocked and therefore maintained within the system. In addition, plant activity leads to the preservation of precipitated hydroxide metal particles (Vymazal et al. 1998). The velocity of the water flow, the velocity of particle settling, the porous volume of the substratum media and the length of the wetland may have an effect on the filtration performance (Sheoran and Sheoran 2006). Sedimentation is another physical process to remove HM, but other processes such as precipitation and the formation of larger particles follow. It does not present alone (Stefanakis et al. 2014f).

2.14.4 Plant uptake

Perhaps the most effective mechanism for heavy metals removal in the wetlands is biological elimination. Plant uptake probably plays a key role in accepted biological processes for assimilating dissolved HM from wastewater in wetlands (Sheoran and Sheoran 2006; Marchand et al. 2010). Roots uptake HM and spread them to the remaining parts of plants. Nevertheless, a small percentage is translocated to the other parts of the plant (e.g. shoots and leaves) (Bonanno and Lo Giudice 2010). The harvest of the above-ground plant thus only contributes a small percentage of the total removal of HM in CWs (Marchand et al. 2010). Although a small percentage of HM is eliminated by plant, studies comparing plant and un-plant systems mostly result in conflicting data with respect to plant significance (Lee and Scholz 2007). The availability of organic matter through the degradation of dead plant material is a key point that is often ignored (Stottmeister et al. 2003). Over time, organic crop-derived matter in wetlands continuously supports sites for metal sorption and precipitation, as well as microbial carbon sources, thus fostering long-term processing (Jacob and Otte 2004; Batty and

Younger 2004). Furthermore, plants may lead to HM elimination by other processes such as filtration, sedimentation, and adsorption, and by achieving improved bed aeration (Kosolapov et al. 2004).

2.14.5 Microbial activities

The biofilm includes microorganisms that can interact with metals and metalloids and can influence their mobility and speciation across a number of mechanisms (Marchand et al. 2010). Uptake and storage of heavy metals by microorganisms represent a measurable amount, their metabolic processes play the most important role in heavy metal removal (Hallberg and Johnson 2005). Metal reduction to non-mobile forms was documented via microbial action in wetlands (Sobolewski 1999).

Reduction of sulphates and co-precipitation with metals is known as the major mechanism for HM removal from wastewater. Bacteria which reduce sulphate, such as *Desulfovibrio spp*., precipitate metals (e.g. Zn, Cu, Fe) and form insoluble precipitates (Marchand et al. 2010). This process can be a long-term sink for the elimination of HM since anoxic precipitated metals linger in sediments or media grains (Kosolapov et al. 2004). The mechanism is positively influenced by parameters such as pH values > 5.5 and redox potential below -100 mV. Reduction of sulphates is found in wastewater at high numbers, which means they require high volumes of carbon and energy sources. The low temperatures can also have a negative effect on the mechanism (Stein and Hook 2005). oxidising bacteria, such as the *Thiobacillus spp*, under aerobic conditions, or *Thiomonas*, facilitate the oxidation of sulphides to sulphites and then to sulphates and they are assumed to be involved in ferrous iron oxidation (Hallberg and Johnson 2005).

2.15 Performance of constructed wetlands

During the last five decades, the constructed treatment wetlands have grown into an effective treatment system that can be used with all types of wastewater, such as sewage, domestic, municipal, agricultural, industrial, landfill leachate and stormwater runoff. CWs of various types differ in their main design characteristics as well as in the processes which are responsible for the performance. But organic removal is high in all kinds of constructed wetlands, see Table 2.5 (Vymazal 2010). The most common form of describing CW performance is to reduce concentration by percentage and remove mass by percentage (Kadlec and Wallace 2009a). Removal efficiency (RE) of pollutants in CWs was calculated, based on concentrations (Equation 2.3), and loads (Equation 2.4).

$$RE = \frac{C_{inf} - C_{eff}}{C_{inf}} \times 100\% \qquad (2.3)$$

where the concentrations of the influent and effluent (mg/l) are denoted by $\mathrm{C_{inf}}$ and $\mathrm{C_{eff}}$ respectively.

$$RE = \frac{(C_{inf} \times Q_{inf}) - (C_{eff} \times Q_{eff})}{(C_{inf} \times Q_{inf})} \times 100\% \qquad (2.4)$$

where inflow and outflow pollutant mass load (mg) are denoted by $\mathrm{C_{inf}} - \mathrm{Q_{inf}} = \mathrm{M_{inf}}\ (mg)$, and $\mathrm{C_{eff}} - \mathrm{Q_{eff}} = \mathrm{M_{eff}}\ (mg)$ respectively.

Although constructed wetland types FWS and VF are mostly aerobic in the microbial degradation processes, anoxic and anaerobic processes prevail in CW type HF. The efficiency of the treatment is similar for FWS and HF CWs while the percentage efficiency for VFCWs is higher because of the higher hydraulic loading rate (Vymazal 2010). The deposition of suspended solids in all types of CWs is extremely high. Table 2.5 also indicate that in FWS CWs, the hydraulic retention time is usually lower than in sub-surface flow CWs.

Table 2.5 Treatment efficiency percentages of different CWs types.

Type	BOD5			TSS			TN			NH_4-N			TP			Reference
	NO	**HLR**	**%**	**NO**	**HLR**	**%**	**NO**	**HLR**	**%**	**NO**	**HLR**	**%**	**NO**	**HLR**	**%**	
FWS	50	4.1	74	52	4.8	77	29	4.9	45	40	5.4	48	52	5.4	34	(Vymazal and Kröpfelová 2008)
	51	3.3	72	52	4.1	68	192	-	58	-	-	53	207	-	50	(Bulc 2006)
	-	-	-	-	-	-	116	8.9	47	118	7.3		282	12.3	49	(USEPA 2000)
	-	-	-	-	-	-	366	3.2	41	59	3.1	39	52	3.5	35	(Kadlec and Wallace 2009a)
HF	438	11.8	75	367	15.4	75	208	10.6	43	305	14.1	39	272	11.4	50	(Vymazal and Kröpfelová 2008)
	-	-	11	-	-	-	99	9.1	33	213	7	30	-	-	-	(Kadlec and Wallace 2009a)
VF	125	8.2	90	98	9.7	89	99	9.1	43	129	8.4	73	118	8.2	56	(Vymazal and Kröpfelová 2008)
	8	29	80	8	29	-	8	29	58	8	29	58	8	29	37	(Stefanakis and Tsihrintzis 2012)

NO: number of CWs; HLR: hydraulic loading rate (cm/d); %: treatment efficiency (Eff, in %)

Table 2.5 also shows nutrient removal efficiency in different types of CWs. P retention in all types of constructed wetlands is low and CWs are rarely constructed with P being the only main target of treatment. In wetlands, P cycling has shown that soil/peat accumulation is the main long-term sink of phosphorus (Richardson et al. 1996). Manufactured substrate materials such as LECA (lightweight clay aggregates) or by- and waste products such as furnace steel slags have recently been tested in constructed wetlands (Jenssen and Krogstad 2003; Vohla et al. 2005; Lucas 2015). With these substrates, P removal is very high, but it is important to recognise that precipitation and sorption are saturable methods, and over time the sorption decreases.

Table 2.5 also shows TN removal, which is usually low due to low nitrification in HF CWs with water-saturated and low or zero denitrification in FWS and VFCWs (Vymazal and Kröpfelová 2008; Kadlec and Wallace 2009; Vymazal 2007). In VFCWs, very high nitrification occurs but there is no denitrification due to fully aerobic conditions in the vertical bed (Brix and Arias 2005). To obtain highly efficient total nitrogen removal, VFCWs could be combined with HF CWs which, by contrast, do not nitrify but provide acceptable conditions for nitrate reduction formed during nitrification in VF beds (Vymazal and Kröpfelová 2008; Kadlec and Wallace 2009; Vymazal 2007; Brix and Arias 2005). In all kinds of CWs, plant uptake only takes effect when plants are harvested. However, the quantity sequestered from the aboveground biomass is generally very low and does not exceed 10% of the nutrient load (Vymazal and Kröpfelová 2008).

In conclusion, all kinds of CWs are powerful in the removal of organics and suspended solids, although nitrogen removal is lower but could be improved using a mix of different types of CWs together. P removal is generally low unless the substrate used is made of special media with a high sorption power. CWs need very limited or zero energy input, and thus the operational and maintenance expenses are much cheaper than conventional treatment solutions. Besides the treatment, CWs are also planned as dual or multipurpose environments that may provide other natural systems such as flood prevention, carbon sequestration, or habitat for wildlife. The design parameters, operation and maintenance have all been direct effect elements on the performance of CWs.

2.16 Numerical models for constructed wetlands

The large variability of typologies and operating techniques of CWs, and the reality that they operate under the effect of their environmental conditions, appears to make each CW special in its kind, and laboratory studies are usually the only representative of the system being studied. The growing use of CWs in various countries for wastewater treatment, combined with very strict water quality specifications, was a catalyst for developing better modelling techniques as design tools (Rousseau et al., 2004). Above all, available CW models can be divided into two kinds: black box (i.e. empirical/statistical) and process based. Unlike process-based models that considered various physical, chemical, and biological processes, a process is not represented by the black box models. Therefore, approaches to black box modelling failed to compensate for the inherent complexity of the CW operating processes. In past years, several researchers have studied and thoroughly examined both modelling approaches (Langergraber 2008; García et al. 2010; Kumar and Zhao 2011; Samsó and Garcia 2013a; Samsó 2014; Meyer et al. 2015).

A mathematical model can be defined simply as an effort to translate into mathematical terms the conceptual understanding of a natural-world system or process (conceptual model) (Boltz et al. 2010; D'Acunto et al. 2019). Thus, mathematical models for CWs are a series of algebraic or differential equations in forms of mathematical expressions (Samsó 2014). Among the many wetland-based processes, those originating from microorganisms' metabolisms are key to describing their global operating (Samsó and García 2013b). Biokinetic models are called the mathematical models which describe the rates at which microbial mechanisms occur (Samsó 2014).

Also, numerical models contain the use of certain forms of spatial and/or temporal discretisation techniques to calculate solutions to mathematical equations (Samsó 2014). Numerical modelling is an invaluable tool, as it makes it possible to observe the results of difficult conceptual models under different controlled conditions and to test their significance and how they allow a greater understanding of the processes concerned (Oberkampf and Trucano 2016).

The main objectives of modelling are to get a better understanding of the processes that occur in CWs such as physical, biological, chemical transformation and degradation. Nonetheless, literature scanning shows a comprehensive range of contaminant removal processes accounted for by current models, their assets/limitations, and possible considerations to maximise their potential for use in different types of CW systems. Many studies have been published in the field of CW modelling. One note is that the different model classifications vary from one author to the next (Rousseau et al. 2004; Langergraber 2008; García et al. 2010; For these authors, kinetic first-order models are in the category of black boxes. However, Rousseau et al. (2004) claimed that these models could be categorised as regression equations, first-order models, Monod-models, and mechanistic (process-based models).

- **Black box models:** In many studies, black box models were used to design and predict the input-removal efficiency of CWs, without seizing the internal processes that regulate treatment processes. Several researchers published satisfying results from using these models but highlighted some incompleteness associated with their common features. Very limited kinds of pollutants (organics and nutrients) have generally been tested using such models. The most widely used among black box approaches is the first-order model, which is especially suited for sizing the systems (GARCÍA et al. 2010). Table 2.6 displays the principal features and limitation of each black-box model.

Table 2.6 Black-box models for CWs, their main features and limitations.

Models	Principal features	Limitations	References
Regression models	Principally been focused on empirical analysis of the relationship between inlet and outlet pollutant concentrations from the wetlands instead of on internal mechanism data.	Based on input/output data instead of on internal process data; over-simplification;	(Rousseau et al. 2004 ; Tang et al. 2009).
First-order models	Non-linear deterministic approach.	Unable to model unexpected events, variations in input flows and concentrations or internal storage changes.	(Kadlec 2000;Kadlec and Wallace 2009; Rousseau et al. 2004).
Monod models	Reflects first-order reactions with relatively low concentrations but high concentrations of zero-order rate reactions.	Prevents complete pollutant decomposition (low at low concentration reaction rate).	(Langergraber and Šimůnek 2005).
Time-dependant Retardation model	Over time, reference simulated removal levels decrease; first and quicker biodegradable substances are removed easily. Left solution with fewer biodegradable components with slower kinetics of removal; more consistent parameters for COD removal data around different depths and at different loads in CWs.	Needs tracer studies for measuring these constants in the rate of removal.	(Shepherd et al. 2001).
Tank-In-Series (TIS) model	Characterises pollutant movement as it crosses the wetland and its discharge at the outlet, Extreme vulnerability to high rates to pollutant removal to the character of the DTD (distribution of time for detention).	Based on I/O data instead of internal process data.	(Kadlec 2003).
Neural Networks (ANN)	Simulates the system and/or functional aspects of biological neural networks and simulates removal of phenol from wastewater from olive mills.	Low regression factor for removing NH3.	(Nayak et al. 2006; Akratos et al. 2009; Yalcuk 2013).

- **Process-based models:** Examine and categorise the current mechanistic models for CWs into the following categories (Langergraber 2008; Langergraber 2011):
  - Models of the hydraulic behaviour and single-solute transportation in CWs
  - Models of reactive transport for saturated conditions

- Models of reactive transport for variably saturated conditions.

Regarding these process-based models being able to simulate CW's internal processes, they pose numerous features and limitations. Therefore, some models are addressed in the following literature review:

- **FITOVERT** software is a multi-component numerical reactive transport model (Giraldi et al. 2010) specifically designed to simulate and predict the conduct and treatment properties of the vertical subsurface flow (VSSF)-CWs under varying saturated porous media. Actually, the FITOVERT model was developed primarily to overcome the weaknesses associated with the wetland models so far developed (Langergraber 2011) that can primarily modulate HSSF CWs. Essentially, the FITOVERT model comes in the forms of hydraulic and biochemical modules together with techniques regulating the transport of dissolved/particulate matter, obstruction of the wetland environment, evapotranspiration, and oxygen transfer (Defo et al. 2017).

  FITOVERT modelling of the vertical flow in unsaturated porous substrates is based on Richards and van Genuchten; Equation 2.5 (Giraldi et al. 2010). Aside from the theoretical basis, FITOVERT also involves numerous technical aspects of the VFCW, which is going to make it a helpful design tool (Stefanakis et al. 2014c).

$$\frac{\partial \theta}{\partial t} = + \frac{\partial}{\partial z}\left[k\left(\frac{\partial h}{\partial z} - 1\right)\right] \qquad (2.5)$$

where the volumetric water content is θ, the time is t (seconds), the spatial coordinate is z (meters: positive downwards), the unsaturated hydraulic conductivity is k (ms/cm), and the potential matrix is h (m).

- **HYDRUS-2D-CW2D**: Served as a starting point for the creation of CW2D. This model use to simulate systems receiving a high load of pollutant and oxygen transport through the plant root (Langergraber and Šimůnek 2005). Also, this model can solve the Richards equation for saturated and unsaturated environments and provides a convection equation and heat and a mass transport dispersion equation. The main disadvantage of this model is that so far only dissolved pollutants are considered and the model during dry periods cannot predict degradation of contaminants.

  Module CW2D used to study CWs’ hydraulic behaviour. The system used consists of various gravel layers of different sizes, planted with Arundo donax (Langergraber 2008). The outcome demonstrates that the simulated and analysed data for the pilot scale CWs exhibited a close fit. The simulation outcome of Toscano et al. (2009) also showed a near fit to the experimental data when they modelled the two-sub-flow CWs of the pollutant removal pilot scale. Morvannou et al. (2014) researched the fate of nitrogen using gravel via a VF CW, handling raw wastewater directly from the house.

Their findings showed that NH4-N was substantially adsorbed into organic matter and then transformed to NO3-N, and that heterotrophic biomass was predominantly present in the layer of sludge (first 20 cm). Both these studies however measured the hydraulic actions of CWs, and removal of pollutants using sand and gravel as the main substrates in VF CWs.

- **PHWAT:** Numeric models for simulating pH variations and mechanisms of clogging, bacteria attachment and flow-induced biofilm removal, redox and surface complexion reactions associated with ASM-based nutrients and organic contaminants, combined with GW flow model MODFLOW (variably saturated conditions) (Brovelli et al. 2007). With PHREEQC, apart from the biokinetic reactions, full water chemistry and interactions between sediment and water can be modelled. PHWAT can also model bio-clogging, the attachment of bacteria and the flow-induced detachment of the biofilm. This model provides a growth-limiting expression to compensate for bacterial growth-induced porosity reduction. It has limitation of simulation of the effect of biomass growth on the hydraulic and hydrodynamic properties of porous saturated media in particular (Samsó 2014).
- **HYDRUS-2D-CWM1:** A new version of the wetland module software for HYDRUS-2D (Langergraber and Šimůnek 2012). The latest version provides the option of choosing between the already implemented CW2D and the newly implemented biokinetic versions of CWM1. HYDRUS-2D-CWM1's only shift in relation to HYDRUS-2D-CW2D is therefore the biokinetic pattern.

  Simulations were run to render a numerical proof of the two biokinetic models being implemented in HYDRUS (Langergraber and Šimůnek 2012). The authors compared findings in a 20 by 20 cm vertical domain with simplified versions of the two biokinetic models. The findings showed that the two biokinetic models in HYDRUS-2D have been implemented correctly. Also, HYDRUS-2D was used to replicate the simulations carried out by Llorens et al. (2011) achieving various tests. It was used for heat transfer and root effects associated with saturated and unsaturated conditions, removal of COD, N and S, ammonium adsorption method used for simulation: HYDRUS-2D. This used only a small number of environmental pollutants/nutrients (Pálfy and Langergraber 2014).
- **STELLA** is a graphical programming language developed to better understand the nonlinear dynamic system in CWs for system dynamic study. Pimpan and Jindal (2009) clarified how the FWS CWs planted with bulrush for cadmium removal using STELLA software are adsorption, desorption and plant uptake. They explained the mixture of clay, loam, soil and sand for adsorption, desorption, and plant uptake.

Ouyang et al. (2011) also used the model for nitrogen removal. The main mechanism for the removal of nitrogen in VFCWs includes organic nitrogen deposition and hydrolysis, nitrification and denitrification processes, leaching through the material region, and plant uptake. Kumar et al. (2011) used dewatered alum sludge modelling the fate of phosphorous in VFCWs. Research results showed that approximately 72% of phosphorus was removed by adsorption, while 20% was removed through plant uptake. Ouyang (2008) used the STELLA modelling to create a dynamic model for the uptake and translocation of pollutants from a soil–plant ecosystem (UTCSP).

2.17 Summary

From the literature review, it is clear that after years of studies and implementation, CWs can be beneficial for worldwide stormwater management, protecting local watercourses, attenuating flooding and enabling re-use of surface runoff for non-potable purposes, thus reducing the burden on drinking water sources. In general, it contributes to the improvement of the aquatic ecosystem. The review found that CWs can be used to treat stormwater for all the global priority pollutants and current CWs have shown their ability to successfully minimise concentrations of stormwater contaminants. The review shows that improvements in the design and operation of CWs achieved across the years have dramatically increased the efficiency of pollutant removal, and also greatly improved the sustainable implementation of this treatment system.

Although CWs have been widely recommended for treatment, the conventional VFCW design has a limited capacity for nitrate removal which impacts the reduction of TN, a key pollutant in stormwater. In addition, their comprehensive implementation is hindered by a lack of design codes and space.

Considering the highly demanding water quality requirements for stormwater, wastewater treatment and water quality internationally, there has been a need for developing comprehensive guidelines based on further research to use the constructed wetlands for urban stormwater management. Additionally, consideration should be given to the appropriate building materials and climatic conditions for each country or geographic region. More importantly, CW design should be considered for less dense land systems, such as using VF constructed wetlands.

In addition, studies show that CWs not only enhance water quality by eliminating contaminants such as hydrocarbons, suspended solids and heavy metals, but can also minimise flooding and peak flow discharges.

The main drivers behind this study were to address deep understanding of the mechanism of pollutant removal that leads to establishing a VFCW system, which effectively retains a variety of priority pollutants and enhances nitrate removal, and to understand the internal processes that lead to the reduction of these contaminants. This review will thus contribute to the body of research dedicated to understanding stormwater treatment through CWs, and hopefully lead to the availability of improved guidance on their implementation, operation and maintenance.

Chapter 3: Materials and methods

3.1 Introduction

Pilot tests are conducted to refine design parameters, compare design choices, identify operational and management problems, or check reliability, so pilot-scale CWs do not always have to comply with the guidelines. Several studies have used pilot-scale constructed wetlands for different purposes, for example, ten pilot-scale cylindrical, vertical flow constructed wetland units were used to study the effect of various design parameters simulating municipal wastewater (Stefanakis and Tsihrintzis 2009), they also used five pilot-scale units to compare five different substrate media on the performance of Vertical Flow Constructed Wetlands (Stefanakis and Tsihrintzis 2009). Also, G. Baskar and others designed, constructed and operated two pilot-scale horizontal subsurface flow constructed wetlands having two different substrates, gravel and pebble, to compare treatment performance between constructed wetlands with different substrates (Baskar et al. 2014). Also, five pilot-scale units were used to test the effects of porous media, HRT, vegetation, and temperature, on removal efficiency of pilot-scale horizontal subsurface flow constructed wetlands (Akratos and Tsihrintzis 2007).

Experiments in this research form an integral part of the work conducted to resolve the research questions. Although there are no specific codes currently available for designing CWs, the CWs being studied were constructed based on guidelines adopted internationally as well as in the United Kingdom. The design method covered catchment study of typical urban areas in the UK, with a focus on land properties, land use, and meteorological trends over a 33-year period.

In addition, continuous wet and intermittent short-dry and prolonged-dry periods had been simulated in the operational technique based on local trends in the representative urban areas. The slow regime filling was the method of dosing influents into the CWs. The effluents were drained after a 24-hour retention time using a tap at the bottom of each CW to control the draining.

Experimental work was performed over a three-year period investigating the impact of design and operational variables on the long-term success of eight pilot-scale VFCWs. Indicators of efficiency were the variations in physical water quality such as pH, electrical conductivity, and temperature; measured in-situ using a multi-parameter probe. Moreover, the chemical characteristics of water total nitrogen (TN), nitrite (N -NO_2), nitrate (N-NO_3), ammonium nitrogen (N-NH_4), orthophosphate (P-PO_4), total phosphorus

(TP), iron (Fe), zinc (Zn), copper (Cu), nickel (Ni), lead (Pb), cadmium (Cd) and chromium (Cr) were tested.

A spectrophotometer measures the total suspended solids (TSS), nitrogen and phosphorus species. Heavy metals are measured by the plasma-optical emission spectrophotometer (ICP-OES) coupled inductive.

This experiment was run for 908 days approximately starting on November 16th, 2013, until April 4th, 2017. During the whole period, the experiment was suspended for limited periods of around eight weeks due to reasons such as new year holidays or the like. The experiments were prepared and operated firstly by Lucas (2015) and Kiiza (2017) for 544 days. During this research, the same experiment had been run for the period from November 17th, 2015 to March 4th, 2017. While this study undertook the analysis, investigation and discussion of the results and data collected was undertaken during the total period from the beginning of the operation until the date of its discontinuation in March 2017.

Generally, the eight pilot-scale VFCWs were subject to the experiment based on variables, conditions, and operating parameters, while tested according to what is shown in Table 3.1. Whereas the current study is to examine long-term pollutants immobilisation in eight pilot-scale VFCWs operated with various design and operation wetland characteristics to tackle the effects on treatment performance during the continuous operation and monitoring for more than 900 days. Thus, each CW was designed to monitor the effects of these various conditions side-by-side making it easy to distinguish, which in line with other studies used similar VFCW design (Hatt et al. 2007a; Stefanakis and Tsihrintzis 2012). More details are given in the following sections.

Table 3.1 Experiment designs, operation conditions and variable parameters of pilot-scale VFCWs.

Factors		Substrate Evaluation				WWAR Evaluation		Wet-dry Regime Evaluation	
VFCW		CW1	CW2	CW3	CW4	CW5	CW6	CW7	CW8
WWAR (%)		2.5%	2.5%	2.5%	2.5%	5%	1.5%	2.5%	2.5%
Wet-dry regime		Wet conditions	Wet conditions	Wet conditions	Wet conditions	Wet conditions	Wet conditions	Partially dry conditions	Extended dry conditions
Substrate composition (by depth)	0-45 mm	Loamy sand	Loamy sand	Fine gravel	Blast furnace slag	Loamy sand	Loamy sand	Loamy sand	Loamy sand
	45-55 mm	Sand	Sand	Med gravel	Sand	Sand	Sand	Sand	Sand
	55-60 mm	Fine gravel	Fine gravel	Coarse gravel	Fine gravel	Fine gravel	Fine gravel	Fine gravel	Fine gravel
Factor tested		(Control unit)	(Control duplicate)	Media type	Media type	WWAR (5%)	WWAR (1.5%)	Wetting and drying regime	Wetting and drying regime
Volume per day		22.5 l	22.5 l	22.5 l	22.5 l	11.3 l	37.6 l	22.5 l	22.5 l
Loading times per week		3	3	3	3	3	3	Cycle 1 week Wet (3) 1 week Dry	Cycle 1 week Wet (3) 4 weeks Dry
Total volume per week/cycle		67.5 l/W	67.5 l/W	67.5 l/W	67.5 l/W	33.9 l/W	112.8 l/W	67.5 l/cycle	67.5 l/cycle

3.2 Pilot-scale VFCW setup

On the roof of the third floor of the South Buildings, School of Engineering at Cardiff University, eight pilot-scale physical models of HDPE pipe with high-structured wall had been designed and installed to be used as VFCWs for treating urban stormwater. Figure 3.1 displays a view of the system of eight pilot-scale CWs. The CWs have been numbered CW1, CW2, CW3, CW4, CW5, CW6, CW7 and CW8. The CWs were run as vertical downflow systems, and various operating criteria were applied depending on the variables which were used to investigate each individual CW.

Asset International Ltd produced the structured-wall HDPE pipes that housed the CWs. Each pipe provided an inner diameter of 400 mm, and a height of 1000 mm (minimum diameter available). The pipes had been sealed off with HDPE plastic at one end, thus providing the CW foundation. At the centre of this sealed end, a main outlet tap was installed on the base of the CW, and an external tap was mounted for overflow but not necessary. Figure 3.2 shows a typical pilot-scale CW, made from a single length of pipe.

Figure 3.1 Experimental set-up of the eight pilot-scale CWs of HDPE pipes.

As mentioned earlier, the design method covered catchment studies of typical urban areas in the UK, with a focus on land properties, land use, and meteorological trends over a 33-year period in addition to using meteorological data to size the VFCWs based on 1-5 % WWAR (wetland area to watershed area ratio). More details are mentioned in the following sections.

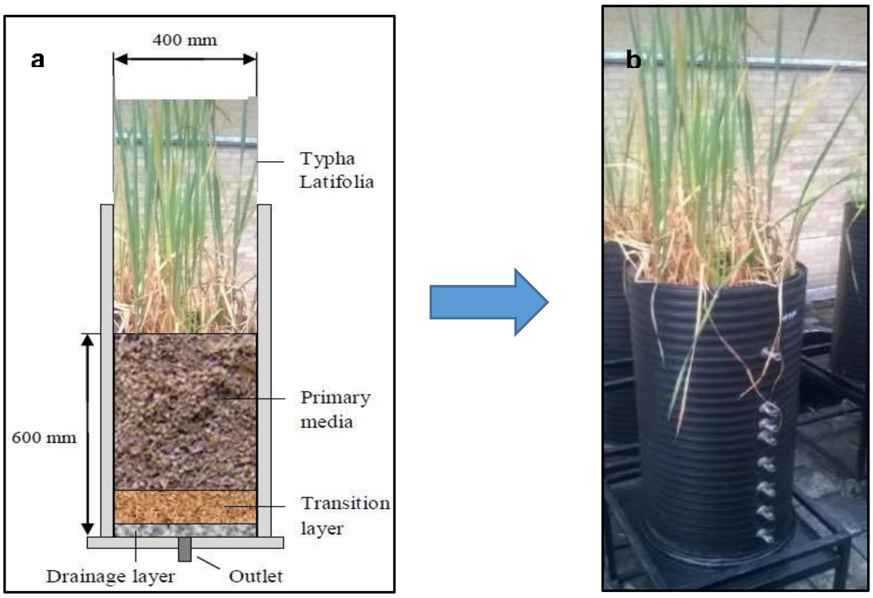


Figure 3.2 A schematic plot of a pilot-scale CW (a) and its implementation using HDPE pipe (b).

After the experimental work had started, the collected samples had been analysed in the Characterisation Laboratories for Environmental Engineering Research (CLEER), located at the Cardiff School of Engineering on the ground floor of the South Buildings.

3.3 Urban stormwater: data collection and preparation

The urban stormwater data used in this research, such as the average annual rainfall (AAR), is based on Met Office data from several stations located in urban areas across the UK from 1978 to 2011. This time span was used to provide accurate averages based on a long duration. Below are the stations from which the data was obtained:

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

Figure 3.3 shows the distribution of those stations across the UK. For each region in the UK at least one station provided data on rainfall for an urban area, and the distribution is well distributed across the chart.

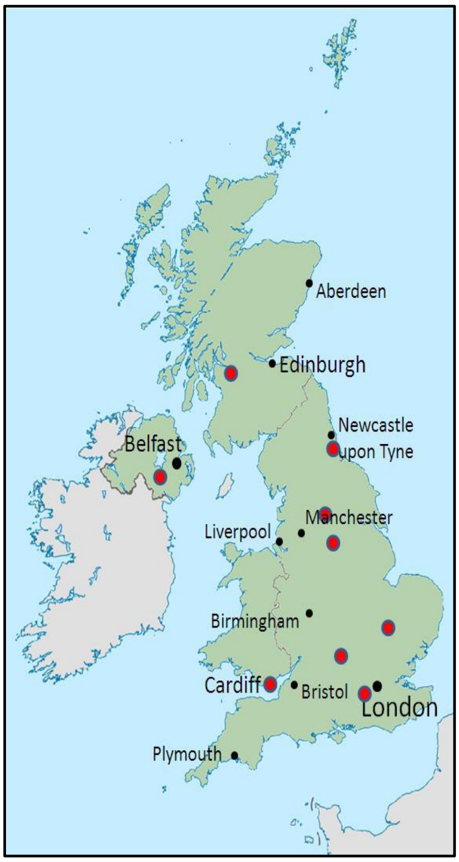


Figure 3.3 Places of weather stations (identified by red markers) from which data on rainfall is collected.

3.3.1 Average rainfall

The hydraulic load volume (HLV) for stormwater treatment is dependent on rainfall patterns. Certain catchment predictions of rainfall are made based on data from the region from previous precipitation. Two important factors in deciding the HLV are the size of a catchment and the volume of precipitation.

The rainfall values (in mm) are given at each station for each month of each year. To give an average annual rainfall (AAR) value, these figures were averaged for each year, and then an AAR value was determined for 1978 to 2011, inclusive. The AAR values were then combined for each of the nine stations to give an AAR for urban areas in the UK (see Table 3.2).

Table 3.2 Urban rainfall data in the United Kingdom, 1978-2011 (Met Office).

Station	Corresponding District	AAR for period 1978 – 2011 (inclusive) (mm)	No. of days with AAR >1 mm, 1978 – 2011 (inclusive)
Armagh	Northern Ireland	816	178
Bradford	NW England & N Wales	873	166
Cambridge	East Anglia	561	115
Cardiff	S Wales & SW England	1143	156
Durham	E & NE England	663	131
Heathrow (London)	SE & Central S England	600	121
Oxford	Midlands	653	130
Paisley	West Scotland	1250	194
Sheffield	Midlands	833	130
The AAR UK Average		**821.33**	**146.78**

The "rainy days" figure is counted as the number of days with a rainfall of > 1 mm. The Met Office publishes monthly and annual reports for the number of rainy days in the following regions of the United Kingdom:

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

The Average Annual Rainfall values reported at each station were matched to their respective district figures for the average number of rainy days experienced per year (1978-2011) in that region.

From rainfall data for the period of 1978 to 2011, the AAR value of 821 mm for UK urban areas, along with a corresponding value of 147 rainy days were calculated and provided in Table 3.2.

3.3.2 Concentration of inflow pollutants

Quality of inflow pollutants was chosen to match an urbanised catchment. The research on urban stormwater pollution by Duncan (1999), Pitt et al. (2004) and others listed in the literature review has established a key for stormwater contaminants that have been reported in the UK and European cities. The results reflect rising pollutants from stormwater in various catchments and their respective average concentrations. In this experiment the catchment form of interest is the highly urbanised catchment. Consequently, the mean concentrations in the literature have been modified according to this study's objectives.

Table 3.3 displays the selected pollutants along with their target influent concentration levels, and the chemical grade of the laboratory that would be applied to reach the needed concentration for each pollutant.

3.3.3 Semi-synthetic urban stormwater

In this study, semi-synthetic urban stormwater was used instead of natural stormwater, or totally synthetic stormwater. It is very difficult to provide natural urban stormwater regularly and it was not available at the site in the necessary amounts at specified times. It can also produce a high degree of variability in concentrations and characteristics of the inflow, whereas 100% synthetic stormwater is less reflective of actual runoff. Semi-synthetic urban stormwater is a solution that allows for an ideal measure of control over concentrations of inflow, while at the same time better reflecting natural runoff as it was generated from the sediment of stormwater.

The semi-synthetic stormwater was created by mixing real sediment of stormwater with dechlorinated tap water and adding lab-grade chemicals to create the needed concentrations of contaminants where possible. At first, the sediment was obtained from a stormwater runoff pond in Nant y Briwnant (north of Cardiff) and then from gulley pots in the Cardiff University, School of Engineering car park. After three months of processes the sediment source changed due to the lack of access to the pond, particularly after storms (floods made collecting the sediments challenging). The sediments collected have been wet-sieving through a 1 mm sieve; FAWB (2009) proposes this upper limit for the particle size of the solids to mimic runoff which has not gone through a pre-treatment facility. The wet-sieving process provides slurry: a mixture of high concentrations of solids with water. Then, the right TSS concentration of this slurry was calculated using standard methods (APHA 2012).

Table 3.3 Target influent pollutants concentration, chemical additions, range of measured influent concentration, and upper discharge limits.

Pollutants	Target influent concentration (mg/l)	Measured range of influent concentration (mg/l)	Upper discharge limit (mg/l)	Chemical additions for semi-synthetic stormwater
TSS	180	98-290	717.5	Road sediment
TN	3	3.440-11.300	0.207	Ammonium chloride (NH_4Cl)
NO_2-N	-	0.000-0.150	0.098	--
NO_3-N	-	0.000-0.700	0.574	--
NH_4-N	-	0.560-4.426	0.002	--
TP	0.45	0.857-1.452	0.230	Di-Potassium hydrogène phosphate (K_2HPO_4) and di-Sodium hydrogen phosphate (Na_2HPO_4)
PO_4-P	-	0.534-1.389	0.029	--
Fe	2.9	0.129-20.246	1.148	Iron (II) Chloride tetrahydrate ($FeCl_2.4H_2O$)
Cr	0.025	0.000-0.662	-	Chromium nitrate ($Cr(NO_3)_3$)
Ni	0.04	0.014-1.021	-	Nickel (II) chloride hexahydrate ($NiCl_2.6H_2O$)
Pb	0.16	0.011-6.766	28.701	Lead nitrate ($Pb(NO_3)_2$)
Cu	0.07	0.005-0.745	9.184	Copper (II) chloride dihydrate ($CuCl_2.2H_2O$
Zn	0.35	0.062-1.934	-	Zinc sulphate heptahydrate ($ZnSO_4.7H_2O$)
Cd	0.005	0.000-0.022	-	1000 mg/l standard solution

The slurry sample was analysed in the CLEER (Characterisation Laboratories for Environmental Engineering Research) laboratory at Cardiff University to determine the current concentration of each of the pollutants mentioned in Table 3.3. Where concentrations of pollutants were found to be less than target inflow levels, chemicals of laboratory grade were applied to the slurry to reach those targets. Equation 3.1 was used to calculate the slurry volume needed for the total target semi-synthetic runoff volume.

$$V_S = \frac{TSS_T \ X \, V_{ST}}{TSS_S} \qquad (3.1)$$

where: V_S means volume of slurry (l), TSS_T means target TSS concentration (mg/l)

V_{ST} means volume of semi-synthetic stormwater (l), TSS_S means slurry TSS concentration (mg/l).

The calculated volume from Equation 3.1 was mixed with dechlorinated tap water until the target volume of semi-synthetic stormwater was achieved (V_{ST} volume). As indicated by FAWB (2009), adding 1 mg/l of sodium thiosulfate is recommended to dechlorinate the tap water. Finally, the mixture was continuously stirred for 10 minutes to achieve a uniform sediment distribution in water and adsorption of contaminants to the particles of the solids.

3.3.4 Quality of the influent stormwater

For each dose treated at the eight pilot-scale VFCWs, influent stormwater quality was calculated. A conservative approach was undertaken for preparing slurry and mixing to reduce the differences in the consistency of the powerful stormwater. It confirmed that the processed semi-synthetic stormwater had concentrations of contaminants within the literature ranges in Table 3.3. The consistency of the quality of stormwater influent was thus relatively stable.

It should be noted that the content of the natural sediment used to represent the stormwater used in the experiments had slightly higher concentrations of contaminants than the ones recorded in the literature. Nevertheless, certain contaminants, like Cd, Cr, and Ni, were below the urban stormwater standard levels. In order to achieve concentrations of pollutant factors, fixed amounts of chemicals of laboratory grade were applied to increase the concentration of specific elements.

Likewise, the concentration of influent TSS was less changeable since pre-determined amounts of sediment slurry were applied to the dechlorinated tap water in defined quantities. De-chlorination reduced the reaction of chlorine with pollutants, as well as reducing chlorine effects on essential microbial species.

Interestingly, influents examined during the study's first seven weeks showed that heavy metals were primarily particulate and as such may be bound to suspended solids, which is explained in more detail in Chapter 4.

3.4 Design criteria of the experiments

To understand the relationship between the design parameters and performance efficiency of stormwater treatment in VFCWs, the experiment was divided into three parts to test and evaluate three of the design parameters: (i) the substrates of the main layer, (ii) Wetland/Watershed Area Ratio (WWAR), and (iii) wet-dry regime of influent loading. While CW1 and CW2 were the control CWs in the three groups as follows:

1- Evaluation of the performance behaviour of CWs based on the type of substrate under operating conditions shown in Table 3.4 was investigated in CW1, CW2, CW3 and CW4.
2- The effect of Wetland/Watershed Area Ratio (WWAR) on the stormwater treatment performance of pilot-scale VFCWs numbers CW1, CW2, CW5 and CW6. The variable parameters regarding this effect are illustrated in Table 3.5.
3- The effect of wet-dry regime on the pollutants removal performance of VFCWs from the stormwater. The effect was investigated through pilot-scale VFCWs numbers CW1, CW2, CW7 and CW8. The experiment conditions of these CWs are clarified in Table 3.6.

Table 3.4 Design and operation conditions to evaluate the removal performance of VFCWs based on the substrate type.

Substrate Evaluation					
CW		**CW1**	**CW2**	**CW3**	**CW4**
WWAR (%)		2.5%	2.5%	2.5%	2.5%
Wet-dry regime		Wet conditions	Wet conditions	Wet conditions	Wet conditions
Substrate layers (by depth)	0-45 mm	Loamy sand	Loamy sand	Fine gravel	Blast furnace slag
	45-55 mm	Sand	Sand	Med gravel	Sand
	55-60 mm	Fine gravel	Fine gravel	Coarse gravel	Fine gravel
Factor tested		(Control)	(Control duplicate)	Media type	Media type
Loading volume per day		22.5 l	22.5 l	22.5 l	22.5 l
Loading frequency per week		3 times/week	3 times/week	3 times/week	3 times/week
Loaded volume per week		67.5 L/W	67.5 L/W	67.5 L/W	67.5 L/W

Table 3.5 Design and operation conditions to evaluate the impact of changing WWAR on the pollutant removal efficiency in VFCWs.

WWAR Evaluation					
CW		**CW1**	**CW2**	**CW5**	**CW6**
WWAR (%)		2.5%	2.5%	5%	1.5%
Wet-dry regime		Wet conditions	Wet conditions	Wet conditions	Wet conditions
Substrate layers (by depth)	0-45 mm	Loamy sand	Loamy sand	Loamy sand	Loamy sand
	45-55 mm	Sand	Sand	Sand	Sand
	55-60 mm	Fine gravel	Fine gravel	Fine gravel	Fine gravel
Factor tested		Control (WWAR 2.5%)	Control duplicate (2.5%)	WWAR (5%)	WWAR (1.5%)
Loading volume per day		22.5 l	22.5 l	11.3 l	37.6 l
Loading frequency per week		3 times/week	3 times/week	3 times/week	3 times/week
Loaded volume per week		67.5 L/W	67.5 L/W	33.9 L/W	112.8 L/W

Table 3.6 Design and operation conditions to evaluate the impact of changing wet-dry regime on the pollutant removal efficiency in VFCWs.

Wet-dry regime Evaluation					
CW		**CW1**	**CW2**	**CW7**	**CW8**
WWAR (%)		2.5%	2.5%	2.5%	2.5%
Wet-dry regime		Wet conditions	Wet conditions	Partially dry conditions	Extended dry conditions
Substrate layers (by depth)	0-45 mm	Loamy sand	Loamy sand	Loamy sand	Loamy sand
	45-55 mm	Sand	Sand	Sand	Sand
	55-60 mm	Fine gravel	Fine gravel	Fine gravel	Fine gravel
Factor tested		(Control unit)	(Control duplicate)	Wetting and drying regime	Wetting and drying regime
Loading volume per day		22.5 l	22.5 l	22.5 l	22.5 l
Loading frequency per week		3 times/week	3 times/week	3 times/week followed 1 week dry	3 times/week followed 4 weeks dry
Loaded volume per week		67.5 l/W	67.5 l/W	67.5 l/ 2W	67.5 l/5W

3.4.1 Substrate selection and the configuration

The common substrates used in vertical CW stormwater subsurface-flow systems are sand and gravel. Similar stormwater treatment systems with sand-based CWs have shown strong removal of heavy metals (Hatt et al. 2007a; Li and Davis 2009), and heavy metals are among the major contaminants of interest in stormwater runoff. The Facility for Advancing Water Biofiltration (FAWB) guidelines recommend the use of loamy sand in stormwater biofiltration technologies because of its high compaction permeability, organic matter content (increasing water holding capacity), low nutrient content, and good vegetation support (Blecken et al. 2009; FAWB 2009).

Therefore, firstly, in six out of the eight CWs (CW1, CW2, CW5, CW6, CW7 and CW8), loamy sand was used as the main substrate; see Figure 3.4a.

Secondly, gravel is widely available and cheap; it has been successful in its use as a CW substrate in suspended solids and heavy metals removal (Hatt et al. 2007b). Accordingly, CW3 was packed with gravel as its primary substrate, transfer layer, and drainage layer outlet; see Figure 3.4b.

Thirdly and lastly, granulated blast furnace slag (BFS) (diameter 4 - 12.5 mm) was chosen as the main substrate in CW4; see Figure 3.4b.

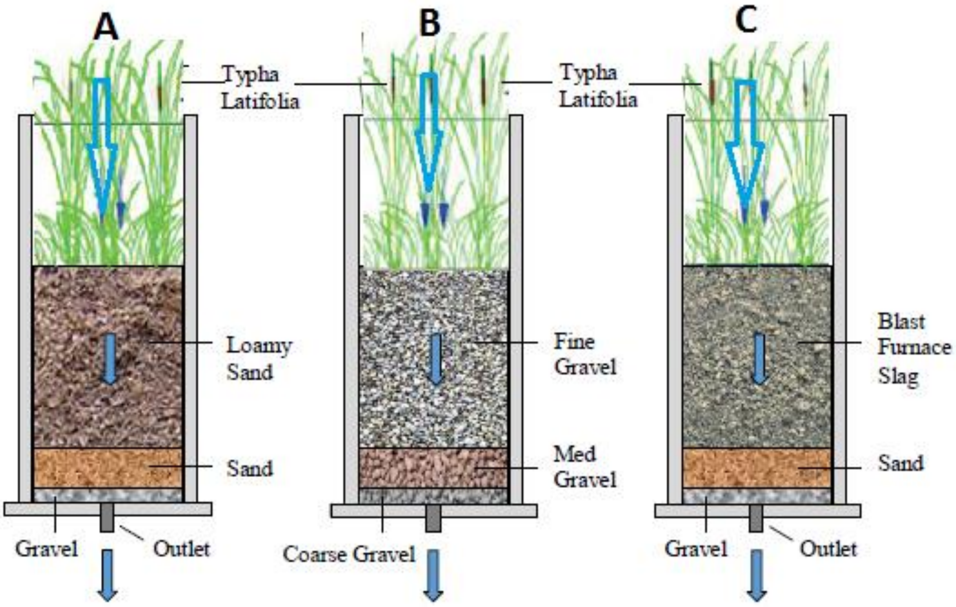


Figure 3.4 Cross-sections of the VFCWs: (A) loamy sand (B) graded gravel (C) BFS.

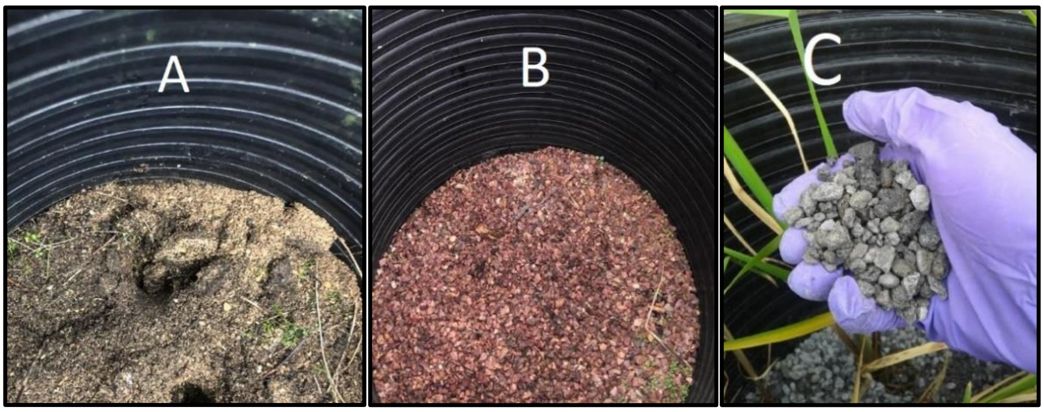


Figure 3.5 Substrates loamy sand (A), fine gravel (B), and blast furnace slag (C).

BFS is a manufacturing by-product, with high adsorption potential for heavy metals and phosphorus (Grüneberg and Kern 2001;Taylor 2006; Asuman Korkusuz et al. 2007). In stormwater treatment systems, heavy metals and phosphorus are key pollutants and the use of a by-product makes BFS a potentially valuable and renewable resource for use in CWs. Figure 3.5 shows the three type of substrates.

Fine gravel of a diameter of 6 mm was used as a drainage layer in every CW and all structures (apart from CW3, in which all layers are gravel) containing a transfer layer of sharp sand to ensure that none of the main substrate was transferred to the drainage layer. In CW3, the transition layer consists of medium size of gravel (10 mm), while the drainage layer consists of 20 mm diameter coarse gravel. Depending on price, local availability and sustainability, the primary substrates were used.

The eight pilot-scale CWs have a total substrate depth of 0.6 m, representing values found in literature and other research studies. The height of 0.6 m is 100 mm deeper than the depth defined by Feng et al. (2012), but with the inclusion of a required transition/drainage layer 150 mm deep, it was agreed that an additional 100 mm of total depth would be desirable to ensure that the primary substrate will have plenty of surface area for adsorption and other contaminant removal procedures. The UK vertical-flow CWs have been typically designed to a depth of 0.5–0.8 m (Cooper 1996). Such typical depths are selected to provide enough hydraulic retention time (HRT) for the efficient treatment of conventional vertical-flow CWs. There have been several pilot-scale studies equivalent to this experiment using 0.8 m deep cells (Scholz 2004; Blecken et al. 2009; Fletcher et al. 2010). As other studies indicate a 0.5 m depth gravel filter was ideal for removing sediment and heavy metals (Hatt et al. 2007a), it was suggested that 0.5 m be an appropriate depth for the treatment of stormwater infiltration (Feng et al. 2012).

3.4.1.1 Physical properties of the substrates

Soil bulk density ($D_b = m_s/V_t$) is the ratio of oven-dried solid mass (m_s) to soil bulk volume (V_t) that includes solid volume and pore space between the soil particles (Blake and Hartge 1986a). Bulk density is a commonly used physical property; it is a measure of soil compaction condition and is used to transfer water percentage by weight to volume content, to calculate porosity when particle density is known, and to estimate soil volume weight that is too high for convenient weighting (Hao et al. 2019).

The particle density ($D_p = m_s/V_s$) refers to the mass (m_s) of solid soil particles (V_s) in a unit volume. The pore space between the particles is not considered (Blake and Hartge 1986b).

Three samples of each substrate were collected then all of them were dried for 24 hours in a hot-air oven at 105°C to a constant weight. The weight the dry sample was then measured (weight of the container full - weight empty container). The dry weight of the soil was recorded, and the volume of the cylinder was calculated (volume of a cylinder is pi x radius squared x height). The calculated bulk density and particle density of the samples are listed in Table 3.7, while the typical substrate properties generally used in CWs are shown in Table 3.8.

Table 3.7 The bulk and particle density of the selected substrates.

Substrates	Sample No.	Bulk density (g/cm3)		Particle density (g/cm3)	
		Per Sample	Average	Per Sample	Average
Loamy Sand	LS1	1.730	1.674	2.626	2.607
	LS2	1.704		2.604	
	LS3	1.588		2.592	
Fine Gravel	FG1	1.505	1.475	2.685	2.658
	FG2	1.471		2.547	
	FG3	1.449		2.743	
Blast Furnace Slag	BFS1	0.356	0.362	2.186	2.161
	BFS2	0.371		2.175	
	BFS3	0.358		2.123	

Table 3. 8 Substrates hydraulic properties widely used in CWs.

Substrates type	Effective size, D_{10} (mm)	Porosity, n (%)	Hydraulic conductivity, K_s (m^3/m^2.day)
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

3.4.1.2 Chemical properties of the substrates

The elemental analysis of the three primary substrate forms (loamy sand, fine gravel, and blast furnace slag) was determined from the substrate stock samples used to configure the eight VFCWs.

Eleven samples were collected, three from raw substrate stock of loamy sand, fine gravel and BFS before being used for treating the urban stormwater, and one sample from each pilot-scale CW after the experiments had terminated. Two core samples (length 350 mm and 75 mm in diameter) were taken from each CW. The samples were dried for 24 hours at 105°C. After that, a representative dry sample weighing 500 g was taken using the riffle box method according to British Standards (BSI 1998). The dissolution process involved the separate weighing of finely crushed powdered samples (< 100 μm) to which 2 ml of hydrofluoric acid (HF) was applied and the mixture was left to stand overnight. Then 3 ml of aqua regia (50:50 ratio of HCl and HNO_3) was applied, and 25 minutes of dissolution using an Anton-Paar Multiwave 3000 microwave operated at 190°C. Complexation (neutralisation of the HF) was accomplished by adding 12 ml of 4% boric acid solution before the final solution of deionised water was made up to 50 ml (Wilson et al. 1997; Pérez-esteban et al. 2013). The generated solutions were analysed with the inductive plasma-optical emission spectrophotometer, ICP-OES 2100 DV (Perkin Elmer), for Ca, Al, Fe, Mg, Mn, Pb, Si, and Zn.

In addition, The SC-144DR Sulphur and Carbon Analyzer was used for measuring sulphur, total carbon and inorganic carbon.

3.4.2 Plants

Typha latifolia plants (density = 64 plants / m^2, see Figure 3.6) were planted on each CW unit. Typha has many advantages: it is found worldwide, is successful in metal removal, and is known for its appropriateness for surface runoff treatment (Ellis et al. 2003a).

Figure 3.6 Typha Latifolia used as a CW plant.

3.4.3 Sizing of VFCWs

The CW surface area would be calculated, under actual design conditions, by the scale of the catchment where it is placed. The surface area is calculated as a percentage of watershed area size, and this is referred to as the Wetland/Watershed area proportion (WWAR). A CW with a WWAR value of 5% means that the CW's surface area is equal to 5% of the total catchment area. Due to the unpredictable nature of the rainfall and the different treatment criteria in different catchments, the design of CWs for stormwater treatment is so complex that there are no design codes that define a WWAR value that should be used; instead, the value is usually taken from regulations and recommendations. An Ellis et al. (2003a) study showed that values of 1-5% are common, and it suggests using a 2-3% WWAR. Ideally, the WWAR value should be as low as possible in order to minimise land acquisition without affecting treatment.

In this phase, the process of sizing was effectively reversed. The surface area of a CW is limited by the fact that the pilot scale systems used the minimum usable diameter of HDPE pipes (400 mm). Instead of beginning with a watershed area and measuring the surface area of the CW, the area of the CW itself is defined and the representative area of the catchment is calculated, which can be handled by the system. Firstly, the CW surface area was determined based on a cross-sectional circular area of the HDPE pipe. A diameter of 0.4 m provides a cross-sectional area of 0.126 m^2, for all eight CWs.

In the experiment, three independent WWAR values were used to evaluate the system's output under various charging situations. Such figures amounted to 1.5%, 2.5% and 5%. WWAR regulation was 2.5%, as it comes within Ellis et al.'s guideline of 2-3% (Ellis et al. 2003b). This WWAR value was applied to CW1, 2, 3, 4, 7 and 8. CW5 had a WWAR of 5% to examine to what degree pollutant control is enhanced by increasing a CW's representative surface area. CW6 had a 1.5% WWAR to assess whether the CW system would demonstrate efficient removal of contaminants while taking up only a very small area of the catchment.

Representative areas of catchment handled by the systems are estimated as:

For WWAR of 5% = $0.126\ X\ \frac{100}{WWAR} = 0.126\ X\ \frac{100}{5} = 2.52\ m^2$

For WWAR of 2.5% = $0.126\ X\ \frac{100}{WWAR} = 0.126\ X\ \frac{100}{2.5} = 5.04\ m^2$

For WWAR of 1.5% = $0.126\ X\ \frac{100}{WWAR} = 0.126\ X\ \frac{100}{1.5} = 8.4\ m^2$

3.4.4 Hydraulic loading

One of the factors that affects the efficiency of SSFCWs is the hydraulic loading rate (HLR). The HLR is the flow added per unit of time to the filter surface. It expresses itself in m/day or cm/day. The HLR is inversely variable as the retention time for a given SSFCW depth and based on the CW configuration (Torrens et al. 2009; Saeed and Sun 2012). HRTs applied to the VFCW pilot scale were calculated from long-term meteorological records data, namely the annual rainfall measured in urban areas in the UK.

3.4.5 Runoff entering CW system

For each event, the average rainfall depth (event = 1 rainy day) is calculated based on the date and result shown in Table 3.4 as follows:

$$ARE = \frac{AAR}{RD_S} = \frac{821}{147} = 5.59\,\frac{mm}{event}$$

where: ARE means average rainfall per event, AAR means average rainfall per event, RD_s means number for rainy days per year.

Representative sizing values were calculated in Section 3.4.3 for 1.5%, 2.5%, and 5% WWARs. Following guidelines from the SUDS Handbook, an 80% impervious catchment is proposed (CIRIA 2007). Thus, the volumes of influent dose were calculated as below:

$$For\ WWAR\ 5.0\% = 5.59\ L/m^2\ X\ 2.2\ m^2\ \ X\ \ 0.8\ \ = 11.3\ L/Event$$

$$For\ WWAR\ 2.5\% = 5.59\ L/m^2\ X\ 5.04\ m^2\ \ X\ \ 0.8\ \ = 22.5\ L/Event$$

$$For\ WWAR\ 1.5\% = 5.59\ L/m^2\ X\ 8.40\ m^2\ \ X\ \ 0.8\ \ = 37.6\ L/Event$$

Subsequently, the number of rain events per week was determined by dividing the total number of rainy days in a year by 52 (weeks in a year), accordingly:

$$Rainy\ events\ per\ week = \frac{147}{52} = 2.8 = 3\ times\ per\ week$$

Therefore, the weekly volumes of influent had been estimated as follows:

$$For\ WWAR\ 5.0\% = 3\ x\ 11.3\ \ = 33.9\ \ L/week$$

$$For\ WWAR\ 2.5\% = 3\ x\ 22.5 = \ 67.5\ \ L/week$$

$$For\ WWAR\ 1.5\% = 3\ x\ 37.6\ \ = 112.8\ L/week$$

The stormwater loading regime calculated according to the equations above are summarised in Table 3.9.

Table 3.9 Semi-synthetic urban stormwater loading regimes details across the pilot-scale VFCWs.

Loading routine case	WWAR	Pilot-scale CW number	Wetting/drying regime	Dosing patterns
1	2.5%	CW1, CW2, CW3 & CW4	Wet conditions	3 doses X 22.5 l= 67.5 l/week
2	5.0%	CW5	Wet conditions	3 doses X 11.3 l= 33.9 l/week
3	1.5%	CW6	Wet conditions	3 doses X 37.6 l= 112.8 l/week
4	2.5%	CW7	Partially dry conditions (PDC)	3 doses X 22.5 l= 67.5 l/week cycle 1 week Wet to 1 week Dry
5	2.5%	CW8	Extended dry conditions (EDC)	3 doses X 22.5 l= 67.5 l/week cycle 1 week Wet to 4 weeks Dry

3.4.6 Wetting and drying periods

Inflow regime no. 4 (see Table 3.7) comprised of intermittent wet (three doses weekly) and dry weeks (zero doses weekly). The trend was: wet for one week; dry for one week; wet for one week; dry for one week etc. The aim of this scheme was to repeat dry weather spells for the short term and to determine their effect on CW efficiency. It also provides some reflection of the UK's changeable weather, where patterns of rainfall can be more stochastic in nature relative to other countries experiencing regular seasons of monsoons. This flow system has been termed "partial dry conditions" or PDC.

Inflow regime no. 5 (see Table 3.9) was a system of both rainy and dry weeks. This structure is intended to evaluate the CW system's output when enduring long stretches of decreased rainfall/drought. The trend was: wet for one week (three doses weekly); dry for four weeks (zero doses/four weekly); wet for one week; dry for four weeks etc. This system has been referred to as "extended dry conditions," or EDC. The wet to dry weeks' ratio was based on the decreased rainfall in East Anglia in spring 2011. The Met Office reported a three-month span regarded as especially warm and dry. In March 2011 the area recorded just 2.1 days of rain > 1 mm, followed by 1.8 days in April and four days in May. That's a total of eight rainy days in three months. Based on this data the wetting and drying regime was determined as follows:

- The March-May duration consists of 13 weeks, totalling 39 wet days according to the defined dose schedule of three doses per week.

- There were only eight rainy days in the 2011 drought which gives a ratio of eight wet days: 31 dry days
- Therefore, wet to dry ratio was estimated by 31/8 = 3.9 ≈ 4 and taken, as 1:4
- As this experiment is performed in weeks, there was a single rainy week for regime no. 3 followed by four dry weeks in one period
- For any "dry season" there were three full cycles representing long periods of drought. The CWs were dosed using regime 1, during the "dry seasons."

As shown in Figure 3.1, which CW units were used to examine the effects of the different dry periods and the unit wetting/drying regime.

3.4.7 Additional considerations for deriving the loading volumes

The physical processes that turn rainfall into runoff are dynamic and highly variable and cannot be reliably reproduced. However, some mathematical models and equations were developed using simplifying assumptions and empirical evidence to simulate hydrological processes and to predict the volumes and rates of runoff. Choosing the correct design or equation depends on parameters such as the drainage area size and availability of data. Therefore, although volumes of loading dosed in VFCWs were generated from 33-year rainfall data (as explained in Section 3.4.5), variations in storm strength, duration, and frequency may not have been accurately simulated. As well as the Wallingford Method (Sewers. 1981) was used for comparative purposes to calculate the volumes of stormwater runoff/loading considering differences in storm strength, duration and frequency. Firstly, the UK's proposed minimum return period is 10 years (Ellis et al. 2003b), while the Environment Agency in England and Wales recommends designs for flood-prone catchments that can cope with a 1:200-year flood (Shutes et al. 2005). In fact, both the Environment Agency (England/Wales) and the US Environmental Protection Agency support the Schueler recommendation (1992) for CWs to maintain 90% of the storm events. So, a storm event consisting of a one-minute duration and 30-year return period (AAR was generated from 33-year data) was selected for comparison, and the measured loading levels are provided in Table 3.10.

Table 3.10 states that attenuation and storage of peak flows may be needed to reduce extra runoff that may result from new catchment developments so that VFCWs can serve the additional purpose of reducing stormwater runoff volume and rate; ensuring that stormwater is properly handled prior to discharge into the receiving waterway; and that groundwater quality is protected.

Table 3.10 Estimated runoff from a catchment at Cardiff (Wales).

Catchment details		Design storm details			
M5-60 (mm)	19	Simulated area (m2)	8.40	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 runoff (mm/hr)	207.6	207.7	207.8
Routing	1.3	Design Rainfall Intensity (l/s/m2)	0.006	0.006	0.00677
coefficient		Percentage Runoff (%)	88.87	88.87	88.87
Total design runoff (l/s)			0.43	0.26	0.13

Furthermore, both the rainfall occurrence and the region it falls on are factors that can affect the subsequent runoff. High intensity rainfall, for example, would usually produce a greater peak discharge than rainfall over a longer period. Similarly, highly porous or permeable soils which can easily absorb rainfall will produce a lesser amount of runoff than soils with more restrictive infiltration. In addition, dense vegetation tends to intercept and help infiltrate the rainfall, thus reducing the volumes and rates of runoff. In comparison, impervious areas such as roadways and rooftops avoid infiltration and increase the volumes and rates of runoff, whereas areas with shorter accumulation periods would have higher peak runoff levels than those with longer runoff periods. However, if all these variables are accounted, then CWs built to manage the highest peak flows or loads will produce massive, over-engineered processes. Effluent quality levels will also have to be greatly lowered. Instead, following preliminary treatment, flow volumes above design limits will have to be redirected or discharged directly into receiving waters. Similarly, runoff associated with the first flush following long precedent dry periods will result in highly polluted flows that could easily interrupt and mobilise the contaminated substrate and damage the vegetation of the wetlands. The design of a full-scale VFCW will therefore consider an acceptable design storm return time, which in turn defines the size and volume of the wetlands.

3.5 Hydrological budget of the VFCWs

The net change in the volumes of influent and effluent water was controlled using Equation 3.4, the dynamic water balance. Subsequently, the effects of precipitation and evapotranspiration were considered in the calculations of the mass balance.

$$D_s = Q_{in} + (P - ET - I)\, X\, A - Q_{out} + Q_R + GW_{in} \qquad (3.2)$$

where: D_s is net volume change (m^3/d), Q_{in} means daily inflow to each unit (m^3/d), P means daily precipitation rate (m/d), ET means rate of evapotranspiration (m/d), I means rate of infiltration (m/d), A means CW surface area (m^2), Q_{out} means daily outflow from CW (m^3/d), Q_R means catchment runoff (m^3/d), GW_{in} means groundwater inlet (m^3/d) which is neglected.

The daily precipitation (P) was thus equal to Cardiff City's Met Office record, while due to the small CW surface area, water loss due to evaporation was considered negligible. Likewise, the rate of evapotranspiration (ET) was extracted from the investigated wetland macrophyte literature values for the ratio (ET/E) (Dong et al. 2011).

3.5.1 VFCWs hydraulics

VFCWs were dosed through sluggish batch inflows and drained at the bottom of each CW unit via a control tap. After the first batch the patterns were replicated 24 hours later. The VFCWs were drained at the end of the processing time, opening the outlet tap at the bottom of each VFCW. Outflow volume and velocity of the eight VFCWs were measured by Kiiza (Kiiza 2017), based on the results obtained, Table 3.1.1 shows a representation of the hydraulics of the eight pilot-scale VFCWs.

Table 3.11 The inflow, outflow volumes and discharge velocity.

CW no.	WWAR (%)	Substrate	Inflow (Ll)	Threshold velocity (m/s)	Outflow (l)
CW1	2.5	Loamy sand	22.5	0.764	21.2
CW2	2.5	Loamy sand	22.5	0.822	20.8
CW3	2.5	Gravel	22.5	0.969	22.4
CW4	2.5	Blast furnace slag	22.5	0.999	22.4
CW5	5.0	Loamy sand	11.3	0.587	11.2
CW6	1.5	Loamy sand	37.6	0.939	34.4
CW7	2.5	Loamy sand	22.5	0.881	21.4
CW8	2.5	Loamy sand	22.5	0.852	21.6

A Gardena 8188-29 Automated Electronic Water Smart Flowmeter (8.5 mm internal diameter) was used to measure the effluent discharges. In all VFCWs, the discharge velocities decreased with the discharge time. Typically speeds of all CWs ranged from 0.59–0.99 m/s, higher than those recorded in Torrens et al. (2009), possibly attributable to discrepancies in the rate of hydraulic loading and the size of the unit of pilot-scale CW investigated.

The unit CW5 of the loamy sand substrate recorded the lowest velocity. Gravel and BFS media in CW3 and CW4 units however reported slightly higher velocities than all loamy sand CWs (Figure 3.7). The disparity in outflow velocities is proportional to the size of the media grain. The larger particle size and thus the more porous gravel and BFS had higher outflow velocity compared to the fine and small particles of loamy sand VFCWs.

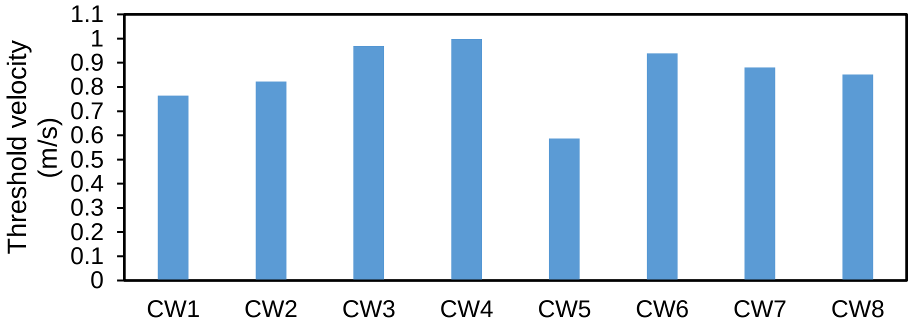


Figure 3.7 Threshold discharge velocities of the VFCWs.

On the other hand, the loamy sand unit CW6 (1.5% WWAR) produced discharge velocities like that of BFS and gravel units (2.5% WWAR). The reasonably high velocity of discharge in CW6 may have been due to the pressure caused by the load of the large volume semi-synthetic stormwater (37.6 L). Both gravel and BFS substrates had the lowest infiltration ability, while unit CW6 retained the most stormwater amongst the loamy sand VFCWs. Nevertheless, there was no clogging during the experimental phase in all the CWs. It indicates the biofilters were ideal for handling powerful loads. In addition, the environmental conditions, loading systems, and rest times between inflows were enough for drying and mineralising pollutants removal.

3.6 Experiments operation

The study's experiments were designed and carried out for 544 days by Lucas (Lucas 2015) and Kiiza (Kiiza 2017). Using the same method and steps used in the previous studies, all VFCWs continued to be operated on an experimental scale using a gentle slow filling. The experiment begins with the preparation of the appropriate amount of semi-synthetic stormwater, which was described in Section 3.3.3. In the VFCWs the influents stormwater was dosed on the same week for three consecutive days as outlined in Table 3.9 and figure 3.8 On Monday of each week, stimuli were dosed into the VFCW and replicated on two non-consecutive days (i.e. Monday, Wednesday, and Friday). But the regime was repeated on three consecutive days of the same week on occasions when dosing was not performed on a Monday.

During the feeding, the semi-synthetic stormwater was carried in a five litres graduated bucket from the mixing container to each VFCW. In each CW cell, influential stormwater prepared from the slurry was directly and slowly poured onto the top surface of the media during the filling stage. The slow feeding method has been used to mitigate the effect of high flow on the biofilter media structure.

Also, the existence of plants in the CW units further decreased the impact on the media dissemination of the leading stream. In addition, a sequence of five passes were applied to CWs 1, 2, 3, 4, 7, 8, and three passes for WC5 and eight passes for CW6, so that the semi-synthetic stormwater dosed in the VFCWs was of equal concentration. The experiment operation procedure is summarised in Figure 3.8 This study aimed to highlight the effect of fixed long retention time on pollutant removal in tidal flow VFCWs. Furthermore, it is recommended that this value allows enough time to treat bacteria, degradable organics, and toxic species contained in fractions of finer solids (Halcrow/UPRC 2000). This fixed extended retention time would allow for anoxic conditions to generate in the CW to aid the denitrification process. Therefore, in the pilot-scale CWs each dose of stormwater was retained for 24 hours. The water was released from the bottom of the CWs through the outlet tap exactly 24 hours after the inflow dosing.

3.6.1 Sample collection procedure

The experimental samples collected were analysed in the Characterisation Laboratories Environmental Engineering Research (CLEER), located at Cardiff School of Engineering on the ground floor of the South Buildings.

Inflow sampling was performed three times a week (one for each dose), thus outflow sampling was limited to once a week because of analytical cost constraints. Every week outflow analysis was adequate to perform a thorough study due to the extended time span during which the experiment was performed. Inflow samples of semi-synthetic stormwater were taken from the mixing tank immediately before the dosage.

From the outlet at the bottom of each CW unit, outflow samples were taken after the 24 hour-retention period at the time of release. Samples were taken during rainy weeks only for those units that were experiencing dry weeks.

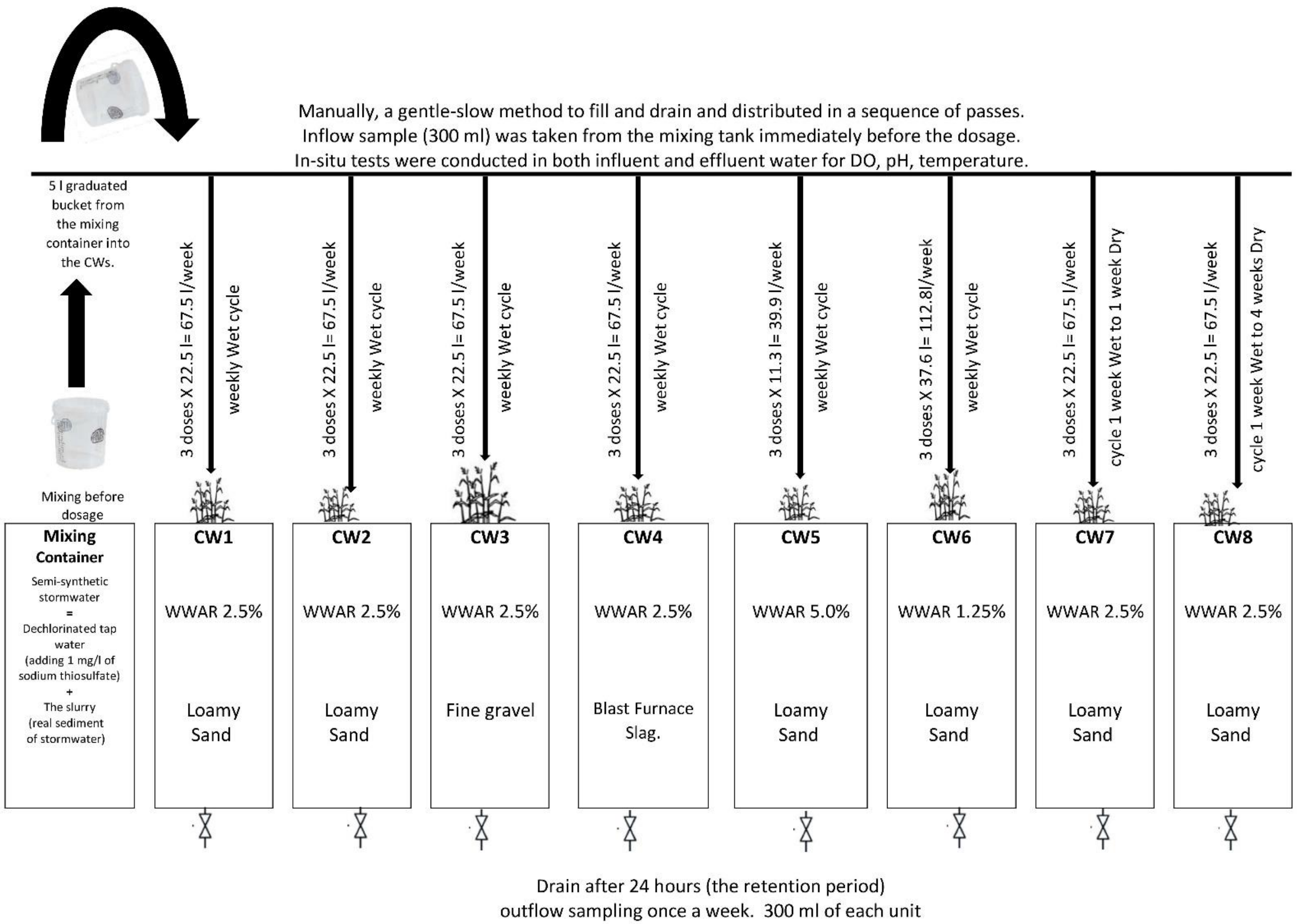


Figure 3.8 Schematic diagram for experiment operation procedure at variable conditions.

3.6.2 Laboratory analysis

Total suspended solids (TSS), total nitrogen (TN), ammonium-nitrogen (NH4-N), nitrite-nitrogen (NO_2-N), total phosphorus (TP), orthophosphate (PO_4-P), total Fe, Zn, Pb, Ni, Cd, Cr, Cu, pH, temperature, and electrical conductivity (EC) were the parameters measured and recorded. The dissolved metal concentrations were also analysed over a seven-week duration only during the experimental process due to time and budget constraints and serves as a supporting analysis to the main experiment. In the last period of operation, starting from day 454, dissolved oxygen (DO) was measured as well. None of the samples were filtered except at the seven-week analysis where the samples were divided into filtered and unfiltered samples to partition the concentration of heavy metals and TP. Filtering was done directly after the samples had been collected using vacuum filtering through a 0.45 µm filter.

In-situ tests were conducted in both influent and effluent water for DO, pH, temperature and EC, while all other pollutant concentrations were measured in the laboratory using the samples taken at the time of dosing (for influent) or releasing (for effluent). 300 ml bottles made of polyethylene were used to collect the samples.
Water samples of 40 ml volumes were acidified with nitric acid (HNO3) for metal analysis and stored in a fridge at a temperature of < 4°C, as suggested by standard methods (APHA 2012). TSS tests were conducted immediately after sample collection so no additional storage requirements were needed. TSS was measured using a pre-set program in the DR3900. Samples of 10 ml were placed in the Hach sample bottles and shaken vigorously before analysis.

The pH, temperature, DO, and EC measurements were recorded using a HANNA HI 98194 multiparameter meter. Heavy metals and TP concentrations were measured using an Optima 210 DV ICP OES (optical emission spectrometer coupled inductively with plasma, Perkin Elmer). The ICP detection limits are illustrated in Table 3.12. The concentrations of TN, NH4-N, NO2-N, NO3-N, PO4-P, and TSS were measured using a benchtop spectrophotometer from Hach Lange DR3900.

Table 3.12 The lower detection limits of ICP-OES.

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

The detection limits for spectrophotometers are included in Table 3.13 TN and PO4-P were analysed using Hach Lange's cuvette tests, for which all the analytical reagents needed were given, along with the analytical vessels. Prior to testing, TN required digestion at 100°C, and this was accomplished with the use of the Hach Lange LT-200 thermostat. NH4-N concentrations were measured using the "Nessler" method which requires a pre-analysis addition of Nessler liquid reagent. NO2-N and NO3-N were measured using reagents for powder pillows (diazotisation and reduction of cadmium, respectively).

Table 3.13 The lower detection limits of the Hach Lange DR3900 benchtop spectrophotometer.

Parameter	Lower concentration detection limit (mg/l)
TSS	5.0000
TN	0.1000
NH4-N	0.0212
NO2-N	0.0020
NO3-N	0.0100
PO4-P	0.0500

Furthermore, this included internal instrument calibration (Optima 210 ICP-OES) and then the determination of system detection limits for each item measured in the research (Tables 3.8 and 3.9). The limit of detection was achieved by multiplying the standard deviations of the 20 blank replicates. The blanks were produced from a Milli-Q analytical reagent water purification device (Millipore), using ultrapure de-ionised water. The blank samples were tested against solutions prepared by a high purity ICP multi-element calibration method being diluted successively. The lower standard level of calibration was set at 0.10 mg/l while the upper limit was 10 mg/l. While variable, the findings in

Tables 3.12 and 3.13 indicate that the detection limits ranged from 0.001 mg/l to 0.005 mg/l for all the elements.

Chapter 4: Evaluation and characterisation of long-term urban stormwater pollutants immobilisation

4.1 Introduction

Although the increasing use of CWs within urban areas to reduce stormwater pollutants has been investigated, long-term performance evaluation under seasonal effects, with frequent wetting and drying events utilising different substrates has been limited. Therefore, the need to deeply understand the underlying issues of pollutants removal performance, removal mechanisms, substrates effect, and the changing of physical stormwater characteristics has become a necessity. The eight pilot-scale CWs were designed and constructed to investigate different variable design aspects on overall removal under long-term operation conditions.

In this chapter, the first four cells of pilot-scale CWs were included in the long-term performance evaluation where three substrates of loamy sand, gravel, and BFS were used and a wetting and drying regime of 22.5 l three times a week was applied (wetland/watershed area ratio 2.5%). Therefore, the specific objectives of this chapter are (i) to evaluate the changing of the substrates chemical characteristics before and after long-term operation and in the same time analysis and differentiate between the removal of pollutant particulate and dissolved fractions; (ii) to perform the long-term removal behaviour of solids, heavy metals, and nutrients from semi-synthetic urban stormwater, compare between the substrates for the best performance by exploring the removal mechanisms ; (iii) to fully understand the mechanisms of the N transformation fractions within the substrates in the nitrification and denitrification processes; and (iv) to track the changes in hydrogen ion concentration, electrical conductivity, and temperature of the influent stormwater and the treated stormwater and link the changes with the kinetics of the pollutant from the liquid phase to solid phase.

4.2 Mass balance analysis of solids, heavy metals, and nutrients removal

Despite the fact that the eight pilot-scale stormwater VFCWs all contained the same volume of the three main substrates (loamy sand, gravel, and blast furnace slag (BFS)), every substrate had a different bulk density and porosity. Moreover, the application of various wet-dry operation regimes for the loamy sand substrate makes it difficult for data explanation and comparison between the various design factors and operating conditions. Therefore, to empower relative examinations between VFCWs, a mass balance approach was utilised based on the mass of the used substrate and amount of loaded pollutant. Thus, the mass of influent pollutant into the system per kg of the substrate and the mass of pollutant removed by the system per kg of substrate per each poured volume were computed (see Equation 4.1 and 4.2).

$$PL_d = \frac{C_i \times V}{M} \tag{4.1}$$

$$R_d = \frac{(C_i - C_e) \times V}{M} \tag{4.2}$$

where: PL_d is the discrete pollutant loading (mg/kg), R_d is the discrete pollutant removal (mg/kg) of substrate, C_i is the influent pollutant concentration (mg/l), C_e is the effluent pollutant concentration (mg/l), V is the inflow semi-synthetic urban stormwater volume (l), and M is the mass of the used substrate (kg).

To represent the outcoming data from the system in a scientific and comparable way, the accumulated inflow volume into the system (V_a) in litre measuring units was calculated according to the applied wet-dry operation condition of each CW (see Equation 4.3).

$$V_a = V + V \times N_i \tag{4.3}$$

where N_i is the number of times that semi-synthetic stormwater was poured into the pilot-scale VFCW since the first loading (number of the cycle).

4.3 Chemical characteristics of the substrates

Before treating semi-synthetic urban stormwater by loamy sand, gravel, and BFS substrates, the chemical compositions of these substrates were dominated by a high content of Ca, Fe and Mg and TC (except BFS regarding TC content), see Table 4.1. Additionally, the BFS substrate followed by a loamy sand substrate has a significant amount of silica content 118 mg/g and 48 mg/g respectively. The calcium silicates could play a major role in pollutants removal through their high activity of electrochemical heterogenetic surface with easy calcium silicates hydrolysation (Dimitrova 1996). The substrates also contain a minor amount of Al in the following order: 45 mg/g of BFS; > 13 mg/g of loamy sand; > 4 mg/g of gravel, which again can give a preferential removal for BFS over the others, where the sorption of metal ions on alumina silicates is effective in alkaline solution generated by releasing hydroxyl ions as a result of the dissolution process (Dimitrova 2000).

After passing the semi-synthetic urban stormwater through these substrates over more than two and half years of tidal flow operation CWs, a clear reduction in Ca content with an increase in metals ions concentrations was noticed in the chemical analysis of these substrates, as can be seen in Table 4.1. When the stormwater contacts with the substrates (loamy sand and BFS), the Ca concentration in the liquid increases due to the dissolution, resulting in replacing and exchanging Ca ions in the substrates (especially BFS) with metals.

Table 4.1 Elemental composition analysis for the substrates utilised in the pilot-scale CWs before and after treating semi-synthetic urban stormwater.

Elemental	Substrates chemicals characteristics						
	Before treatment			After treatment			
				Loamy sand		Gravel	BFS
	Loamy sand	Gravel	BFS	CW1	CW2	CW3	CW4
	mg/g						
Zn	0.35	0.26	0.13	0.57	0.55	0.22	0.31
Cu	0.01	-	-	0.15	0.18	0.01	0.03
Pb	-	-	-	0.06	0.03	-	-
Cd	-	-	-	-	-	-	-
Cr	0.15	-	-	0.26	0.21	0.10	0.41
Ni	-	-	-	0.36	0.23	-	0.19
Fe	62.82	43.61	12.51	63.11	64.59	84.02	64.09
Ca	317.29	197.81	232.96	289.22	297.47	188.08	215.58
Mg	5.68	89.11	39.88	4.56	5.02	88.59	38.12
K	3.13	0.97	5.44	2.56	3.23	2.15	4.81
Al	13.18	3.48	45.86	11.76	11.96	4.70	46.86
Mn	0.42	1.09	2.26	0.38	0.40	2.10	3.43
Si	48.41	26.28	118.40	41.68	42.45	25.81	116.07
S	0.07	0.42	6.58	0.35	0.36	1.12	4.44
TC	114.48	137.70	2.98	118.08	117.72	125.24	9.91
IC	89.30	115.50	0.13	88.60	79.30	110.10	2.60
OC	25.18	22.20	2.85	29.48	38.42	15.14	7.31

From Table 4.1, there was an increase and slight decrease in organic carbon (OC) content and inorganic carbon (IC) content, respectively, before and after using the substrates, which could be explained by the effectiveness of using CWs as a bio-retention and adsorption system at the same time.

4.4 Stormwater pollutants partitioning analysis

To fully understand the removal mechanisms of stormwater constituents (mainly heavy metals and P), a clarification of which forms of these metals and P are present in stormwater and their relative removal is needed. Therefore, a partitioning analysis for influent and effluent stormwater was conducted. The mean percentages and the variations of heavy metals and phosphorus partitioning and their total and dissolved concentrations for influent and treated semi-synthetic urban stormwater were monitored over seven weeks of analysis, as shown in Table 4.2. Partitioning analysis between dissolved and particulate phases displayed that Fe and Cr were about 100% entirely particulate metals, while a range of 45% to 98% was found in solid phase for Cd, Ni, Zn, Pb, and Cu. Although several studies claimed that most of the heavy metals in urban stormwater are attached and/or adsorbed into particulates (Maniquiz-Redillas and Kim 2014; Djukić et al. 2016; Gill et al. 2017), no clear correlations between TSS and heavy metals and P were observed, which could be explained by either the weak adsorption process between dissolved metals and TSS (Maniquiz-Redillas and Kim 2014) or precipitation of these anions and cations alongside the fine particles usually found in roads (i.e. sand, clay) in smaller and variable weight relative to SS.

The partitioning analysis between the dissolved and particulate phases of analysed parameters in the treated semi-synthetic stormwater are summarised in Table 4.2. It can be noticed that there was effective removal for Pb, Ni, Cd, Cr, and Cu with effluent concentrations below the detection limits, indicating acceptable removal for these ions under a wide range of CW design and operation. Although 100% of Fe and 88% of Zn was found as particulate in the influent stormwater, nonetheless, their fractions were detected as mostly particulate and dissolved fractions respectively (except CW4 that predominantly removed Zn to below the detection limit which could be due to the effectiveness of BFS physicochemical properties in the pollutants retention). However, an increasing Zn dissolved fraction from the inflow to outflow in all loamy sand CWs was found while it was reduced in gravel CW and completely removed in BFS CW, as shown in Figure 4.1; this will be explained more in Chapter 5.

Table 4.2 Mass balance of heavy metals and phosphorus partitioning analysis of the semi-synthetic urban stormwater influent and after passing through eight pilot-scale CWs (mean ± SD).

CW	TSS mg/l	Phase	Heavy metals							P
			Fe	Zn	Pb	Ni	Cd	Cr	Cu	
Influent			%							
		Particulate	99.69 ±0.82	88.16 ±5.53	98.49 ±2.17	83.94 ±13.47	52.65 ±51.57	100.00 ±0.00	99.05 ±2.52	37.00 ±9.76
		Dissolved	0.31 ±0.82	11.84 ±5.53	1.51 ±2.17	16.06 ±13.47	47.35 ±50.83	0.00 ±0.00	0.95 ±2.52	63.00 ±9.76
			mg/l							
	179.000 ±21.674	Total	4.485 ±0.265	0.575 ±0.048	0.373 ±0.084	0.041 ±0.023	0.014 ±0.023	0.014 ±0.010	0.130 ±0.019	0.986 ±0.052
		Dissolved	0.013 ±0.030	0.066 ±0.020	0.006 ±0.007	0.009 ±0.011	0.014 ±0.025	0.000 ±0.000	0.001 ±0.002	0.623 ±0.093
1	28.857 ±5.581	Total	0.202 ±0.026	0.090 ±0.064	0.004 ±0.004	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.326 ±0.048
		Dissolved	0.002 ±0.003	0.133 ±0.057	0.001 ±0.001	0.000 ±0.000	0.008 ±0.015	0.000 ±0.000	0.004 ±0.004	0.313 ±0.064
2	11.571 ±4.894	Total	0.068 ±0.037	0.085 ±0.046	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.345 ±0.055
		Dissolved	0.001 ±0.002	0.103 ±0.028	0.002 ±0.004	0.000 ±0.000	0.001 ±0.002	0.000 ±0.000	0.003 ±0.002	0.343 ±0.097
3	11.714 ±3.653	Total	0.248 ±0.076	0.023 ±0.010	0.008 ±0.007	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.277 ±0.050
		Dissolved	0.000 ±0.001	0.027 ±0.010	0.002 ±0.003	0.000 ±0.000	0.002 ±0.005	0.000 ±0.000	0.000 ±0.000	0.243 ±0.057
4	9.857 ±3.270	Total	0.044 ±0.017	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.282 ±0.057
		Dissolved	0.000 ±0.001	0.000 ±0.000	0.003 ±0.007	0.000 ±0.000	0.002 ±0.005	0.000 ±0.000	0.000 ±0.000	0.258 ±0.074
5	11.571 ±3.910	Total	0.060 ±0.015	0.082 ±0.011	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.250 ±0.057
		Dissolved	0.000 ±0.000	0.095 ±0.007	0.001 ±0.002	0.000 ±0.000	0.000 ±0.001	0.000 ±0.000	0.003 ±0.003	0.234 ±0.074
6	20.500 ±4.796	Total	0.133 ±0.031	0.039 ±0.009	0.000 ±0.001	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.316 ±0.059

CW	TSS mg/l	Phase	Heavy metals							P
			Fe	Zn	Pb	Ni	Cd	Cr	Cu	
		Dissolved	0.001 ±0.002	0.052 ±0.010	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.358 ±0.047
7	27.750 ±3.304	Total	0.191 ±0.044	0.083 ±0.019	0.005 ±0.009	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.314 ±0.030
		Dissolved	0.001 ±0.008	0.104 ±0.005	0.004 ±0.005	0.000 ±0.000	0.003 ±0.006	0.000 ±0.000	0.003 ±0.003	0.292 ±0.065
8	18.167 ±9.283	Total	0.113 ±0.055	0.060 ±0.013	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000	0.306 ±0.059
		Dissolved	0.113 ±0.055	0.078 ±0.009	0.000 ±0.000	0.000 ±0.000	0.003 ±0.007	0.000 ±0.000	0.001 ±0.001	0.368 ±0.232

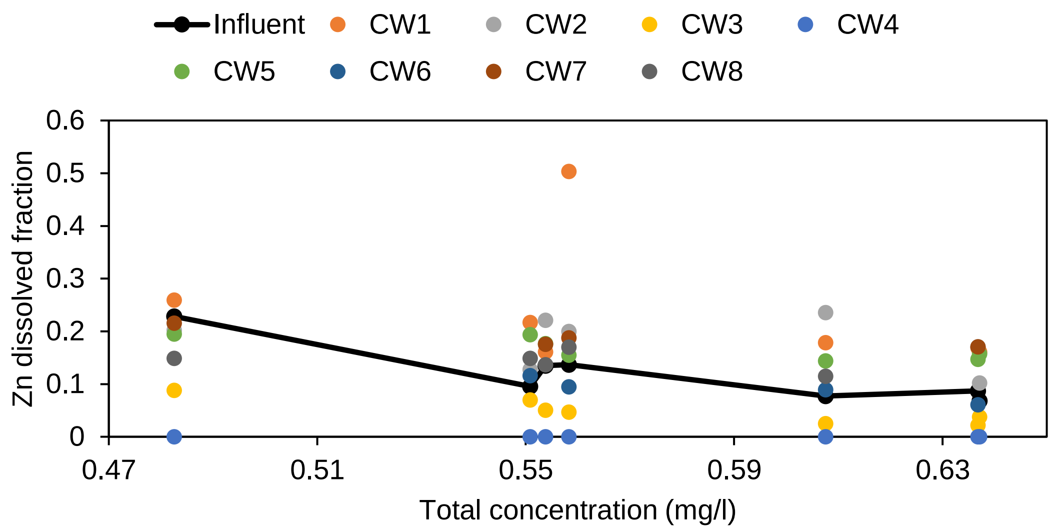


Figure 4.1 Influent and effluent Zn dissolved fraction relative to the total influent concentration resulting from seven weeks of partitioning analysis.

Additionally, P particulate fraction was almost retained within all eight CWs and about 50% to 70% of influent dissolved was removed within the substrates' particles, indicating the acceptable biochemical retention characteristics of these substrates. Similar results were found by Shrestha et al. (2018) who analysed more than 800 samples at bio-retention CW to find higher PO_4-P concentration (69%) than particulate-P (31%) in the effluent TP concentration. However, the partitioning analysis was run for only seven weeks of operation and a complete picture of performance is discussed in the next sections.

To explore the result of influent semi-synthetic stormwater and find out how the total pollutant concentration is related to its dissolved fraction, a relation between the dissolved fraction and the total concentration was pointed out. Figure 4.2 demonstrates the dissolved fraction of Zn and TP in influent samples indicating an inverse correlation between total concentration and dissolved fraction. This means more metals entirely particulate at higher total concentrations and these findings coincide with Gill et al. (2017) study.

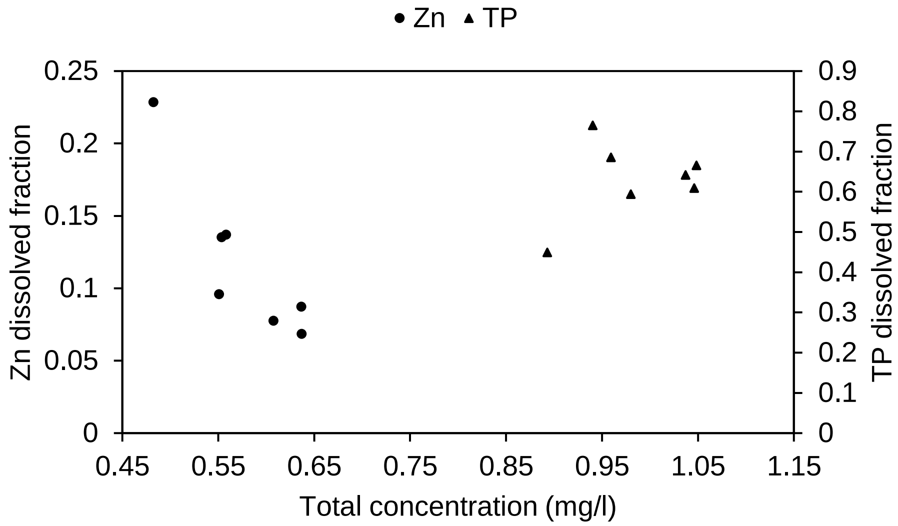


Figure 4.2 Correlation between Zn and TP dissolved fractions and their total concentrations in the influent of semi-synthetic urban stormwater.

4.5 Stormwater pollutants removal evaluation relative to the substrates

4.5.1 Total solids removal

The performance of different substrate types used in the pilot-scale VFCWs with intermittent downflow conditions for TSS removal from semi-synthetic urban stormwater is demonstrated in Figure 4.3a, b, and c for the loamy sand, gravel, and BFS, respectively. The results of the identical design and operation for CWs 1 and 2 were averaged and the standard deviations for the variation in performance were obtained as shown in Figure 4.3a. In general, the removal weight in comparison to the loading weight was constant for the three substrates and there were slight variations in the removal between the influent and effluent TSS for the loamy sand and gravel at the start of loading rate, and then these variations were minimised after the accumulating poured volume reached 2000 l. It should be noticed that the gradual improvement in TSS removal over the accumulated loading volume leads to a reduction this variability. The range of influent TSS loading (29.7 - 87.7 mg/kg) reduced at the systems outlet to achieve a discrete removal range of 21.1 - 64.1 mg/kg, 16.7 - 75.3 mg/kg, and 27.8 - 84.4 mg/kg for loamy sand, gravel, and BFS substrates, respectively.

To compare the performance relative to previous studies, the averages of removal efficiency (mean ± SD) for loamy sand, gravel, and BFS CWs were in the following order: 91.1 ± 6.9%, 95.0 ± 3.4%, 94.5 ± 4.5%, and 94.6 ± 3.0%, indicating that the substrates performed nearly equally, apart from CW1, with the least variation in the removal marked for CW4 (see Table 4.3). However, to rank the CWs according to their performance, a statistical analysis was conducted. Due to the volatile data, and the one-way ANOVA test assumptions of normal distribution and homogeneity of variance, non-parametric analysis (Kruskal-Wallis test) was used to find if the TSS removal performance of CWs using the same wet-dry regime and WWAR and the three substrates are statistically equal or different. The result of the statistical analysis showed that there are significant differences between the first four CWs ($p=0.000$), where CW1 performed differently toward TSS removal from CW2, 3, and 4 ($p < 0.05$) while there were not statistical differences between CWs 2, 3, and 4 ($p = 1.000$). Moreover, these levels of TSS removal are comparable to other studies using similar CW configuration and locate within the range of 72.2 to 99.3% (Babatunde et al. 2008; Blecken et al. 2011).

Suspended solids removal from the inlet water in such a passive treatment process is one of the CW features. As the inlet urban stormwater has continuously loaded to the CWs, the suspended solids are subsequently trapped between and within the pores in a complicated internal removal mechanism. At the beginning of the stormwater loading, the built-up and trapping processes can explain the variation and fluctuation in TSS removals relative to inlet TSS loads in loamy sand and gravel substrates as can be seen in Figure 4.3a and b. Meanwhile, the BFS substrate showed constant TSS removal, relative to inlet load, from the beginning of the loading period, which can be explained by its physicochemical properties and then its affinity for TSS.

The primary TSS removal mechanisms in VFCWs are settling and filtration or interception. These mechanisms depend on solids characterisation of specific water sources (size and constituents). For example, solids in domestic wastewater mainly consist of organic, while metals are the big portion of solids constitution in urban and agriculture stormwaters, which might affect its capturing through the filtration process (Kadlec and Wallace 2009b). Metcalf and Eddy (2014) explained the mechanisms of suspended solids trapping within a granular medium filter which can be classified mainly into straining (particle size and pore size are the main factors), sedimentation where the particle settles on the medium according to Newton law, interception where the particle is removed through contact with the surface of the filtering medium, and physical or chemical adsorption where the particle is attached or bonded to the medium or another attached particle through electrostatic and van der Waals forces or chemical interaction.

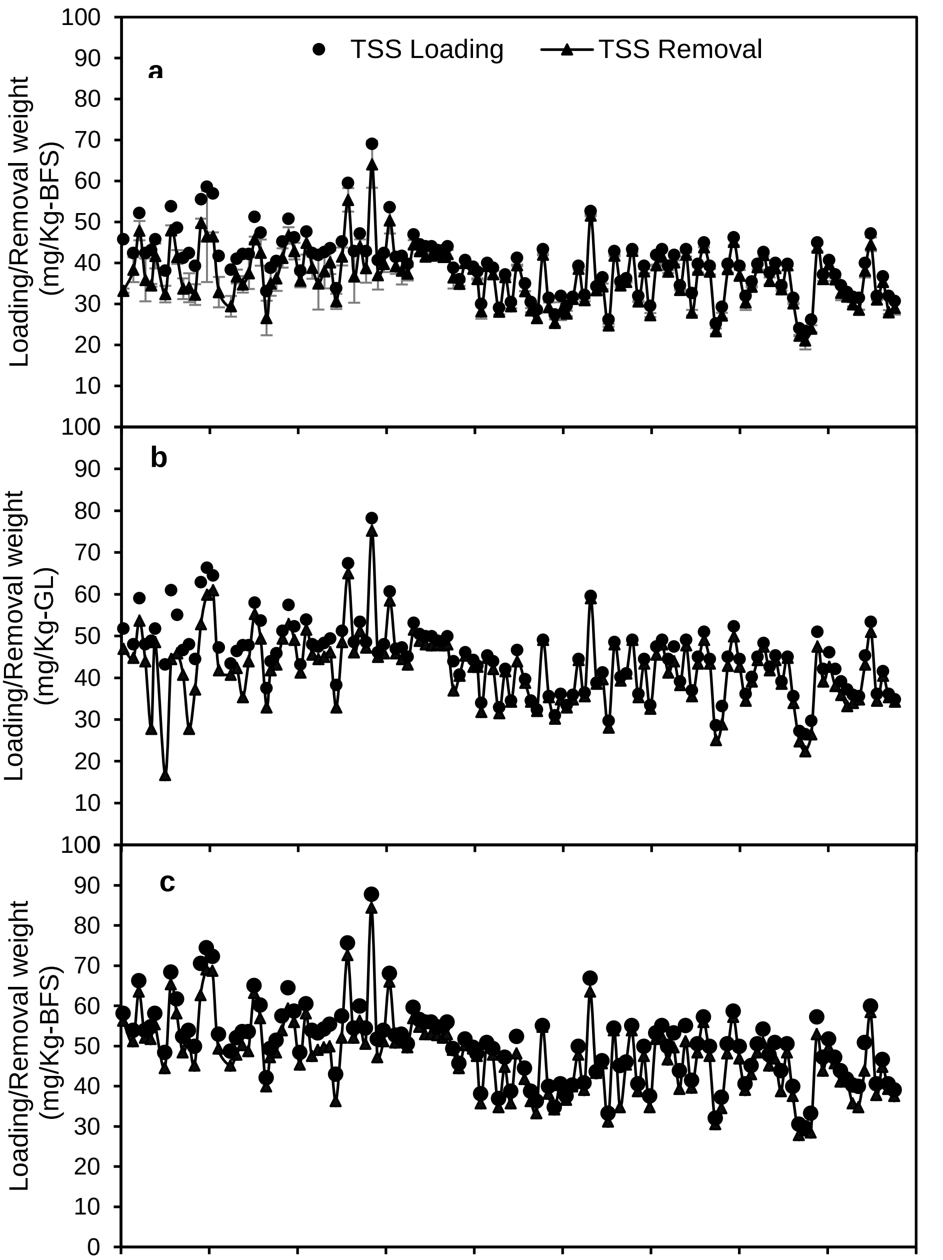


Figure 4.3 The loading and removal weight of TSS from semi-synthetic urban stormwater fed into pilot-scale VFCWs packed with (a) loamy sand substrate of CWs 1 and 2, (b) gravel substrate of CW 3, and (c) BFS substrate of CW 4. Error bars represent the variation in the removal performance of CWs 1 and 2.

The loamy sand used in CWs 1 and 2 contains a high portion of sand particles, thus, it could be suggested that the main TSS removal mechanisms in CWs 1 and 2 packed with the loamy sand substrate are straining and settling with the minor effect of adsorption mechanism on overall removal. Gravel and BFS packed in CWs 3 and 4 have a particle size range of 4 - 8 mm and 4 - 12.5 mm respectively, and straining and sedimentation play the major role in TSS removal from the system and this can be done through flowing the particle down the system with the flow of water. Although the loamy sand has a fine-grain size with two main removal mechanisms, the adsorption mechanisms play a crucial role in the removal process associated with the BFS substrate (CW4), which could be explained by the inherent nature of its physical and chemical properties.

Table 4.3 Averages and standard deviations of removal efficiencies of total solids and heavy metals under three times wet a week.

CW	TSS	Heavy metals%						
		Fe	Zn	Pb	Ni	Cd	Cr	Cu
1	91.1	93.6	75.1	95.5	99.8	99.6	100.0	97.6
	±6.9	±5.0	±17.7	±11.7	±1.3	±2.3	±0.0	±11.9
2	95.0	96.6	78.3	99.9	100.0	100.0	100.0	100.0
	±3.4	±4.8	±15.0	±0.3	±0.0	±0.0	±0.0	±0.0
3	94.5	93.5	93.5	93.9	99.8	100.0	95.11	97.8
	±4.5	±6.9	±6.6	±9.7	±0.6	±0.0	±13.7	±4.9
4	94.6	98.4	99.9	99.9	100.0	100.0	100.0	100.0
	±3.0	±1.5	±0.4	±0.2	±0.0	±0.0	±0.00	±0.0

4.5.2 Heavy metals removal

The general performance of heavy metals removal during the operating time and over the accumulating loaded volume is demonstrated in Figures 4.4 through 4.7 and for the four VFCWs using loamy sand, gravel, and BFS as substrate with 22.5 l loaded three times a week and a 24-hour retention time, while the mean values and the variations of the removal weights are presented in Table 4.3. From those figures, the highest removal performance for the monitored heavy metals accounted for BFS, followed by loamy sand and gravel. Moreover, in Table 4.3, the average values for all heavy metals were between 76% and 100%, indicating that the resulted removal efficiency of heavy metals is comparable with other studies using similar CW configurations (Wang et al. 2015; Mohammed and Babatunde 2017; Walaszek et al. 2018). From the table and figures, a gradual increase in the removal percentage can be noticed as the substrate changed from loamy sand, gravel, and BFS.

Despite the fact that the least substrate weight used in the VFCWs was BFS followed by gravel and sand, the BFS substrate received a higher influent loading rate in the meaning of mg of pollutant to kg of the media, then gravel and loamy sand substrates. The results point out that the studied heavy metals were effectively scraped from their liquid phase to solid phase in the pilot-scale VFCWs; nevertheless, the more heavy metals uptake was pronounced for BFS material weighing 1.28 ± 1.0, 0.17 ± 0.1, 0.16 ± 0.4, 0.03 ± 0.04, 0.001 ± 0.002, 0.014 ± 0.03, and 0.05 ± 0.04 mg/kg (mean ± SD) for Fe, Zn, Pb, Ni, Cd, Cr, and Cu, respectively, relative to their influent loading weight of 1.28 ± 1.01, 0.17 ± 0.09, 0.16 ± 0.38, 0.03 ± 0.04, 0.001 ± 0.002, 0.014 ± 0.03, and 0.05 ± 0.04. It should be noticed that the substrates' performance behaviour for heavy metals removal weight coincides with TSS removal weight, indicating a strong correlation between them affecting the performance.

Although the highest influent loading rate was applied to BFS VFCW as displayed in Figures 4.4 to 4.7, the BFS substrate showed the highest heavy metals uptake. A possible explanation for this removal discrepancy might be that the physicochemical properties of the substrates and the removal mechanisms play a major role in the removal differences.

Figure 4.4a, b, and c provides the experimental data on Fe influent and removal weights for the loamy sand, gravel, and BFS, respectively, with removal weight ranges of 0.005 – 4.757 mg/kg, 0.018 – 4.854 mg/kg, and 0.036 – 6.102 mg/kg. It is apparent from these figures that the Fe removal was high, relative to the inflow loading, and constant even with the extreme loading of around 500 l of accumulating stormwater, indicating constant removal performance under variable Fe loading conditions. Comparing the three main substrates' results of iron removal, it can be seen that the high removal weight accompanied the BFS substrate. Although iron presents as almost entirely particulate - associate form in the inflow of urban stormwater - its ionic status depends on oxidation and reduction reactions which relate to redox potential and pH. However, there were no effluent dissolved forms of Fe from CWs 3 and 4 and minor dissolved forms appeared from CWs 1 and 2 as shown in partitioning analysis, indicating loamy sand had less ability to adsorb the dissolved fraction and the high biological activity in these CWs might contribute in reducing or oxidise Fe resulting in its remobilisation to the effluent.

For Zn removal performance, the substrates showed similar high removal weight patterns, however, the removal weight was continuously less for loamy sand in comparison to gravel and BFS and more variable relative to inflow loading weight (see Figures 4.4a, b, and c for Zn removal). The removal rates were in the following ranges: 0.002 - 0.452 mg/kg of loamy sand, 0.008 - 0.470 mg/kg of gravel, and 0.015 - 0.585 mg/kg of BFS. To compare the results of the current study with previous ones, removal percentages were obtained (in Table 4.3) and the percentages for loamy sand (CW1 and 2), gravel (CW3), and BFS (CW4) were 75.1, 78.3, 93.5, and 99.9% respectively. These results are in line with those of previous laboratory-scale and pilot-scale studies, where the reported removal efficiencies located between 42% and 99% (Hatt et al. 2007a; Hatt et al. 2007b; Blecken et al. 2009; Blecken et al. 2011; Tromp et al. 2012; Wang et al. 2015; Gill et al. 2017).

The peaks of removal weight patterns coincided in behaviour during the period of study for all media and the main differences can be explained by the main associated removal mechanisms. The potential removal mechanisms for all these divalent cation heavy metals mainly include sedimentation, precipitation with sulphides under anaerobic condition and co-precipitation, adsorption and plant uptake (Kadlec and Wallace 2009b), which in return depend on (not restricted to) substrate, pollutant characteristics, and microbial activities. As it has been shown in the influent and effluent heavy metals partitioning section that about 11.82% of Zn is in its dissolved form, it is possible, therefore, that the major removal mechanisms are the same as explained in Section 4.3.1. In addition to the main mechanisms of straining and settling, physical and chemical adsorption mechanisms seem to play a major role in the discrepancy of removal weights with a preference for BFS. The inherent physicochemical properties are the vital component of Zn adsorption. Blast furnace slag undergoes hydrolysis reaction resulting in increasing hydroxyl ions slowly, this reaction is accompanied by ion exchange between slag's calcium content and the hydrogen ions in the influent (Dimitrova 2002). Thus, the gradual changing of the 24-hour incubated stormwater within BFS particle into alkaline condition could be evidence of Zn precipitation or co-precipitation and ion exchange or adsorption. It has been reported that Zn adsorption is flavour under slight acid to neutral pH solution conditions (Rieuwerts et al. 1998; Blecken et al. 2011) where most metals bind better at higher pH, due to less competition from protons for adsorption sites (Metcalf and Eddy 2014).

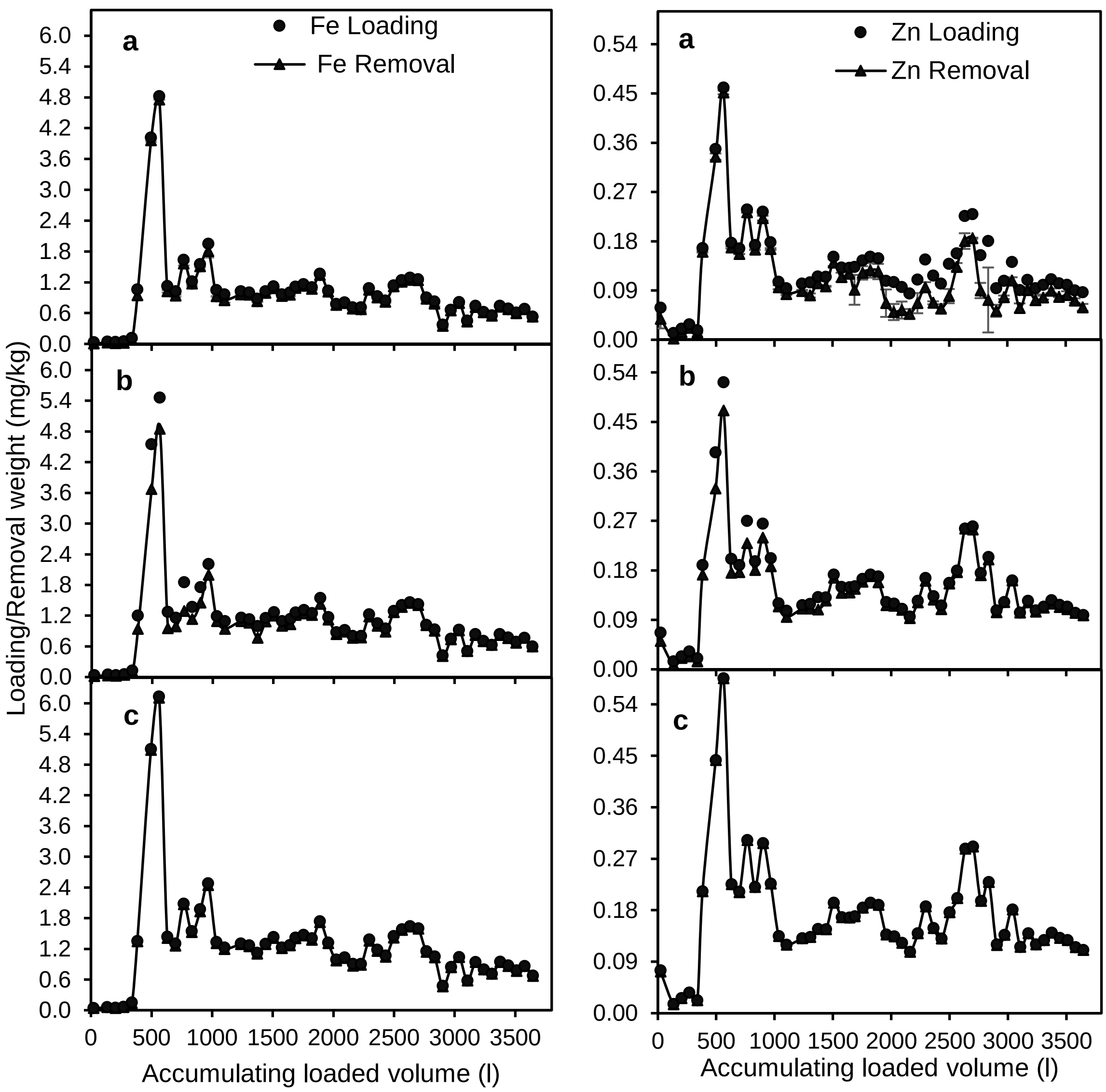


Figure 4.4 The loading and removal weight of Fe and Zn from semi-synthetic stormwater fed into pilot-scale constructed wetland packed with (a) loamy sand substrate of CWs 1 and 2, (b) gravel substrate of CW3, and (c) BFS substrate of the CW4. Error bars represent the variation in the removal performance of CWs 1 and 2.

The removal behaviour of Pb, Ni, Cd, Cr, and Cu by the studied substrates was continuously constant at high retention levels during the period of the experiments. As can be seen from Figures 4.5 to 4.7, the removal weights relative to heavy metals loading rates were almost the same, indicating high performance. Figures 4.5a, b, and c show respectively the Pb removal performance of loamy sand, gravel, and BFS during the studied period. A completed removal was achieved by all the substrates except for gravel where some detectable effluent concentrations on the early stage of the operation were found. From these figures, it can be noticed at accumulating pollutant loading of 1000 l that there were variations on the performance of CWs 1 and 2 (both loamy sand) and

CW3 (gravel), while consistent removal performance was attained within BFS particles (CW4) even when applying high loading rates. This discrepancy in the performance can be related to the progress of the formation of a thin layer on the top of the CW generated from TSS sedimentation during the experiment time and additionally to the involved removal mechanism. As discussed in the partitioning section of the seven-week influent and effluent of heavy metals analysis, Pb was mostly found in the particulate form associated with the CWs influent, therefore, straining and sedimentation mechanisms are the vital control on the Pb removal. The 24-hour retention time of suspended particles (including metals in particulate form) occupying inside CWs had a crucial impact on converting those particles from stabilised to destabilised status within the semi-synthetic urban stormwater. As can be seen from Figures 4.5a, b and c, the removal weights were not in high values and more variable up to the loading volume of 1000 l for loamy sand and gravel substrates. This performance behaviour could indicate that the more particles settle and accumulate within the medias' grains and on the top layer, the more removal and then higher performance than at the start could be attained. Thus, with the progress in operation, loamy sand and gravel substrates become more efficient in retaining both fraction forms. On the contrary, the removal weight for Pb within BFS particles was constant even when applying the highest pollutant loading weight, indicating that BFS could effectively remove both Pb fractions through mainly physical and chemical removal mechanisms. The average removal efficiencies achieved between 93 and 99% which are comparable and within the performance line of other studies that reported removal efficiencies of Pb using similar pilot-scale or field-scale CWs (Hatt et al. 2007a; Hatt et al. 2007b; Blecken et al. 2011; Feng et al. 2012; Gill et al. 2017).

Nickel removal patterns were constant through all substrates with no detected effluent Ni concentration to achieve nearly 100% removal (see Table 4.1 and Figures 4.4a, b and c for Ni removal). This removal performance coincides with and is higher than other studies using CWs to treat urban stormwater, which could be explained by differences in influent concentration levels, pollutant characteristics, retention time, substrate type, and CW configuration (Birch et al. 2004; Scholz 2004; Tromp et al. 2012).

The high Ni removal performance could be explained mainly through physical and chemical retaining mechanisms happening within particles of the substrates and minorly via plant uptake. Straining and settling of the predominantly Ni particulate form (about 84% found in the influent) are the more reasonable assumption for physical removal alongside TSS removal. Moreover, partitioning analysis revealed that all of the dissolved part of the Ni in the effluent was below the measuring limit, which can be explained by

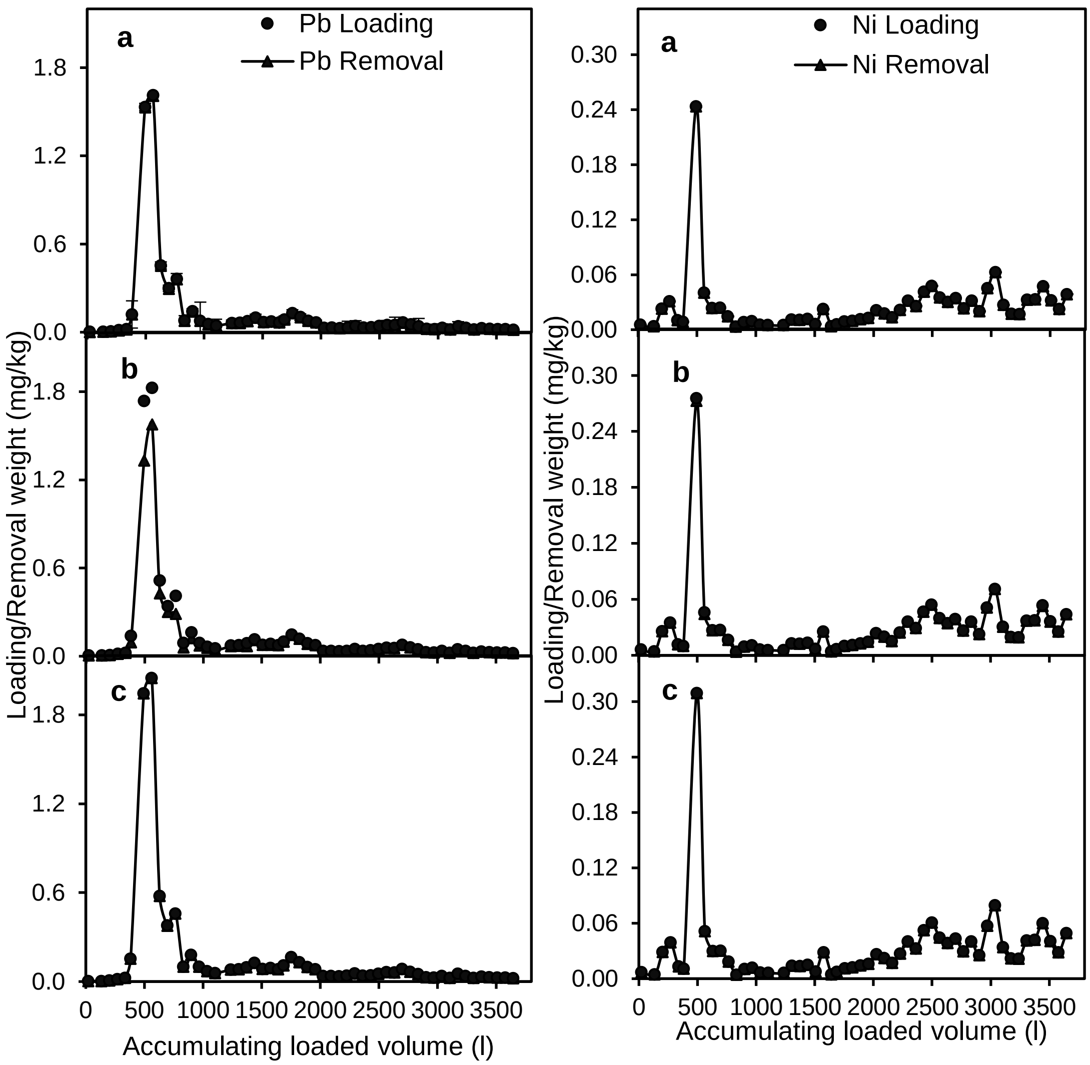


Figure 4.5 The loading and removal weight of Pb and Ni from semi-synthetic stormwater fed into pilot-scale constructed wetland packed with (a) loamy sand substrate of CWs 1 and 2, (b) gravel substrate of CW3, and (c) BFS substrate of CW4. (Error bars represent the variation in the removal performance of units 1 and 2)

its removal being accomplished through the chemical adsorption mechanisms. Although various adsorption mechanisms of ion exchange, co-precipitation and chelation and/or plant uptake might contribute to dissolved metal removal (Metcalf and Eddy 2014; LeFevre et al. 2015; Gill et al. 2017), a contrary debate provides different routes about plants' ability for heavy metals uptake (Adams et al. 2013). Most investigations on CWs treating urban stormwater exploring the overall significance of the different heavy metals removal mechanisms have shown sedimentation to be the predominant process compared to plant uptake (Walker and Hurl 2002; Hatt et al. 2009; Z. Zhang et al. 2012; Šíma et al. 2019). According to the Ni removal line throughout sampling times, there was constant removal performance in the pilot-scale CWs with effluent concentrations below the detection level before, during, and after macrophyte establishment, which confirms the eliminating role of plant Ni uptake.

Although all treated semi-synthetic urban stormwater samples had Cd concentrations below the detection limit (0.0013 mg/l), there is a clear steady performance in CWs 1 – 4 (see Figures 4.6a, b, and c for Cd loading/removal weight). In a similar previous study, Blecken et al. (2011) found 58 Cd-samples out of total 75 cases with Cd effluent concentrations below the 0.0007 mg/l detection limit, while Hatt et al. (2009) found all the collected effluent samples below the detection limit of 0.001 mg/l. A comparison of the findings with those of other studies confirms that the outcomes from these CWs complement the abilities of comparable CWs to accomplish high Cd removal performance. It was impractical to state precisely how well Cd removal performance compares to other similar studies, where the maximum detected removal efficiency that could be attained was 68%. However, other studies with similar configurations or field-scale investigations have reported Cd retention efficiency > 90% (Blecken et al. 2011; Wang et al. 2015).

Cadmium retaining could be elucidated through straining and settling as the predominant removal mechanisms for particulate fraction and chemical adsorption for dissolved fraction, where it was perceived in the partitioning analysis section that partitioning of Cd in the semi-synthetic stormwater influent was 55% particulate-bond phase and 45% dissolved phase. Thus, all the substrates were effective to remove Cd via physical and chemical retaining mechanisms.

From Cr loading/removal weight data in Figures 4.6a, b, and c, it is apparent that all substrates retained Cr effectively to below the detection limit, except two points at stormwater loading volume of around 500 l of gravel substrate. A possible explanation for this might be that gravel substrate has a big pore size at the beginning of stormwater loading which allows smaller particles to escape with the effluent, later these pores become smaller with the continuous stormwater loading to become more efficient in trapping smaller particles. In influent semi-synthetic stormwater partitioning analysis, 100% of Cr was found entirely particulate-bounded, thus it is fair to assume physical removal mechanisms were predominant.

The CWs perform similar to pilot-scale and field-scale CW studies regarding Cr retention, where the mean removal efficiency achieved > 95% in all three substrates, which is located within the results of other studies ranging 64% -99% (Feng et al. 2012; Šíma et al. 2019).

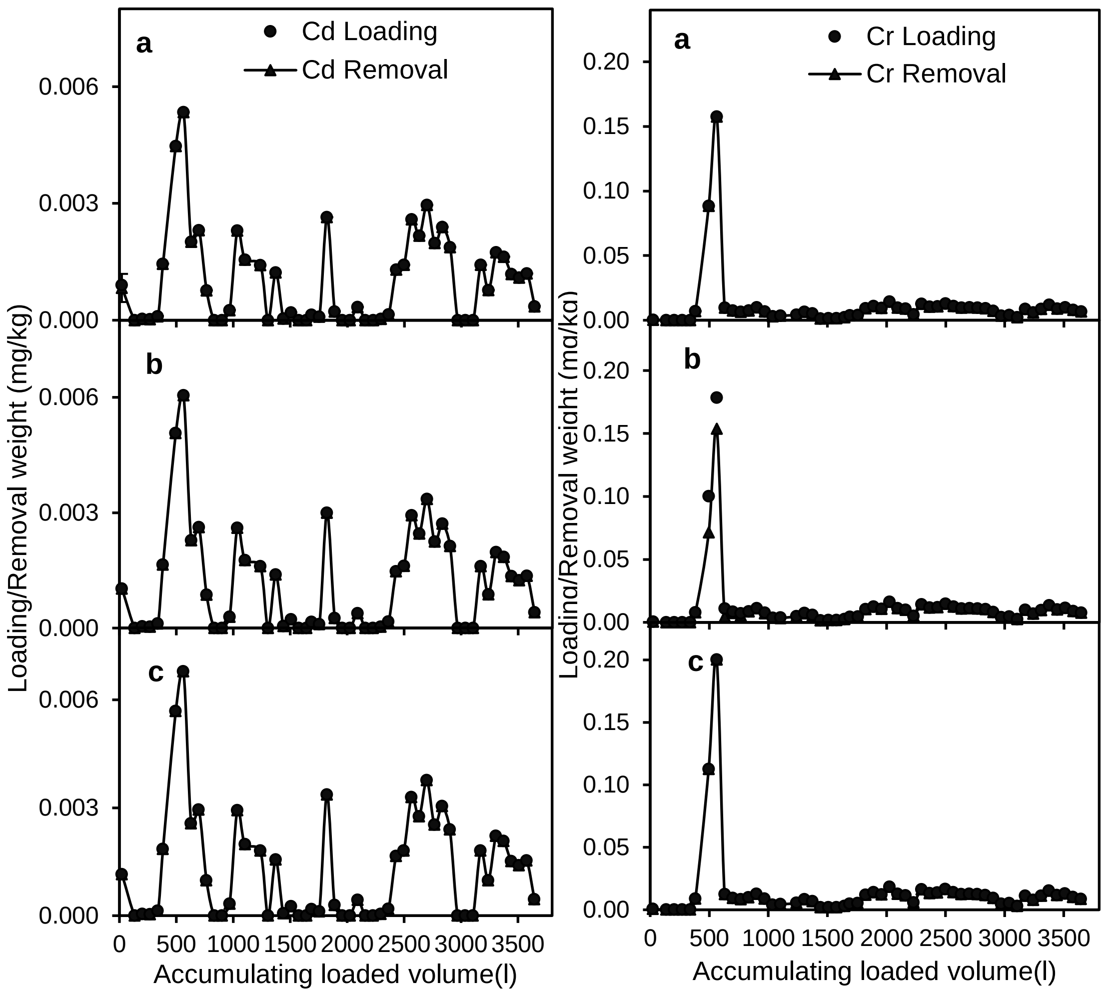


Figure 4.6 The loading and removal weight of Cd and Cr from semi-synthetic stormwater fed into pilot-scale constructed wetland packed with (a) loamy sand substrate of CWs 1 and 2, (b) gravel substrate of CW3, and (c) BFS substrate of CW4. Error bars represent the variation in the removal performance of CWs 1 and 2.

Figure 4.7 demonstrates Cu loading and removal weight patterns in CWs 1 and 2 (mean values are presented), 3, and 4. Cu was effectively reduced to an undetectable level in loamy sand, gravel, and BFS except for the four sampling points between 500 l and 900 l of accumulated stormwater loaded to CWs. However, the removal efficiency and effluent concentrations display that CWs outperform other similar studies of pilot-scale or field-scale CWs attainting a removal efficiency range of 60% - 95% (Hatt et al. 2007a; Li and Davis 2009; Tromp et al. 2012; Wang et al. 2015; Gill et al. 2017; Šíma et al. 2019).

In partitioning analysis of influent stormwater, Cu was found totally in the particulate-bound fraction, thus it is possible to propose Cu retention mechanisms as the same as TSS removal processes of straining and sedimentation. However, detectable dissolved levels were measured in CWs 1 and 2, which might be because of oxidation and reduction processes due to high microorganisms' activities and pH dropping as a result of nitrification, denitrification and humic acids from plant growth, death, and decomposition.

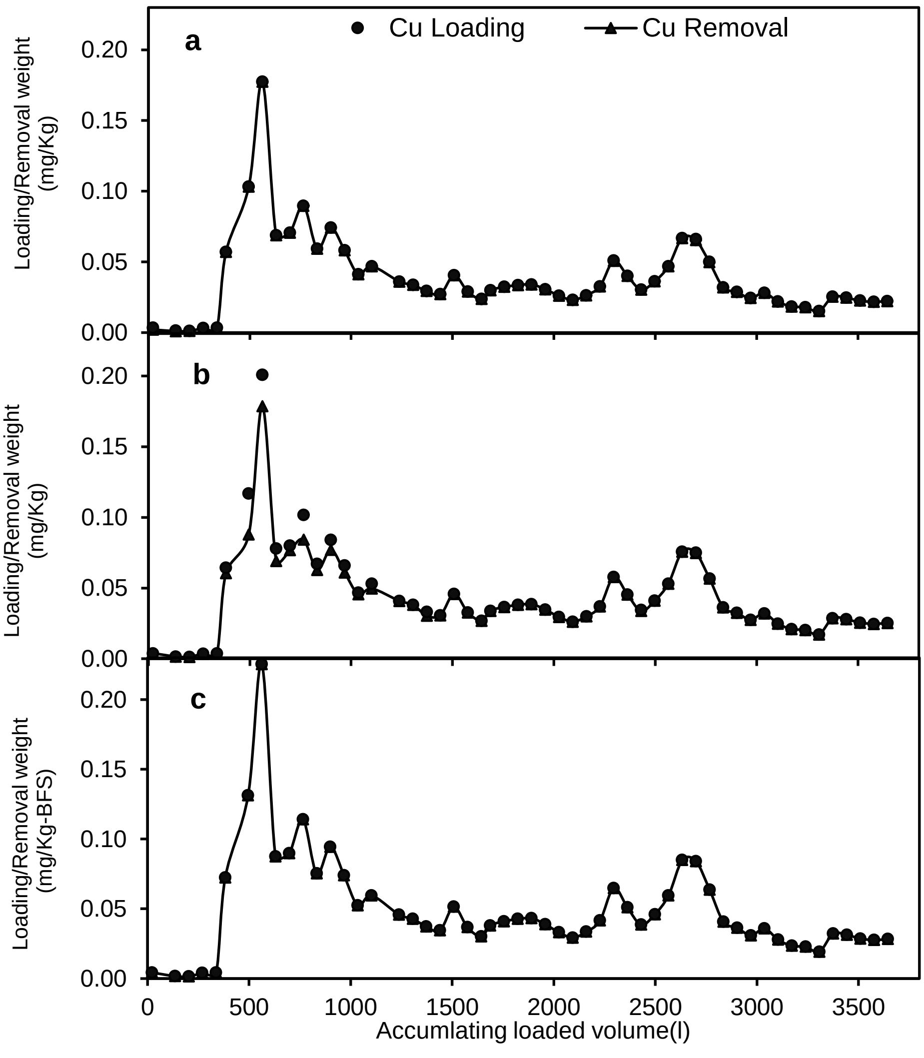


Figure 4.7 The loading and removal weight of Cu from semi-synthetic stormwater fed into pilot-scale constructed wetland packed with (a) loamy sand substrate of CWs 1 and 2, (b) gravel substrate of CW3, and (c) BFS substrate of the CW4. Error bars represent the variation in the removal performance of CWs 1 and 2.

The differences in performance between the substrates were evaluated statistically using a non-parametric independent Kruskal-Wallis test for the detected effluent metals only (Fe and Zn). The test showed that the Fe removal performance differed significantly between CW1 (loamy sand) and CW3 (gravel) with both CWs 2 (loamy sand) and 4 (BFS) ($p = 0.000$) while CWs 1 and 2 performed similarly to CWs 3 and 4 respectively ($p = 1.000$). For Zn removal, the two identical CWs of loamy sand showed statistically similar removal performance ($p = 1.000$) otherwise the Zn removal performance differed significantly between the CWs ($p = 0.000$).

4.5.3 Nutrients removal

Nitrogen and phosphorus removal from various contaminated pointed and non-pointed discharge sources have always attracted attention. When these nutrients discharge into surface water, they become a significant hazard for the ecosystem of the water body and impair water quality via changing the dissolved oxygen levels to less than living requirements for aquatic life. Thus, samples of influent and effluent were analysed for N and P fractions including TN, NH_4-N, NO_2-N, NO_3-N, TP, and PO_4-P. These nutrients fractions were used to understand and investigate the removal behaviour in pilot-scale CWs using the tidal flow regime, as explained in detail in the following sections.

4.5.3.1 Nitrogen

The N transformation and removal in CWs can be controlled by the nitrification-denitrification process, N uptake (assimilation), adsorption, ammonia volatilization, mineralisation (ammonification) (Sun et al. 2017; Dagenais et al. 2018). In order to fully investigate and understand N transformation routes within the substrates in tidal flow CWs, fractions of TN including NH_4-N, NO_2-N, and NO_3-N were measured which represent the total inorganic fraction of N. Therefore, the organic bound nitrogen (organic-N) can be computed from finding the difference between TN value and summation of the measured fractions according to Equation 4.4.

$$\boldsymbol{Organic - N = TN} - [(\boldsymbol{NH_4 - N}) + (\boldsymbol{NO_2 - N}) + (\boldsymbol{No_3 - N})] \qquad (4.4)$$

The influent concentrations of nitrogen fractions in semi-synthetic urban stormwater during the operation time of CWs are presented in Figure 4.8. As can be seen from the figure, the major fraction of TN was organic-N (range 0.236 – 7.089 mg/l) followed by NH_4-N (range 0.560 – 4.426 mg/l) and NO_3-N (range 0 – 0.7 mg/l). While NO_2-N was mostly under the detection limit of 0.002 mg/l in influent and effluent flow. However, these undetectable concentrations were considered zero to enable the conducted research to explore comprehensively the N transformation routes in combination with other forms of N.

Table 4.4 lists the mean values and standard deviation of effluent N forms and removal efficiencies attained in CWs 1 to 4. The treated outcomes show a decrease in TN and

NH_4-N in the main three substrates, and an increase in NO_2-N and NO_3-N concentrations from the inlet to outlet of the pilot-scale CWs. More details about the transformation of N components over the time of operation are closely illustrated to deeply understand the mechanisms behind N reduction in the tested CWs.

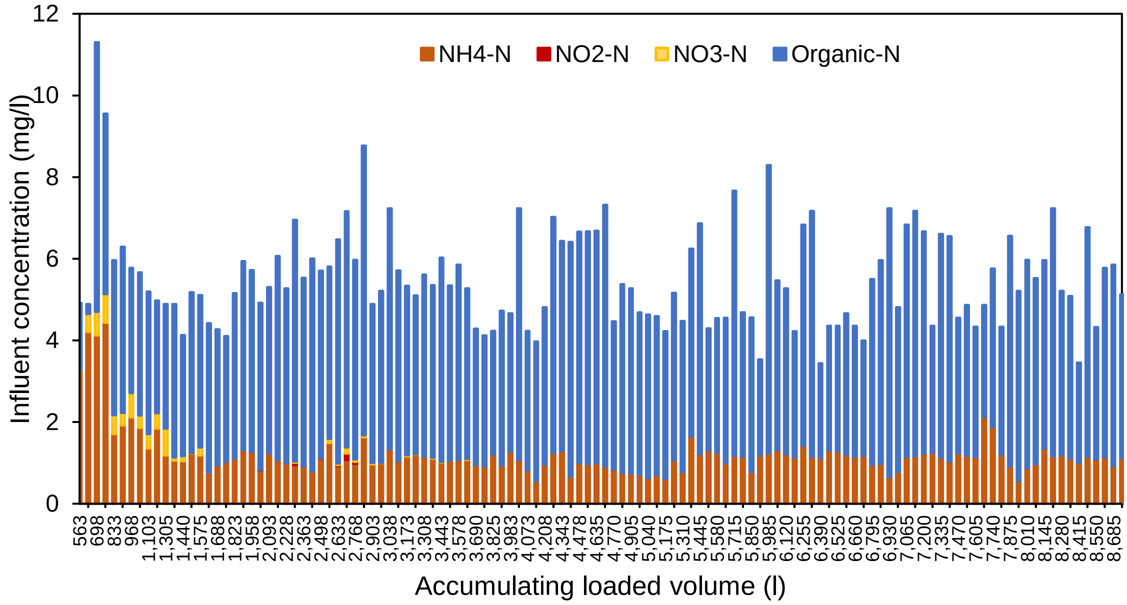


Figure 4.8 Influent N species of semi-synthetic urban stormwater for the pilot-scale CWs.

Table 4.4 Average values and their variations of N fractions transformation and removal percentages over the operation time, the removal percentages with negative sign mean an increase in the concentration in the outflow.

CW	Effluent Concentration (mg/l)					Removal %				
	TN	NH_4-N	NO_2-N	NO_3-N	Organic-N	TN	NH_4-N	NO_2-N	NO_3-N	Organic-N
1	1.288 ±1.089	0.127 ±0.166	0.005 ±0.009	0.380 ±0.574	0.777 ±0.684	76.8 ±16.4	89.5 ±6.6	-85.0	-704.7	81.2 ±15.7
2	1.288 ±0.937	0.101 ±0.049	0.007 ±0.013	0.291 ±0.466	0.894 ±0.677	76.5 ±14.8	90.9 ±4.6	-168.5	-516.6	77.8 ±16.7
3	1.912 ±0.969	0.077 ±0.043	0.004 ±0.006	0.626 ±0.582	1.204 ±0.673	65.4 ±14.6	93.4 ±2.8	-59.6	-1225.9	70.9 ±15.6
4	1.457 ±0.851	0.084 ±0.104	0.016 ±0.049	0.305 ±0.478	1.052 ±0.596	73.2 ±14.1	92.9 ±4.3	-551.0	-545.9	73.3 ±15.9

4.5.3.1.1 Total nitrogen removal

Total nitrogen reduction relative to the inlet concentration improved over the time of pollutants loaded into CWs 1 to 4 (see Figures 4.8 and 4.9). Because of the identical design and operation of CWs 1 and 2, the average values of their results and the variation on the reduction performance are computed and represented in Figure 4.9a. The gradual TN reduction improvement increased as the bioactivity of microorganisms in the pilot-scale CWs enhanced. The reduction in TN effluent concentration and TN removal efficiency reached the maximum values in CWs 1, 2 and 4 at the accumulating inflow volume of 3308 l where loamy sand and BFS served as substrates. While the progression in the TN reduction within gravel grains was much slower than the other three CWs, indicating more time was required in CW3 to mature and establish the biofilm. After this peak point in TN reduction, the removal efficiency declined to a steady level for all CWs. Therefore, the average values listed in Table 4.4 do not represent the actual meaning for TN removal efficiency as the CW needs time to mature. From Table 4.4, the average TN removal efficiency over the whole operation time is located between 65% ± 14% and 76% ± 16%, meanwhile, the maximum removal efficiency achieved at 3308 l accumulating inflow volume was 98%, after this point, loamy sand, BFS, and gravel substrates behaved constantly with minor variation in the following order: 81% ± 7.4% > 76% ± 8.9% > 74% ± 8.2%. However, the non-normal distributed TN data over monitoring time statistically showed no differences between loamy sand CWs and BFS CW ($p \geq 0.06$) while the analysis resulted in significant differences in the TN removal performance between gravel CW versus loamy sand and BFS CWs ($p \leq 0.005$). Comparison of these results with those of similar pilot-scale stormwater CWs confirms that TN removal performance in the current CWs was effective and favourably comparable in terms of removal efficiency. However, some studies have reported an increase in TN concentrations effluent as a result of enhancing N forms transformation in the various biological processes. Wang et al. (2017) outlined a TN removal efficiency ranging from 53 to 84% while in another study average TN removal efficiency was found between -241 and -79% (Bratieres et al. 2008).

4.5.3.1.2 Organic–nitrogen compound

Organic-nitrogen represents the major fraction of TN influent which is 77% as mean value (see Figure 4.8). However, the removal efficiencies of this fraction were less in comparison with NH_4-H fraction for loamy sand, gravel, and BFS in this following order: CW1 > CW2 > CW4 > CW3 (see Table 4.4 and Figure 4.9). The variations in removal could be marked to the lack of biological mineralisation (ammonification) process by which organic-N transfers biologically to ammonium occurring in both aerobic or anaerobic conditions (Metcalf and Eddy 2014; Shrestha et al. 2018). As the progression of biofilm fixed on the CWs media increases with the time of operation, the removal rate for loamy sand CWs and BFS enhanced, to reach the maximum removal at 3308 l accumulating inflow volume. Later, the removal decreased to a steady level of conversion. In gravel media, the progression in the biofilm generation and then the biological activities were slower than the other two media and this resulted in less organic-N removal.

Whereas the average removal efficiencies for organic-N mineralisation in gravel and BFS were 71% and 73% over more than 900 days of applying the semi-synthetic stormwater, the organic-N removal efficiency in loamy sand VFCWs (CW1 and CW2) recorded higher transformation rates than the others (81% and 78% respectively). In comparison with full-scale treatment units, Sartoris et al. (2000) reported a two-year average value of 65% for organic-N transformation in field-scale constructed wetland used as a secondary wastewater treatment unit, while Zhou and Hosomi (2008) reported a 22% average removal value over two years of treating a nutrient-polluted river using constructed wetland planted forage rice.

The rate of this process depends on temperature, pH value, carbon to nitrogen ratio, nutrient availability, and CW media. The required temperature and pH for optimal ammonification are reported in a range of 40 – 60°C and 6.5 – 8.5 respectively (Reddy et al. 1984; Vymazal 1995). Influent temperature and pH ranges of semi-synthetic urban stormwater flowing to CWs were between 7.5 and 25.3°C and 6.8 and 8.1 respectively. However, the organic-N removal activity reached its maximum within loamy sand and BFS substrates even with influent stormwater at outside optimal temperature. The temperature can slow down the process where Songliu et al. (2009) stated that the optimum temperature for denitrifying bacteria is in a range of 20 – 40°C and the process decelerates at a temperature below 15°C and almost terminates at a temperature below 5°C. After the point of organic-N reaching the maximum reduction in its effluent for all media, despite the long time required for biofilm generation on gravel to be matured, the organic-N levels increased to almost within constant rates. Gradual increase of organic-N after accumulating inflow volume of 3308 l could be marked to the decay of cells and tissues containing organic-N which had been biologically generated from inorganic-N in the assimilation process (Kadlec and Wallace 2009b; Metcalf and Eddy 2014).

4.5.3.1.3 Ammonium–nitrogen compound

The fraction of ammonium-nitrogen was significantly reduced from inflow load relatively in constant rate by at least 90% via the nitrification process. Thus, the reduction values listed in Table 4.4give a good indication for typical NH_4-N removal behaviour in the first four CWs. In this process, nitrifying bacteria, with oxygen availability, oxidizes NH_4-N into NO_2-N and then the latter is simultaneously oxidised to NO_3-N (see Equations 4.5 to 4.7) (Metcalf and Eddy 2014). The type of bacteria in tidal flow CWs is facultative heterotrophic which is active under aerobic and anaerobic conditions (Maciolek and Austin 2006; Austin et al. 2007), where ammonium and nitrite are the carbon donors, while oxygen is the electron acceptor.

Ammonium oxidation step: $2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O$ *(4.5)*

Nitrite oxidation step: $2NO_2^- + O_2 \rightarrow 2NO_3^-$ *(4.6)*

Total oxidation reaction: $NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$ *(4.7)*

CWs 1 and 2, packed with loamy sand media, behaved pretty much the same for NH_4-N reduction (90% reduction). However, CWs packed with gravel (CW3) and BFS (CW4) media introduced a relatively higher performance than loamy sand CWs to achieve about 93% reduction with a slight preference for gravel media. It is encouraging to compare these results of NH_4-N reduction with that found by previous studies of similar experiment configurations, with reduction values between 60% and 95% (Nanbakhsh et al. 2007; Zhang et al. 2011; Martín et al. 2013; Du et al. 2014; Zhi et al. 2015). The novel design of tidal flow CW effects on the NH4-N reduction can be clearly demonstrated by comparing it with other CW configurations. In a pilot scale horizontal flow CW used to treat nutrient-polluted water river, Zhou and Hosomi (2008) found a 21% average reduction in NH4-N during the 2004 operation, and this value decreased significantly to -12.5% in 2005, while Sartoris et al. (2000) reported 20% the daily total ammonia removal nitrogen in field-scale horizontal flow CW treating secondary effluent of wastewater treatment plant. The differences in NH_4-H reduction between the substrates could be interpolated by the differences in the void volumes, where gravel had the biggest void volume followed by BFS and loamy sand. Therefore, the larger void volume the more oxygen enters the CW due to the tidal flow regime, which leads to oxidising more NH_4-N, which is already adsorbed into the media and biofilms during the stormwater loading.

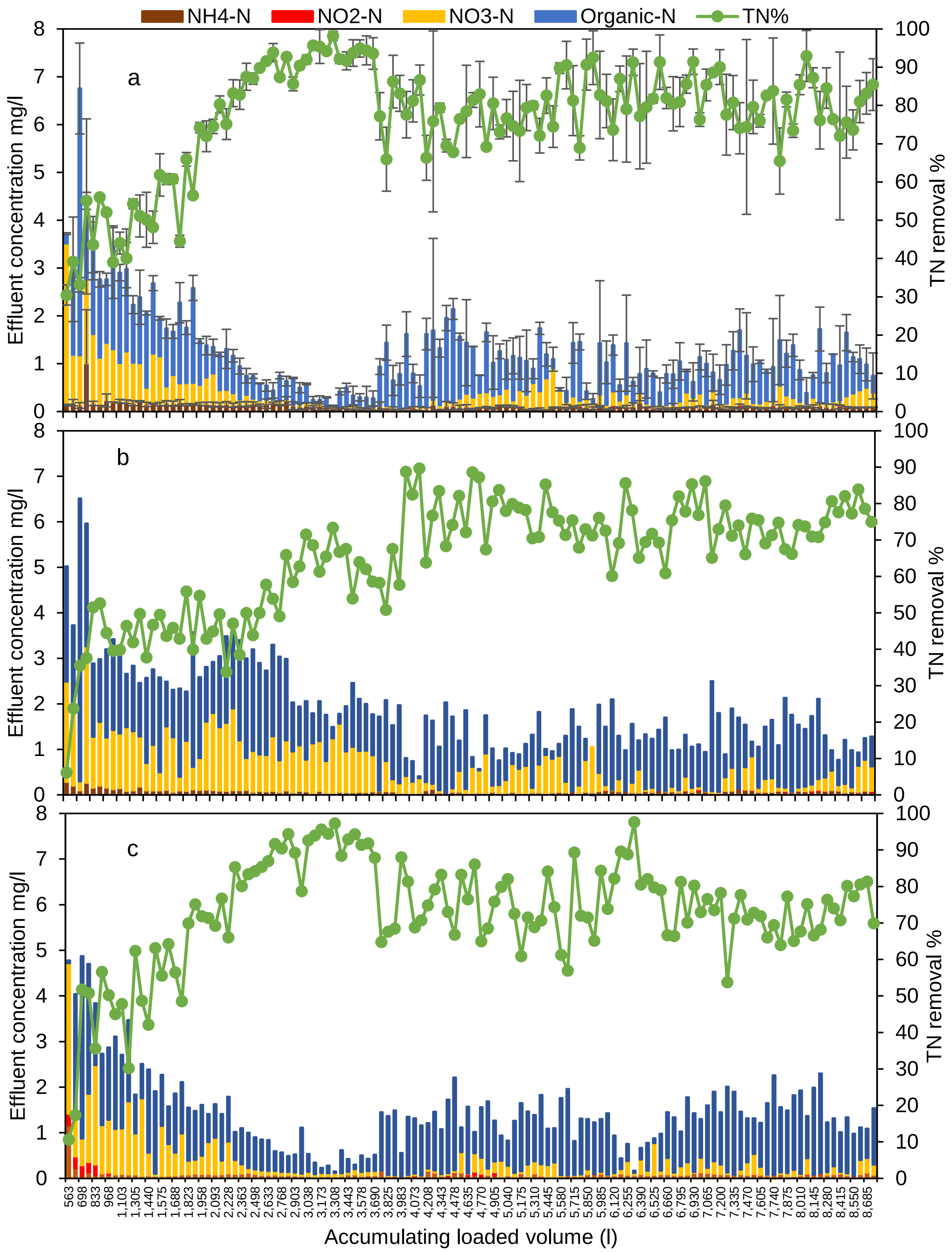


Figure 4.9 Percentage removal of TN and effluent concentrations of N fractions of treated semi-synthetic urban stormwater for (a) CWs 1 and 2 (average and standard deviation are presented), (b) CW3, and (c) CW4.

4.5.3.1.4 Nitrite-nitrogen compound

From Figure 4.8 and Table 4.4, it can be noticed that NO_2-N concentrations increased from almost zero value in inflow stormwater to a range of 0.004 to 0.016 mg/l in outflow with maximum variation 0.049 mg/l for CWs 1 to 4. The same behaviour has been reported that both NO2-N and NO3-N concentrations increase from the inflow to outflow in different configurations of CW (Chang et al. 2014; Pelissari et al. 2014; Tan et al. 2017). This increment in NO_2-N concentrations was likely to increase due to the nitrification process where heterotrophic bacteria oxidise NH_4-N resulting in NO_2-N in the first step of the nitrification process. Oxygen supplementation to the CWs is a vital factor in this N transformation process where oxygen is an electron acceptor. The figures listed in Table 4.4 represent the mean values for the whole operation time of CWs. However, Most of the NO_2-N concentrations in the outlets of loamy sand, gravel, and BFS CWs were undetectable (see Figures 4.9a, b and c), which marks simultaneous transformation of NH_4-N to NO_2-N compound which is further oxidised to NO_3-N fraction as a result of the second phase of the nitrification process (see Equations 4.5 to 4.6). According to Equation 4.6, this process releases hydrogen ions as a result of the NH_4-N oxidation to NO_2-N leading to pH dropping in the effluent as can be noticed for CWs 1, 2, and 3 (see Figures 4.11a and b) which was not the same in CW4. In CW4, effluent pH was elevated due to the inherent properties of BFS causing high alkalinity effluent, as a result of calcium silicate dissolution from the media (Dimitrova 1996; Dimitrova 2000; Khelifi et al. 2002), even with H^+ releasing from the nitrification. Therefore, it is fair to assume that the process of nitrification is effective and successfully transforms NH_4-N to NO_2-N and then to NO_3-N.

4.5.3.1.5 Nitrate-nitrogen compound

There were clear increments in NO_3-N concentrations from inflow to outflow of CWs 1 to 4 which can be noticed from the comparison between Figures 4.8 and 4.9. The NO_3-N resulted from NO_2-N oxidising in the nitrification process under aerobic conditions, which is one of the good oxygenation features of tidal vertical flow CWs, as discussed in the previous section. This N fraction is reduced as a terminal electron acceptor, resulting from carbon oxidation under anaerobic or anoxic conditions, to produce gaseous N forms (N_2O, and N_2) in a process called denitrification (Kadlec and Wallace 2009b; Metcalf and Eddy 2014). The denitrification process consists of biologically oxidising the carbon source as an electron donor and then reducing NO_3-N, as electron acceptor instead of oxygen, to NO_2-N in the first step, meanwhile, the final step includes reducing NO_2-N to nitric oxide (NO), then nitrous oxide (N_2O) and finally to N gas, which can be summarised in Equation 4.7. The N forms transformed effectively in both nitrification and denitrification or anoxic processes through the decrease in NH_4-H concentrations and lack of NO_2-N concentrations in the outflow for all CWs, and the differences in the removal efficiencies refer to the biological activities.

$$NO_3 \rightarrow NO_2 \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad (4.8)$$

Another evidence of effective denitrification process was the sum of effluent concentrations of NO_2-N and NO_3-N in CWs 1 to 4 which were between 0.298 and 0.630 mg/l which are much less than 2 mg/l as recommended for complete denitrification of wastewater (Metcalf and Eddy 2014). From Table 4.4, the NO_3-N removal percentage increased 516% for loamy sand CWs to about 1226% for gravel. However, many previous studies have found negative removal efficiencies in lab or field-scale researches (Blecken et al. 2010; Zhang et al. 2011; Dagenais et al. 2018; Shrestha et al. 2018).

At the beginning of CWs operation, the levels of NO_3-N were high in all CWs which was misleading of inadequate denitrification even though the tidal flow regime in the CWs was applied to enhance this process. However, as the semi-synthetic urban stormwater was intermittently applied to the CWs, the organism community increased and generated biofilm on the media leading to better performance in NO_3-N removal. From Figure 4.9, the NO_3-N effluent concentrations decreased over time as the systems matured, indicating that the denitrification capabilities improved in the CWs.

4.5.3.2 Phosphorus

Partitioning analysis in Section 4.3 showed that about 63 ± 9.76% of TP is in a dissolved fraction and the rest in particulate form in the influent semi-synthetic urban stormwater. The particulate fraction was almost completely removed in all CWs relative to its small percentage, while the major dissolved fraction was found in the outflow. Although the major fraction is dissolved P and the particulate fraction almost removed, the laboratory analysis for TP in inflow and outflow was continued and then terminated until a complete picture of TP removal behaviour was confirmed. This was achieved at an accumulated inflow volume of 3645 l. Meanwhile, orthophosphate fraction analysis was terminated at the end of the whole experiment to track its removal efficiency within these CWs.

4.5.3.2.1 Total phosphorus

The average percentages of TP removal range from 71 ± 5.5 to 77 ± 8.8 for CWs 1 – 4 for more than two and half years of operation. The total evaluation of CW performance is comparable to other previous studies with pilot- or field-scale CWs (53 - 86%) (Hatt et al. 2007a; Hatt et al. 2009; Martín et al. 2013). However, Zhang et al. (2011) achieved an average TP removal of 93% using a biofilter CW under wet-dry conditions by adding a carbon source and creating a submerged zone, which explains the high TP removal values attained in this system where these operating conditions enhanced the denitrification process and improved plant growth leading to high nutrient removal values. Moreover, Zhang et al. (2011) used semi-synthetic stormwater with about 50% of the TP in particulate form.

From Figure 4.10a, a clear TP removal improvement with the progress of operation can be noticed in CWs 1 and 2, to increase from 60 to 91%, as an average value for both CWs. Meanwhile, the removal efficiency for gravel and BFS CWs slightly declined to 60 and 70% respectively. This discrepancy in the performance could be referred to the effectiveness of the bio-retention structure which was more active in loamy sand CWs than the other two substrates. It was noticed that loamy sand was capable of supporting the vegetation very well while the plants started to change colour and they grew even less after planting in gravel and BFS substrates.

In bio-retention treatment systems, P adsorption to the media is the major removal process where reactive P fraction can strongly bond to aluminium and ferric hydroxides/oxides and/or precipitate with calcium in slow adsorption reaction (LeFevre et al. 2015). However, TP reduction depends not only on dissolved fraction removal but also on the removal of the particulate fraction. The latter fraction was successfully removed via either straining and/or sedimentation in the same TSS removal mechanisms, or decomposed consequently through the nitrification and denitrification processes.

4.5.3.2.2 Ortho-phosphorus fraction

The average PO_4-P removal values and its variations were in the following order: (86.8% ± 7.7) CWs 1 and 2 > (75.1% ± 7.4) CW3 > (73.8 ± 8.1) CW4. However, it was found by using an independent Kruskal-Wallis test that pairs of loamy sand CWs and the gravel CW with the BFS CW behaved similarly in terms of phosphate retention ($p = 1.000$) while both gravel and BFS CWs differed significantly from loamy sand CWs ($p = 0.000$). In comparison with previous studies that have a similar CW design, the current results for both TP and PO_4-P were comparable and located within the range of other research (77 – 94%) PO_4-P (Sim et al. 2008; Martín et al. 2013; Shrestha et al. 2018). As can be seen from Figure 2.10a, the PO_4-P removal efficiency improved with time in the loamy sand

CWs and this was not the case with the gravel and BFS CWs in Figures 4.10b and c. These variations in PO_4-P reductions unsurprisingly mimicked the TP removal behaviour. Hence the majority fraction of TP was phosphate as discussed in the partitioning analysis.

Adsorption and/or precipitation in addition to the biological or plant uptake can contribute to reducing the dissolved forms of P in the CWs. This was continuously monitored and visualised in the shrinkage in the size of the plants and the changing of their colour over time in gravel and BFS CWs; therefore, P uptake by plants was unlikely to contribute significantly to total removal as the plants struggle to grow in these granulated substrates. Meanwhile, the removal improved within loamy sand particles over time even though the well-established plants died during the winter, indicating more than one removal mechanism was associated.

Although phosphate adsorption into Fe and Al hydr(oxides) in CWs is usually coincided with acidic conditions (LeFevre et al. 2015) and over the time of experiments, none of the CWs exhibited acidic conditions, Babatunde and Zhao (2010) and Al-Tahmazi and Babatunde (2016) and other studies have shown that the P adsorption into metal hydr(oxides) increases as pH solution decreases and P adsorption more likely depends on the activity of these metals. The Fe and Al content in all substrates was less than or equal to 6.3% and in most cases these metals' content increased after the CWs shut down, indicating it is highly unlikely that phosphate might be adsorbed to the metal hydr(oxides) in such a condition (alkaline condition and more metals accumulating on substrates' particles). Thus, it was considered that phosphate adsorption mechanisms to the metal hydr(oxides) did not play a major role in the P removal in the pilot-scale CWs.

Elemental composition analysis showed that the Ca content is the primary element especially for loamy sand (32%) and BFS (23%), which is considered the most important substrate characteristic for its role in P removal within particles of calcareous soils usually used in CWs. Because of the electrochemical heterogenetic surface of the substrates, Ca can easily be hydrolysed in solution causing pH elevation because of the released hydroxide (Dimitrova 2000). Ca favours precipitation with P as sparingly soluble calcium phosphate minerals especially at slight alkaline conditions (Metcalf and Eddy 2014). The mean value of influent pH was 7.45 (± 0.31) and with high Ca concentration it is more likely that P is removed via precipitation than adsorption. It has been reported that calcium phosphate precipitation will spontaneously happen at pH solutions greater than 7 (Al-Tahmazi and Babatunde 2016). Therefore, it is proposed that the dominant P retaining mechanism in the CWs is calcium phosphate precipitation.

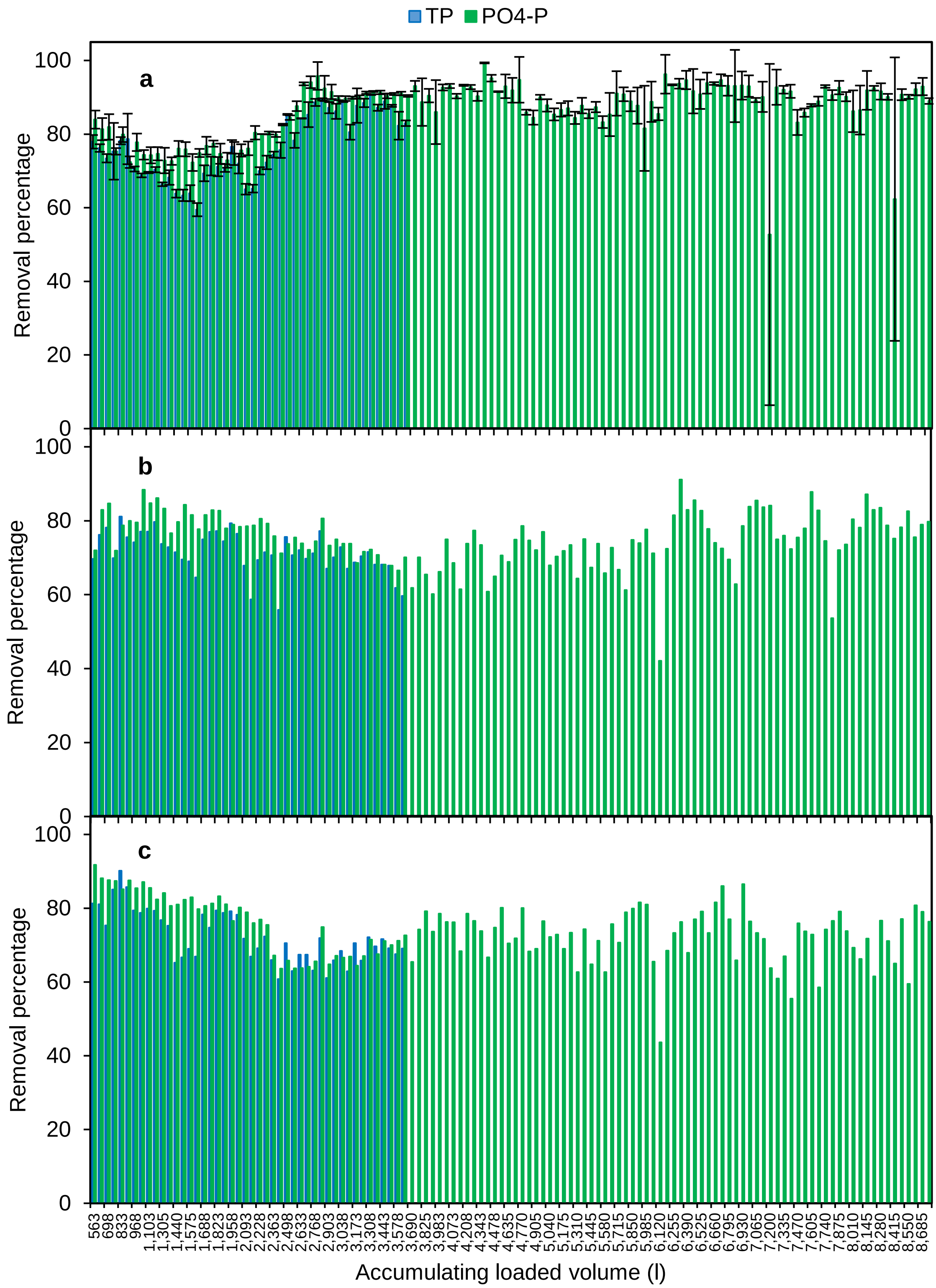


Figure 4.10 TP and PO_4-P removal patterns from semi-synthetic urban stormwater of loamy sand CWs (a – mean standard deviation presented for CWs 1 and 2), gravel CW (b – CW3), and BFS CW (c - CW4).

4.6 Physical properties of semi-synthetic stormwater

Constructed wetland pH, EC, and temperature measurements are useful parameters because the changing of these physical properties might be an indicator of various chemical and biological activities within the CWs. The inflow and outflow physical properties of semi-synthetic urban stormwater were recorded during samples occasion for the whole experiment period as shown in Figure 4.11 for CWs 1 to 4. The both in- and outflow temperatures fluctuated depending on seasonal time. The influent recorded temperature was in the range of 7.5 to 25.3°C while the effluent temperature across the CWs was found slightly less from the inflow, due to retention time overnight with high variability in the environment temperature during the day, and was located in the range of 6.9 to 23.5°C. It can be noticed from Figure 4.11 that the temperature increased during the summer season and started to decrease during the autumn season to reach minimum values in the winter season. The incubated stormwater temperature within CW substrates has a vital impact on both chemical reactions and microorganisms' activities. Dimitrova (2002) found that the temperature significantly influences metal adsorption characteristics through affecting the Ca dissolution rate and the hydroxide ions concentration processes when he used BFS to remove Pb. The increment in temperature, and in conjunction with pH above neutral values, enhances the transformation of ammonium to free ammonia (Kadlec and Wallace 2009b). An early study has shown that the rate of both denitrification and dissimilation of nitrate reduction to ammonium increase with increasing temperature (Rahman et al. 2019). In the current study, the plant growth was effective during spring and summer seasons especially in loamy sand CWs and then high nitrogen removals were achieved, due to high microorganisms' activities.

The electrical conductivity of the inflow stormwater ranged from 0.28 to 0.46 ms/cm and this range was almost doubled in the outflow from CWs 1 and 2, with minor increments in CW3, and moderate increases in CW4, as can be seen clearly in Figure 4.11a, b, and c. The difference in the EC values between the inflow and outflow was a result of the cations and anions formed from the dissolution of different ions from the substrates as well as the associated biological activity, which was more pronounced within the particles of loamy sand and BFS substrates than gravel substrate.

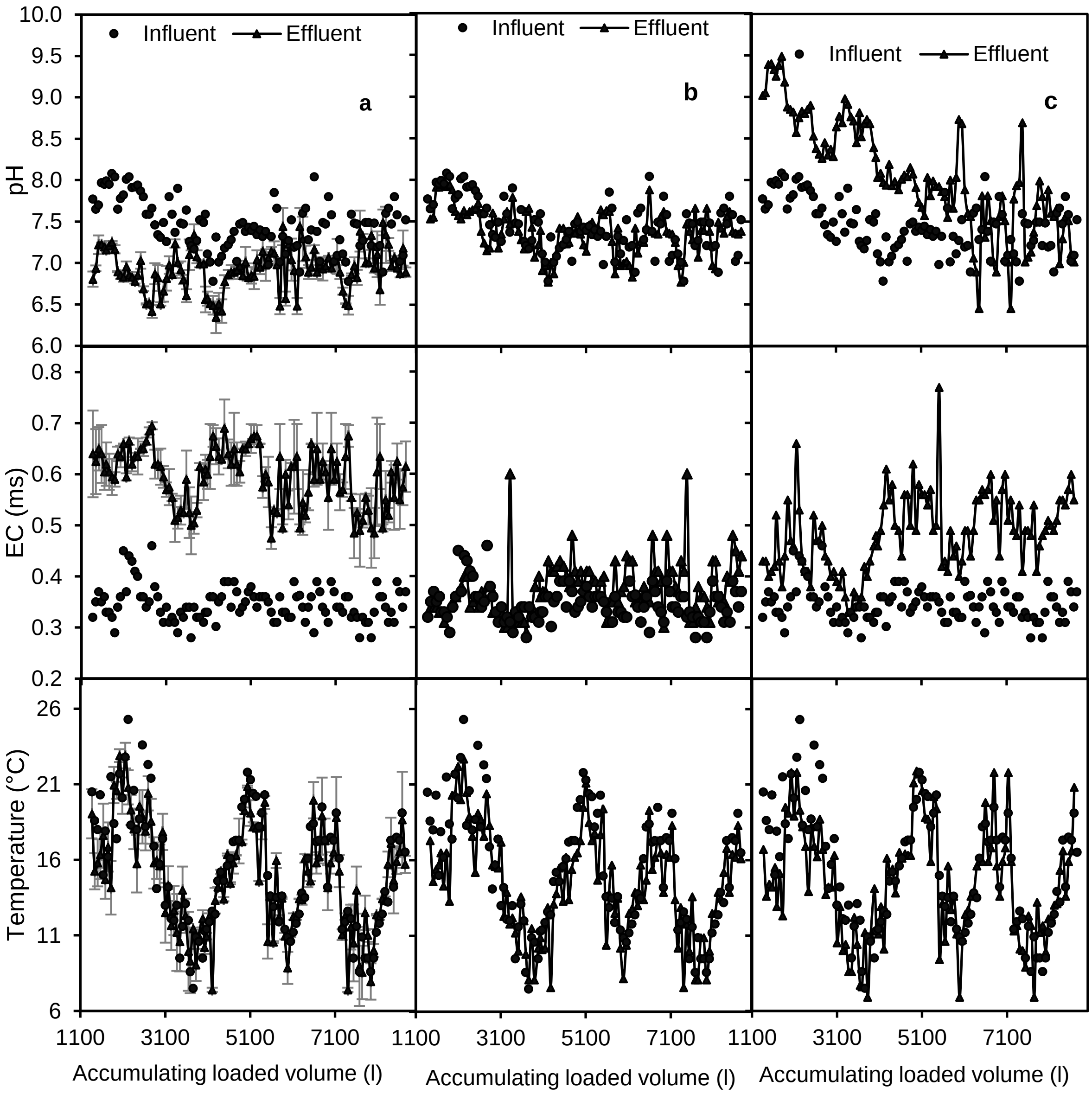


Figure 4.11 Influent and effluent physical properties of semi-synthetic stormwater: (a) CWs 1 and 2 of loamy sand (average values and standard deviation are presented); (b) CW3 of gravel; and (c) CW4 of BFS.

To provide a healthy ecosystem in CW, the inflow hydrogen ion concentration should be located between 6.5 and 9.0. From Figure 4.11, it can be noticed that the pH range values of the inflow stormwater were almost within the recommended range, where the optimal nitrification rates take place at a pH range of 7.5 to 8.0. Ammonium oxidation is pH-dependent and the oxidation process decreases crucially at pH values below 7 (Kadlec and Wallace 2009b; Metcalf and Eddy 2014). In addition to its effect on biological activities, pH plays a vital role in the chemical reactions. This could be through controlling the chemical phase of hyd(oxides) of Fe, Al, and Mn, Ca precipitation, and dissolution.

The pH range is more likely to be influenced by the physicochemical properties of the substrates and the biological activities. In the current study, the outflow hydrogen ion concentrations from the three substrates had three different roots of behaviour, see Figure 4.11. The loamy sand substrate showed mostly effluent pH less than the influent, which could be explained by the high biological activities leading to increased hydrogen ions as discussed in Section 4.5.3.1 and Equation 4.7. Gravel CW had a slight decrease in hydrogen ion concentration in comparison with the influent pH of stormwater; this might be explained by the weak microorganisms' activities, hence the least nitrogen removal was noticed in gravel CW.

One of the BFS CW features is exhibiting alkaline outflow conditions due to the dissolution which is declining with time as the media becomes exhausted (Dimitrova 2002; Kostura et al. 2005). However, the final effluent pH was a combination of the effect of metals dissolution from the structure of the BFS and the biological process activities. Organic substances resulted from the cycle of growth, death, and decomposition of the plant in CWs are another source of natural acidity which might too cause a drop in pH values. The higher pH dropping in loamy sand CWs than the other two substrates was not only due to the effective N removal but also due to the cycle of plant growth, death and decomposition during different seasons. However, the final range values of effluent pH were slightly acid in some cases in loamy sand CWs and circumneutral conditions with the consistency of prolonging performance.

4.7 Summary

This section summarised the main outcomes from the performance evaluation for the removal of solids, heavy metals, and nutrients from semi-synthetic urban stormwater in the long-term operation of pilot-scale CWs. The focus of this chapter was on the first four CWs using loamy sand, gravel, and BFS as main substrates and wet-dry operation conditions of 22.5 l three times a week. The chemical composition analysis of the substrates before and after treating urban stormwater showed a clear changing of their chemical content, especially loamy sand and BFS. The Ca content on the prementioned substrates was reduced by about 8% and 7% respectively, indicating Ca dissolution coincided with pH elevation in the BFS CW as a result of exchanging of metals with the hydroxyl ions on the substrates' surfaces. The heavy metals content in all the substrates was increased as evidence of adsorption or ion exchange of these ions on the substrates' surfaces. OC content was increased markedly in all substrates due to the biological activities.

Straining, settling, and interception removal mechanisms for TSS and metals entirely particulate mainly explained the removal through CWs. However, adsorption mechanisms play a major role in differences in the removal between the substrates. Total removal for N was successfully achieved through ammonification (converting organic-N to NH_4-N), nitrification and denitrification (increasing NO_3-N concentration) processes. N species transformation was consistent within the matured substrate and this rate of transformation was variable between the CWs depending on microorganism's activity. P removal mechanisms were mainly explained by Ca phosphate precipitation, adsorption into metal hydr(oxides) and plant uptake for dissolved fraction while particulate fraction was immobilised through the same SS removal mechanisms.

Mass balance analysis showed that the BFS CW had higher SS and heavy metals removal weights than loamy sand and gravel CWs. On removal percent comparison base, the CWs attained high SS and heavy metals removal percentages which are comparable with other researchers' results of the same experiment configurations or field-scale study. N species transformation performance was acceptable and consistent in the last one and half years of operation; the resulted species are comparable with other studies where decreasing organic-N, NH_4-N and increasing NO_3-N and in some detectable NO_2-N were indicating of the activity of the tidal flow regime providing the balance between the aerobic and anoxic/anaerobic condition with present facultative heterotrophic bacteria. These required conditions seemed to be ideally available in loamy sand CWs and to a lesser extent in BFS and then gravel. The highest fraction of TN in the effluent was organic-N followed by NO_3-N. P removal was more effective in loamy sand CWs then BFS and gravel which was explained by active plant growth for P uptake in addition to other removal mechanisms.

Chapter 5: The influence and modelling of operation conditions on VFCW retention behaviour

5.1 Introduction

The widely used CWs for stormwater clarification by retaining various pollutants involve complex physical, chemical, and biological removal mechanisms. However, these mechanisms most likely depend on the loaded stormwater volume and the frequency of the loaded volume besides other factors, such as present vegetation, physical properties of influent stormwater, influent pollutant concentration, and substrate characteristics. Therefore, six pilot-scale VFCWs were designed to understand the effect of three cases of wetland/watershed catchment area ratio (WWAR) and three cases of wet-dry regime conditions on the removal behaviour. Two identical CWs were the connection between the two cases of operation (CW1 and 2). Furthermore, it is very easy to compare the influent and effluent pollutant concentrations and then calculate the removal percentage, which is unlikely to give very limited information to be used in performance prediction and CW design. Thus, a generalised prediction model based on a variety of design and operation conditions is required.

Therefore, the following objectives set for this chapter are:

1- Investigate, understand, and compare the effect of changing WWAR values on TSS, heavy metals, and nutrients removal.
2- Investigate, understand, and compare the effect of various dry-wet regime conditions on TSS, heavy metals, and nutrients removal.
3- Build and assess a statistical prediction model generalising the various operating conditions.

In order to compare and understand the performance behaviour, mass balance equations, mentioned in Chapter 4 were used to normalise the removal data according to applied operation condition. The non-parametric statistical analyses were utilised to support and deeply understand the impact and the difference. Partial least squares regression analysis (PLS) was implemented to build a general model to cover all the operating conditions.

5.2 Removal behaviour under different wetland/watershed area ratios

Three different wetland/watershed area ratios of 5%, 2.5%, and 1.5% have been experimented in the pilot-scale CWs of 5, 1 and 2, and 6 respectively. The impact of WWAR changing on the removal performance behaviour of the prementioned CWs was deeply examined for predominant urban stormwater pollutants. These CWs with the same substrate (loamy sand) have the same wet-dry regime (three times wet a week) with 24 hours of stormwater occupation time. Thus, the WWARs were the only parameter being investigated for its effect on the removal of TSS, heavy metals, and nutrients from semi-synthetic urban stormwater. The tidal flow regime was operated to follow three times semi-synthetic urban stormwater loading a week periodically. The loading rates for CW5, CW1 and CW2, and CW6 were 11.3 l, 22,5 l, and 37.6 l respectively per 24-hour retention time. The resulted data were explored, discussed, and tested statistically to show the impact and the significant differences, as illustrated in the following sections.

5.2.1 TSS removal

The distribution of TSS removal percentages across 5%, 2.5%, and 1.5% WWARs is demonstrated in Figure 5.1. At the start time of semi-synthetic urban stormwater loading to VFCWs, low TSS removal values were recorded which represented as outliers relative to the total removal performance, which was more pronounced in CW2. After the stormwater continued being loaded in various volumes, more TSS were strained, settled, and attached with loamy sand particles according to the removal mechanisms explained in more detail in Chapter 4. All the pilot-scale VFCWs with various WWAR values performed similarly, apart from CW1 and CW2, with almost the same lower, median, and upper TSS removal percentages. Where the mean TSS removal percentage values were in the following order: 91.1% (CW1) < 92.3% (CW5) < 93.9% (CW6) < 95.0% (CW2). However, despite the difference between CW1 and CW2, the non-parametric statistical analysis showed there were no significant differences between the CWs' performance of 2.5% WWAR and 1.5% WWAR, while a significant impact of changing WWAR value from 5% to 2.5% on the TSS removal was found; see Table 5.1. At 5% WWAR value, the stormwater volume loaded three times a week in the cycle was 11.3 l while with 2.5% WWAR value, the loaded volume increased to 22.5 l three times a week in cycle indicating that the more stormwater applied to CW the more suspended solids trapped on and between substrate particles, making a layer on the substrate surface and reducing spaces between the particles, thus the removal performance increased. Increasing the stormwater loading volume leads to an increase the amount of TSS load to the CW causing improved removal performance in a shorter time in comparison with lower values of WWAR. This was not clearly identified in CW6 which received the highest loading volume because of unexpected operation difficulties causing to shift the commissioning of the experiment in this unit until week 24.

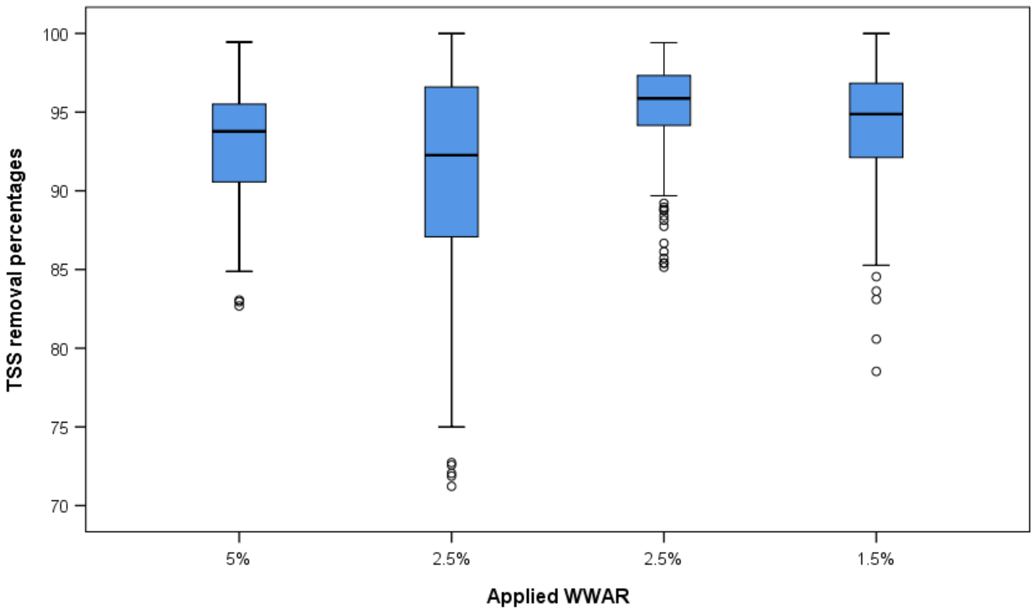


Figure 5.1 Error bars of TSS removal performance differences between loamy sand CWs of 5, 1 and 2, and 6 operated under 5%, 2.5%, and 1.5% WWAR respectively.

The two identical CWs, 1 and 2, showed a significant difference in the TSS removal performance which could be explained by many reasons. Although the gradual grain size of loamy sand particle in all the instructed CWs was the same, it is possible that CW1 had different particle size arrangements due to unavoidable misconstruction of the WC layers during the installation. This might affect the pore size distribution which results in a poor straining mechanism or even inflow shortcuts as a result of unequal flow distribution within these unstratified layers. Moreover, the frequent pouring of stormwater could disturb the previously accumulated solids between the substrate particles or prevent from generating a layer of settled solids on the surface which could be the reason for this difference. Additionally, the substrate of CW1 might have more fine particles than the others which could be washed out during the processes of loading and discharging of stormwater causing higher effluent TSS concentrations in the early stage of CW operation as reported elsewhere (Hatt et al. 2007a).

Table 5.1 Statistical Kruskal-Wallis comparison results between CWs with different WWAR values for pollutants removal from urban stormwater, where the significant difference in the performance is accepted if the significance level is 0.05 or lower.

Pollutant	WWAR	5%	2.5%	2.5%	1.5%
	CW	5	1	2	6
TSS	5	1.000	1.000	0.000	0.334
	1		1.000	0.000	0.104
	2			1.000	1.000
	6				1.000
Fe	5	1.000	0.183	0.081	0.003
	1		1.000	0.000	0.000
	2			1.000	1.000
	6				1.000
Zn	5	1.000	1.000	1.000	0.842
	1		1.000	1.000	1.000
	2			1.000	1.000
	6				1.000
TN	5	1.000	1.000	1.000	1.000
	1		1.000	1.000	1.000
	2			1.000	1.000
	6				1.000
PO_4-P	5	1.000	0.000	0.000	0.000
	1		1.000	1.000	0.000
	2			1.000	0.000
	6				1.000

A successful TSS removal performance of both 2.5% (CW2) and 1.5% (CW6) was achieved in comparison with removal performance of 5% (CW5). CWs received large inflow stormwater volume, meaning high SS loaded on a short time leading to more solids aggregate in the CW, thus reducing remobilisation of previously captured solids providing adhesive surfaces that improve the removal performance as stated elsewhere (Blecken et al. 2010). Thus, both CW2 and CW6 of 2.5% and 1.5% WWARs respectively are the most suitable for TSS removal as the substrate structure built up quickly in a short time of operation. However, with the progression of the operation time, all CWs showed a constant TSS removal performance at a high level.

5.2.2 Heavy metals removal

The treated semi-synthetic urban stormwater in VFCW1, 2, 5, and 6 at different WWARs had heavy metals concentrations of Pb, Ni, Cd, Cr, and Cu below the detection limits except for Fe and Zn which were within the measuring limits. Therefore, the focus in this section is on the removal performance of Fe and Zn at 5%, 2.5%, and 1.5% WWAR operation conditions. To show the impact of WWAR changing on the removal of these two metals from urban stormwater, removals based on substrate weight and the loaded volume, and in comparison with the loaded weight fraction values were demonstrated. Moreover, statistical analysis was used to distinguish the significant differences in the removal performance between the VFCWs at various WWAR levels.

In Figure 5.2, it was clear high performance and comparable at the same time of Fe removal weight in all CWs. It can be seen from the figure that even with a gradual increase in Fe loading from 5% WWAR (CW5) to 1.5% WWAR (CW6), the removal weight in comparison to the loading weight was constant, apart for the first few weeks of operation, especially in CW1. In comparison between the CWs, the highest removal weight was accounted for in CW6 which was loaded with the highest Fe weight, then followed by CW1 and CW2, and the least was CW5 where the lowest Fe weight was loaded, indicating constant removal performance even with applying high Fe load. The Fe removal percentage mean values were in the following: 93.6 (CW1) < 95.7 (CW5) < 96.6 (CW2) < 98.6 (CW6). High variation in the performance in the first few weeks of operation was recorded for CW1, CW2, and CW5 generating standard deviation in the removal percentage values of 5.0, 4.8, and 4.3 respectively, while CW6 was constant in the removal performance with the least variation of 1.3%. After 1200 l of accumulating loaded urban stormwater, the variation in the Fe removals was constant in most cases, especially in CW1 and CW2. However, the statistical analysis confirmed a significant effect of WWAR on Fe removal when the ratio changed from 5 to 1.5%, while changing the ratio from 2.5% and 1.5% did not affect the Fe removal significantly, as shown in Table 5.1.

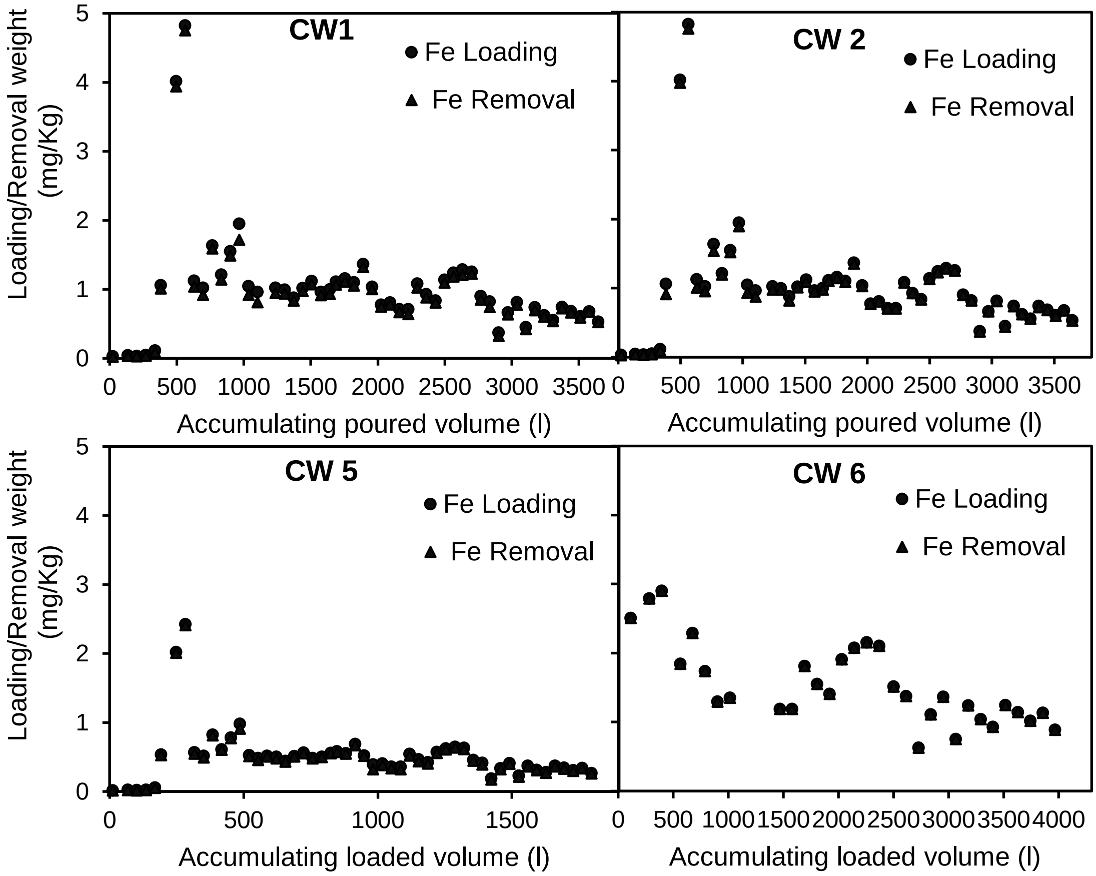


Figure 5.2 Performance of pilot-scale CW1, CW2, CW5, and CW6 with the applied WWAR of 2.5%, 2.5%, 5%, and 1.5% respectively for Fe removal based on the comparison between loaded weight and removal weight of Fe per unit weight of the loamy sand substrate.

Although the general performance and main removal mechanisms of heavy metals were demonstrated in Chapter 4, a more thorough explanation about how the different applied WWAR values could affect the removal performance is required. The partitioning analysis of seven weeks showed that Fe in the semi-synthetic urban stormwater (influent) was entirely particulate and there was no clear correlation between the particulate Fe form and TSS which could be interpreted by the weak bonding and/or precipitation of the Fe with the normal sand and clay found in the roads in smaller and variable weight relative to the solid fraction. In the same partitioning analysis for each effluent from the VFCWs (except CW4 using BFS), a clear high correlation between the effluent TSS and particulate form of Fe was found (R^2 located between 0.688 and 0.961), indicating that the Fe was mainly removed alongside TSS in the same removal mechanisms of straining, sedimentation, and adsorption to already attached or previously settled solids. The relation between the effluent Fe and TSS concentrations at three levels of WWAR is presented in Figure 5.3. This relation, in most cases, increased as the WWAR value decreased which could indicate that the more stormwater loaded (coincided with the least WWAR value) to CW, the higher the TSS removal and consequently more Fe retention in CW resulting in high correlation, as the R^2 increased from 0.6168 at 5% AWWAR value to 0.8876 at 1.5% WWAR value.

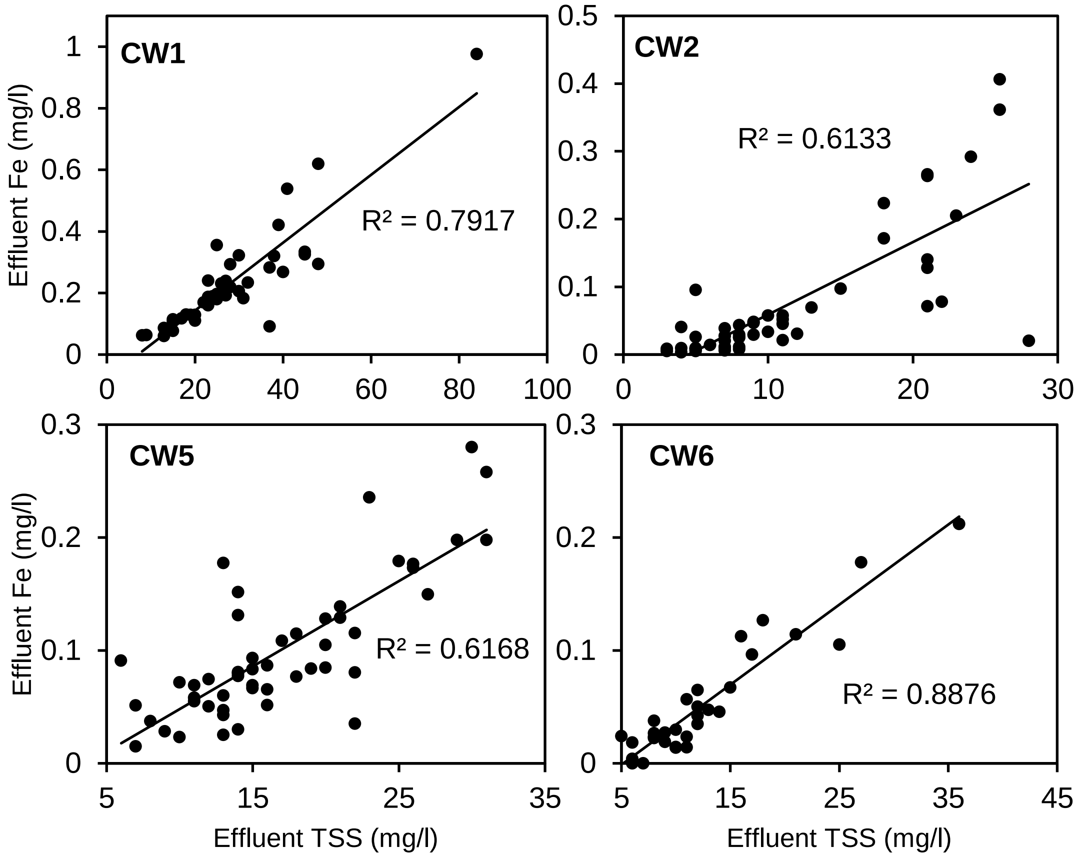


Figure 5.3 Relationship between the effluent concentrations of TSS and Fe at WWAR percentages of 5% (CW5), 2.5% (CW1), 2.5% (CW2), and 1.5% (CW6).

The zinc removal performance of VFCWs with various WWAR values is demonstrated in Figure 5.4. The removal distribution over the accumulating loaded stormwater is based on the loaded volume per cycle to distinguish between the performances. As the highest WWAR value means the lowest Zn loaded to CW and vice versa, thus the high loading weight of Zn found in CW6 and lowest found in CW5. The mean values of Zn removal percentages over the whole of the experiment period were 75%, 77%, 78%, and 86% for CW1, CW5, CW2, and CW6 respectively. To find if there is a significant difference in the removal performance, the Kruskal-Wallis test results, shown in Table 5.1 showed that there is no significant effect of changing AWWAR value on the Zn removal performance.

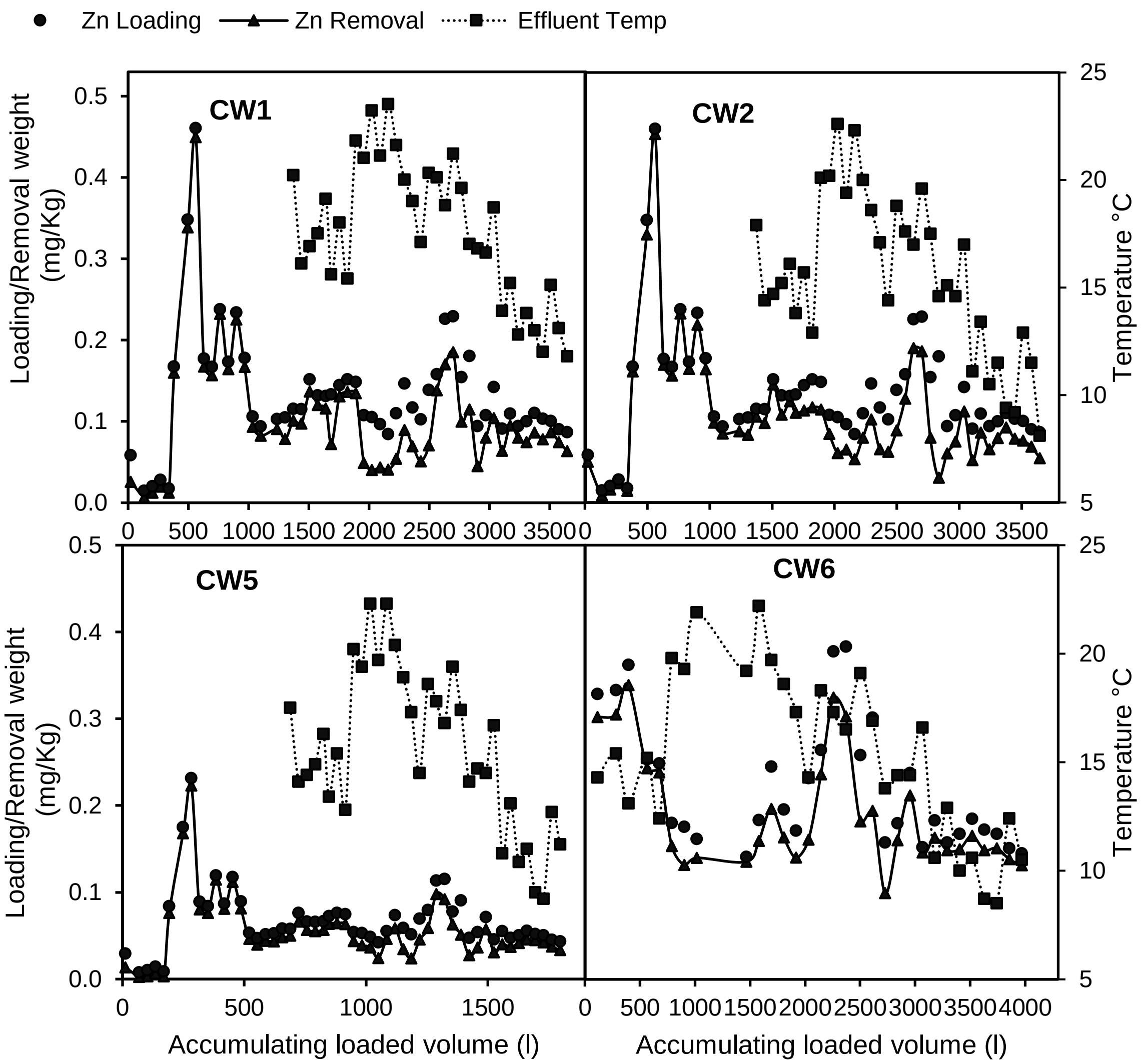


Figure 5.4 Performance of pilot-scale CW1, CW2, CW5, and CW6 with applied WWAR of 2.5%, 2.5%, 5%, and 1.5% respectively for Zn removal based on the comparison between loaded weight and removal weight of Zn per unit weight of loamy sand and the outflow temperature.

The removal weight was the highest in CW6 of 1.5% AWWAR and this weight decreased as the value of WWAR increased to 5%. However as shown in Figure 5.4, the CWs showed inconsistent Zn removal weights; as an example, in CW1 and CW2 the removal moved from the same scale of removal weight, relative to the Zn loading weight to different behaviour at the accumulating stormwater volume of 1950 l and then the removal changed to a steady removal level from the accumulating volume of 3170 l to the end of the experiments. It is clear from Figure 5.4 that the variation in the removal consistency at those ranges of accumulating volume is associated with increasing the effluent temperature. The temperature impact on Zn removal could be related to an increase in biological activity and then the release of the previously adsorbed Zn through the processes of growth, decay, and decomposition of the biological-based system. However, there was not a clear direct trend between the temperature and removal behaviour which is also confirmed elsewhere (Blecken et al. 2011). Moreover, it has been noticed from the partitioning analysis discussed in Chapter 4, that there was an increase in Zn dissolved fraction from inflow to outflow in only loamy sand CWs. The loamy sand CWs showed active growth of *Typha latifolia* and the first sign of growth was in March 2014, then the plant established well during spring and summer seasons before the signs of dying appeared in October, until they became completely brown on November 2014. Thus, the active plant growth indicated an increase in biological activity and then the decomposition process of *Typha Iatifolia* during the winter season resulted in DOM release and consequently release of the previously adsorbed Zn. This life cycle of growth, death, and decomposition in such a bio-retention regime could cause elevating Zn dissolved fraction in the outflow. However, plant uptake play a minor role in the metals removals from stormwater to contribute 0.2 to 7% of total removal as observed by Read et al. (2008) where uptake was usually determined either experimentally or through mass balance calculation (Dietz and Clausen 2006; Muthanna et al. 2007; Sun and Davis 2007). This can be confirmed more in CW3 and CW4 which used gravel and BFS as substrates where both attended high Zn removal, hence the removal of the dissolved fraction was achieved even with hardly any growth of *Typha Iatifolia* in both CWs. In the partitioning analysis, about 88% of total influent Zn was in a particulate bounded form which could be removed via sedimentation, filtration, coprecipitation, or adsorption, therefore it is suggested that the majority of Zn form was removed via the prementioned mechanisms. All loamy sand CWs showed higher biological activity, concerning nitrification and denitrification processes than gravel and BFS as discussed in Chapter 4 and later sections. Thus, the activities of the microorganisms in loamy sand CWs might play the vital role in releasing the immobilised Zn, that was previously removed, under the anaerobic condition to permit increasing the dissolved fraction level in the outflow, as it been confirmed elsewhere (Sansalone et al. 1995; Sun and Davis 2007; Maniquiz-Redillas and Kim 2014).

5.2.3 Nutrient removal

5.2.3.1 Nitrogen removal

One of the bio-retention system features is effective in N removal, however, the applying of variable volumes of urban stormwater could affect the performance of these systems. Therefore, three different values of WWAR were elaborated to examine carefully the N species transformation under nitrification and denitrification processes. Figure 5.5 shows the N species transformation from the inflow to outflow at variable stormwater loading which matched the WWAR values of 5%, 2.5%, and 1.5% applied in CW5, CW1 and 2, and CW6 respectively; mean and standard deviation for the performance of CW1 and CW2 were present as they both had the same operating conditions and both produced the same removal performance. The concentration picture of these two N species was completely changed and consequently an increase in NO_3-N level mostly in the effluent via a combination of ammonification, nitrification, and denitrification processes as explained in detail in Chapter 4. From Figure 5.5, all CWs operated at three levels of WWAR values exhibited similar N species transformation and then similar TN removal efficiency performance behaviour. The mean values and the variation in the TN removal efficiencies for CW5, CW1, CW2, and CW6 were 76.1% ± 19.8, 76.8% ± 16.4, 76.5% ± 14.8, and 76.3% ± 12.1, respectively. The high variation in the TN removal reflected the gradual increase in N species reduction as the microbial community increased and this removal behaviour reached a steady level as the CW matured with the minor effect of ambient conditions such temperature, and pH. However, statistical analysis was conducted to find if WWAR has an impact on N removal behaviour, the results of non-parametric independent samples test showed no significant differences in TN removal under 5%, 2.5%, and 1.5% WWAR operation conditions.

The close performance in terms of N species transformation and then TN removal at different levels of urban stormwater loading could be reasoned to the long retention time of 24 hours being applied which was probably more than enough even for the highest loading volume of stormwater (represented 1.5% WWAR value). At the first time of operation, the microbial community started to confound between the loamy sand particles which could be clearly seen from the inconsistency in the performance regarding N species transformation and TN removal efficiency; see Figure 5.5. After the microbial community established very well in the CWs, N transformation routes and TN removal were more stable. The fully matured CWs would need less retention time to achieve the same removal performance for higher loading rate, which could be overcome via enhancing system aeration and then giving a buffer against the urban stormwater increments since a tidal vertical flow regime has been used (Saeed and Sun 2012). Thus, the highest 1.5% WWAR CW showed similar removal performance to the other two values. To support this removal behaviour similarity, Sun et al. (2017) stated that increasing the time of stormwater incubation does not elevate the N removal percentages in mature bio-retention systems.

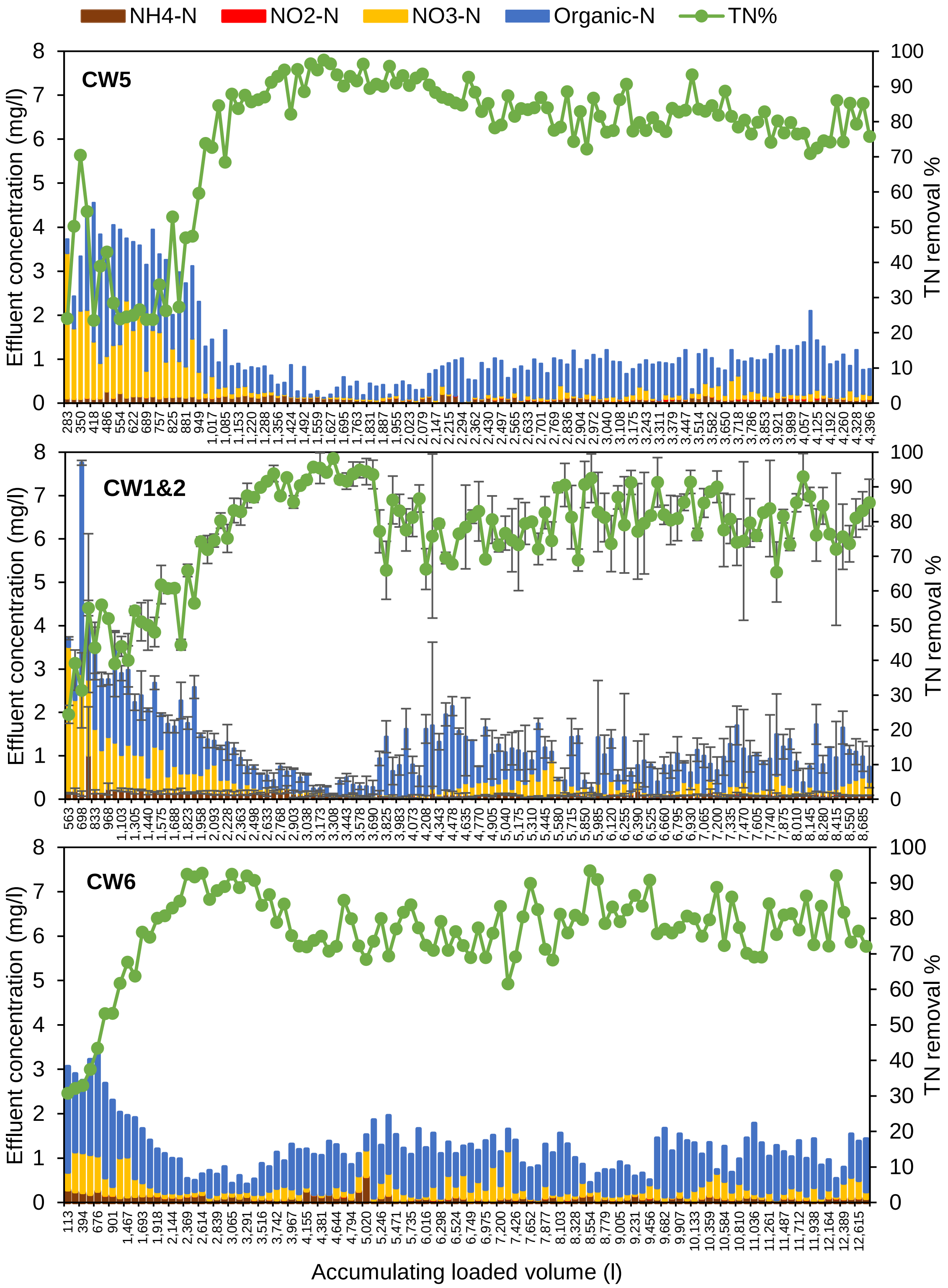


Figure 5.5 Total nitrogen removal efficiency and nitrogen forms transformation in the effluent semi-synthetic urban stormwater, operated under 5% (CW5), 2.5% (CW1&2), and 1.5% (CW6) WWAR values.

5.2.3.2 Phosphorus removal

As discussed in Chapter 4, the majority of P fraction was dissolved, and the particulate P fraction was in most cases completely removed likely via the same TSS removal mechanisms. However, the analysis of TP was tracking until a clear picture of its removal was identified. The distribution of PO_4-P loading and removal weights and the removal efficiency over different loading volumes at 5%, 2.5%, and 1.5% of WWAR values are demonstrated in Figure 5.6. As can be seen from the figure in all CWs that the differences between the loading and removal of PO4-P weights were highly variable at the beginning of stormwater loads and then tend to be stable after the bioretention system established. As more stormwater was loaded to the CW (in case of CW6), removal weight increased and improved over time, as shown in Figure 5.6. However, the highest removal percentage was accounted for CW5 which has the lowest loading volume and then the removal tended to decrease as the loading volume of stormwater increased, WWAR value increased from 5% to 1.5%. The average values of PO_4-P removal efficiency over the whole time of the experiment were 91.7%, 87.2% and 87.1%, and 82.0% for WWAR values of 5% (CW5), 2.5% (CW1 and CW2), and 1.5% (CW6) respectively. The statistical analysis of the Kruskal-Wallis test showed that there were significant differences in the removal performance at multi-levels of WWAR values ($p = 0.000$), as listed in Table 5.1. However, the removal weight increases as the WWAR values decreased while the removal percentages followed the opposite direction as it compares between the influent and effluent concentration.

As has been explained in the previous chapter, the removal mechanisms mainly depend on the phosphate calcium precipitation and minorly on the plant uptake and adsorption to metals oxyhydroxides. Thus, the higher stormwater loading volume the higher Ca dissolution from the loamy sand substrate required to precipitate the extra loaded PO_4-P, which clearly appeared after the accumulating loaded volume reached about 6000 l. Another minor factor that could play a role in the variance of removal performance is the plant and microbial activities, by consuming more P as required in their biomass and after the decay of dead plants causing P release resulting in increasing effluent concentration and then variation in the removal. An earlier study (Shrestha et al. 2018) confirmed that a high loading rate of stormwater had consistently negative impacts on P removal efficiency of bio-retention systems via pollutants mobilisation, and moreover, Martín et al. (2013) found significant differences in P removal efficiency calculated at different heights on VFCW during the seasons, which confirmed the effect of plant uptake and microbial activity on the variation on the removal. The differences in the output could be clarified on what base the comparison has been made, and by normalising the influent and effluent concentration to the loading rate a real picture of the performance is obtained.

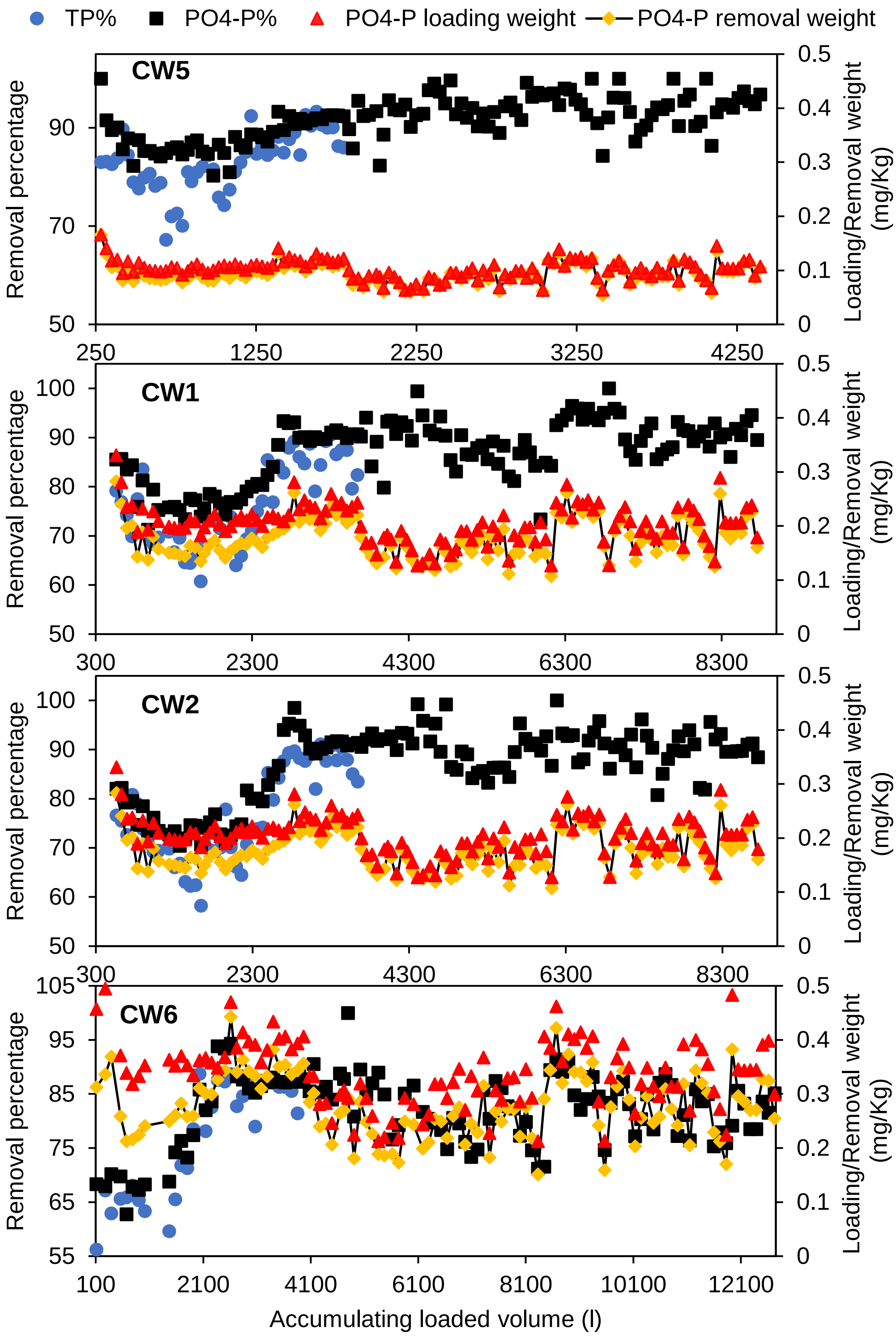


Figure 5.6 Variation of TP and PO_4-P removal percentages and effluent temperature over the accumulated volume of the stormwater loaded at 1.5%, 2.5%, and 5% AWWAR values to CW5, CW1 and CW2, and CW6 respectively.

5.3 Removal behaviour under different wet-dry regimes

Three wet-dry regimes were utilised in CW1 and CW2 as wet condition (WC), CW7 as partial dry condition (PDC), and CW8 as extended dry condition (EDC). The loaded semi-synthetic stormwater of each prementioned CW was the same (22.5 l) with a 24-hour retention time. The loading frequencies were three times loading a week for WC CWs, three times loading a week followed by one dry for PDC CW7, and one week wet of three times loading followed by four weeks dry in the cycle for EDC CW8; more detail in Chapter 3. In these operation arrangements, the CWs have been evaluated for TSS, heavy metals, and nutrients removal variation, which is based on data exploring, comparison, and statistical analysis.

5.3.1 TSS removal

Despite the inequality in the TSS removal performance of CW1 and CW2 operated under the same wet-dry regime condition (WC), there was a gradual decrease in the average value of the TSS removal percentage when the applied regime changed from WC to PDC and then to EDC over the whole time of experiments, as presented in Figure 5.7. The average values of the TSS removal for WC CW1 and CW2, PDC CW7, and EDC CW8 were 93.1%, 91.5%, and 92.1% respectively. The non-parametric Kruskal-Wallis test of independent samples results displayed statistically no significant differences in the TSS removal between PDC regime and EDC regime while the WC regime performed toward TSS removal differently to the other two regimes.

The performance behaviour of wet-dry regimes mimicked the behaviour of applying different values of WWAR, where the less frequent loading volume the less TSS loading weight and the less TSS removal percentages are obtained. However, this effect of stormwater loading volume seems to be lessened when the drying period increases from wet operating conditions to partially or extended dry conditions. During the dry periods, the previously precipitated particles and organic matter undergo shrinkage due to evaporation, which leads to increase porosity. This is probably dependent on the length of dry time, weather condition (i.e., temperature, humidity, rain rate), and media type. Thus, the filtration capacity of PDC and EDC CWs increases resulting in reducing the chances of capturing suspended particles. However, in the rewetting period, the substrate will swell again and reduce the porosity, and then the physical removal mechanisms of suspended particles will improve over the time of rewetting. This behaviour was expected as the removal mechanisms of suspended particles were sedimentation and straining. The output from the experimental and statistical analyses of applying various wet-dry regime conditions is matched with other previous studies (Muthukaruppan et al. 2002; Hatt et al. 2007a).

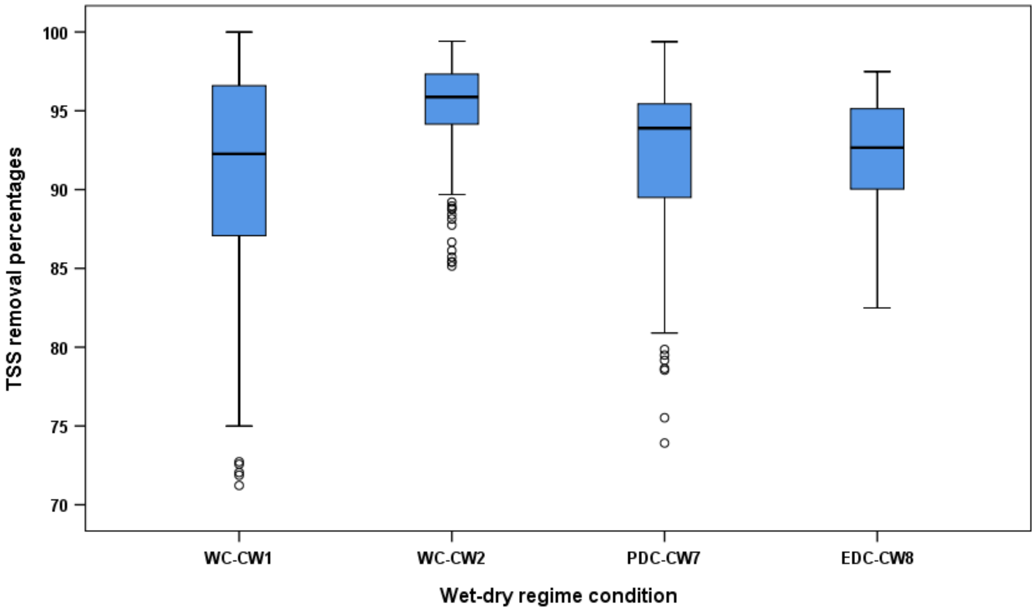


Figure 5.7 Error bars of TSS removal performance differences between loamy sand CWs of CW1 and CW2, CW7, and CW8 operated under three levels of wet-dry regime condition.

5.3.2 Heavy metals removal

As in the case of applying variable WWAR values, the effluent concentrations of heavy metals of Pb, Ni, Cd, Cr, and Cu from VFCWs operated at a different level of wet-dry regime conditions were below the detected limits, however, effluent concentrations of Fe and Zn were measured. Therefore, the only focus in the heavy metal removal section was on the Fe and Zn.

Figures 5.2 (CW1 and CW2) and 5.8 (CW7 and CW8) display the Fe loaded and removal weight performance relative to the discrete loaded volume per unit weight of the loamy sand at wet-dry regime conditions of WC, PDC, and PDC, respectively. Apart from the variation in the removal at the earlier stage of operation, all CWs showed similar removal behaviour even with high loading weight applied in several points as could be seen in the figures. The average removal values of these CWs at multi-levels of wet-dry regime conditions were approximately similar to each other (the removal of 94.3% was the same in CW7 and CW8, 93.6% for CW1, and 96.6% for CW2, where both operated as WC scenario). Moreover, the Kruskal-Wallis independent samples test found that the wet-dry regime operation conditions do not affect the Fe removal performance.

Table 5.2 Statistical Kruskal-Wallis comparison results between CWs with different wet-dry regimes for pollutants removal from urban stormwater, where the significant difference in the performance is accepted if the significance level is 0.05 or lower.

Pollutant	Wet-Dry regime (Wet times/week-Dry/week)	3-0	3 - 0	3 - 1	3 - 4
	CW	1	2	7	8
TSS	1	1.000	0.000	1.000	1.000
	2		1.000	0.000	0.000
	7			1.000	1.000
	8				1.000
Fe	1	1.000	0.000	1.000	0.964
	2		1.000	0.121	0.577
	7			1.000	1.000
	8				1.000
Zn	1	1.000	1.000	1.000	1.000
	2		1.000	1.000	1.000
	7			1.000	1.000
	8				1.000
TN	1	1.000	1.000	1.000	0.082
	2		1.000	1.000	0.378
	7			1.000	1.000
	8				1.000
PO_4-P	1	1.000	1.000	1.000	1.000
	2		1.000	1.000	1.000
	7			1.000	1.000
	8				1.000

.

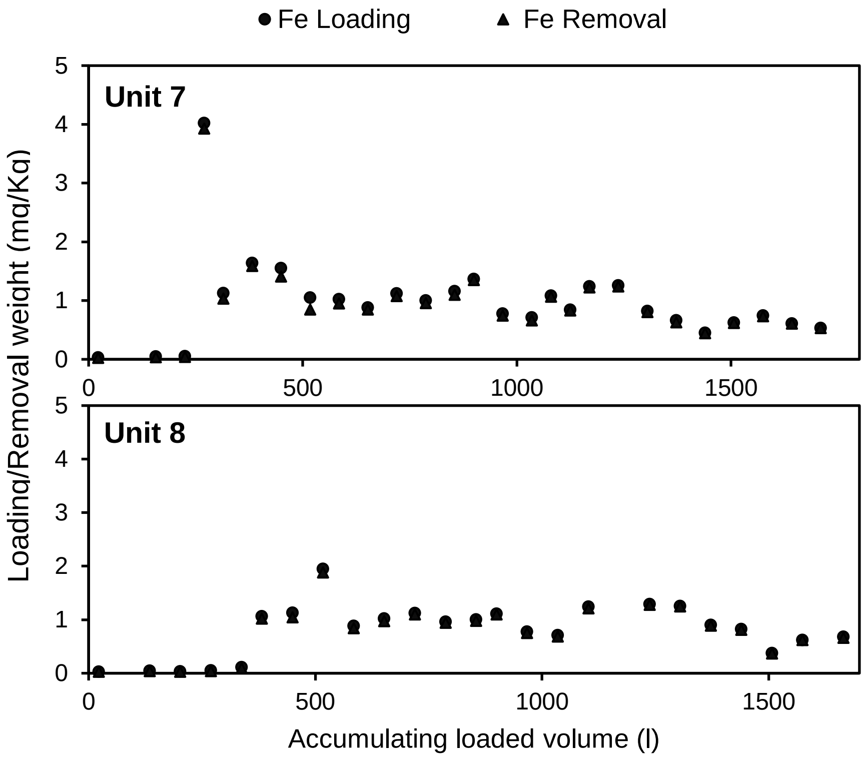


Figure 5.8 Fe removal based on the comparison between loaded weight and removal weight of Fe per unit weight of loamy sand substrate in PDC CW7 and EDC CW8.

As mentioned in Chapter 4 and Section 5.2.2, influent Fe was entirely particulate bound metal. Therefore, the Fe removal mechanisms are assumed the same as TSS removal mechanisms. Thus, a high relationship between the effluent TSS and Fe was found in all cases of the wet-dry regime, as present in Figure 5.3 for CW1 and CW2 and Figure 5.9 for CW7 and CW8. This finding reflects those of Hatt et al. (2007b) who also found that the rewetting of bio-retention systems after an extended dry period does not influence the heavy metals removals.

While Zn loading and removal weights with effluent temperature under three levels of wet-dry regime conditions are illustrated in Figures 5.4 (for CW1 and CW2), and 5.10. All the CWs expressed constant removal performance except the segments coincided with increasing the temperature which caused an elevation in the dissolved fraction of Zn due to the increase in biological activities as explained in Section 5.2.2.

The average values of removal efficiency were 75.1%, 78.3%, 84.7%, and 82.5% for CW1, CW2, CW7, and CW8 respectively. However, the non-parametric test showed that the extended dry period does not impact on the removal ($p = 1.000$). Nonetheless, it seems that PDC and EDC improved the Zn removal in comparison with the WC case. A possible explanation for this slight difference in the removal might that partially and extended dry regimes lessen the microbial activities and thus reduce dissolved Zn releasing under anaerobic or anoxic condition. Moreover, the rewetting of the substrate's particles following a period of drying enhances the previously adsorbed pollutant diffusion more into particle surface leading to a rejuvenation of the adsorbent surface (Zhao et al. 2009; Bai et al. 2014; Callery et al. 2016). This process could improve the adsorption characteristics especially for the increasing level of the dissolved fraction.

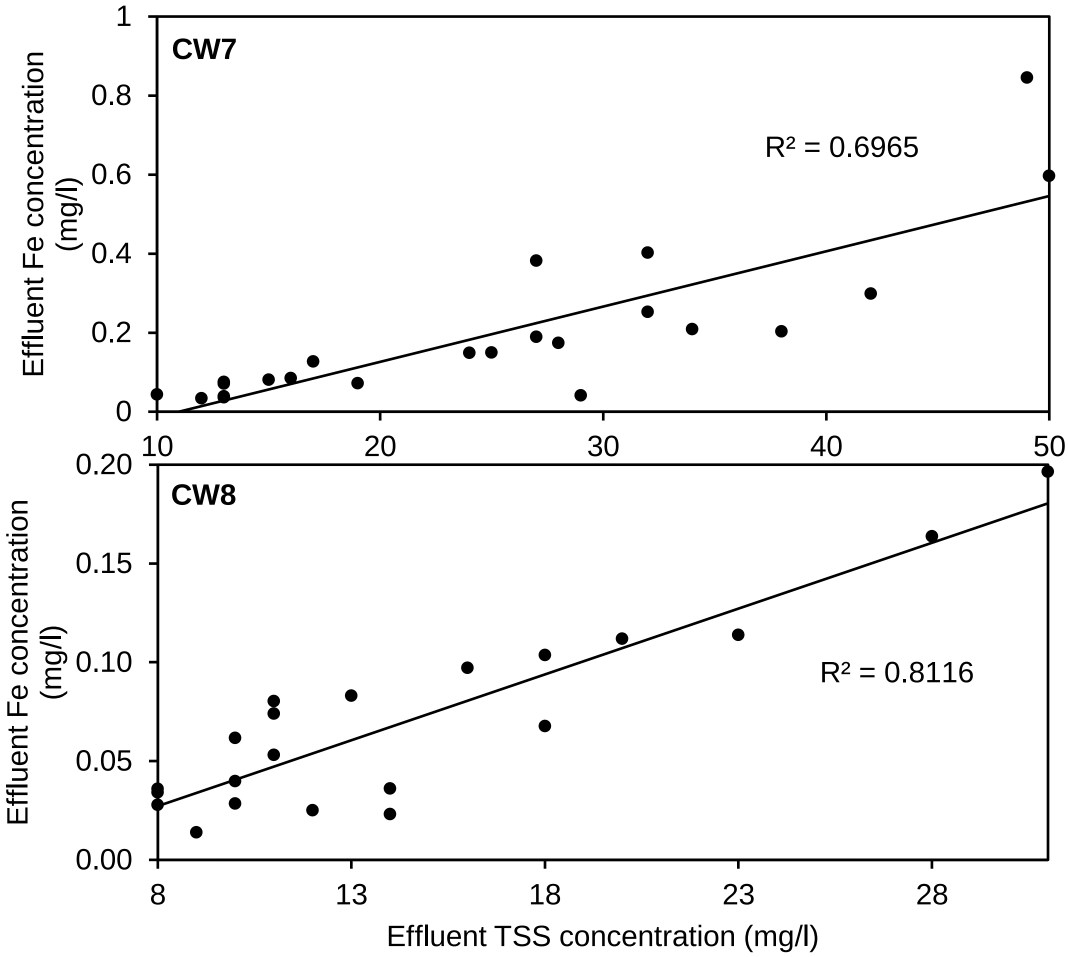


Figure 5.9 Relationship between the effluent concentrations of TSS and Fe at wet-dry regime conditions of PWC and EWC in CW7 and CW8 respectively.

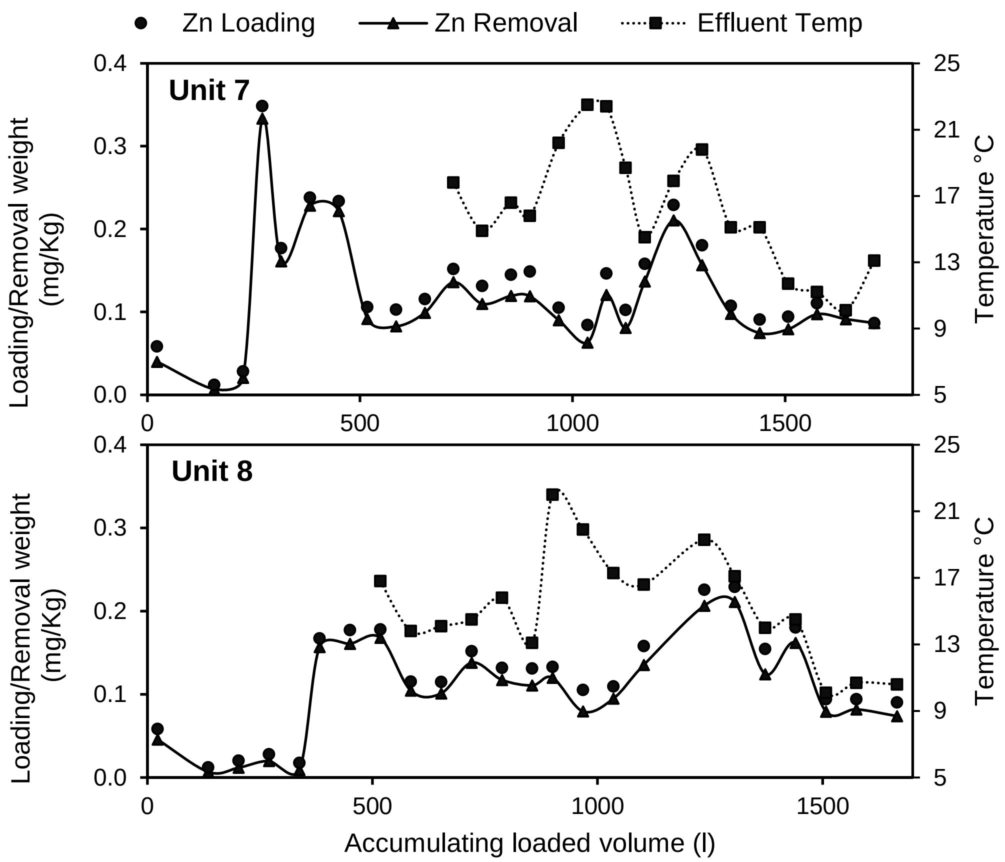


Figure 5.10 Zn removal based on the comparison between loaded weight and removal weight and the outflow temperature of the loamy sand substrate under the wet-dry regime of PDC and EDC in CW7 and CW8 respectively.

5.3.3 Nutrient removal

5.3.3.1 Nitrogen removal

Nitrogen species transformation from the influent and effluent and TN removal efficiencies under WC, PDC, and EDC are demonstrated in Figure 5.5 for CW1and CW2 (mean values and the variation in the performance presented) and Figure 5.11 for CW7 and CW8. From comparing these figures, the differences in effluent N species were almost the same between the three wet-dry regimes with no significant differences in the performance. Furthermore, the TN removal behaviour increases in all conditions as the CWs mature with the operation progressing. The mean values of TN removal percentages were 76.8%, 77.8%, and 74.6% for WC, PDC, and EDC regimes respectively. These mean values showed very close removal performance with a little decline in the condition from WC or PDC to EDC. However, the Kruskal-Wallis test showed that the removal performance of the CWs under the three levels of the dry-wet regime was statistically equal, as shown in Table 5.2.

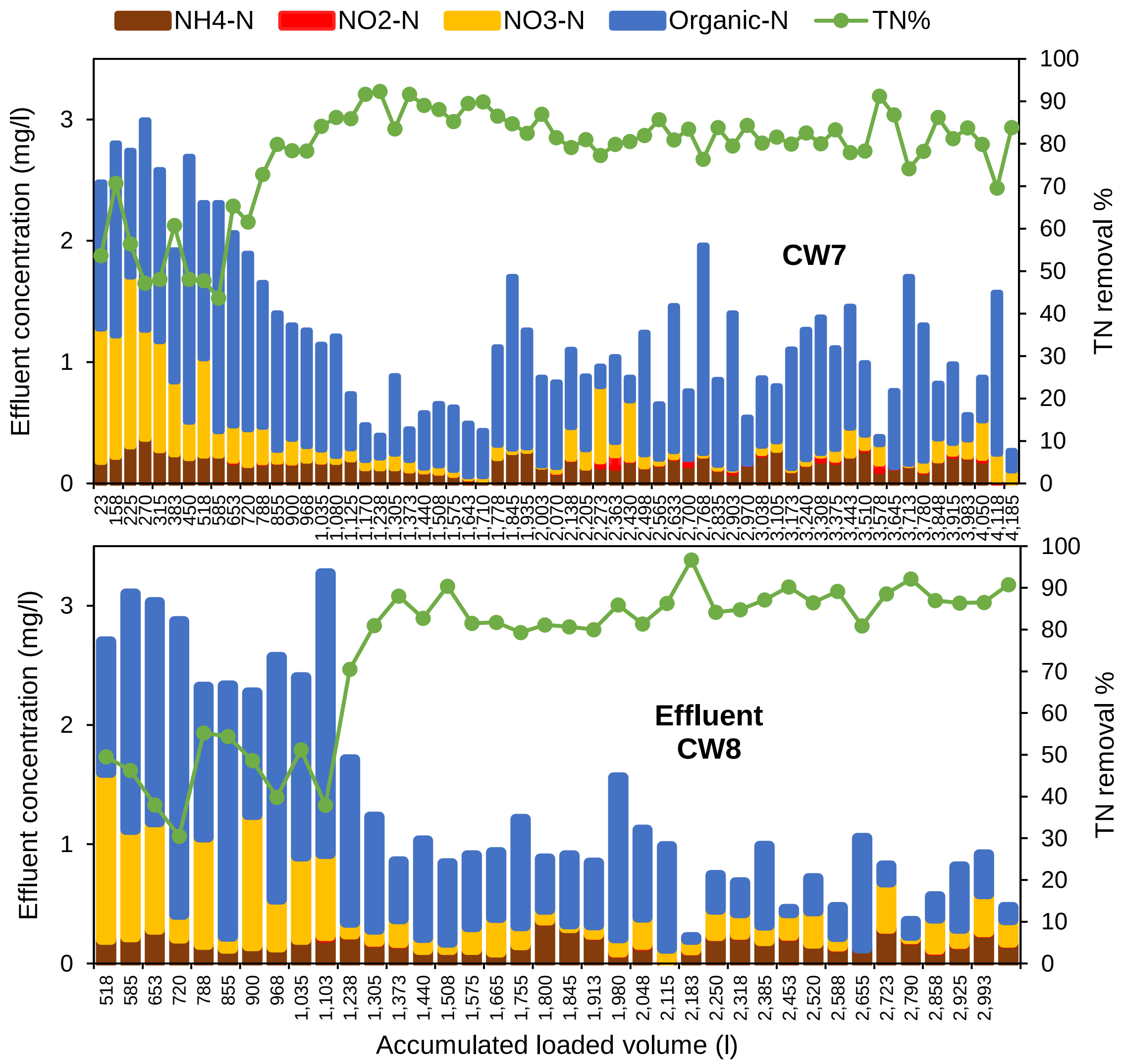


Figure 5.11 Total nitrogen removal efficiency and nitrogen species transformation between the influent and effluent semi-synthetic urban stormwater before and after pilot-scale VFCWs, respectively, operated under dry and extended dry–wet regimes of CW7 and CW8 respectively.

The close similarity in N species transformation in all cases of wet-dry regimes indicated successful ammonification, nitrification, and denitrification processes and that a microbial community established very well in WC CWs, and to lesser in EDC CW, as the denitrification process decreases due to the drying period (Rahman et al. 2019), where the longer dry condition could impact on the availability of microbial community growth and affects TN removal. The drying condition increases the mineralisation rate of organic nitrogen via aerobic microbial, leading to accumulating cell-bound NH4-N which in rewetting condition is released into the water from dying bacteria during the drying period. Then, under flavour aerobic conditions, the released NH4-N is transformed to NOx-N (Scholz et al. 2002; Hatt et al. 2007a). These dry and rewetting operation conditions could lead to an increase in effluent concentrations of both NH4-N and/or NOx-N in addition to the high level of effluent organic-N. The hypothesised increasing concentrations were not significantly noticed in the effluent of the current study. This could be elucidated by the availability of enough moisture content in the loamy sand substrate due to relatively high humidity and rainy UK weather, enabling the microbial community in CWs to survive and remain active until the rewetting time. Thus, it could be concluded that partial and extended dry conditions applied in this study did not inhibit the activity of heterotrophic organisms and then did not affect TN removal performance.

5.1.1.1 Phosphorus removal

The orthophosphate removal behaviour of the VFCWs operated under variable wet-dry regime conditions was almost the same in WC CW1 and CW2 (Figure 5.6), PDC CW7, and EDC CW8 (Figure 5.12). Despite the decline in the removal weights or the corresponding removal efficiency at the beginning of the operation, the removal improved over time in all operation cases. Of particular notice was the continuous increase in the PO_4-P removal, and with less variation was observed in EDW CW. The averages and standard deviation values for EDW CW8, PDW CW7, and WC CW1 and CW2 over the experiment time were 86.9% ± 4.4, 86.9% ± 5.3, and 87.2% ± 6.5 & 87.1% ± 7.3, respectively. The statistical analysis also confirmed that the CWs behaved similarly in terms of P removal under variable conditions of the wet-dry regime.

The results are in line with other studies using unplanted VFCWs to treat stormwater in a range of wetting and drying regime conditions where P was not influenced by the rewetting following extended dry periods compared with wet periods (Hatt et al. 2007a). Other researchers have noticed that the tidal and intermittent loading regimes enable adsorbate molecules to diffuse further into the adsorbent surface before the next loading (Babatunde et al. 2010; Sengupta and Pandit 2011; Bai et al. 2014; Callery et al. 2016). However, as the dry period increases, outflow concentrations are likely to increase upon rewetting as a result of oxyhydroxides aging and release of the cell-bound P from dead bacteria during the drying period (Scholz et al. 2002). In the current study, the effluent P concentration in the PDC and EDC was continuously lower than the influent, and the N species transformation did not differ significantly as evidence of microbial community activity and without decay on the biomass or releasing P under extreme dry conditions.

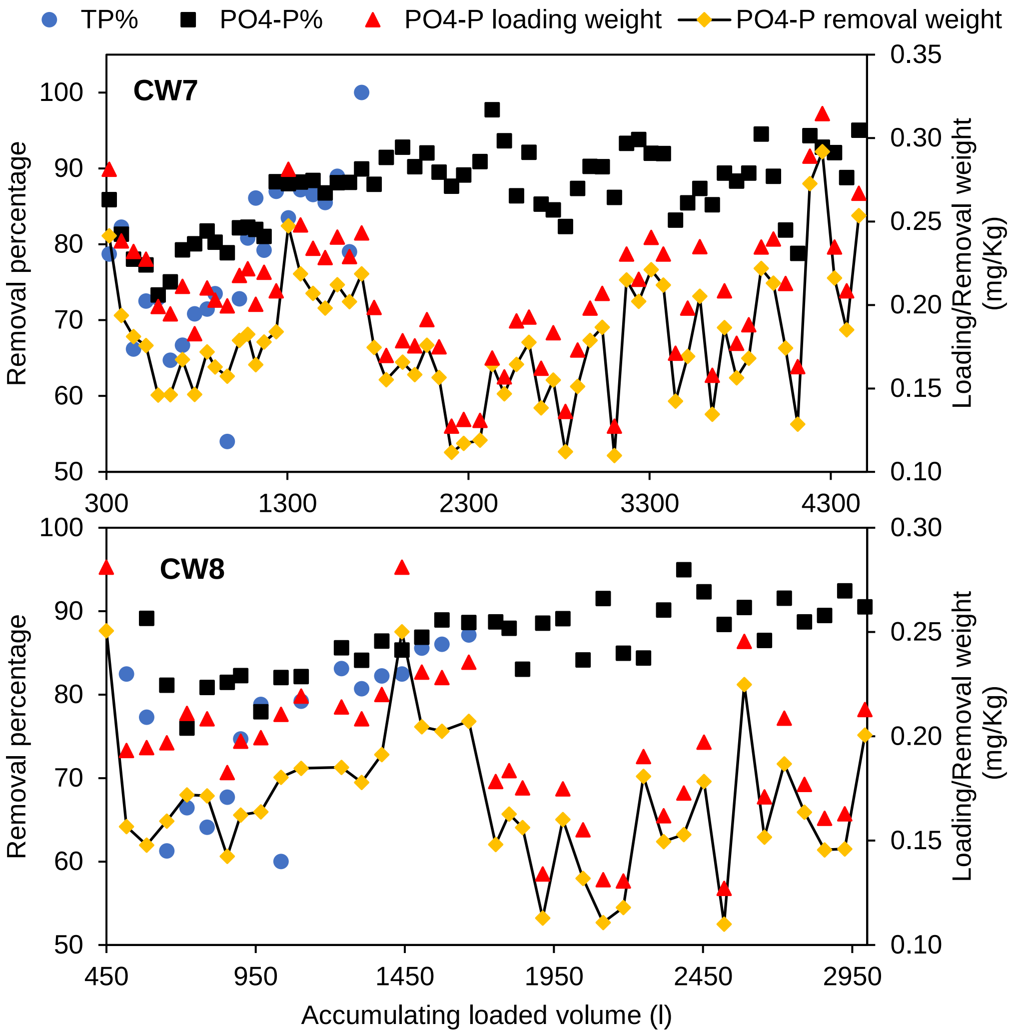


Figure 5.12 Variation of TP and PO_4-P removal percentages, loading, and removal weights over the accumulated volume of the stormwater loaded in variable wet-dry regime conditions.

5.4 Statistical analysis

Because of the complexity of pollutants removal in the ecosystems as a result of a combination of physical, chemical, and biological processes, it has become difficult to point out which mechanism is dominant to remove specific pollutants. Moreover, the common and easy way to evaluate CW performance is to compare the influent and effluent target pollutant concentration to compute the removal percentage, which has very limited implementations in terms of design or performance prediction. Therefore, a generalised statistical model based on long-term monitoring of pollutant removal performance coincided with variable design and operation conditions parameters has become a necessity for future applications.

In the current study, three wet-dry regimes and three loaded stormwater volumes (WWAR) were implemented using pilot-scale VFCWs packed using loamy sand substrate and planted with *Typha latifolia.* Instead of taking each condition of operation as a case for modelling the performance, all conditions were gathered to generalise the performance, as diagrammed in Figure 5.13. The accumulating stormwater volume loaded to the VFCWs is increased gradually when the conditions are dry and the discrete loaded volume convert to wet and high load values. Thus, the removal performance of loamy sand CWs was considered in the statistical prediction-based model for the variety of operating conditions within the same physicochemical characteristics. For this reason, CW3 and CW4 using gravel and BFS substrates with the same operation conditions were not included in the statistical analysis. The average values for the monitored parameters in the identical CW1 and CW2 were used to reduce the errors resulting from the differences in the output results and the over correlation of duplicated input. Thus, CW2 in the model represents the average values for the removal performance of CW1 and CW2.

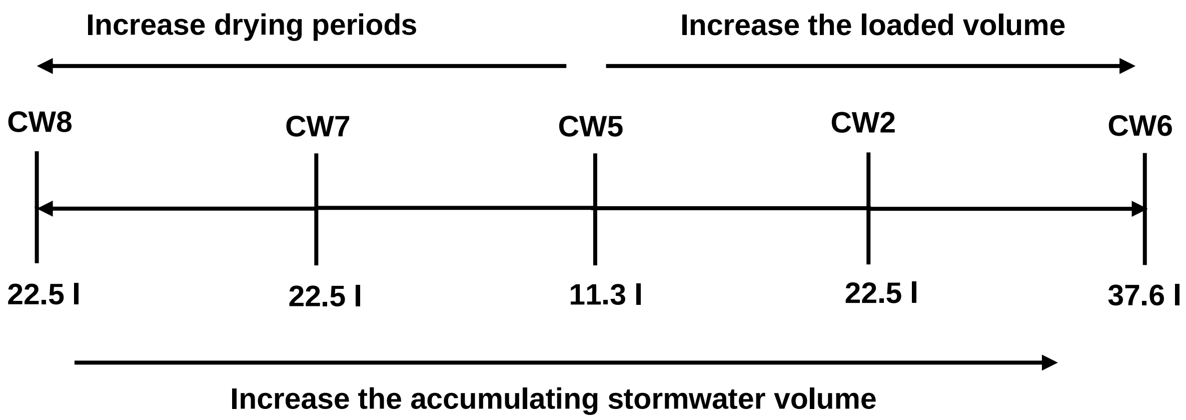


Figure 5.13 Schematic diagram for the variable operation conditions included in the generalisation statistical prediction model (mean values were taken for the symmetrical CW1 and CW2 represented as CW2).

5.4.1 Data preparation and the correlation

The monitoring procedure for performance of different pollutants removal was differently scheduled, therefore, the monitored data of physical stormwater properties, TSS, heavy metals, and nutrients were divided into two data sets. The first data set included pH, T, EC, TSS, Fe, Zn, TN, and TP which were used to predict Fe, Zn, and TP. The other heavy metals (Pb, Ni, Cd, Cr, and Cu) were not used in the statistical analysis as their effluent concentrations were undetectable. The second data set included pH, T, EC, TSS, TN, and PO_4-P which were used to predict TN and PO_4-P. In addition to these parameters, the accumulating stormwater volume was also included in the analysis for both sets which recognised the condition of the operation, where CW8 with EDC had the least accumulating volume while CW6 with 1.5% WWAR value had the highest accumulating volume etc. Moreover, the pollutants loading and accordingly their removal depend on the substrate weight and the discrete loaded volume. Thus, the mass balance equations (4.1 to 4.3) mentioned in Chapter 4 were the key point to distinguish the differences in the performance behaviour of CWs under various conditions.

In order to specify which of the monitored parameters under the various operations of VFCWs were the most correlated, data were screened and tested statistically to track the correlations. The loaded and removal weights of pollutants in both data sets, and also stormwater physical characteristics of stormwater and accumulating volume (V_a), were first explored for outliers, data normality distribution, and then bivariate statistical analysis. The predictor variables (independents) represent V_a, the influent stormwater pH, T, and EC and loading weights of TSS, Fe, Zn, TN, TP, PO_4-P while the response variables (dependents) represent the removal weights of Fe, Zn, TP, TN, and PO_4-P. From these analysing procedures, Table 5.3 and Table 5.4 were eluted for the first and second data set respectively. The non-parametric bivariate correlation coefficients (r) and their statistical significance assigned with an asterisk were listed on these prementioned tables; Spearman's correlation was used as the data violated the parametric assumptions. The r value is usually used to measure the size of an effect and r values of ± 0.1 mean a small effect, ±0.3 mean moderate effect and ± 0.5 is a large effect. The r values usually locate between -1 and +1 and the sign indicates the correlation direction (Field 2013). On both data sets, V_a had a positive effect on TP-RW and PO_4-RW at a significant level of 0.01 which means the removal increases with the increasing of the accumulating stormwater with the time of operation and this matched the previously discussed results in Section 5.1.2.3, where the removal weight increased as the WWAR value decreased from the 5% to 1.5%. pH had a positive effect on Fe-RW and negative on TP-RW which in both cases with increasing pH encourages Fe oxidation and consequently reduces the TP removal by small to moderate effect classification. As expected for both data sets, the loading weights of TSS, Fe, Zn, TN, TP, PO_4 had the most significant positive effect on the removal weights of Fe, Zn, TP, TN, PO_4.

Table 5.3 Correlation coefficients between the influent physical properties of stormwater, pollutants loading, and pollutants removal based on first data set extracted from five CWs operated at different operation conditions.

Parameter	V (l)	pH	T (°C)	EC (ms/cm)	TSS-LW[a] (mg/Kg)	Fe-LW (mg/Kg)	Zn-LW (mg/Kg)	TN-LW (mg/Kg)	TP-LW (mg/Kg)	Fe-RW[b] (mg/Kg)	Zn-RW (mg/Kg)	TP-RW (mg/Kg)
V_a (l)	1.000	-0.438**	-0.319**	-0.062	0.326**	-0.076	0.063	0.371**	0.420**	-0.054	-0.058	0.492**
pH		1.000	0.442**	0.079	-0.043	0.283**	0.127	-0.049	-0.173*	0.275**	0.151	-0.249**
T (°C)			1.000	0.422**	-0.029	0.225**	0.153	-0.006	-0.111	0.218**	0.115	-0.163*
EC (ms/cm)				1.000	-0.001	0.077	0.055	0.052	-0.020	0.067	-0.042	-0.044
TSS-LW (mg/Kg)					1.000	0.757**	0.823**	0.877**	0.892**	0.757**	0.772**	0.853**
Fe-LW (mg/Kg)						1.000	0.917**	0.704**	0.621**	0.997**	0.905**	0.563**
Zn-LW (mg/Kg)							1.000	0.793**	0.751**	0.920**	0.960**	0.719**
TN-LW (mg/Kg)								1.000	0.884**	0.706**	0.729**	0.863**
TP-LW (mg/Kg)									1.000	0.628**	0.704**	0.972**
Fe-RW (mg/Kg)										1.000	0.908**	0.572**
Zn-RW (mg/Kg)											1.000	0.664**
TP-RW (mg/Kg)												1.000

[a] is the loading weight, [b] is the removal weight
* is statistically significant at level of 0.05, ** is statistically significant at level of 0.01.

Table 5.4 Correlation coefficients between the influent physical properties of stormwater, pollutants loading, and pollutants removal based on second data set extracted from five CWs operated at different operation conditions.

Parameter	V (l)	pH	T (°C)	EC (ms/cm)	TSS-LW[a] (mg/Kg)	TN-LW (mg/Kg)	PO_4-LW (mg/Kg)	TN-RW[b] (mg/Kg)	PO_4-RW (mg/Kg)
V_a (l)	1.000	-0.422**	-0.322**	-0.101*	0.246**	0.367**	0.364**	0.434**	0.416**
pH		1.000	0.398**	-0.178**	0.149**	-0.027	0.098*	-0.126**	0.040
T (°C)			1.000	0.455**	0.053	0.020	0.036	-0.062	-0.015
EC (ms/cm)				1.000	-0.013	0.051	-0.010	0.044	-0.029
TSS-LW (mg/Kg)					1.000	0.83**	0.879**	0.734**	0.838**
TN-LW (mg/Kg)						1.000	0.815**	0.941**	0.790**
PO_4-LW (mg/Kg)							1.000	0.742**	0.984**
TN-RW (mg/Kg)								1.000	0.746**
PO_4-RW (mg/Kg)									1.000

[a] is the loading weight, [b] is the removal weight
* is statistically significant at level of 0.05, ** is statistically significant at level of 0.01.

5.4.2 General statistical prediction model

In order to locate the best multivariate model, which can predict and explain the variation of the pollutants removal weights from the independent variables of physical stormwater properties and pollutants loading weights based on multilevel of operation conditions in VFCW, a partial least squares regression analysis (PLS) was used. 80% of the original data were used as a training set and the rest (20%) were chosen randomly as a testing set after model construction. PLS extracts a set of latent factors from the independent variable (matrix X) and dependent variables (matrix Y). The extracted latent factors should explain as much of the covariance on both matrixes as possible. Therefore, the extraction was stopped when there was no significant change in the declination of the predicted residual sum of squares (PRESS) or simply it is the sum of the squared Y distances to the model, as SPSS software provides these values within the output. The prediction quality was assessed using the residual sum of squares (PRESS) which is defined as the summation of the squares of the differences between the measured and the predicted dependent values. The smaller values of PRESS, the better model prediction, with a value of 0 meaning ideal prediction (Abdi 2010). Thus, six latent factors were extracted for both data sets, as shown in Table 5.5 and Table 5.6.

Table 5.5 Proportion of variance explained for X and Y matrixes by the extracted latent factors from independent and dependent variables respectively and models' coefficients resulted from PLS regression analysis of the first data set.

Latent factors	X Variance	Cumulative X variance	Y Variance	Cumulative Y variance (R^2)	Adjusted R^2
1	0.532	0.532	0.728	0.728	0.726
2	0.266	0.798	0.153	0.881	0.880
3	0.071	0.870	0.042	0.924	0.922
4	0.037	0.906	0.018	0.942	0.940
5	0.024	0.930	0.013	0.955	0.953
6	0.051	0.981	0.005	0.959	0.958

Model coefficients

Dependent variables	Constant	Independent variables							
		V (l)	pH	T (°C)	TSS-LW	Fe-LW	Zn-LW	TN-LW	TP-LW
					(mg/Kg)				
Fe-RW (mg/Kg)	-0.288	1.11E-05	0.037	-0.002	0.004	0.796	1.77	-0.008	-0.83
Zn-RW (mg/Kg)	-0.019	-8.65E-06	0.006	-0.001	-0.001	0.017	0.813	-0.007	0.133
TP-RW (mg/Kg)	0.173	1.16E-05	-0.018	-0.002	0.000	-0.067	0.533	0.036	0.419

Table 5.6 Proportion of variance explained for X and Y matrixes by the extracted latent factors from independent and dependent variables respectively and models' coefficients resulted from PLS regression analysis of the second data set.

Latent factors	X Variance	Cumulative X variance	Y Variance	Cumulative Y variance (R^2)	Adjusted R^2
1	0.414	0.414	0.784	0.784	0.783
2	0.143	0.557	0.066	0.850	0.849
3	0.115	0.672	0.047	0.896	0.895
4	0.175	0.848	0.013	0.910	0.909
5	0.076	0.924	0.019	0.929	0.928
6	0.033	0.957	0.015	0.944	0.943

Model coefficients

Dependent variables	Constant	Independent variables					
		V (l)	pH	EC (ms/cm)	TSS-LW	TN-LW	PO_4-LW
					(mg/Kg)		
TN-RW (mg/Kg)	1.182	2.76E-06	-0.136	-0.459	-0.002	0.835	-0.025
PO_4-RW (mg/Kg)	0.134	-2.13E-07	-0.014	-0.048	0.000	-0.004	0.901

The predicted models for both data sets were tested for their validation using the randomly chosen 20% as testing data, which had been excluded from the resulted models in PLS analysis. This step was done as a cross-validation procedure to check if the resulted models could be generalised to data from VFCW treating urban stormwater. the predicted values for the dependent variables for both training and testing data were calculated according to models' parameters listed in Table 5.5 and Table 5.6 for first and second data sets. The measured values (observed values) of Fe-RW, Zn-RW, TP-RW, TN-RW, and PO_4-RW were drawn against their predicted values, as shown in Figure 5.14. As can be seen from the figure, high-fitting values were obtained in all cases with almost the same prediction when the model moved from the training data to the testing data.

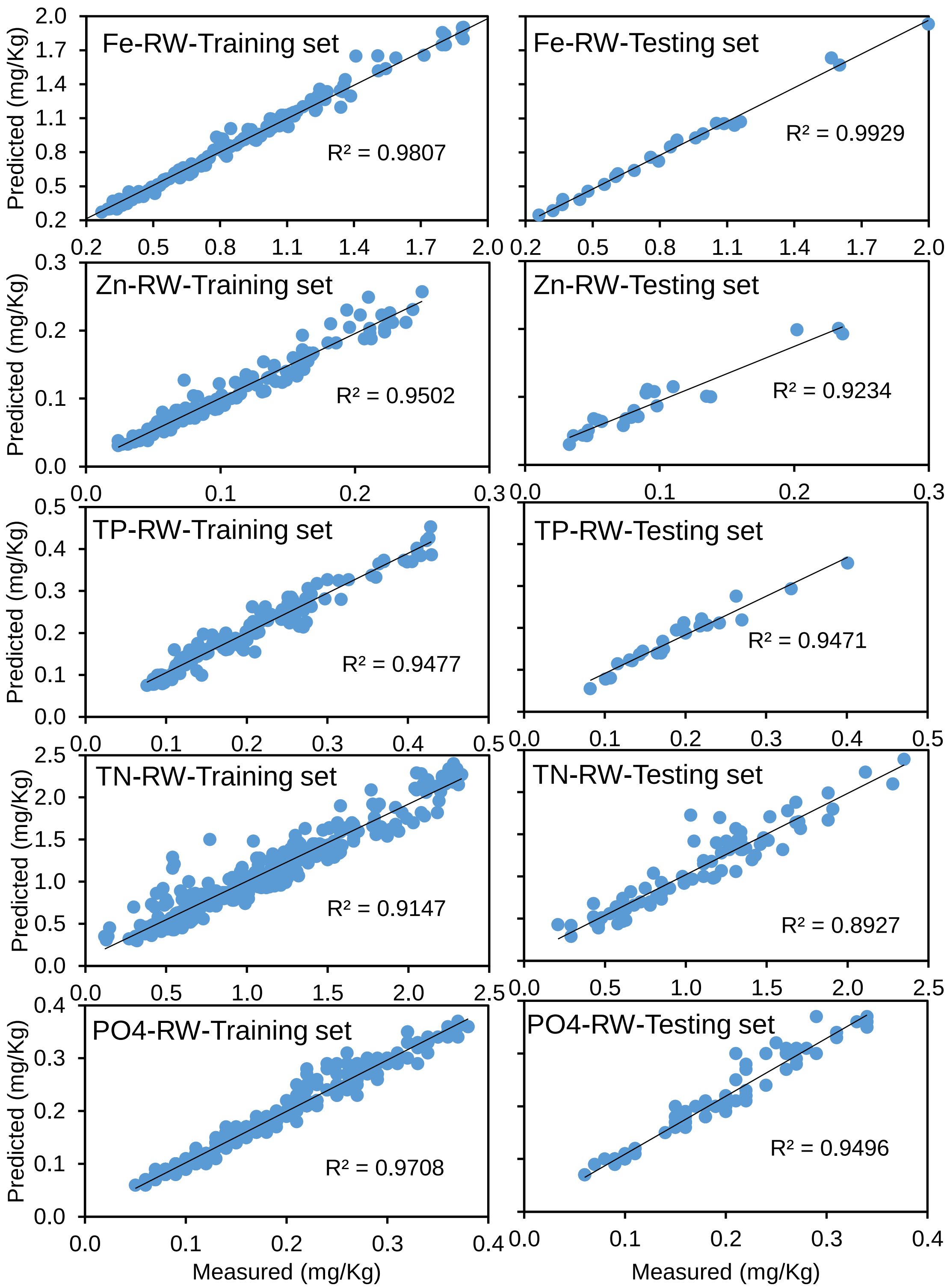


Figure 5.14 A correlation fitting comparison between the training and testing data as a model validation test for the measured versus predicted data of Fe, Zn, and TP removal weights (first data set) and TN and PO4 removal weights (second data set).

The high-fitting quality was obtained from the first data set used to model the CWs removal behaviour for Fe-RW, Zn-RW, and TP-RW which could be further supported by calculating the PRESS values 0.538, 0.023, and 0.062 for training data and 0.045, 0.001, and 0.012 for testing data respectively. In opposite, the second data set for prediction of TN-RW and PO4-RW showed noises around the prediction line especially with the TN case where the R^2 changed from 0.915 to 0.893 as the model used to validate the prediction power on external data. However, the PRESS for training and testing data was found to have changed from 84.17 to 8.012 and from 15.45 to 0.058 for TN-RW and PO_4-RW respectively. This was expected for the TN modelling as this process depends not merely on the media type and stormwater characteristics but also mainly on the microbial community that controls the nitrification and denitrification processes, which was not included in the model. Despite some noises on the data, the model was able to estimate closer prediction values to the testing data set as the PRESS dropped to 8.012.

The generalised prediction models were used to estimate the values of the dependent variable from the independent variables depending on the models' parameters mentioned in Tables 5.5 and 5.6 for each case of operating condition. The generated constants and the parameters of the models from all the data gathered from six CWs experimented at various operation conditions can be used to predict the individual long-term pollutant removal behaviour of each CW. The comparison between the measured values and the estimated ones for Fe-RW, Zn-RW, TP-RW, TN-RW, and PO4-RW against the accumulating loaded stormwater volume for CW8, CW7, CW5, CW2, and CW6 were demonstrated in Figures 5.15 and 5.16. It is clear from Figure 5.15 that high-fitting quality was present in all cases with minimal differences between the measured and the predicted dependent variables. The strength of fittings was expected which reflected the test result of the models' robustness, explained in the above section. Moreover, the measured data showed a consistent removal behaviour which reinforced the strength of prediction, as can be seen in Figure 5.15. On the contrary, TN-RW and PO_4-RW measured data exhibited persistent fluctuation which probably explained the variation between the measured and the predicted values. These differences were more pronounced in TN-RW than PO_4-RW that could be clarified for microbial activity within the CWs influenced by another vital factor not included in the model, such as the oxygen availability and facultative heterotrophs bacteria would both contribute significantly and improve the prediction. This analysis procedure can be utilised as a new method to generate a prediction model for various passive treatment systems in addition to the generalised models in this study that can be applied to other pilot- or field-scale systems with the same configuration.

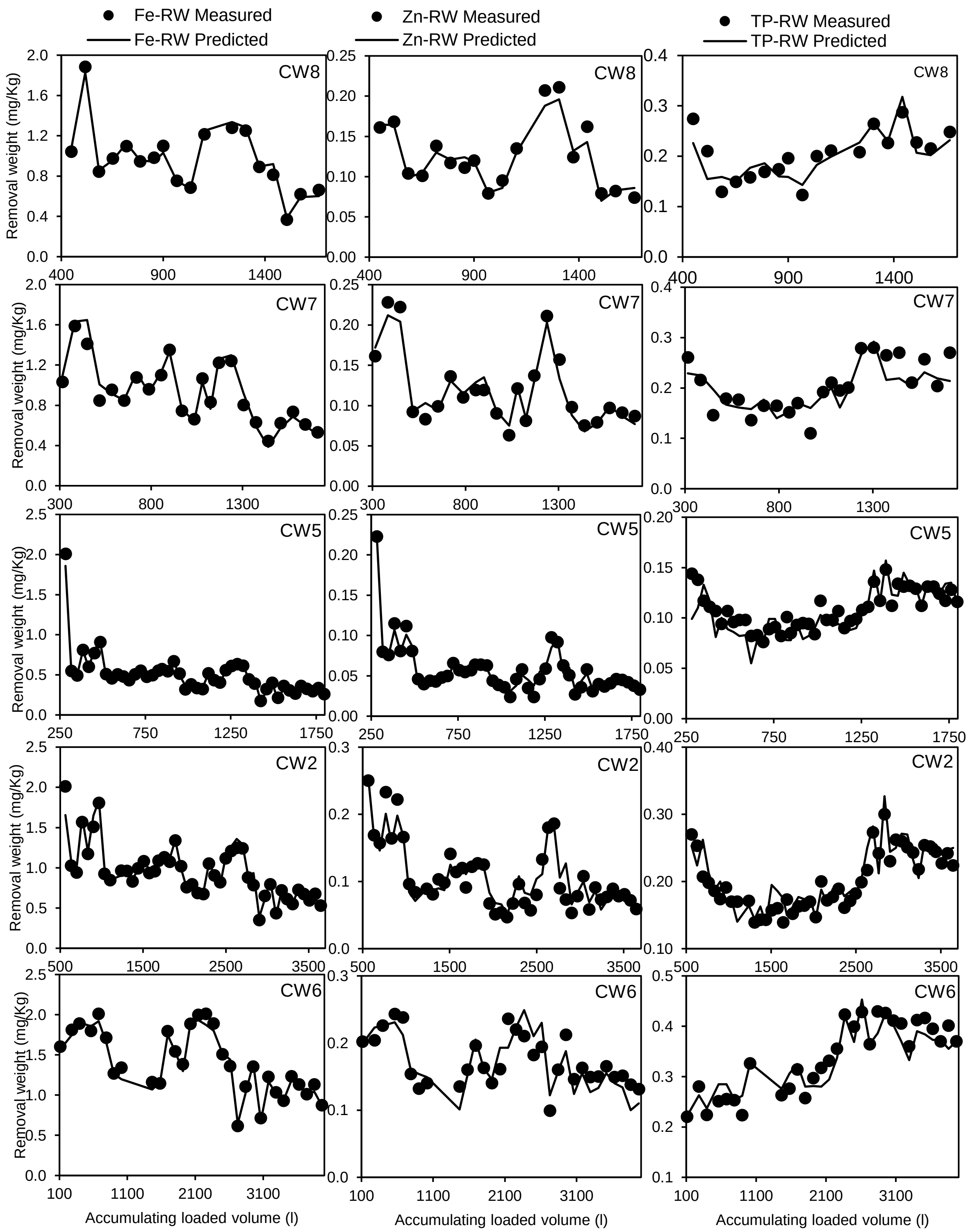


Figure 5.15 The measured and predicted values of Fe-RW, Zn-RW, and TP-RW at variable operation conditions of wet-dry regimes and WWARs resulted from generalised model of PLS.

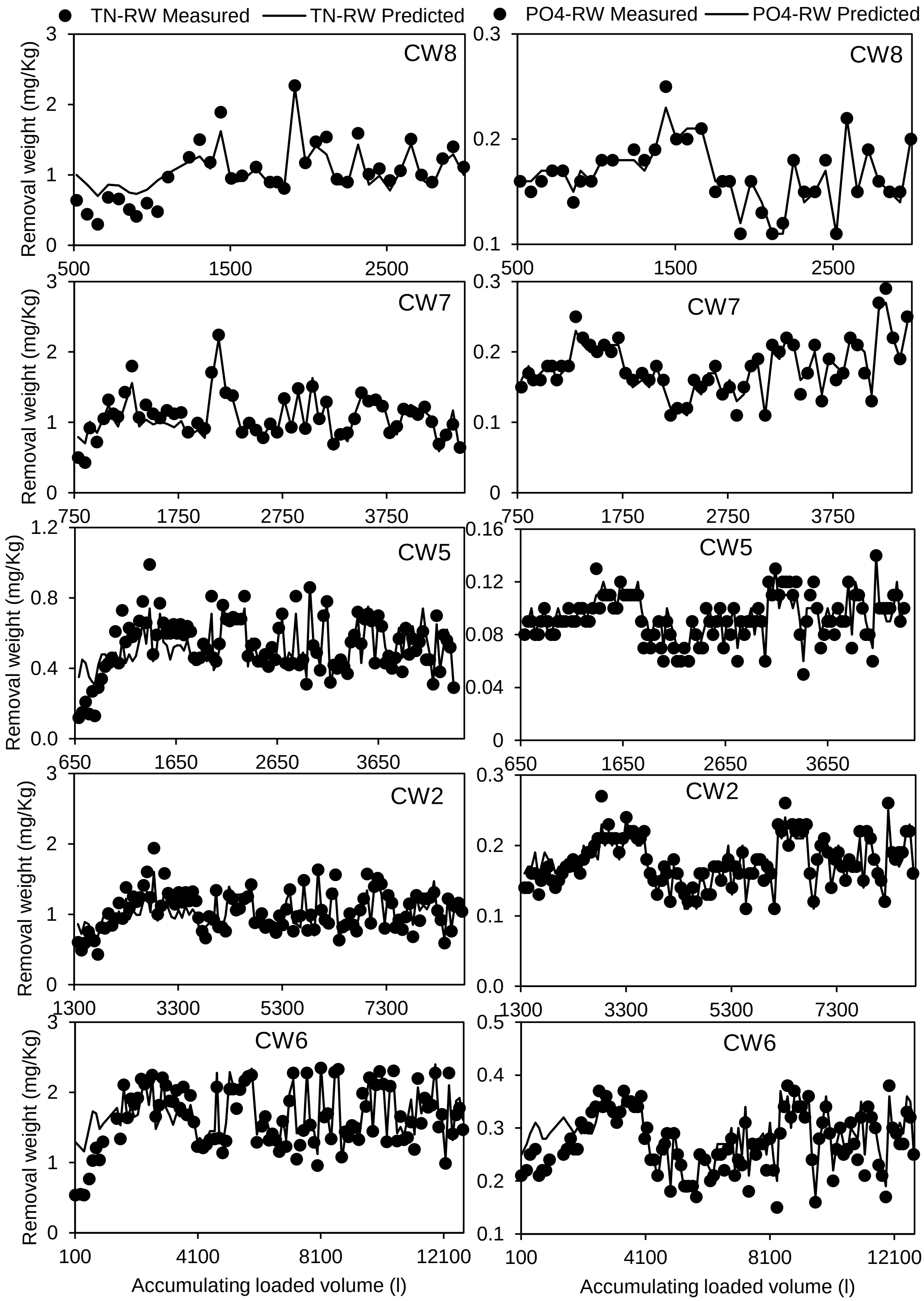


Figure 5.16 The measured and predicted values of TN-RW and PO4-RW at variable operation conditions of wet-dry regimes and WWARs resulted from generalised model of PLS regression.

5.5 Summary

This chapter discussed the effect of changing WWARs and wet-dry regime conditions on the pollutant removal performance of pilot-scale VFCWs using loamy sand as a substrate. The high stormwater loading rate coincides with the low WWAR values resulting in increasing TSS removal, which was confirmed statistically. There was a significant difference in TSS removal with the WWAR value decreased from 5% to 2.5%, as more TSS retained in a shorter time with high loading. For heavy metals, the detected concentrations in the effluent were only Fe and Zn, and therefore the discussion was limited for those two metals. Fe was effectively removed at a constant level in comparison to its loading weight. The removal more likely correlated to TSS removal as this relation increased with increasing the WWAR value. Statistical differences in Fe removal were found between 5% WWAR CW and 2.5% and 1.5% WWAR CWs, indicating Fe removed alongside in the same removal mechanisms with TSS. Zn removal was more variable in comparison with Fe removal due to the effect of microbial activity on increasing the dissolved Zn fraction, while the statistical analysis displayed no effect of changing WWAR value on the removal. Although different N species loading weight to CW5, CW1 and CW2, and CW6 due to applied 5%, 2.5%, and 1.5% WWAR respectively were implemented, none of the CWs displayed outperformance behaviour toward N species transformation and then TN removal efficiency. The TN removal percentages were in the range of 76.1 – 76.8% without statistical impact of changing WWAR on the removal. After the CWs matured, the 24-hour retention is probably more than enough even with the case of 1.5% WWAR CW. This might be the reason why the N removal was not influenced by changing WWAR values. A 1.5% WWAR CW6 displayed the highest variation on both PO4-P and TP removal weight than the other two. while on the percentage removal base comparison, 5% WWAR CW5 showed the highest significant removal percentage followed by 2.5% and 1.5% WWAR. The variation in the removal weight probably occurred because the high P loading required additional Ca dissolution from the loamy sand to remove the former via precipitation, or it might be belonging to releasing the previously utilised P in the cell structure due the decomposition process.

Applying WC, PDC, and EDC of the wet-dry regime was also investigated. TSS removal decreased gradually when the operation condition changed from WC to PDC and EDC, which is probably due to increasing porosity as a result of shrinkage during the dry period and thus affecting the removal mechanisms. The statistical analysis confirmed this impact on TSS removal only between WC and the other two cases. This operation regime did not impact on Fe and Zn removal performance significantly. The wet-dry regime seems to improve the Zn removal to increase the removal to 85% and 83% in the case of PDC and EDC respectively in comparison to 78% in the case of WC. The PDC and EDC could improve the pollutant diffusion more into the particle surface and thus rejuvenate the adsorbent surface. The applied wet-dry regime did not affect significantly the N species transformation and TN removal efficiency, indicating that the microbial community was able to survive during the drying period. Orthophosphate removal behaviour was not influenced significantly by the PDC and EDC and the average values of 87% and 87%, respectively were the same in WC.

The data of all the above operation conditions were gathered to construct a statistical prediction model. Because of the monitoring experiment program associated with two periods of measuring, the data was split into two sets. The first set used pH, T, EC, TSS-LR, Fe-LR, Zn-LR, TN-LR, and TP-LR as predictors and Fe-RW, Zn-RW, and TP-RW as responses. The second data set included pH, T, EC, TSS-LR, TN-LR, PO_4-LR as predictors, and TN-RW and PO_4-RW as responses. On both data sets, 80% of data were selected randomly as training data and the rest as testing data to check the robustness of the prediction models using data not used for model generation. PLS regression analysis was used. The number of latent factors was selected based on calculating PRESS value for each factor and latent factor generating was stopped at an insignificant decrease in PRESS value. The models were validated using the testing data set and calculating the PRESS. Models' parameters and explanations in the data variance were listed. The measured data against the predicted data were drawn with a high-fitting degree.

Chapter 6: Modelling nitrogen dynamics in tidal flow constructed wetlands

6.1 Introduction

It has become encouraged to use environmentally friendly and cost-effective treatment units around the worlds such as constructed wetlands (Nairn and Mitsch 2000; Ellis et al. 2003a; Birch et al. 2004; Fisher and Acreman 2004; Kadlec and Wallace 2009b; Lee et al. 2009; Babatunde et al. 2010; Merriman et al. 2012; Stefanakis et al. 2014f). Such passive treatment of constructed wetlands (CWs) usually involves complex pollutant removal mechanisms classified mainly into physical, chemical, and biological removal processes. Several studies have been conducted to investigate these processes, especially N (Gray et al. 2000; Liu et al. 2005; Jia et al. 2011; Saeed and Sun 2012; Stefanakis et al. 2014f; Zhi et al. 2015).

In general, CWs are classified into free water surface CWs, horizontal subsurface CWs, and vertical flow CWs. The novel tidal flow regime has been used to the advantage of enhancing oxygen supply in VFCWs which allows for diffusion of oxygen molecules further into media and the biofilm generated on the media surface, leading to a rejuvenation in the media before the next wastewater loading. This loading strategy in conjunction with biological processes leads to inconsistency in the effluent of different pollutants, especially N forms. To simulate the N forms dynamics (ammonium, nitrate, and organic N) in VFCWs with complex removal mechanisms, a combination of mathematical models has become a necessity to understand the underlying mechanisms.

Modelling N forms transformation and removal in CWs is vital with regards to deeply understanding the behaviour of N forms dynamics in such passive treatment systems. It has been mentioned that the STELLA software has been widely applied in biological, ecological and environmental sciences, including its application in CW (Ouyang 2008; Joergensen and Fath 2011; Ouyang et al. 2011; Kumar et al. 2015; Mohammed and Babatunde 2017; Mayo et al. 2018). Moreover, STELLA software has low truncation error and a fast convergence on given initial values, making it a preferable software over the others listed in literature review chapter.

Therefore, in this chapter, the fate, transformation, and removal routes of NH4-N, NO3-N, and organic-N in VFCWs receiving stormwater in tidal flow operation conditions were investigated via the development of a mathematical model in STELLA v9.0.2 (Structural Thinking and Learning Laboratory with Animation) software. Experiment conditions, influent and effluent data in addition to the parameters and constants which were either examined in a laboratory or obtained from previous studies were gathered and computed to generate a N transformation model. STELLA software is a quantitative system modelling software that permits modellers to specify system elements, their interrelations, and the direction of the relation. Consequently, the parameter values and the mathematical equations to describe model elements and the correlations can be specified by the modeller, and at the same time, the modeller can control and track the behaviour of the individuals. The following objectives are set in this chapter:

1- To develop a dynamic model simulating different compounds of N forms transformations
2- To determine the interaction of N transformation processes
3- To specify the efficiency of various removal processes.

6.2 Ammonium nitrogen adsorption

Ammonium nitrogen adsorption is one of the important processes in N transformation dynamics. Therefore, batch experiments were carried out to investigate the NH4-N adsorption by loamy sand media. The effects of adsorbent dose (loamy sand) and the equilibrium time on the adsorption of various pollutants usually found in the stormwater were investigated by Lucas (2015). Based on this study, the optimum conditions of equilibrium time and mass of loamy sand used in the adsorption experiments were 24 hours and 0.5 g respectively. The loamy sand was air-dried loamy sand (for two weeks) and then grounded for particle size less than 2 mm. Ammonium stock solution was prepared from dissolving $(NH_4)_2SO_4$ salt in deionised water. A set of bottles with NH4-N initial concentration of 1, 5, 10, 25, and 50 mg/l with 1:200 of solid-liquid ratio was agitated for 24 hours at 180 rpm. After the equilibrium time had set, the mixtures were withdrawn, filtered, and analysed for the residual NH4-N concentration using a Hach DR3900 spectrophotometer according to the measuring procedure. NH4-N uptake (q_e) in mg/g unit was computed using Equation 6.1.

$$q_e = \frac{(C_i - C_e) \times V}{m} \tag{6.1}$$

where C_i and C_e are the initial and final NH4-N concentrations in mg/l unit, V is the volume of the solution in l unit, and m is the mass of loamy sand used in the batch experiments in g unit.

The resulted equilibrium data were fitted with the Langmuir and Freundlich models. The models' equation and their corresponding parameters resulted from fitting are listed in Table 6.1. As can be seen from the table, the adsorption data fitted well in both models. However, Freundlich isotherms expressed slightly higher fitting for equilibrium data (R^2= 0.992) than Langmuir, therefore, it was considered in the NH4-N adsorption process.

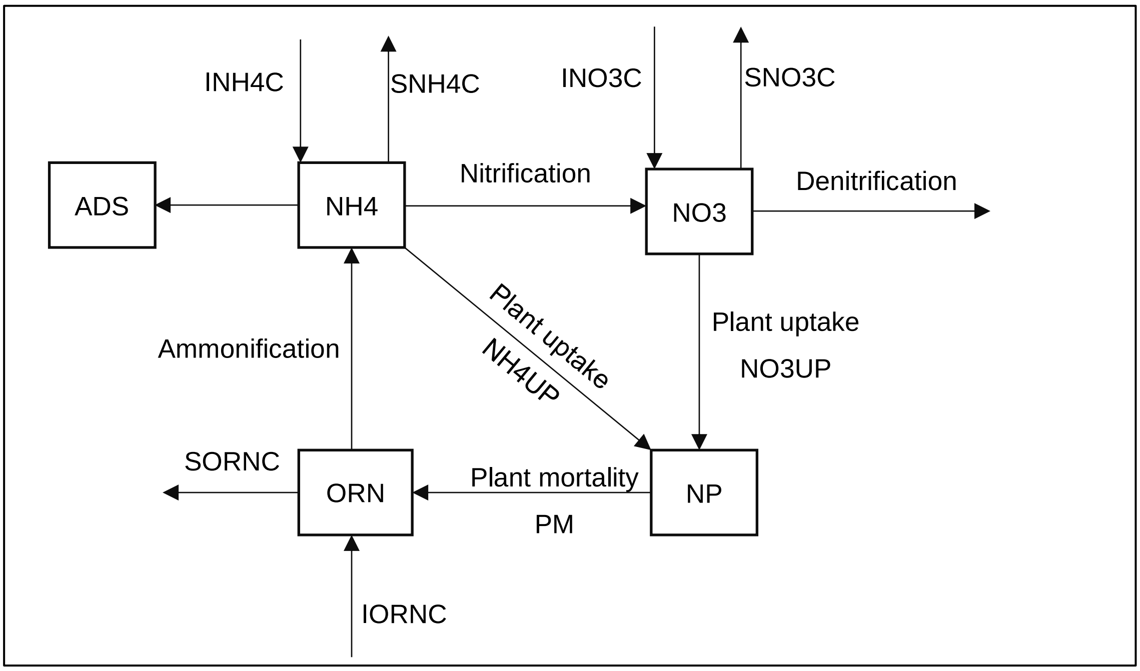
Table 6.1 The linearised equations of adsorption isotherms, their parameter values, and strenght of fitting.

Model	Equation	Parameter definition	Value	R^2
Langmuir	$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m}$	Q_m is the maximum adsorption capacity (mg/g)	12.285	0.979
		b is Langmuir adsorption constant (l/mg)	0.0372	
Freundlich	$\log q_e = \log K_f + \frac{1}{n} \log C_e$	K_f is the Freundlich constant (l/g)	0.42658	0.992
		n is the heterogeneity factor	1.14233	

6.3 Nitrogen transformation model

The forms of nitrogen transformation were first modelled mathematically by generating a conceptual diagram (theoretically developed diagram) based on data availability, the knowledge of the ecosystem, and the objectives of this study (Joergensen and Fath 2011). Figure 6.1 shows the proposed conceptual diagram for nitrogen forms transformation in urban stormwater VFCW comprised of state variables, forcing functions, and processes. The developed diagram was then drawn into STELLA software in more detail, as illustrated in Section 6.3.1. The entered forcing functions in addition to the influent concentrations of organic-N (IORNC), ammonium (INH4C), and nitrate (INO3C) were urban stormwater tidal flow rate (Fd), temperature (T), pH, mass of loamy sand (M), and influent dissolved oxygen (IO2). The state variables of the model were organic-N (ORN), ammonium-N (NH4), nitrate-N (NO3), ammonium adsorption into loamy sand (ADS), and nitrogen in plants (NP). While the N forms transformation processes were ammonification, nitrification, denitrification, plant uptake, and plant mortality.

The observed data of influent and effluent and the relevant mathematical equations with the included parameters and constants were entered into a STELLA conceptual model. The details of these steps were explained in Section 6.3.2. After clearly identify the system parameters, boundary conditions (scale), the required observed data (influent and effluent), and initial conditions, the model was calibrated using a trial-and-error procedure through changing the values of model parameters until the best fit between the simulated and observed N forms values was obtained. Then, sensitivity analysis was performed to identify the most parameters that affect the model performance. The final step was to validate the resulted calibrated model by using an independent data set to observe model prediction strength. More details were illustrated in Section 6.3.3.



Figur 6.1 Therotical proposed conceptual diagram of N forms transformation in urban stromwater VFCW.

6.3.1 Model conceptualisation

System dynamics modelling software, STELLA v.9.0.2 (Structural Thinking Experiential Learning Laboratory with Animation) is a well-known useful tool for graphic and dynamic simulation of biological processes (Joergensen and Fath 2011). In such a system, a dynamic relationship between variables, parameters, and the associated processes as a linkage step can be represented as a loop diagram of stocks and flows. The key feature of STELLA software involve stocks which are the state variable for accumulations, flows which are the processes leading into or out of the stocks, converters which are the auxiliary variables presented by a constant value or by values depending on other variables or graphical functions, and connectors which are used to connect between a model's elements. The complete conceptual model for stormwater N dynamics in VFCWs operated under the tidal flow condition is demonstrated in Figure 6.2. The figure shows a conceptual model of six major procedures and mechanisms of N dynamics in the VFCW operated under tidal flow conditions. These procedures are included in this study: (1) application of semi-synthetic urban stormwater to the VFCW, (2) transformation of organic-N to NH4-N (ammonification/mineralisation), (3) transformation of NH4-N to NO3-N (nitrification), (4) transformation of NO3-N to N gas (denitrification), (5) NH4-N and NO3-N uptake by the plants, and (6) NH4-N adsorption by the main media (loamy sand). Nitrite was not considered in the model as both of its influent and effluent concentrations were under the detected limit (< 0.002 mg/l). additionally, ammonia volatilisation was not taken into account since this process is neglected at the natural pH of CWs.

Therefore, the developed models have five state variables consisting of organic-N (ORN), ammonium-N (NH4), nitrate-N (NO3), nitrogen in the plants (NP), adsorption of NH4-N (ADS), all expressed in mg of N per day unit. Where the VFCWs were designed to operate at various conditions of wet and dry regimes, the observed data of influent and effluent N fractions from CW1 and CW2 were only used to model N transformation dynamics since both pilot-scale VFCWs were designed to receive a flow rate of 22.5 l per day loaded three times every week. The average values of the effluent observed data were selected in the model because of the consistency in the N removal behaviour for the operation period from 545 to 908 days. 80% of data (day 545 – 831) were used for model calibration and the rest (day 832 – 908) were used for model validation. Therefore, the first step in the N dynamic model construction is the tidal flow regime. The simulated tidal flow resulting from the sub-model, presented in Figure 6.3, showed the frequent loading of 22.5 l/day every week, based on three loading times a week.

The semi-synthetic urban stormwater incubated in the VFCWs during the loading day have 24 hours as the retention time. Thus, a 1 1/day (DT) simulation time step was chosen in the developed model. The 4th order Runge-Kutta method is selected to solve the model differential equations. The mass balance calculations for the state variables that explain the state or the condition of the biosystem are included. The state variable, processes, parameters, and auxiliary variables included in the model are defined in Table 6.2.

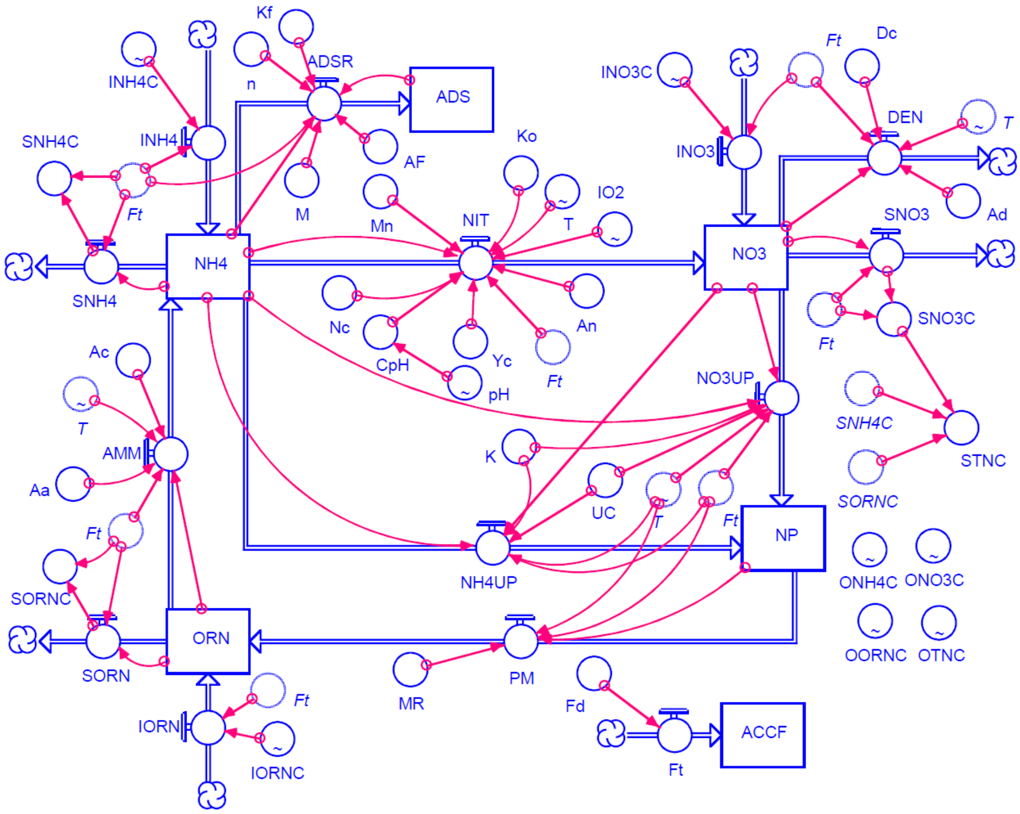


Figure 6.2 Conceptual STELLA diagram of N transformation dynamics in tidal VFCW treating semi-synthetic urban stormwater, all terms are defined through Section 6.3.1 to 6.3.3 and in Table 6.2.

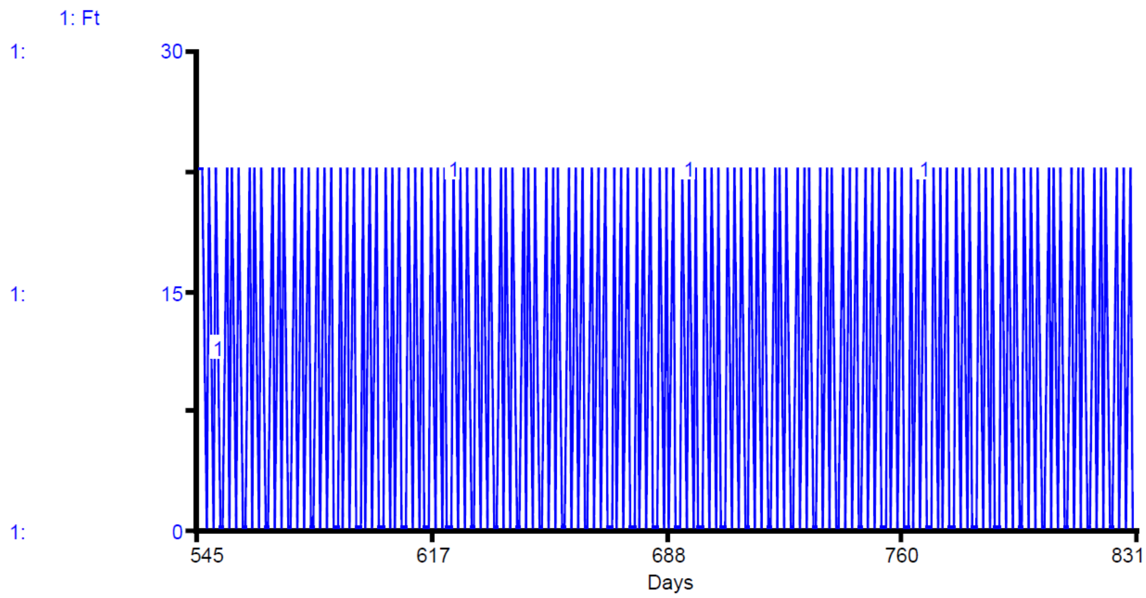


Figure 6.3 Simulation of the tidal flow (Ft) regime of three times a week loading for the 80% calibration data.

6.3.2 Mathematical formulation

The quantitative descriptions of various processes involved in the model are represented through mathematical formulas. The formulas assist in quantifying the rate of N transformation mechanisms and processes acting in the system. Thus, a general mass balance formula can be formulated for the material that undergoes various reaction rates of production, consumption, inflow, outflow, removing, and accumulation. If the material concentration is C in mg/l and the volume of stormwater loaded into the VFCW is V in l unit. A mass balance of the material can be presented (Equation 6.2).

$$F_o \times C_o + \sum P_r = F_e \times C + V \times \frac{dC}{dt} \tag{6.2}$$

where F_o and F_e are the inflow and outflow of the VFCW in l day^{-1} unit respectively, Co is the material influent concentration in mg/l unit, while the term V(dC/dt) is the material concentration changing rate in mg/day and P_r is the process reaction rate in mg/day unit.

Ammonification is one of the N transformation processes involving the biological transformation of organically combined N to NH3-N. This process is described as first-order kinetics (Martin and Reddy 1997; Joergensen and Fath 2011) including the Arrhenius equation to embed the temperature factor as in Equation 6.3.

$$AMM = ORN \times Ac \times Aa^{(T-20)} \tag{6.3}$$

In which AMM is the ammonification rate (mg/day), ORN is the amount of organic-N, Ac is the ammonification rate constant (1/day), and Aa is the Arrhenius temperature constant for AMM.

The nitrification process is modelled based on the hypothesis that nitrate generation by the nitrifying bacteria is the rate-limiting step (Fritz et al. 1979). The effect of temperature, dissolved oxygen, and pH on the growth of the bacteria was also included in the modelling of this process. The Monod model kinetics is used as shown in Equation 6.4.

$$NIT = \frac{Nc}{Yc} \times CpH \times \frac{NH4}{NH4+Mn} \times \frac{IO2}{IO2+Ko} \times An^{(T-20)} \tag{6.4}$$

where Nc is the nitrification rate (1/day), Yc is the nitrifying bacteria yield constant, Mn is the Michaelis-Menten half-saturation constant for nitrification (mg/l), IO2 is the influent dissolved oxygen concentration (mg/l), An is the Arrhenius temperature constant for nitrification, and CpH value is calculated by the influence of pH on the biofilm growth using Equation 6.5.

$$CpH = \begin{cases} 1 - 0.833 \times (7.2 - pH) & for\ pH \geq 7.2 \\ 1 & for\ pH < 7.2 \end{cases} \tag{6.5}$$

To model the transformation rate of NO3 to N gas in the process of denitrification, a first-order kinetics process combined with the effect of temperature in the form of the Arrhenius equation is applied (Joergensen and Fath 2011), as shown in Equation 6.6.

$$DEN = NO3 \times Dc \times Ad^{(T-20)} \tag{6.6}$$

where Dc is the denitrification rate constant (1/day) and Ad is the Arrhenius temperature constant for denitrification (unitless).

The rate of NH4 uptake by the plants (NH4UP) is modelled using a first-order equation including the Arrhenius temperature factor. The uptake model is based on the assumption that it is proportional to the available concentration of inorganic-N (Martin and Reddy 1997). The mathematical formula used to model NH4UP is represented in Equation 6.7.

$$NH4UP = UC \times \left(\frac{NH4}{NH4+K}\right) \times \left(\frac{NH4}{NH4+NO3}\right) \times 1.05^{(T-20)} \tag{6.7}$$

where UC is the N demand for biomass production which is the productivity of the biomass multiplied by the N biomass ratio (mgN/ day), while K is the Michaelis-Menten half-saturation constant for plants uptake (mg/l). Similar to NH4UP modelling, nitrate uptake rate (NO3UP) by plants is modelled using Equation 6.8.

$$NO3UP = UC \times \left(\frac{NO3}{NO3+K}\right) \times \left(\frac{NO3}{NO3+NH4}\right) \times 1.05^{(T-20)} \tag{6.8}$$

The growth of plants in the VFCWs would eventually decay. Their mortality is proportional to the N content in the plants' biomass. Thus, plant mortality (PM) is expressed in the model, following Equation 6.9.

$$PM = NP \times MR \times 1.05^{(T-20)} \tag{6.9}$$

where MR is the plants' mortality rate (1/day).

Ammonium can be easily adsorbed to loamy sand media and the generated biofilm. As described in Section 6.2, NH4-N adsorption followed the Freundlich isotherm model. The adsorption process can be represented in the N adsorption model by the equilibrium between NH4-N concentration in urban stormwater and NH4-N concentration in the adsorbent. Therefore, the adsorption process (ASDR) can be expressed as in Equation 6.10.

$$ASDR = AF \times (NH4 - Ft \times (\frac{ADS}{M \times Kf})^{n} \tag{6.10}$$

where Af equals to 0.897, which depends on the experimental results, M is the total amount of adsorbent (g), Kf is the Freundlich constant (l/g), and n is the heterogeneity factor.

6.3.3 Calibration, validation and sensitivity analysis

The STELLA software develops a set of differential equations derived from the conceptual diagram. The mathematical equations of mass balance transformation of N components discussed in the previous section were entered in STELLA. The influent and effluent observed data resulted from the operation of VFCW 1 and 2, which include influent NH4-N concentration (INH4C), influent of NO3-N concentration (INO3C), influent organic-N concentration (IORNC), influent TN concentration (ITN), influent oxygen concentration (IO2), T, pH, effluent NH4-N concentration (ONH4C), effluent NO3-N concentration (ONO3C), effluent organic-N concentration (OORNC), and effluent TN concentration (OTN), along with the parameters and auxiliary variables were either entered directly or entered using the graphical function. After the STELLA model was constructed and before estimating the N transformation dynamics, the model was calibrated using a trial-and-error procedure. To achieve this, the selected parameter values were adjusted until obtaining the best match between the simulated results and observed data. The goodness fitting of the model and prediction bias of either under- or overestimation was evaluated by calculating the mean percentage error (MPE), which gives an easily comparable metric, according to Equation 6.11:

$$MPE = \frac{100}{n}\sum_{i=1}^{n}\frac{N_O - N_P}{N_O} \qquad (6.11)$$

where n is the number of the experimental data point, while N_O and N_P are the value of N form observed and predicted from the STELLA model respectively. A negative error of MPE means that the model predictions tend to overestimate experimentally effluent N form concentration, whereas a positive error means an underestimation.

An important step to examine model reliability, which follows the model calibration, is the validation of the model. The resulted data for an operation period of 832 days to 908 days was used for model validation. The objective of the validation is to assess how well the model simulated the input values from independent data to fit the observed effluent ones.

Table 6.2 Summary description of state variables, processes, and parameters used in the modelling N forms transformation.

Symbol	Unit	Definition	Literature range	Source	Calibration
		State variables			
NH4	mg N/day	Amount of ammonium-N available for various processes	-	-	-
NO3	mg N/day	Amount of nitrate-N available for various processes	-	-	-
ORN	mg N/day	Amount of organic-N available for various processes	-	-	-
ADS	mg N/day	Amount of ammonium adsorbed in loamy sand	-	-	-
NP	mg N/day	Amount of N found in plant	-	-	-
		Processes			
AMM	mg N/day	Ammonification	-	-	Equ. 6.3
NIT	mg N/day	Nitrification	-	-	Equ. 6.4
DEN	mg N/day	Denitrification	-	-	Equ. 6.5
NH4UP	mg N/day	Ammonium-N uptake by plants	-	-	Equ. 6.7
NO3UP	mg N/day	Nitrate-N uptake by plants	-	-	Equ. 6.8
MP	mg N/day	Mortality of plants	-	-	Equ. 6.9
ADSR	mg N/day	Adsorption	-	-	Equ. 6.10
Ft	l/day	Tidal flow rate	-	-	-
		Parameters			

Symbol	Unit	Definition	Literature range	Source	Calibration
Ac	1/day	Ammonification rate (transformation rate of ORN into NH4)	0.5 – 0.8	(Joergensen and Fath 2011)	1.9
Aa	-	Arrhenius temperature constant for AMM	1.02 – 1.06	(Joergensen and Fath 2011)	1.02
Nc	1/day	Nitrification rate (transformation rate of NH4 into NO3)	0.1 – 1.5, 14	(Joergensen and Fath 2011;Kumar et al. 2015))	1.6
Yc	-	Nitrifying microorganisms yield constant	0.03 – 0.13	(Charley et al. 1980)	0.039
Mn	mg/l	Michaelis-Menten half-saturation constant for nitrification	0.01 – 1.0	(Joergensen and Fath 2011)	0.05
Ko	mg/l	Michaelis-Menten half-saturation constant for oxygen consumption	0.1 – 2.0	(Joergensen and Fath 2011)	0.1
An	-	Arrhenius temperature constant for NIT	1.02 – 1.07	(Joergensen and Fath 2011)	1.05
Dc	1/day	Denitrification rate (transformation rate of NO3 into N gas)	0.25 – 5.0	(Joergensen and Fath 2011)	0.25
Ad	-	Arrhenius temperature constant for DEN	1.05 – 1.12	(Joergensen and Fath 2011)	1.05
Uc	mg N/day	Inorganic-N demand equals to biomass production multiplied by N biomass ratio		Estimated	11.34
K	mg/l	Michaelis-Menten half-saturation constant for plant uptake	0.0 – 1.0	(Joergensen and Fath 2011)	0.05
Mr	1/day	The mortality rate of plant	0.006, 0.001	(Martin and Reddy 1997; Joergensen and Fath 2011)	0.001
		Others			
INH4C; ONH4C	mg/l	Influent and effluent (observed) NH4-N concentration respectively		Observed data	GF*
INO3C; ONO3C	mg/l	Influent and effluent (observed) NO3 concentration respectively		Observed data	GF*
IORNC; OORNC	mg/l	Influent and effluent (observed) organic-N concentration respectively		Observed data	GF*

Symbol	Unit	Definition	Literature range	Source	Calibration
OTN	mg/l	Effluent (observed) total nitrogen		Observed data	GF*
IO2	mg/l	Influent dissolved oxygen concentration		Observed data	GF*
pH	-	Influent pH of semi-synthetic urban stormwater		Observed data	GF*
T	°C	Temperature		Observed data	GF*
M	g	Amount of loamy sand		Calculated	94436
AF	-	Adsorption constant	0.0 - 100	(Joergensen and Fath 2011)	0.897
Fd	l/day	Semi-synthetic urban stormwater flow rate		Experiment	22.5

*is a graphical function to input the observed data as a time series

To have a clear overview of the most sensitive parameters, forcing function, or sub-models to the state variables in the model, sensitivity analysis is applied. Practically, the sensitivity analysis (S) is implemented by changing the parameters, the forcing functions, or the sub-models (P) to observe the corresponding response on the state variable (X), as shown in Equation 6.12.

$$S = \frac{\partial X/X}{\partial P/P} \tag{6.12}$$

Hence the higher the value of S, the more important the parameter. Meanwhile, the relative change in the parameter is selected based on the experimental knowledge as to the certainty of the parameters (Joergensen and Fath 2011).

6.4 Result and discussion

6.4.1 Nitrogen forms simulation – calibration and validation

In the calibration step, the input parameters were either resulted from the experimental measurements, calibrated, or taken from the literature (see Table 6.2). The model calibration was achieved using a trial-and-error procedure by adjustment of the most significant parameters until the mean error for differences between the predicted values and observed data are as close as possible to zero. A comparison of the model simulation results and observed effluent data was carried out for the operation period of 545 to 831 days of VFCW 1 and 2 for model calibration, while the operation period of 832 to 908 days was used for model validation, as can be seen in Table 6.3. From the comparison of the observed and simulated data in Table 6.3, a clear overview of the model effectiveness to predict the effluent concentration of different N forms was noticed. Although the model in calibration and validation cases showed a reasonable and very close prediction range (for example simulated results for model calibration of SNH4C range from 0.02 to 0.18 mg/l while observed effluent ONH4C range from 0.04 to 0.15 mg/l), the mean values of both observed and simulated different N forms were almost the same in both cases of model calibration and validation.

The observed and the simulated values of NH4C, NO3C, ORNC, and TN in the effluent from pilot-scale VFCW under tidal flow condition for calibration and validation are demonstrated in Figures 6.4 and 6.5. From these time series figures, all the individual observed values of all N forms were predicted with a high degree of agreement on both cases of data set. Generally, the model seems to overestimate the observed values for NH4-N, NO3-N, and TN in calibration and validation steps with values of -5.43, -0.19, and -13.38, -0.53, -0.34, and -13.36 respectively, while underestimation of 1.96 and 1.08

accounted for organic-N in model calibration and validation respectively. However, these values of MPE listed in Table 6.3 are highly acceptable in comparison with 10% to 33% MPE found from simulation of heavy metals removal in CW using STELLA software (Mohammed and Babatunde 2017).

Table 6.3 Comparison between the effluent observed concentrations of different N forms in loamy sand VFCW and the simulated ones for model calibration and validation.

Model	N form	Observed (mg/l)		Simulated (mg/l		MPE%
		Range	Average	Range	Average	
Calibration	**NH4-N**	0.04 – 0.15	0.09	0.02 – 0.18	0.09	-5.43
	NO3-N	0.13 – 0.18	0.16	0.14 – 0.18	0.16	-0.19
	Org-N	0.30 – 0.89	0.56	0.35 – 0.81	0.54	1.96
	TN	0.52 – 1.15	0.82	0.62 – 1.27	0.92	-13.38
Validation	**NH4-N**	0.04 – 0.15	0.09	0.03 – 0.14	0.10	-0.53
	NO3-N	0.15 – 0.19	0.17	0.16 – 0.18	0.17	-0.34
	Org-N	0.38 – 0.81	0.59	0.36 – 0.81	0.58	1.08
	TN	0.59 – 1.08	0.85	0.63– 1.27	0.97	-13.36

The model efficiency was also evaluated using the determination coefficient (R^2) by finding the correlation between the observed effluent N forms and the model output. Figures 6.6 and 6.7 compare the correlation among the observed data and simulated results of the model calibration and validation for NH4-N, NO3-N, organic-N, and TN. The R^2 value is an indicator of the direction and strength of the correlation, the closer the value to 1 the stronger the linear correlation. The value of R^2 above 0.5 is considered a valid linear relationship (Field 2013). The highest correlation was found with observed and simulated data of NH4-N for both model calibration and validation R^2 0.7153 and 0.903 followed by the organic-N with R^2 of 0.773 and 0.780 respectively. Meanwhile, the other correlations of N forms (NO3-N and TN) were significant and acceptable linear relation (R^2 = 0.541 alt least). These results seem to be consistent with other research using STELLA software to model N transformation dynamics either in VFCW or in subsurface horizontal CW. For example, Ouyang et al. (2011) found an R^2 of 0.693 for the linear correlation between the effluent measured TN at the bottom of the VFCW and the simulated results, while Mayo et al. (2018) modelled N transformation and removal in field-scale CW to obtain the R^2 of 0.6, 0.58, and 0.64 between the resulted data from the STELLA software and the measured values for NH4-N, NO3-N, and TN respectively. The differences in the model prediction efficiencies in the current research and previous studies are a reflection of the inherent properties combined with each study such as the used media, pollutant loading rate, flow type, and so on. Thus, from the model results, it can be assumed that the constructed model sufficiently simulates N transformation dynamics in the pilot-scale VFCW operated under tidal flow condition.

Although the removal process activity in biochemical systems increases when the biofilm is generated, the processes responsible for N transformation dynamics more likely depend on the temperature, pH, C/N ratio, nutrient availability, oxygen concentration, and CW configuration (Fritz et al. 1979; Kadlec and Wallace 2009b; Lee et al. 2009). These processes include organic matter decomposition, mineralisation/ammonification, nitrification, and denitrification (Kadlec and Reddy 2001). The ammonification rate is fast in the oxygenated zone and then decreases as the condition changes from aerobic to facultative and anaerobic (Lee et al. 2009). The model output range of AMM was 20.956 – 55.120 mg/day. However, no direct correlation between the influence factors and AMM rate was drawn, which indicates their limited impact on the process.

Unlike the ammonification process, It was found, from the results of the developed model of N form transformations in STELLA software, that both processes of nitrification (transfer NH4-N to NO3-N) and denitrification (transfer NO3-N to N gaseous) related highly to the temperature, with R^2 equal to 0.945 and 0.971 respectively (figures are not shown). The processes increased to reach the highest rates during the peak summer season and then decreased when the temperature decreased during the winter season. A recent study by Pan et al. (2020) found in the N simulation model that the denitrification rate was the highest at high water temperature and unsaturated flow conditions. Another interesting aspect observed in this study is the elevation in NO3-N effluent concentration which indicates that nitrification acts as a vital factor in oxidising NH4-N to NO3-N in VFCWs operated under tidal flow (enhanced oxygen supply). In such systems, the nitrification successfully retains NH4-N, but it is limited in denitrification.

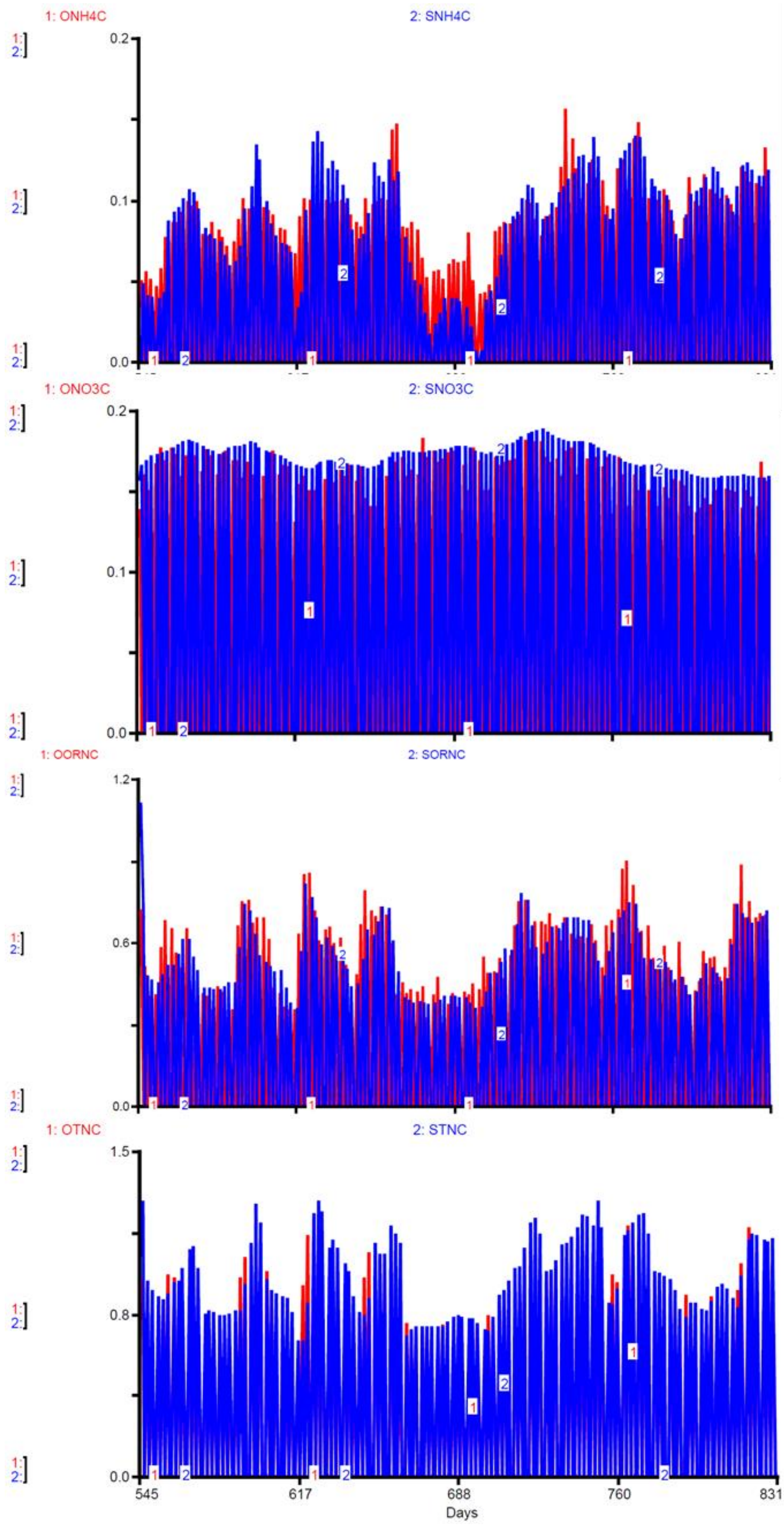


Figure 6.4 Comparison of the simulated and observed values of NH4-N, NO3-N, organic-N, and TN measured in mg/l unit resulting from model calibration.

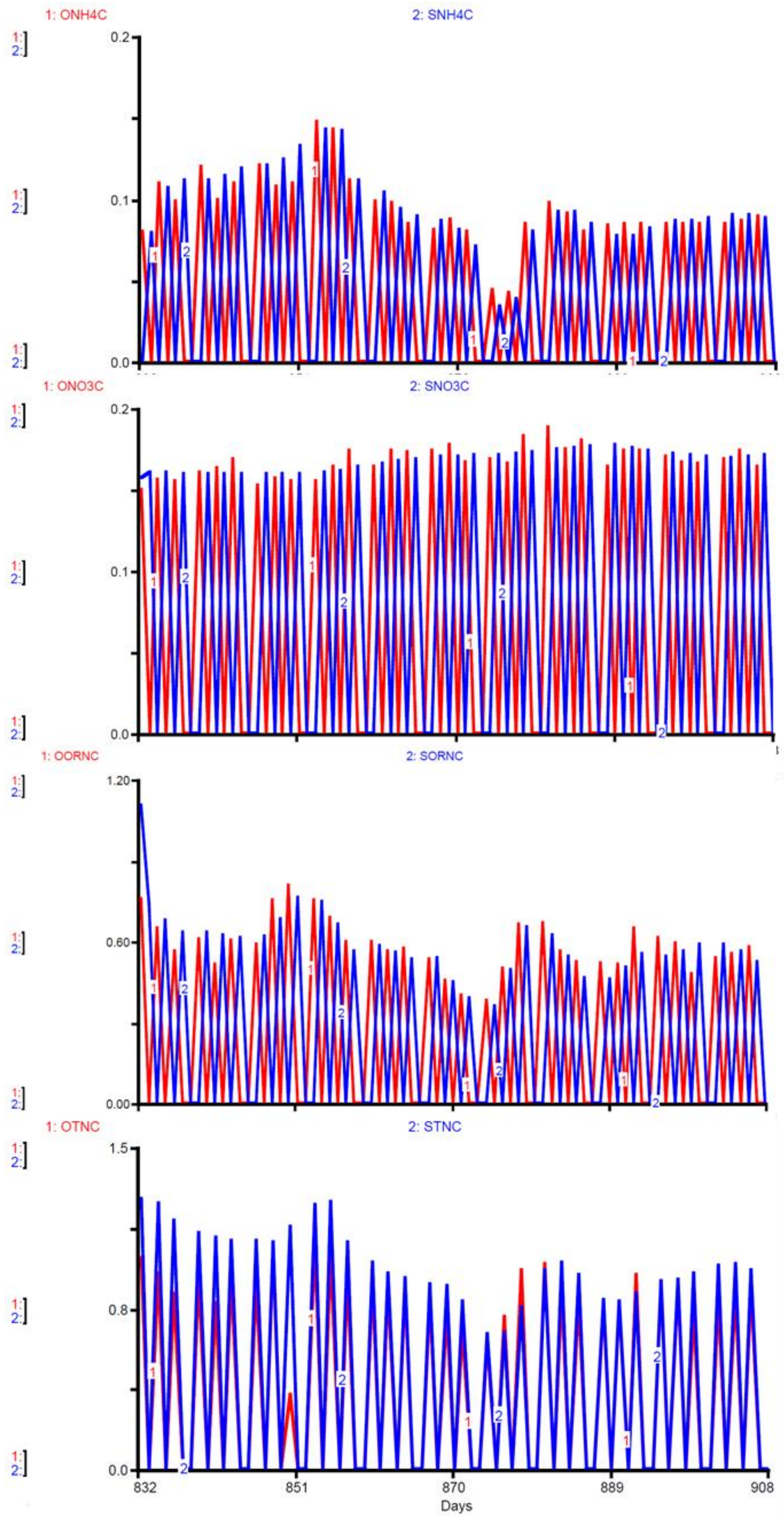


Figure 6.5 Comparison of the simulated and observed values of NH4-N, NO3-N, organic-N, and TN measured in mg/l unit resulting from model validation.

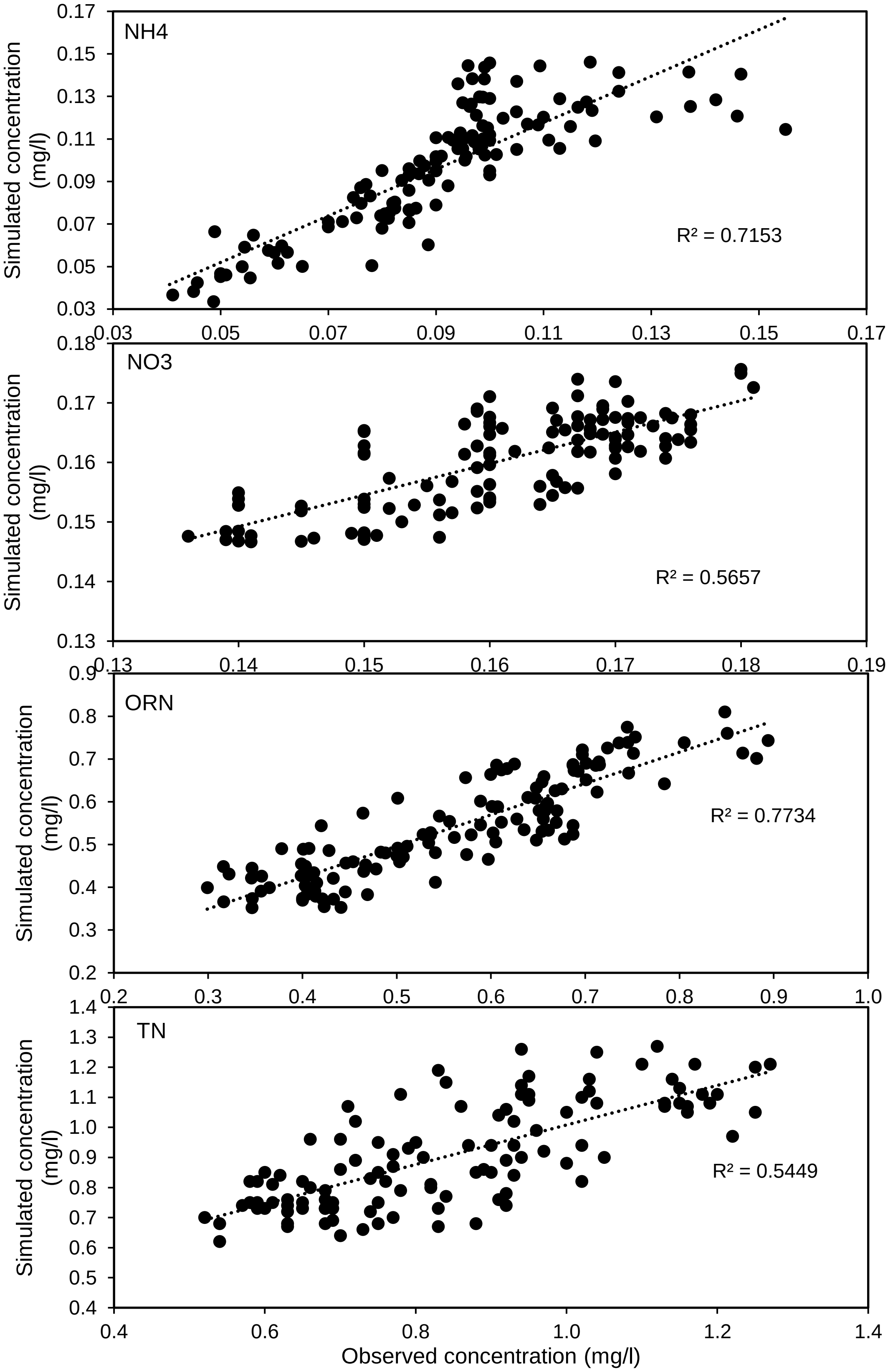


Figure 6.6 Comparison between model-predicted and field-observed effluent concentrations of NH4-N, NO3-N, organic-N, and TN in tidal VFCW in the case of model calibration.

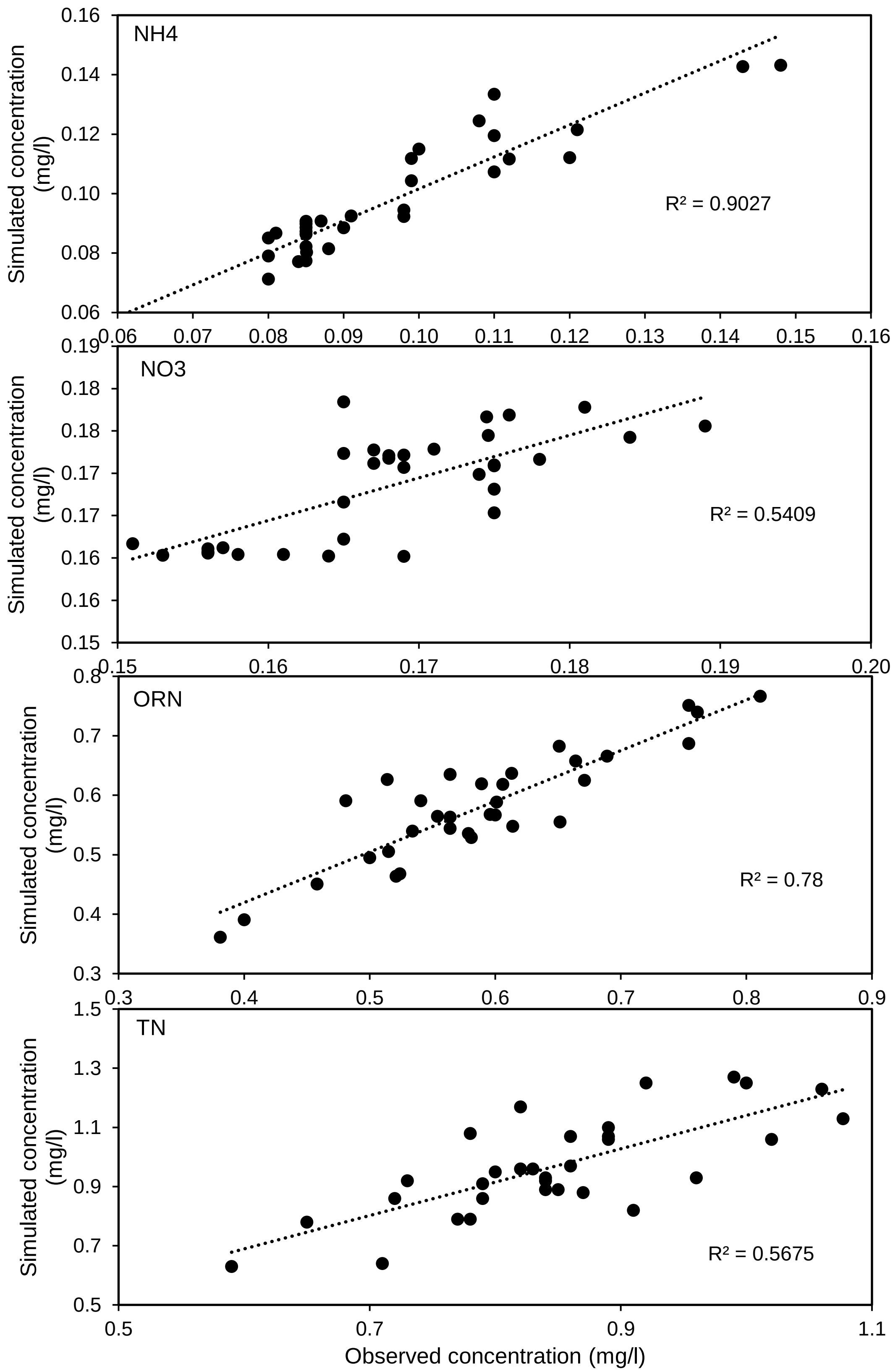


Figure 6.7 Comparison between model-predicted and field-observed effluent concentrations of NH4-N, NO3-N, organic-N, and TN in tidal VFCW in the case of model validation.

6.4.2 Sensitivity analysis

The most sensitive model components can be identified clearly using sensitivity analysis. The sensitivity of the model was determined by testing the most parameters that likely have an important impact on the state variables. Therefore, parameters of Ac, Nc, Dc, Yc, Uc, Mn, Ko, K, Mr, and Fd were tested and only five of them were selected as the most important parameters. The sensitivity of these parameters was calculated based on changing the parameter value by ±10% and then computing the sensitivity value based on the relative changing on the state variable using Equation 6.12. The magnitude of the changes in the parameter values of ±10% (except Fd) is usually enough to show the parameter ‘s importantly in N dynamics within the biochemical system, and this range is also selected in previous studies (Joergensen and Fath 2011; Kumar et al. 2015). Whereas, the percentage of change in Fd was 5% and 6.7%, which were computed based on the flow rate of 11.3 l/day (CW5) and 37.6 l/day (CW6), respectively, relative to the modelled flow rate of 22.5 l/day (CW1 and CW2). The sensitivity of the tested parameters, by decreasing and increasing them by 10%, to state variables of NH4, NO3, ORN, ADS, and NP is listed in Table 6.4. The sensitivity results clearly point out that Ac, Nc, Dc, and Yc parameters have a greatly significant impact on NH4 and NO3 state variables, therefore, their values should be determined accurately. Opposite of that, changing the listed parameters indicates no impact on the ORN, ADS, and NP except the changing of Ac, Nc, and Yc by ±10% which would make a change of ADS of at least 19%. This impact on the ADS state variable is understandable because these parameters (Ac, Nc, and Yc) all control the NH4-N concentration in the system. Furthermore, the adsorption process is hypothesised that NH4-N adsorption in the system depends on the balance between the influent and equilibrium concentrations. Thus, a -0.190 sensitivity value at increasing Nc by 10% would cause an increasing nitrification rate in the system, and lowering the NH4-N concentration level for adsorption, therefore, it would decrease the ADS state variable value by 19%.

The effect of changing the flow rate on the state variables of NH4, NO3, ORN, and ADS was noticed in the sensitivity analysis. This effect can be translated as the Fd value change of 5% and 6.7%, the NH4 value would be changed by more 100% and 150% respectively, and so on for the rest of state variables. Whereas changing the flow will change the influent daily N forms loading rate and thus a significant effect will be identified in the state variables. Chang et al. (2014) found the same results obtained from modelling N transformation in vertical up-flow CW when the flow rate of wastewater loading increased.

Table 6.4 Sensitivity analysis values of the state variable resulted from the ±10% changing of the parameters.

State variable	Sensitivity value									
	Ac		Nc		Dc		Yc		Fd	
	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-5%	+6.7%
NH4	-0.461	0.444	0.322	-0.135	0.017	-0.016	-0.276	0.291	-1.081	1.567
NO3	-0.059	-0.592	-1.046	1.046	0.735	-0.639	1.160	-0.952	-0.593	0.270
ORN	0.042	-0.05	0.000	0.000	0.000	0.000	0.000	0.000	-1.000	0.988
ADS	-0.219	0.208	0.205	-0.190	0.010	-0.009	-0.211	0.186	-0.556	0.627
NP	-0.001	0.000	-0.001	0.002	0.000	0.000	0.002	-0.001	0.002	0.000

6.4.3 Ammonium nitrogen adsorption

The main substrate used in pilot-scale VFCWs 1 and 2 was loam sand. The substrate has a high Ca content (317 mg/g) followed by Fe (63 mg/g) which can improve adsorption and chemical precipitation processes to retain various stormwater pollutants. According to the batch experiments, NH4-N adsorption equilibrium data fitted well with both Langmuir (R^2=0.979) and Freundlich (R^2=0.992) models with a maximum adsorption capacity of 12.285 mg/g, as listed in Table 6.1. As mentioned before in Section 6.2, the Freundlich model was considered the best fit for NH4-N adsorption in the loamy sand substrate. These results are in agreement with a Piñón-Villarreal et al. (2013) study who found equilibrium adsorption data of 100% loamy sand (soil 2) was best fitted with the Freundlich model, indicating heterogeneity adsorption characteristics of the loamy sand substrate. The NH4-N adsorption was modelled based on the assumption that the adsorption will stop when the influent concentration equals the equilibrium concentration. Based on this, it was observed that the NH4-N adsorption range was between 14.990 and 35.368 mg/day. NH4-N adsorption in biochemical systems is usually loose. As the system matures with the operation progressing, the generated biofilm adsorbs further NH4-H and then tends to transfer the already adsorbed NH4-N to NO3-N in the nitrification process or the adsorbed NH4-N into the substrate releases as the nitrification rate increases and influent NH4-N is low. However, the adsorption rate increases if the NH4-N concentration is increased and this behaviour can be supported by the adsorption variation relative to the mean value (25.245 ± 5.767). During the dry period of CW, the loamy sand is exposed to air which may oxidise the NH4 into NO3-N (Joergensen and Fath 2011), which furthermore justifies the high contribution of this process to TN removal (accounted for 41.576%, see Section 6.4.5, N mass balance). Thus, several aspects such as the physicochemical properties of the substrate, type of the CW, operation design of the wetland, and plant availability can significantly impact on the rate and extent of these biochemical reactions.

6.4.4 Nitrogen plant uptake

Plants utilise NH4-N and NO3-N as N source in addition to carbon, oxygen, hydrogen, and phosphorus as the main constituents of the plants' biomass. Menten first-order reaction equation in conjecting the effect of temperature on the uptake rate of N forms was used. In constructed wetlands, The N plants uptake depends mainly on the concentration of NH4-N and NO3-N in the stormwater and the temperature. A high correlation between the NO3UP and T was found from the N plants uptake model (R^2=0.837) which was not the case with NH4UP(R^2=0.413) as shown in Figure 6.8. Although, the nature of the plants prefers NH3-N as N source over NO3-N as the former is more reduced energetically than NO3-N (Kadlec and Wallace 2009b), *Typha latifolia,* used as the plants in VFCW, has the ability to utilise both prementioned N forms. This can be confirmed by the model simulation results whereas the average percentages of NH4UP and NO3UP contributed to the total NP were 88.2% and 11.8% respectively. However, NO3-N may become an N source for plant growth if the water contains a high concentration of NO3-N. However, the average percentage of NO3UP plants uptake was 3.733 ± 0.588, which is relatively higher than NH4UP plants (2.287 ± 0.307). The TN removal percentages accounted for NH4UP and NO3UP resulted from the model were 3.40% and 6.15% respectively. These figures of N forms plants uptake closely match other previous studies with a 4.4 - 6.55% range of plants uptake contribution (Ouyang et al. 2011; Kumar et al. 2015; Mayo et al. 2018).

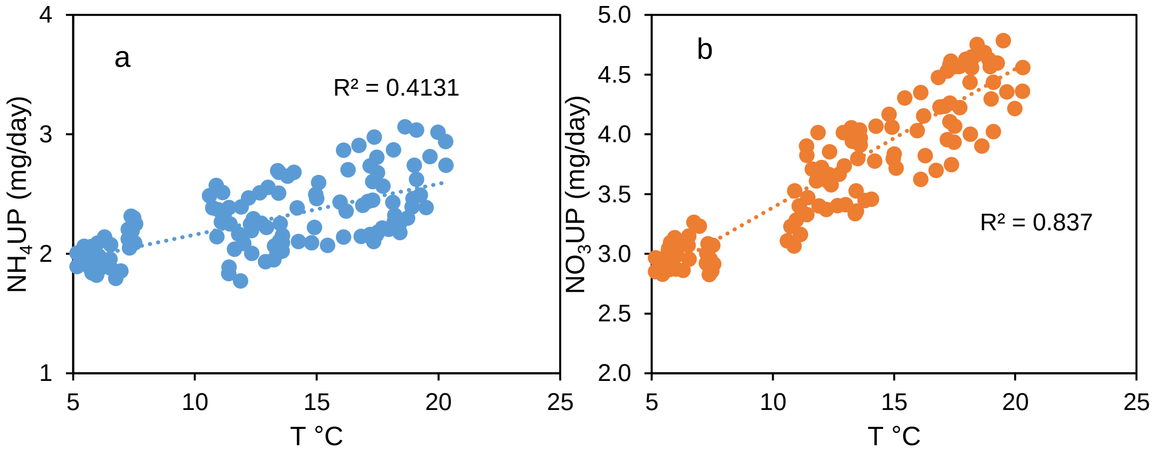


Figure 6.8 The relationship of ammonium plant uptake with temperature (a) and nitrate plant uptake with the temperature (b).

The N plants uptake more likely depends on the concentration availability of both forms in stormwater and temperature (Martin and Reddy 1997; Mayo et al. 2018). Thus, this behaviour of N forms assimilation in plants gives an explanation of the increasing values of NO3UP with the temperature rising rather than NH4UP.

6.4.5 Nitrogen mass balance in the VFCW

The nitrogen transformations model not only simulates the transformation rate and provides the prediction of N forms within various processes, but it also enables the modeller to calculate the mass balance of N forms allocation in these processes. The mass balance of nitrogen transformation dynamics between various forms is demonstrated in Figure 6.9. The values of N forms flowing into and from one state variable to another represent the average data for the operation period of 545 – 831 days. The N forms received from the semi-synthetic stormwater per day were measured to be 47.617 mg of organic-N, 13.089 mg of NH4-N, and 0.015 g of NO3-N. Afterward, ammonification, nitrification, adsorption, denitrification, and plant uptake and decay were estimated based on the N model simulation. The results of model calibration determined 2.287 mg and 3.852 mg of NH4-N and NO3-N plants uptake respectively, from which 0.218 mg of organic-N released through plants decomposition per day, leaving 5.921 mg/day as the net N uptake by the plant from water, which can be removed from the system through plant harvesting. Nevertheless, a 35.671 mg/day out of the total amount of organic-N (47.617 + 0.218) mg/day was transferred into NH4-N in the ammonification process leaving 12.215 mg/day of organic-N in effluent water. Denitrification removes 11.539 mg/d of N gas being emitted to the atmosphere from the system leaving 3.582 mg/day in treated water.

The major N removal mechanisms in stormwater VFCWs presented in N mass balance Figure 6.8 are NH4-N adsorption, accounting for 41.58%, denitrification accounted for 19.00%, and plant uptake accounted for 9.55%. Thus, the total N removal from the influent resulted from the prementioned processes all together was 70.13%. Whereas the largest part of removal via NH4-N adsorption into the loamy sand substrate is responsible for removal of 25.245 mg/day, denitrification records 11.539 mg/day removal and 5.802 mg/day will be removed if the plants are harvested. It is encouraging to compare these figures of removal percentages contributed by various processes with that found by Ouyang et al. (2011) who found that denitrification was responsible for 18% of TN loss in pilot-scale VFCWs, 6% of TN accounted for plant uptake, and 22% of TN was removed via other mechanisms such volatilisation, adsorption, and deposition.

Mass balance analysis allows identifying any potential N sources and is helpful in specifying effective possible routes to remove N in the CW. Although the above calculations based on the average values were almost accounted for in the mass balance analysis, the individual calculation posed some differences in unidentified masses. The calculations of mass balance in Figure 6.8 showed unaccounted for N mass of 0.906 mg/day from the total input N mass of 60.721 mg/day. This unaccounted for N mass could be elicited for by laboratory measurement error in the N forms, since the measured values are in low concentrations, or it could be that the model underestimates the rate of various processes involved in the N dynamics. The output of the current study is in agreement with other studies that modelled N transformation mechanisms in CWs, as mentioned by Kadlec and Wallace (2009) for N mass balance in demonstration wetland, and also Liu et al. (2005) found that the total unbalance N mass of 570 g/day out of the total influent mass of 2929 g/day resulted from modelling N transformation in subsurface flow CW.

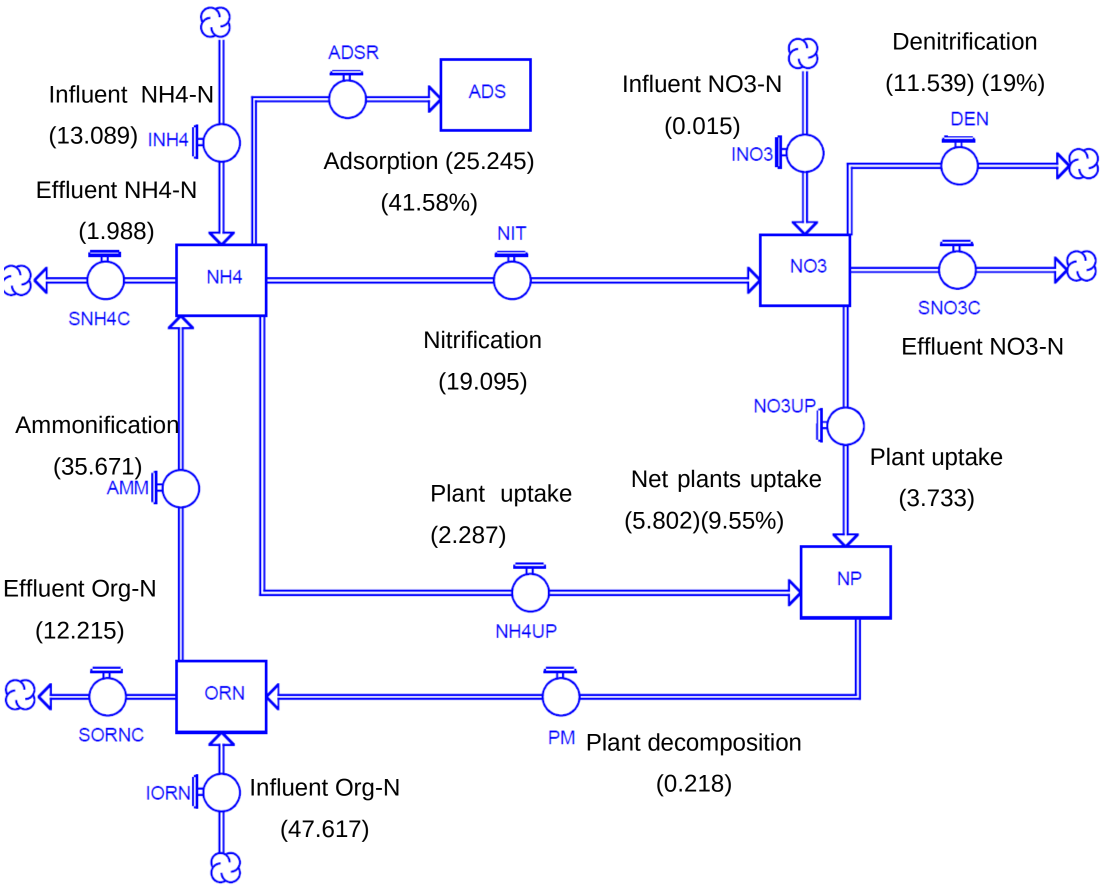


Figure 6.9 Mass balance of nitrogen transformation dynamics in stormwater VFCW operated under tidal flow condition measured in mg/day.

6.5 Summary

This chapter included modelling N forms transformation in pilot-scale VFCWs treating semi-synthetic urban stormwater in tidal flow strategy. Experimentally measured data of CW1 and CW2 (mean values were taken) for the operation period from 545 to 908 days were used to simulate N forms dynamics utilising STELLA software. The processes and potential mechanisms used in the model included ammonification/mineralisation, nitrification, denitrification, ammonium nitrogen adsorption, and plants uptake. The sensitivity analysis revealed that Ac, Nc, Dc, and Yc were the most important parameters in the system and changing them ±10% would influence significantly on the daily masses of NH4, NO3, and ADS, while changing the applied flow rate from 22.5 l/day to either 11.3 l/day (flow applied to CW5) or 37.6 l/day (flow applied to CW6) impacted significantly on the daily masses of NH4, NO3, ORN, and ADS. The model was calibrated to have a reasonable agreement with observed effluent data of N forms. Accepted prediction efficiencies were found between the observed and model output for both model calibration and validation. Mass balance analysis showed that the major route for N removal was through NH4-N adsorption accounting for 41.58% of TN followed by denitrification and plants uptake accounting for 19% and 9.55% respectively. This study demonstrates that the model could be used to predict N forms transformation in stormwater VFCWs using loamy sand as the main media and under the same operating conditions.

Chapter 7: Conclusions and recommendations

7.1 Conclusions

This study advanced our deep understanding the underlying removal mechanisms from urban stormwater in VFCWs using tidal flow strategy under long-term operation, investigated the influence of the novel design aspects on the priority stormwater pollutants to construct a generalised statistical prediction model, and finally modelling of the N forms transformation mechanisms to examine the contribution of various processes of ammonification, nitrification, denitrification, plants uptake, and adsorption on the removal. To meet the study objectives, eight VFCWs were constructed to achieve variable design and operation conditions in which was divided into three main parts. The first part was to evaluate and characterised the VFCWs stormwater pollutants' immobilisation under variable physicochemical properties of the substrates. The second part was allocated to investigate the effect of various WWAR ratios and wet-dry conditions on the removal and also to generate a general statistical model prediction the performance at various operation conditions. The last part was to identify and model the N forms transformation using STELLA software.

The main conclusions from this study are as below:

- The long-term retaining of suspended solids, heavy metals, P an N evaluation for VFCWs 1 and 2, 3, and 4 packed with loamy sand, gravel, and BFS respectively with WWAR% of 2.5 and three times a week loading rate showed generally variable retaining percentages of suspended solids, heavy metals, and P. Mass balance analysis based on loading rate (22.5 l/day) and amount of the substrate used in VFCW showed that the retention performance was higher in BFS than loamy sand and gravel substrates, which furthermore was confirmed statistically using ANOVA test and also confirmed using chemical composition analyses for the former substrates before and after treating the urban stormwater for about two and half years. The Ca contained in BFS and loamy sand was reduced by about 8% and 7% respectively, evidence for Ca dissolution resulting in exchange of metals with the hydroxyl ions on the surface of the substrates and removing P alongside Ca precipitation. Due to the biological activities, the OC content was raised promising biochemical treatment units to remove both metals and nutrients at the same time. Because of Fe and Zn mostly being present in the urban stormwater as particulate forms, their removals and most of the other heavy metals were highly related to the removal of suspended solids. Although

BFS showed a relatively high performance in retaining suspended solids and heavy metals, N forms removals were more pronounced in the loamy sand VFCWs as a result of the biological activities and plants fixation. P plants uptake might play a key role for its effective retention in loamy sand VFCWs in addition to adsorption and precipitation, which gave preference for loamy sand VFCWs rather than the other two substrates.

- Various operation conditions of WWAR of 1.5, 2.5, and 5% of urban stormwater loading were implemented in VFCWs 1, 2, 5, and 6. The long-term experimental analysis demonstrated statistically to explore the influence and to generate prediction model able to estimate the removal with a high level of accuracy. Suspended solid retaining increased significantly with decreasing WWAR% from 5 to 2.5, as more suspended solids were retained in a shorter time with high loading rate. All heavy metals were retained effectively under the various operation conditions of loading rates and wet-dry regimes with effluent concentration below the detection limits except Fe and Zn. Fe retention was consistent in comparison to its loading rate and the retention was more likely related to suspended solids removal. The statistical analysis showed differences in the performance when the loading rate changed from 11.3 l per day to 22.5 and 37.6 l per day, indicating Fe retained in the same removal mechanisms of suspended solids. While Zn retention was variable at different levels of WWAR% which could be due to the effect of biological activities on dissolved organic matter and then release Zn effluent concentration. The effect of changing WWAR% on Zn retention in loamy sand VFCWs was not accounted for by any statistical differences in the removal. The TN retention percentages range was between 76.1 and 76.8 for the three levels of WWAR%, therefore, no statistical differences in the performance of TN removal was recorded, indicating the biochemical processes are the key role in the removal mechanisms. P retention showed high variability in the case of a WWAR% of 1.5, while the highest significant removal percentages accounted for by a WWAR% of 5.
- The wet condition (WC), partial dry condition (PDC), and extended dry condition (EDC) modes of wet-dry conditions seemed to impact the urban stormwater pollutants retention differently. The PDC and EDC causes increment in the porosity as a result of shrinkage of the previously trapped solids and may be the generated biofilm. This operation strategy affected the removal mechanisms of suspended solids, as the results showed significant decreasing in the removal when the wet-dry strategy changed from WC to PDC and EDC. However, this operation conditions did not influence Fe and Zn removal performance

significantly, instead an improvement in Zn retention was noticed. The PDC and EDC increased the removal percentage of Zn from 78% in WC condition to 85% and 83% respectively, which could be due the enhancement in the diffusion characteristics of the substrate and reduction in Zn oxidation. However, these operation regimes did not affect significantly the TN removal efficiency. The PO4-P removal value of 87% was the same at all three conditions.

- The experimental results of three levels of both WWAR% and wet-dry strategy were gathered to construct a general statistical prediction model using partial least square analysis. The mass balance based on the mass of the substate and the loading weight for influent and effluent experimental data of TSS, Fe, Zn, TP, TN in additional to pH, T, and the accumulative stormwater was applied. Six latent factors were extracted to explain the most variation of 98.1%, 95.9%, and 95.6%, 94.4% in independent (x matrix) and dependent (Y matrix) variables respectively. A high degree of accuracy between the predicted and measured (observed) data was obtained in both data sets to predict Fe, Zn, TP, TN, and PO4-P at various operation conditions of WWAR% and wet-dry strategy.
- A dynamic model for nitrogen forms transformation was constructed using STELLA software to understand their complex removal in such biochemical VFCWs 1 and 2 with a WWAR% value of 2.5 (22.5 l per day, three time a week). The mathematical equations for the processes of ammonification (organic-N transforming to NH4-N), nitrification (NH4-N transforming to NO3-N), denitrification (NO3-N transforming to N gas), NH4-N adsorption, and nitrogen plants uptake were developed as the main N forms removal mechanisms. The predictive values of different N forms from the calibration and validation models were in a good agreement with the observed (measured) effluent concentrations with acceptable and comparable MPE% ranging from -13.38 to 1.96. Sensitivity analysis for the effect of changing model parameters on N forms dynamics showed that ammonification rate constant, nitrification rate constant, denitrification rate constant, and nitrifying bacteria yield constant had the greatest influence on the state variables of NH4, NO3, and adsorption. Meanwhile, changing the loading rate from 22.5 l/day to 11.3 l/day or 37.6 l/day would influence significantly the whole proposed mechanisms except plants uptake. Furthermore, the results from the model demonstrated that the main route for N removal was through NH4-N adsorption process which accounted for 41.58% of TN adsorbed to the loamy sand and/or biofilm followed by denitrification and plants uptake accounting for 19% and 9.55% respectively.

7.2 Recommendations for further work

This study has highlighted the impact of designs' criteria on pollutant removal in tidal flow VFCWs. Nevertheless, the findings of these pilot-scale studies can be difficult to scale up, as the real physical processes that turn rainfall into runoff are complex and highly complicated and cannot be reproduced with absolute certainty. Simplifying assumptions were therefore made to allow the experiments to be performed, as data were produced by the experimental design, materials, and methods which illustrate that tidal-flow VFCWs are cost-effective for stormwater treatment. Understanding of the mechanism of pollutant removal processes in VFCWs to treat stormwater remains exceedingly difficult. Some critical areas of study remain pertinent to advance our understanding of the urban water cycle, which may be summarised as follows:

- Field studies must be performed to complete the findings of this research. Through it, the load volumes will be determined at each precipitation event, based on the strength of the rainfall and not on the average annual precipitation. Similarly, the 24-hour retention period applied in this research did not consider conditions in which rainfall could last longer than one day. Whereas design storm events will result in flow-based retention time, such that more severe storm events than the design event will have a shorter retention period, whereas smaller storm events will retain longer.
- Climate change impacts on urban hydrology can contribute to changes in the extent and duration of rainfall events. Consequently, there is a growing need to consider these possible adjustments and the sizes they will occur at. In addition, the effects that certain events could have on stormwater systems, flood risk and water quality should be considered. Moreover, as populations continue to expand within urban areas, the effects of global warming on water supplies remain unclear, where rapidly sustainable management of rainfall and stormwater runoff are promoting renewable water yields.
- Using tidal flow strategy would enhance the oxygen supply to systems which impacts positively on the nitrification but at the same time the denitrification process is becoming lacking. Therefore, further work is required to investigate oxygen levels at different depth of CW columns and how the decreasing or increasing will affect the processes of N forms dynamics.
- Furthermore, to overcome the lack of denitrification process in VFCWs under tidal flow strategy, an investigation for the effect of the CW depth on oxygen

availability and how this could change the condition from aerobic or anoxic to anaerobic conditions are required to develop the design.

- Although a wide range of urban stormwater priority contaminants were investigated in this research, urban stormwater can carry a variety of alternative pollutants. To enhance our knowledge and to identify the underlying removal mechanisms of these contaminants, therefore, further examination to identify the capability of the current tidal floe VFCW design to remove these pollutants such as polycyclic aromatic hydrocarbons (PAHs), different herbicides and oil and grease is needed.
- Ammonium-nitrogen adsorption to media is not constant and can be released or used by the nitrifying bacteria during the resting time. Therefore, the kinetics of the adsorbed NH4-N and organic matter degradation during the resting time should be further identified. This could provide key information to optimise the operation parameters, such as loading rate and wet-dry period.
- Clear relationships were found between the removal of TSS and Fe and Zn at different operation conditions. Further investigations are required to determine the particle size distribution of TSS and the capacity to adsorb and desorb various urban stormwater pollutants at various wet-dry conditions.

References

Abdi, H. 2010. Partial least squares regression and projection on latent structure regression (PLS Regression) Wiley Interdisciplinary Reviews: Computational Statistics Volume 2, Issue 1. *Wiley Interdisciplinary Reviews: Computational Statistics* 2(1), pp. 97–106.

Adams, A., Raman, A. and Hodgkins, D. 2013. How do the plants used in phytoremediation in constructed wetlands, a sustainable remediation strategy, perform in heavy-metal-contaminated mine sites? *Water and Environment Journal* 27(3), pp. 373–386.

Adeola, S., Revitt, M., Shutes, B., Garelick, H., Jones, H. and Jones, C. 2009. Constructed Wetland Control of Bod Levels in Airport Runoff. *International Journal of Phytoremediation* 11(1), pp. 1–10.

Aguirre, P., Ojeda, E., García, J., Barragán, J. and Mujeriego, R. 2005. Effect of water depth on the removal of organic matter in horizontal subsurface flow constructed wetlands. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering* 40(6–7), pp. 1457–1466.

Akratos, C.S., Papaspyros, J.N.E. and Tsihrintzis, V.A. 2009. Artificial neural network use in ortho-phosphate and total phosphorus removal prediction in horizontal subsurface flow constructed wetlands. *Biosystems Engineering* 102(2), pp. 190–201.

Akratos, C.S. and Tsihrintzis, V.A. 2007. Effect of temperature, HRT, vegetation and porous media on removal efficiency of pilot-scale horizontal subsurface flow constructed wetlands. *Ecological Engineering* 29(2), pp. 173–191.

Al-Tahmazi, T. and Babatunde, A.O. 2016. Mechanistic study of P retention by dewatered waterworks sludges. *Environmental Technology & Innovation* 6, pp. 38–48.

APHA 2012. *Standard Methods for the Examination of Water and Wastewater (22nd ed).*

Aryal, R., Vigneswaran, S., Kandasamy, J. and Naidu, R. 2010. Urban stormwater quality and treatment. *Korean Journal of Chemical Engineering* 27(5), pp. 1343–1359.

Aryal, R., Kandasamy, J., Vigneswaran, S., Naidu, R. and Lee, H.S. 2011. Review of stormwater quality, quantity and treatment methods part 2: Stormwater: Quality modelling. *Environmental Engineering Research* 16(4), pp. 143–149.

Asuman Korkusuz, E., Beklioğlu, M. and Demirer, G.N. 2007. Use of blast furnace granulated slag as a substrate in vertical flow reed beds: Field application. *Bioresource*

Technology 98(11), pp. 2089–2101.

Austin, D., Maciolek, D., Davis, B. and Wallace, S. 2007. Damköhler number design method to avoid clogging of subsurface flow constructed wetlands by heterotrophic biofilms. *Water Science and Technology* 56(3), pp. 7–14.

Ávila, C., Matamoros, V., Reyes-Contreras, C., Piña, B., Casado, M., Mita, L., Rivetti, C., Barata, C., García, J. and Bayona, J.M. 2014. Attenuation of emerging organic contaminants in a hybrid constructed wetland system under different hydraulic loading rates and their associated toxicological effects in wastewater. *Science of the Total Environment* 470–471, pp. 1272–1280.

Babatunde, A.O., Zhao, Y.Q., O'Neill, M. and O'Sullivan, B. 2008. Constructed wetlands for environmental pollution control: a review of developments, research and practice in Ireland. *Environment international* 34(1), pp. 116–26.

Babatunde, A.O., Zhao, Y.Q. and Zhao, X.H. 2010. Alum sludge-based constructed wetland system for enhanced removal of P and OM from wastewater: Concept, design and performance analysis. *Bioresource Technology* 101(16), pp. 6576–6579.

Babatunde, A.O. and Zhao, Y.Q. 2010. Equilibrium and kinetic analysis of phosphorus adsorption from aqueous solution using waste alum sludge. *Journal of Hazardous Materials* 184(1–3), pp. 746–752.

Bagheri, M., Mirbagheri, S.A., Ehteshami, M. and Bagheri, Z. 2015. Modeling of a sequencing batch reactor treating municipal wastewater using multi-layer perceptron and radial basis function artificial neural networks. *Process Safety and Environmental Protection* 93(April), pp. 111–123.

Bai, L., Wang, C., Huang, C., He, L. and Pei, Y. 2014. Reuse of drinking water treatment residuals as a substrate in constructed wetlands for sewage tertiary treatment. *Ecological Engineering* 70, pp. 295–303.

Baskar G., Deeptha V.T., A.R. 2014. Comparison of Treatment Performance Between Constructed Wetlands With Different substrates. *International Journal of Research in Engineering and Technology* 03(04), pp. 210–214.

Batty, L.C., Baker, A.J.M. and Wheeler, B.D. 2002. Aluminium and phosphate uptake by Phragmites australis: The role of Fe, Mn and Al root plaques. *Annals of Botany* 89(4), pp. 443–449.

Batty, L.C. and Younger, P.L. 2004. Growth of Phragmites australis (Cav .) Trin ex . Steudel in mine water treatment wetlands : effects of metal and nutrient uptake. 132, pp.

85–93.

Bendoricchio, G., Dal Cin, L. and Persson, J. 2000. Guidelines for free water surface wetland design. *EcoSys Bd* 8, pp. 51–91.

Birch, G.F., Matthai, C., Fazeli, M.S. and Suh, J.Y. 2004. Efficiency of a constructed wetland in removing contaminants from stormwater. *Wetlands* 24(2), pp. 459–466.

Blake, G.R. and Hartge, K.H. 1986a. Bulk Density1. In: *Methods of Soil Analysis: Part 1—Physical and Mineralogical Methods*. SSSA Book Series SV - 5.1. Madison, WI: Soil Science Society of America, American Society of Agronomy., pp. 363–375.

Blake, G.R. and Hartge, K.H. 1986b. Particle Density1. In: *Methods of Soil Analysis: Part 1—Physical and Mineralogical Methods*. SSSA Book Series SV - 5.1. Madison, WI: Soil Science Society of America, American Society of Agronomy., pp. 377–382.

Blecken, G.-T., Zinger, Y., Deletić, A., Fletcher, T.D. and Viklander, M. 2009. Impact of a submerged zone and a carbon source on heavy metal removal in stormwater biofilters. *Ecological Engineering* 35(5), pp. 769–778.

Blecken, G.-T., Zinger, Y., Deletić, A., Fletcher, T.D., Hedström, A. and Viklander, M. 2010. Laboratory study on stormwater biofiltration: Nutrient and sediment removal in cold temperatures. *Journal of Hydrology* 394(3–4), pp. 507–514.

Blecken, G.T., Marsalek, J. and Viklander, M. 2011. Laboratory study of stormwater biofiltration in low temperatures: Total and dissolved metal removals and fates. *Water, Air, and Soil Pollution* 219(1–4), pp. 303–317.

Boltz, J.P., Morgenroth, E. and Sen, D. 2010. Mathematical modelling of biofilms and biofilm reactors for engineering design. *Water Science and Technology* 62(8), pp. 1821–1836.

Bonanno, G. and Lo Giudice, R. 2010. Heavy metal bioaccumulation by the organs of Phragmites australis (common reed) and their potential use as contamination indicators. *Ecological Indicators* 10(3), pp. 639–645.

Bratieres, K., Fletcher, T.D.D., Deletic, A. and Zinger, Y. 2008. Nutrient and sediment removal by stormwater biofilters: A large-scale design optimisation study. *Water Research* 42(14), pp. 3930–3940.

Brix, H. 1994. Use of constructed wetlands in water pollution control: Historical development, present status, and future perspectives. *Water Science and Technology* 30(8 pt 8), pp. 209–223.

Brix, H. and Arias, C.A. 2005. The use of vertical flow constructed wetlands for on-site treatment of domestic wastewater: New Danish guidelines. *Ecological Engineering* 25(5), pp. 491–500.

Brovelli, A., Baechler, S., Rossi, L., Langergraber, G. and Barry, D.A. 2007. Coupled flow and hydro-geochemical modelling for design and optimization of horizontal flow constructed wetlands. *2nd International Symposium on 'Wetland Pollutant Dynamics and Control WETPOL 2007' – Extended Abstracts II* (September), p. 2007.

BSI, B. standard 1998. *Methods of test for Soils for civil engineering purposes*. London: British Standards Institute.

Bubb, J.M., Rudd, T. and Lester, J.N. 1991. Distribution of heavy metals in the river yare and its associated broads III. Lead and zinc. *Science of The Total Environment* 102, pp. 189–208.

Bulc, T.G. 2006. Long term performance of a constructed wetland for landfill leachate treatment. *Ecological Engineering* 26(4), pp. 365–374.

Burian, S.J. and Edwards, F.G. 2002. Historical Perspectives of Urban Drainage Steven J. Burian* and Findlay G. Edwards*. *Computer* (479), pp. 1–16.

Butler†, D. and Davies††, J.W. 2000. *Urban Drainage*. 2nd ed. London and New York: Spon Press.

Butler, C. and Pidgeon, N. 2011. From 'flood defence' to 'flood risk management': Exploring governance, responsibility, and blame. *Environment and Planning C: Government and Policy* 29(3), pp. 533–547.

Callery, O., Healy, M.G., Rognard, F., Barthelemy, L. and Brennan, R.B. 2016. Evaluating the long-term performance of low-cost adsorbents using small-scale adsorption column experiments. *Water Research* 101, pp. 429–440.

Chang, N. Bin, Wanielista, M.P. and Xuan, Z. 2014. *Tracer-based system dynamic modeling for designing a subsurface upflow wetland for nutrient removal*. 1st ed. © 2014 Elsevier B.V. All rights reserved.

Chang, Y., Wu, S., Zhang, T., Mazur, R., Pang, C. and Dong, R. 2014. Dynamics of nitrogen transformation depending on different operational strategies in laboratory-scale tidal flow constructed wetlands. *Science of The Total Environment* 487(1), pp. 49–56.

Charlesworth, S. 2017. Sustainable Drainage in Refugee Camps. *New Water Policy and Practice* 4(1).

Charley, R.C., Hooper, D.G. and McLee, A.G. 1980. Nitrification kinetics in activated sludge at various temperatures and dissolved oxygen concentrations. *Water Research*

14(10), pp. 1387–1396.

CIRIA 2007. *The SUDS manual*. London: Construction Industry Research & Information Association (CIRIA), Report C697.

Connolly, R., Zhao, Y., Sun, G. and Allen, S. 2004. Removal of ammoniacal-nitrogen from an artificial landfill leachate in downflow reed beds. *Process Biochemistry* 39(12), pp. 1971–1976.

Cooper, P. 1996. *Reed beds and constructed wetlands for wastewater treatment*. Swindon, Wiltshire: WRc Publications.

Cooper, P., Griffin, P., Humphries, S. and and Adrian, P. 1999. Design of a Hybrid Reed Bed System to Achieve Complete Nitrification and Denitrification of Domestic Sewage. *Water Quality Research Journal of Canada* 40(3), pp. 283–289.

Cooper, P.F., Job, G.D., Green, M.B. and Shutes, R.B.E. 1996. *Reed beds and constructed wetlands for wastewater treatment*. WRc Publications Medmenham, Marlow, UK.

Cronk, J.K. and Fennessy, M.S. 2001. *Wetland plants: biology and ecology.*

Cui, L., Ouyang, Y., Lou, Q., Yang, F., Chen, Y., Zhu, W. and Luo, S. 2010. Removal of nutrients from wastewater with Canna indica L. under different vertical-flow constructed wetland conditions. *Ecological Engineering* 36(8), pp. 1083–1088.

D'Acunto, B., Frunzo, L., Luongo, V. and Mattei, M.R. 2019. Mathematical Modeling of Biofilms. *ACS Symposium Series* 1323, pp. 245–273.

Dagenais, D., Brisson, J. and Fletcher, T.D. 2018. The role of plants in bioretention systems; does the science underpin current guidance? *Ecological Engineering* 120(February), pp. 532–545.

Datta, S.K. De 1995. Nitrogen transformations in wetland rice ecosystems. *Fertilizer Research, Publishers, Kluwer Academic* (42), pp. 193–203.

Davis, A.P., Shokouhian, M. and Ni, S. 2001. Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. *Chemosphere* 44(5), pp. 997–1009.

Davis, A.P., Robert G. Traver2 and Hunt, W.F. 2010. Improving Urban Stormwater Quality: Applying Fundamental Principles. *Journal of Contemporary Water researCh & eduCation UCOWR* (146), pp. 3–10.

Defo, C., Kaur, R., Bharadwaj, A., Lal, K. and Kumar, P. 2017. Modelling approaches for simulating wetland pollutant dynamics. *Critical Reviews in Environmental Science and*

Technology 47(15), pp. 1371–1408.

Dietz, M.E. and Clausen, J.C. 2006. Saturation to Improve Pollutant Retention in a Rain Garden. *Environmental Science & Technology* 40(4), pp. 1335–1340.

Dimitrova, S. 2000. Interaction of blast-furnace slag with heavy metal ions in water solutions. *Water Research* 34(6), pp. 1957–1961.

Dimitrova, S. V. 2002. Use of granular slag columns for lead removal. *Water Research* 36(16), pp. 4001–4008.

Dimitrova, S.V. 1996. Metal sorption on blast-furnace slag. *Water Research* 30(1), pp. 228–232.

Djukić, A., Lekić, B., Rajaković-Ognjanović, V., Veljović, D., Vulić, T., Djolić, M., Naunovic, Z., Despotović, J. and Prodanović, D. 2016. Further insight into the mechanism of heavy metals partitioning in stormwater runoff. *Journal of Environmental Management* 168, pp. 104–110.

DLWC, (Department of Land and Water Conservation) 1998. *The constructed wetland manual vol.1*. DLWC, New South Wales.

Dong, Y., Wilinski, P.R. and Scholz, M. 2011. Impact of Hydraulic Loading Rate and Season on Water Contaminant Reductions Within Integrated Constructed Wetlands.

Dotro, G., Langergraber, G., Molle, P., Nivala, J., Puigagut, J., Otto Stein and Sperling, M. von 2017. *VOLUME 7 Treatment Wetlands*. IWA Publishing.

Drizo, A., Frost, C.A., Grace, J. and Smith, K.A. 1999. Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems. *Water Research* 33(17), pp. 3595–3602.

Du, X., Xu, Z., Li, J. and Zheng, L. 2014. Characterization and removal of dissolved organic matter in a vertical fl ow constructed wetland. *Ecological Engineering* 73, pp. 610–615.

Duncan, H. 1999. *Urban stormwater quality : a statistical overview / Hugh P. Duncan*. Hydrology, C. R. C. for C. ed. Clayton, Vic: CRC for Catchment Hydrology.

Ellis, B. 1991. Urban runoff quality in the UK: problems, prospects and procedures. *Applied Geography* 11(3), pp. 187–200.

Ellis, John Bryan, Shutes, R Brian E and Revitt, D.M. 2003a. *Constructed wetlands and links with sustainable drainage systems.* Environment Agency.

Ellis, J B, Shutes, R B E and Revitt, D.M. 2003b. Guidance Manual for Constructed

Wetlands., p. 112.

Ellis, J.B. and Revitt, D.M. 1982. Incidence of heavy metals in street surface sediments: Solubility and grain size studies. *Water, Air, and Soil Pollution* 17(1), pp. 87–100.

Environment Agency [no date]. Sustainable Drainage Systems (SUDS) Surface water run-off. *Environment Agency*

Faulwetter, J.L., Gagnon, V., Sundberg, C., Chazarenc, F., Burr, M.D., Brisson, J., Camper, A.K. and Stein, O.R. 2009. Microbial processes influencing performance of treatment wetlands : A review. 35, pp. 987–1004.

FAWB 2009. Guidelines for filter media in biofiltration systems (Version 3.01). (June), pp. 1–8.

Feng, W., Hatt, B.E., McCarthy, D.T., Fletcher, T.D. and Deletic, A. 2012. Biofilters for Stormwater Harvesting: Understanding the Treatment Performance of Key Metals That Pose a Risk for Water Use. *Environmental Science & Technology* 46(9), pp. 5100–5108.

Le Fevre, G.H., Paus, K.H., Natarajan, P., Gulliver, J.S., Novak, P.J. and Hozalski, R.M. 2015. Review of dissolved pollutants in urban storm water and their removal and fate in bioretention cells. *Journal of Environmental Engineering (United States)* 141(1)

Field, A. 2013. *Discovering Statistics using IBM SPSS*. Third Edit. SAGE Publications Ltd.

Fisher, J. and Acreman, M.C. 2004. Wetland nutrient removal : a review of the evidence Wetland nutrient removal : a review of the evidence. 8(4), pp. 673–685.

Fitch, M.W. 2014. Constructed Wetlands. *Comprehensive Water Quality and Purification* 3, pp. 268–295.

Fletcher, T.D., Shuster, W., Hunt, W.F., Ashley, R., Butler, D., Arthur, S., Trowsdale, S., Barraud, S., Semadeni-Davies, A., Bertrand-Krajewski, J.L., Mikkelsen, P.S., Rivard, G., Uhl, M., Dagenais, D. and Viklander, M. 2015. SUDS, LID, BMPs, WSUD and more – The evolution and application of terminology surrounding urban drainage. *Urban Water Journal* 12(7), pp. 525–542.

Flood and Water Management Act 2010. Flood and Water Management Act. In: Elizabeth, I. ed. *Flood and Coastal Erosion Risk Management*., p. 111.

Fritz, J.J., Middleton, A.C. and Meredith, D.D. 1979. Dynamic process modeling of wastewater stabilization ponds. *Journal of the Water Pollution Control Federation* 51(11), pp. 2724–2743.

Galfi, H. 2014. Suspended solids and indicator bacteria in stormwater runoff: Sources of bias in field measurements.

García, J., Aguirre, P., Mujeriego, R., Huang, Y., Ortiz, L. and Bayona, J.M. 2004. Initial contaminant removal performance factors in horizontal flow reed beds used for treating urban wastewater. *Water Research* 38(7), pp. 1669–1678.

GARCÍA, J., ROUSSEAU, D.P.L., MORATÓ, J., LESAGE, E., MATAMOROS, V. and BAYONA, J.M. 2010. Contaminant Removal Processes in Subsurface-Flow Constructed Wetlands: A Review. *Critical Reviews in Environmental Science and Technology* 40(7), pp. 561–661.

Garn, H.S. 2002. Surface-Water Quality-Assurance Plan for the Wisconsin District of the U.S. Geological Survey, Water Resources Division.

Geary, P., Saunders, M. and Waters, D. 2003. Stormwater runoff treatment using constructed wetlands. *Water* 30(6), pp. 55–60.

Ghani, a a B., Zakaria, N. a, Chang, C.K. and Ainan, a 2008. Sustainable Urban Drainage System (SUDS) – Malaysian Experiences. *11th International Conference on Urban Drainange, Edinburgh, Scotland,UK* (September), pp. 1–10.

Gill, L.W., Ring, P., Casey, B., Higgins, N.M.P. and Johnston, P.M. 2017. Long term heavy metal removal by a constructed wetland treating rainfall runoff from a motorway. *Science of the Total Environment* 601–602, pp. 32–44.

Giraldi, D., de Michieli Vitturi, M. and Iannelli, R. 2010. FITOVERT: A dynamic numerical model of subsurface vertical flow constructed wetlands. *Environmental Modelling & Software* 25(5), pp. 633–640.

Goonetilleke, A., Thomas, E., Ginn, S. and Gilbert, D. 2005. Understanding the role of land use in urban stormwater quality management. *Journal of environmental management* 74(1), pp. 31–42.

Gower, A.M. (Anthony M.. 1980. *Water quality in catchment ecosystems*. Chichester: Chichester : Wiley.

Grandgirard, J., Poinsot, D., Krespi, L., Nénon, J.P. and Cortesero, A.M. 2002. Performances of constructed wetlands for municipal wastewater treatment in rural mountainous area. *Hydrobiologia* 103(3), pp. 239–248.

Gray, S., Kinross, J., Read, P. and Marland, A. 2000. The nutrient assimilative capacity of maerl as a substrate in constructed wetland systems for waste treatment. *Water Research* 34(8), pp. 2183–2190.

Greenway, M. 2004. Constructed wetlands for water pollution control - Processes, parameters and performance. *Developments in Chemical Engineering and Mineral Processing* 12(5–6), pp. 491–504.

Greenway, M. and Woolley, A. 1999. Constructed wetlands in Queensland: Performance efficiency and nutrient bioaccumulation. *Ecological Engineering* 12(1–2), pp. 39–55.

Greenway, M. and Woolley, A. 2001. Changes in plant biomass and nutrient removal over 3 years in a constructed wetland in Cairns, Australia. *Water Science and Technology* 44(11–12), pp. 303–310.

Groot, de R., Brander, L., van der Ploeg, S., Costanza, R., Bernard, F., Braat, L., Christie, M., Crossman, N., Ghermandi, A., Hein, L., Hussain, S., Kumar, P., McVittie, A., Portela, R., Rodriguez, L.C., ten Brink, P. and van Beukering, P. 2012. Global estimates of the value of ecosystems and their services in monetary units. *Ecosystem Services* 1(1), pp. 50–61.

Grüneberg, B. and Kern, J. 2001. Phosphorus retention capacity of iron-ore and blast furnace slag in subsurface flow constructed wetlands. *Water Science and Technology* 44(11–12), pp. 69–75.

Hallberg, K.B. and Johnson, D.B. 2005. Microbiology of a wetland ecosystem constructed to remediate mine drainage from a heavy metal mine. *Science of the Total Environment* 338(1-2 SPEC. ISS.), pp. 53–66.

Hao, X., Ball, B.C., Culley, J.L.B., Carter, M.R. and Parkin, G.W. 2019. Chapter 57 Soil Density and Porosity. (June)

Harrop, D.O., Mumby, K., Ashworth, J., Nolan, J., Price, M. and Pepper, B. 1990. Air quality in the vicinity of urban roads. *Science of the Total Environment, The* 93(C), pp. 285–292.

Hatt, B.E., Fletcher, T.D. and Deletic, A. 2007. Hydraulic and pollutant removal performance of stormwater filters under variable wetting and drying regimes. *Water Science and Technology* 56(12), pp. 11–19.

Hatt, B.E., Deletic, A. and Fletcher, T.D. 2007a. Stormwater reuse: designing biofiltration systems for reliable treatment. *Water Science and Technology* 55(4), pp. 201–209.

Hatt, B.E., Fletcher, Tim D and Deletic, A. 2007b. Treatment performance of gravel filter media: Implications for design and application of stormwater infiltration systems. *Water Research* 41(12), pp. 2513–2524.

Hatt, B.E., Fletcher, T.D. and Deletic, A. 2009. Hydrologic and pollutant removal performance of stormwater biofiltration systems at the field scale. *Journal of Hydrology*

365(3–4), pp. 310–321.

Huang, J., Reneau, R.B. and Hagedorn, C. 2000. Nitrogen removal in constructed wetlands employed to treat domestic wastewater. *Water Research* 34(9), pp. 2582–2588.

Hubbe, M.A., Metts, J.R., Hermosilla, D., Blanco, M.A., Yerushalmi, L., Haghighat, F., Lindholm-Lehto, P., Khodaparast, Z., Kamali, M. and Elliott, A. 2016. Wastewater Treatment and Reclamation: A Review of Pulp and Paper Industry Practices and Opportunities. *BioResources* 11(3), pp. 7953–8091.

Hunt, W.F., Davis, A.P. and Traver, R.G. 2012. Meeting hydrologic and water quality goals through targeted bioretention design. *Journal of Environmental Engineering (United States)* 138(6), pp. 698–707.

ITRC 2003. Technical and regulatory guidance document for constructed treatment wetlands. *Technology* (December), p. 128.

IWA 2017. *Treatment Wetlands (IWA 2017)*. IWA Publishing,UK.

Jacob, D.L. and Otte, M.L. 2004. Long-term effects of submergence and wetland vegetation on metals in a 90-year old abandoned Pb e Zn mine tailings pond. 130, pp. 337–345.

Jayaratne, R., Seyb, R., Martindale, M. and Li, J.S. 2010. Constructed wetland design practices and performance : an overview. *Stormwater Conference* , pp. 1–17.

Jenssen, P. and Krogstad, T. 2003. Design of constructed wetlands using phosphorus sorbing lightweight aggregate (LWA). *Constructed Wetlands for Wastewater Treatment in Cold Climates, Advances in Ecological Sciences* 11, pp. 259–272.

Jia, W., Zhang, J., Wu, J., Xie, H. and Zhang, B. 2010. Effect of intermittent operation on contaminant removal and plant growth in vertical flow constructed wetlands: A microcosm experiment. *Desalination* 262(1–3), pp. 202–208.

Jia, W., Zhang, J., Li, P., Xie, H., Wu, J. and Wang, J. 2011. Nitrous oxide emissions from surface flow and subsurface flow constructed wetland microcosms: Effect of feeding strategies. *Ecological Engineering* 37(11), pp. 1815–1821.

Joergensen, B. and Fath, S. 2011. *Fundamentals of Ecological Modelling: Applications in Environmental Management and Research*. Elsevier.

Kadlec, R.H. and Knight, R.L. 1996. *Treatment Wetlands.* Lewis Publishers, Boca Raton.

Kadlec, R.H. 2000. The inadequacy of first-order treatment wetland models. 15, pp. 105–119.

Kadlec, R.H. 2003. Effects of pollutant speciation in treatment wetlands design. *Ecological Engineering* 20(1), pp. 1–16.

Kadlec, R.H. and Reddy, K.R. 2001. Temperature Effects in Treatment Wetlands. *Water Environment Research* 73(5), pp. 543–557.

Kadlec, R.H. and Wallace, S.D. 2009a. Summary for Policymakers. In: Intergovernmental Panel on Climate Change ed. *Climate Change 2013 - The Physical Science Basis*. Second edi. Cambridge: Cambridge University Press., pp. 1–30.

Kadlec, R.H. and Wallace, S.D. 2009b. *Treatment Wetlands*. Second edi. CRC Press Taylor & Francis Group, LLC.

Khelifi, O., Kozuki, Y., Murakami, H., Kurata, K. and Nishioka, M. 2002. Nutrients adsorption from seawater by new porous carrier made from zeolitized fly ash and slag. *Marine Pollution Bulletin* 45(1–12), pp. 311–315.

Kiiza, C.J. 2017. *Design and modelling of pollutant removal in stormwater constructed wetlands*. PhD thesis. Cardiff University, Cardiff, Wales, UK.

Kleinmann, R.L.P. 1990. Acid mine water treatment using engineered wetlands. *International journal of mine water* 9(1), pp. 269–276.

Knight, R.L., Kadlec, R.H. and Ohlendorf, H.M. 1999. The use of treatment wetlands for petroleum industry effluents. *Environmental Science and Technology* 33(7), pp. 973–980.

Knight, R.L., Jr, V.W.E.P., Robert E. Borer, A., R. and Jr., C. 2000. Constructed Wetlands for Livestock Wastewater Management. *Ecological Engineering* 15, pp. 41–55.

Knight, R.L., Clarke Jr, R.A. and Bastian, R.K. 2001. Surface flow (SF) treatment wetlands as a habitat for wildlife and humans. *Water science and technology : a journal of the International Association on Water Pollution Research* 44(11–12), pp. 27–37.

Kosolapov, D.B., Kuschk, P., Vainshtein, M.B., Vatsourina, A. V., Wießner, A., Kästner, M. and Müller, R.A. 2004. Microbial processes of heavy metal removal from carbon-deficient effluents in constructed wetlands. *Engineering in Life Sciences* 4(5), pp. 403–411.

Kostura, B., Kulveitová, H. and Lesko, J. 2005. Blast furnace slags as sorbents of phosphate from water solutions. *Water research* 39(9), pp. 1795–802.

Kumar, J.L.G., Wang, Z.Y., Zhao, Y.Q., Babatunde, a O., Zhao, X.H. and Jørgensen, S.E. 2011. STELLA software as a tool for modelling phosphorus removal in a constructed wetland employing dewatered alum sludge as main substrate. *Journal of environmental science and health. Part A, Toxic/hazardous substances & environmental engineering* 46(7), pp. 751–757.

Kumar, J.L.G., Zhao, Y.Q., Hu, Y.S., Babatunde, A.O. and Zhao, X.H. 2015. Nitrogen dynamics model for a pilot field-scale novel dewatered alum sludge cake-based constructed wetland system. *Environmental Technology (United Kingdom)* 36(6), pp. 732–741.

Kumar, J.L.G. and Zhao, Y.Q. 2011. A review on numerous modeling approaches for effective, economical and ecological treatment wetlands. *Journal of Environmental Management* 92(3), pp. 400–406.

Langergraber, G. 2008. Modeling of Processes in Subsurface Flow Constructed Wetlands: A Review. *Vadose Zone Journal* 7(2), pp. 830–842.

Langergraber, G. 2011. Numerical modelling: A tool for better constructed wetland design? *Water Science and Technology* 64(1), pp. 14–21.

Langergraber, G. and Haberl, R. 2001. Constructed wetlands for water treatment. In: Verhoeven, J. T. A. et al. eds. *Minerva Biotecnologica*. Berlin, Heidelberg: Springer Berlin Heidelberg., pp. 123–134.

Langergraber, G. and Šimůnek, J. 2005. Modeling Variably Saturated Water Flow and Multicomponent Reactive Transport in Constructed Wetlands. *Vadose Zone Journal* 4(4), pp. 924–938.

Langergraber, G. and Šimůnek, J. 2012. Reactive Transport Modeling of Subsurface Flow Constructed Wetlands Using the HYDRUS Wetland Module. *Vadose Zone Journal* 11(2), p. vzj2011.0104.

Lee, B.H. and Scholz, M. 2007. What is the role of Phragmites australis in experimental constructed wetland filters treating urban runoff? *Ecological Engineering* 29(1), pp. 87–95.

Lee, C.G., Fletcher, T.D. and Sun, G. 2009. Nitrogen removal in constructed wetland systems. *Engineering in Life Sciences* 9(1), pp. 11–22.

LeFevre, G.H., Paus, K.H., Natarajan, P., Gulliver, J.S., Novak, P.J. and Hozalski, R.M. 2015. Review of Dissolved Pollutants in Urban Storm Water and Their Removal and Fate in Bioretention Cells. *Journal of Environmental Engineering* 141(1), p. 04014050.

Li, H. and Davis, A.P. 2009. Water quality improvement through reductions of pollutant loads using bioretention. *Journal of Environmental Engineering* 135(8), pp. 567–576.

Liu, W., Dahab, M.F. and Surampalli, R.Y. 2005. Nitrogen Transformations Modeling in Subsurface-Flow Constructed Wetlands. *Water Environment Research* 77(3), pp. 246–258.

Llorens, E., Saaltink, M.W. and García, J. 2011. CWM1 implementation in RetrasoCodeBright : First results using horizontal subsurface flow constructed wetland data. 166, pp. 224–232.

Lucas, R. 2015. *Design and experimental assessment of stormwater constructed wetland systems*. PhD thesis. Cardiff University, Cardiff, Wales, UK.

Ma, J., Tracy, K. and Lenhart, J. 2009. Phosphorus Removal in Urban Runoff Using Adsorptive Filtration Media. In: *Proceedings of the StormCon*. Anaheim, CA, USA, pp. 16–20.

Machemer, S.D. and Wildeman, T.R. 1992. Adsorption compared with sulfide precipitation as metal removal processes from acid mine drainage in a constructed wetland. *Journal of Contaminant Hydrology* 9(1–2), pp. 115–131.

Maciolek, D. and Austin, D. 2006. Low Energy Biological Nitrogen Removal by Cation Exchange, Thin Film Oxygen Transfer, and Heterotrophic Nitrification in Sequencing-Batch, Packed-Bed Reactors. In: *Proceedings of the Water Environment Federation*., pp. 1560–1582.

Mæhlum, T. and Jenssen, P. 2003. Design and performance of integrated subsurface flow wetlands in a cold climate. *Constructed Wetlands for Wastewater Treatment in Cold Climates* , pp. 69–86.

Mæhlum, T. and Stalnacke, P. 1999. Removal efficiency of three cold-climate constructed wetlands treating domestic wastewater: Effects of temperature, seasons, loading rates and input concentrations. In: *Water Science and Technology*. Elsevier Science Ltd., pp. 273–281.

Mahmood, Q., Pervez, A., Zeb, B.S., Zaffar, H., Yaqoob, H., Waseem, M., Zahidullah and Afsheen, S. 2013. Natural treatment systems as sustainable ecotechnologies for the developing countries. *BioMed Research International* 2013

Maniquiz-Redillas, M. and Kim, L.H. 2014. Fractionation of heavy metals in runoff and discharge of a stormwater management system and its implications for treatment. *Journal of Environmental Sciences (China)* 26(6), pp. 1214–1222.

Marchand, L., Mench, M., Jacob, D.L. and Otte, M.L. 2010. Metal and metalloid removal in constructed wetlands, with emphasis on the importance of plants and standardized measurements: A review. *Environmental Pollution* 158(12), pp. 3447–3461.

Marshall, G. 2015. *Don't even think about it: Why our brains are wired to ignore climate change*. Bloomsbury Publishing USA.

Martin, J.F. and Reddy, K.R. 1997. Interaction and spatial distribution of wetland nitrogen processes. *Ecological Modelling* 105(1), pp. 1–21.

Martín, M., Gargallo, S., Hernández-Crespo, C. and Oliver, N. 2013. Phosphorus and nitrogen removal from tertiary treated urban wastewaters by a vertical flow constructed wetland. *Ecological Engineering* 61, pp. 34–42.

Matagi, S.., Swai, D. and Mugabe, R. 1998. A review of Heavy Metal Removal Mechanisms in wetlands. *African Journal of Tropical Hydrobiology and Fisheries* 8(1)

Mayo, A.W., Muraza, M. and Norbert, J. 2018. Modelling nitrogen transformation and removal in mara river basin wetlands upstream of lake Victoria. *Physics and Chemistry of the Earth* 105(May 2016), pp. 136–146.

Merriman, L.S., Member, A. and Raleigh, C.B. 2012. Assessing the Development of Ecosystem Services in Constructed Stormwater Wetlands. 7004(12)

Met office 2020. UK climate extremes Select all Add Highest daily maximum temperature records UK climate Highest daily minimum temperature records (online). Available at: https://www.metoffice.gov.uk/research/climate/maps-and-data/uk-climate-extremes.

Metcalf, L. and Eddy, H.P. 2014. *Wastewater engineering : treatment, disposal, and reuse*. New York: McGraw-Hill.

Meyer, D., Chazarenc, F., Claveau-Mallet, D., Dittmer, U., Forquet, N., Molle, P., Morvannou, A., Pálfy, T., Petitjean, A., Rizzo, A., Samsó Campà, R., Scholz, M., Soric, A. and Langergraber, G. 2015. Modelling constructed wetlands: Scopes and aims - a comparative review. *Ecological Engineering* 80, pp. 205–213.

Misra, A.K. 2014. Climate change and challenges of water and food security. *International Journal of Sustainable Built Environment* 3(1), pp. 153–165.

Mohammed, A. and Babatunde, A.O. 2017. Modelling heavy metals transformation in vertical flow constructed wetlands. *Ecological Modelling* 354, pp. 62–71.

Mohammed, A.A. 2017. *Development of an engineered wetland system for sustainable landfill leachate treatment*. PhD thesis. Cardiff University, Cardiff, Wales, UK.

Morvannou, A., Choubert, J.M., Vanclooster, M. and Molle, P. 2014. Modeling nitrogen removal in a vertical flow constructed wetland treating directly domestic wastewater. *Ecological Engineering* 70, pp. 379–386.

Müller, A., Österlund, H., Marsalek, J. and Viklander, M. 2020. The pollution conveyed by urban runoff: A review of sources. *Science of the Total Environment* 709, p. 136125.

Muthanna, T.M., Viklander, M., Gjesdahl, N. and Thorolfsson, S.T. 2007. Heavy Metal Removal in Cold Climate Bioretention. *Water, Air, and Soil Pollution* 183(1–4), pp. 391–402.

Muthukaruppan, M., Chiew, F. and Wong, T. 2002. Size distribution and partitioning of urban pollutants. *Global Solutions for Urban Drainage* , pp. 1–12.

Nairn, R.W. and Mitsch, W.J. 2000. Phosphorus removal in created wetland ponds receiving river overflow. 14, pp. 107–126.

Nanbakhsh, H., Kazemi-Yazdi, S. and Scholz, M. 2007. Design comparison of experimental storm water detention systems treating concentrated road runoff. *Science of the Total Environment* 380(1–3), pp. 220–228.

Nathan, A.J. and Scobell, A. 2012. How China sees America. *Foreign Affairs* 91(5), pp. 33–36.

Nayak, P.C., Satyaji Rao, Y.R. and Sudheer, K.P. 2006. Groundwater level forecasting in a shallow aquifer using artificial neural network approach. *Water Resources Management* 20(1), pp. 77–90.

Newcombe, C.P. and Macdonald, D.D. 1991. Effects of Suspended Sediments on Aquatic Ecosystems. *North American Journal of Fisheries Management* 11(1), pp. 72–82.

Ngwenya, B. 2004. Geochemical processes governing the performance of a constructed wetland treating acid mine drainage, Central Scotland. *Applied geochemistry* 19(11), pp. 1773–1783.

O’Dell, G. 2001. AHA environmental assessment. *Hospitals & health networks / AHA* 75(11), pp. 59–61, 63.

O’Hogain, S. 2003. The design, operation and performance of a municipal hybrid reed bed treatment system. *Water Science and Technology* 48(5), pp. 119–126.

Oberkampf, W.L. and Trucano, T.G. 2016. *Verification and validation in computational fluid dynamics*

Ouyang, Y. 2008. Modeling the mechanisms for uptake and translocation of dioxane in a soil-plant ecosystem with STELLA. *Journal of Contaminant Hydrology* 95(1–2), pp. 17–29.

Ouyang, Y., Luo, S.M. and Cui, L.H. 2011. Estimation of nitrogen dynamics in a vertical-flow constructed wetland. *Ecological Engineering* 37(3), pp. 453–459.

Pálfy, T.G. and Langergraber, G. 2014. The verification of the constructed wetland model no. 1 implementation in HYDRUS using column experiment data. *Ecological Engineering* 68(1), pp. 105–115.

Pan, W., Huang, Q., Xu, Z. and Pang, G. 2020. Experimental investigation and simulation of nitrogen transport in a subsurface infiltration system under saturated and unsaturated conditions. *Journal of Contaminant Hydrology* 231(January), p. 103621.

Pelissari, C., Sezerino, P.H., Decezaro, S.T., Wolff, D.B., Bento, A.P., Junior, O. de C. and Philippi, L.S. 2014. Nitrogen transformation in horizontal and vertical flow constructed wetlands applied for dairy cattle wastewater treatment in southern Brazil. *Ecological Engineering* 73, pp. 307–310.

Pérez-esteban, J., Escolástico, C., Ruiz-fernández, J., Masaguer, A. and Moliner, A. 2013. Bioavailability and extraction of heavy metals from contaminated soil by Atriplex halimus. *Environmental and Experimental Botany* 88, pp. 53–59.

Phillips, I.R. and Greenway, M. 1998. Changes in Water-soluble and exchangeable ions, cation exchange capacity, and phosphorus(max) in soils under alternating waterlogged and drying conditions. *Communications in Soil Science and Plant Analysis* 29(1–2), pp. 51–65.

Pimpan, P. and Jindal, R. 2009. Mathematical modeling of cadmium removal in free water surface constructed wetlands. *Journal of Hazardous Materials* 163(2), pp. 1322–1331.

Piñón-Villarreal, A.R., Bawazir, A.S., Shukla, M.K. and Hanson, A.T. 2013. Retention and transport of nitrate and ammonium in loamy sand amended with clinoptilolite zeolite. *Journal of Irrigation and Drainage Engineering* 139(9), pp. 755–765.

Pitt, R., Maestre, a and Morquecho, R. 2004. The national stormwater quality database (NSQD, version 1.1). *1st Annual Stormwater …* (April 2003), pp. 1–9.

Poleto, C. and Tassi, R. 2012. Sustainable Urban Drainage Systems. *Drainage Systems* (March 2018)

Pucher, B. 2015. SIMULATION OF VERTICAL FLOW FILTERS FOR THE TREATMENT OF DOMESTIC WASTEWATER USING SAND AND ZEOLITE AS. (0540424)

Rahman, M., Grace, M.R., Roberts, K.L., Kessler, A.J. and Cook, P.L.M. 2019. E ff ect of temperature and drying-rewetting of sediments on the partitioning between denitri fi cation and DNRA in constructed urban stormwater wetlands. *Ecological Engineering* 140(January), p. 105586.

Ranieri, E., Gorgoglione, A. and Solimeno, A. 2013. A comparison between model and experimental hydraulic performances in a pilot-scale horizontal subsurface flow constructed wetland. *Ecological Engineering* 60, pp. 45–49.

Read, J., Wevill, T., Fletcher, T. and Deletic, A. 2008. Variation among plant species in pollutant removal from stormwater in biofiltration systems. *Water Research* 42(4–5), pp. 893–902.

Ready, K.R., Kadlec, R.H., Flaig, E. and Gale, P.M. 1999. Phosphorus retention in streams and wetlands: A review. *Critical Reviews in Environmental Science and Technology* 29(1), pp. 83–146.

Reddy, K.R., Patrick, W.H. and Broadbent, F.E. 1984. Nitrogen transformations and loss in flooded soils and sediments. *C R C Critical Reviews in Environmental Control* 13(4), pp. 273–309.

Reed, S.C., Crites, R.W. and Middlebrooks, E.J. 1998. *Natural Systems for Waste Management and Treatment*. 2nd ed. New York, USA: McGraw-Hill, Inc.

Reed, S.C. and Brown, D. 1995. Subsurface flow wetlands—A performance evaluation. *Water Environment Research* 67(2), pp. 244–248.

Richardson, C.J., Qian, S., Craft, C.B. and Quails, R.G. 1996. Predictive models for phosphorus retention in wetlands. *Wetlands Ecology and Management* 4(3), pp. 159–175.

Rieuwerts, J.S., Thornton, I., Farago, M.E. and Ashmore, M.R. 1998. Factors influencing metal bioavailability in soils: preliminary investigations for the development of a critical loads approach for metals. *Chemical Speciation and Bioavailability* 10(2), pp. 61–75.

Rousseau, D.P.L., Vanrolleghem, P.A. and De Pauw, N. 2004. Model-based design of horizontal subsurface flow constructed treatment wetlands: A review. *Water Research* 38(6), pp. 1484–1493.

Saeed, T. and Sun, G. 2012. A review on nitrogen and organics removal mechanisms in subsurface flow constructed wetlands: Dependency on environmental parameters, operating conditions and supporting media. *Journal of Environmental Management* 112, pp. 429–448.

Samsó, R. 2014. *Numerical modelling of Constructed Wetlands for wastewater treatment*. Uni- versitat Polit`ecnica de Catalunya-BarcelonaTech (UPC).

Samsó, R. and Garcia, J. 2013a. BIO_PORE, a mathematical model to simulate biofilm growth and water quality improvement in porous media: Application and calibration for constructed wetlands. *Ecological Engineering* 54, pp. 116–127.

Samsó, R. and García, J. 2013b. Bacteria distribution and dynamics in constructed wetlands based on modelling results. *Science of the Total Environment* 461–462, pp. 430–440.

Sansalone, J.J., Buchberger, S.G. and Koechling, M.T. 1995. Correlations between heavy metals and suspended solids in highway runoff: Implications for control strategies. *Transportation Research Record* (1483), pp. 112–119.

Sansalone, J.J. and Kim, J.Y. 2008. Suspended particle destabilization in retained urban stormwater as a function of coagulant dosage and redox conditions. *Water Research*

Sartoris, J.J., Thullen, J.S., Barber, L.B. and Salas, D.E. 2000. Investigation of nitrogen transformations in a southern California constructed wastewater treatment wetland. *Ecological Engineering* 14(1–2), pp. 49–65.

Scholz, M. 2004. Treatment of gully pot effluent containing nickel and copper with constructed wetlands in a cold climate. *Journal of Chemical Technology & Biotechnology* 79(2), pp. 153–162.

Scholz, O., Gawne, B., Ebner, B. and Ellis, I. 2002. The effects of drying and re-flooding on nutrient availability in ephemeral deflation basin lakes in western New South Wales, Australia. *River Research and Applications* 18(2), pp. 185–196.

Schueler, T.. 1987. *Controlling Urban Runoff - A Practice Manual for Planning and Designing Urban BMPs*. Washington: Metropolitan Washington Council of Governments.

Sengupta, S. and Pandit, A. 2011. Selective removal of phosphorus from wastewater combined with its recovery as a solid-phase fertilizer. *Water research* 45(11), pp. 3318–30.

Sewers., S.T.C. on S. and W.M.W.P. on the H.D. of S. 1981. *Design and analysis of urban storm drainage : the Wallingford procedure. Vol.1, Principles, methods and practice*. Station, H. R. ed. London: London : National Water Council.

Sheoran, A.S. and Sheoran, V. 2006. Heavy metal removal mechanism of acid mine drainage in wetlands: A critical review. *Minerals Engineering* 19(2), pp. 105–116.

Shepherd, H.L., Tchobanoglous, G. and Grismer, M.E. 2001. Time-Dependent Retardation Model for Chemical Oxygen Demand Removal in a Subsurface-Flow

Constructed Wetland for Winery Wastewater Treatment. *Water Environment Research* 73(5), pp. 597–606.

Shrestha, P., Hurley, S.E. and Wemple, B.C. 2018. Effects of different soil media, vegetation, and hydrologic treatments on nutrient and sediment removal in roadside bioretention systems. *Ecological Engineering* 112(January), pp. 116–131.

Shutes, B., Ellis, J.B., Revitt, D.M. and Scholes, L.N.L. 2005. Constructed wetlands in UK urban surface drainage systems. *Water Science and Technology* 51(9), pp. 31–37.

Shutes, R.B.E., Ellis, J.B., Revitt, D.M., Forshaw, M. and Winter, B. 2004. Urban and Highway Runoff Treatment by Constructed Wetlands. *Wetlands Ecosystems in Asia* , pp. 361–382.

Silveira, A.L.L. 2002. Problems of modern urban drainage in developing countries. *Water Science and Technology* 45(7), pp. 31–40.

Sim, C.H., Yusoff, M.K., Shutes, B., Ho, S.C. and Mansor, M. 2008. Nutrient removal in a pilot and full scale constructed wetland, Putrajaya city, Malaysia. *Journal of Environmental Management* 88(2), pp. 307–317.

Šíma, J., Svoboda, L., Šeda, M., Krejsa, J. and Jahodová, J. 2019. The fate of selected heavy metals and arsenic in a constructed wetland. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering* 54(1), pp. 56–64.

Sobolewski, A. 1996. Metal species indicate the potential of constructed wetlands for long- term treatment of metal mine drainage. *Ecological Engineering* 6(4), pp. 259–271.

Sobolewski, A. 1999. A Review of Processes Responsible for Metal Removal in Wetlands Treating Contaminated Mine Drainage. *International Journal of Phytoremediation* 1(1), pp. 19–51.

Songliu, L., Hongying, H., Yingxue, S. and Jia, Y. 2009. Effect of carbon source on the denitrification in constructed wetlands. *Journal of Environmental Sciences* 21(8), pp. 1036–1043.

Srishantha, U. and Rathnayake, U. 2017. Sustainable urban drainage systems (SUDS) – What it is and where do we stand today? *Engineering and Applied Science Research* 44(4), pp. 235–241.

Stefanakis, A., Akratos, C.S. and Tsihrintzis, V.A. 2014a. Constructed Wetlands Classification. *Vertical Flow Constructed Wetlands* , pp. 17–25.

Stefanakis, A., Akratos, C.S. and Tsihrintzis, V.A. 2014b. Introduction. *Vertical Flow*

Constructed Wetlands , pp. 1–16.

Stefanakis, A., Akratos, C.S. and Tsihrintzis, V.A. 2014c. Modeling of Vertical Flow Constructed Wetlands. In: *Vertical Flow Constructed Wetlands*. Elsevier., pp. 165–179.

Stefanakis, A., Akratos, C.S. and Tsihrintzis, V.A. 2014e. Processes and Mechanisms in Sludge Treatment Wetlands. *Vertical Flow Constructed Wetlands* , pp. 209–214.

Stefanakis, A., Akratos, C.S. and Tsihrintzis, V.A. 2014f. Treatment Processes in VFCWs. *Vertical Flow Constructed Wetlands* , pp. 57–84.

Stefanakis, A., Akratos, C.S. and Tsihrintzis, V.A. 2014g. VFCW Components. *Vertical Flow Constructed Wetlands* , pp. 39–55.

Stefanakis, A. and Tsihrintzis, V. 2009. Comparison of different substrate media on the performance of Vertical Flow Constructed Wetlands. *11th International Conference on Environmental Science and Technology (CEST 2009)* (September)

Stefanakis, A.I. and Tsihrintzis, V.A. 2009. Performance of pilot-scale vertical flow constructed wetlands treating simulated municipal wastewater: effect of various design parameters. *Desalination* 248(1–3), pp. 753–770.

Stefanakis, A.I. and Tsihrintzis, V.A. 2012. Effects of loading, resting period, temperature, porous media, vegetation and aeration on performance of pilot-scale vertical flow constructed wetlands. *Chemical Engineering Journal* 181–182, pp. 416–430.

Stein, O.R. and Hook, P.B. 2005. Temperature, plants, and oxygen: How does season affect constructed wetland performance? *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering* 40(6–7), pp. 1331–1342.

Stottmeister, U., Wießner, A., Kuschk, P., Kappelmeyer, U., Kästner, M., Bederski, O., Müller, R.A. and Moormann, H. 2003. Effects of plants and microorganisms in constructed wetlands for wastewater treatment. *Biotechnology Advances* 22(1–2), pp. 93–117.

Sun, G. and Austin, D. 2007. A mass balance study on nitrification and deammonification in vertical flow constructed wetlands treating landfill leachate. *Water Science and Technology* 56(3), pp. 117–123.

Sun, G.J., Zhao, Y., Allen, S. and Cooper, D. 2006. Generating ‘tide’ in pilot-scale constructed wetlands to enhance agricultural wastewater treatment. *Engineering in Life Sciences* 6(6), pp. 560–565.

Sun, X. and Davis, A.P. 2007. Heavy metal fates in laboratory bioretention systems. *Chemosphere* 66(9), pp. 1601–1609.

Sun, Y., Zhang, D. and Wang, Z.W. 2017. The potential of using biological nitrogen removal technique for stormwater treatment. *Ecological Engineering* 106, pp. 482–495.

Sundaravadivel, M. and Vigneswaran, S. 2001. Constructed wetlands for wastewater treatment. *Critical Reviews in Environmental Science and Technology* 31(4), pp. 351–409.

Tan, E., Hsu, T.C., Huang, X., Lin, H.J. and Kao, S.J. 2017. Nitrogen transformations and removal efficiency enhancement of a constructed wetland in subtropical Taiwan. *Science of the Total Environment* 601–602, pp. 1378–1388.

Tang, X., Eke, P.E., Scholz, M. and Huang, S. 2009. Processes impacting on benzene removal in vertical-flow constructed wetlands. *Bioresource Technology* 100(1), pp. 227–234.

Taylor, M. 2006. *An assessment of Iron and Steel slag for treatment of stormwater pollution*. Hamilton New Zealand: asa Australasian (iron & steel) Slag Association Inc , Landcare Research Contract Report: LC0506/064 PREPARED.

Toet, S., Van Logtestijn, R.S.P., Kampf, R., Schreijer, M. and Verhoeven, J.T.A. 2005. The effect of hydraulic retention time on the removal of pollutants from sewage treatment plant effluent in a surface-flow wetland system. *Wetlands* 25(2), pp. 375–391.

Torrens, A., Molle, P., Boutin, C. and Salgot, M. 2009. Impact of design and operation variables on the performance of vertical-flow constructed wetlands and intermittent sand filters treating pond effluent. *Water research* 43(7), pp. 1851–1858.

Tromp, K., Lima, A.T., Barendregt, A. and Verhoeven, J.T.A. 2012. Retention of heavy metals and poly-aromatic hydrocarbons from road water in a constructed wetland and the effect of de-icing. *Journal of Hazardous Materials* 203–204, pp. 290–298.

United Nations/ Department of Economic and Social Affairs and Population Dynamics 2019. World Population Prospects 2019. Available at: https://population.un.org/wpp/Download/Standard/Population/.

Urbanc-Bercic, O. 1996. Constructed wetlands for the treatment of landfill leachates: The Slovenian experience. *Wetlands Ecology and Management* 4(3), pp. 189–197.

Us Epa 2003. Protecting Water Quality from Urban Runoff. *United States Environmental Protection Agency* (February), p. EPA-841-F-03-003.

USEPA 1988. *Design Manual. Constructed Wetlands and Aquatic Plant Systems for*

Municipal Wastewater Treatment. US: Environmental Protection Agency, Office of Research and Development, Center for Environmental Research Information.

USEPA 1993. Subsurface Flow Constructed Wetlands For WasteWater Treatment A Technology Assessment. *USPEA, Office of Water, EPA 832-R-93-008, Washington, D.C* (July)

USEPA 1995. *A Handbook of Constructed Wetlands – Volume 1: General Considerations*. USEPA Region III with USDA, NRCS.

USEPA 2000. Manual Treatment of Municipal Wastewaters. *United States Environmental Protection Agency* (September), p. 165.

Vohla, C., Põldvere, E., Noorvee, A., Kuusemets, V. and Mander, Ü. 2005. Alternative filter media for phosphorous removal in a horizontal subsurface flow constructed wetland. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering* 40(6–7), pp. 1251–1264.

Vymazal, J. 1995. *Algae and element cycling in wetlands.* Lewis Publishers Inc.

Vymazal, J., Brix, H., Cooper, P.F., And, M.B.G. and Haberl, R. 1998. Constructed Wetlands for Wastewater Treatment in Europe. *International Review of Hydrobiology* 83(5-6), p. 500.

Vymazal, J. 2001. *Transformation of nutrients in Natural and Constructed Wetlands.* Backhuys Publishers b.v.

Vymazal, J. 2005. Removal of heavy metals in a horizontal sub-surface flow constructed wetland. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering* 40(6–7), pp. 1369–1379.

Vymazal, J., Greenway, M., Tonderski, K., Brix, H. and Mander, Ü. 2006. Constructed Wetlands for Wastewater Treatment. In: Verhoeven, J. T. A. et al. eds. *Wetlands and Natural Resource Management*. Berlin, Heidelberg: Springer Berlin Heidelberg., pp. 69–96.

Vymazal, J. 2007. Removal of nutrients in various types of constructed wetlands. 380, pp. 48–65.

Vymazal, J. 2009. The use constructed wetlands with horizontal sub-surface flow for various types of wastewater. *Ecological Engineering* 35(1), pp. 1–17.

Vymazal, J. 2010. Constructed wetlands for wastewater treatment. *Water (Switzerland)* 2(3), pp. 530–549.

Vymazal, J. and Kröpfelová, L. 2008. *Wastewater Treatment in Constructed Wetlands with Horizontal Sub-Surface Flow*. pringer Science + Business Media B.V, Dordrecht.

Walaszek, M., Del Nero, M., Bois, P., Ribstein, L., Courson, O., Wanko, A. and Laurent, J. 2018. Sorption behavior of copper, lead and zinc by a constructed wetland treating urban stormwater. *Applied Geochemistry* 97(January), pp. 167–180.

Walker, D.J. and Hurl, S. 2002. The reduction of heavy metals in a stormwater wetland. *Ecological Engineering* 18(4), pp. 407–414.

Wang, J., Zhang, P., Yang, L. and Huang, T. 2015. Adsorption characteristics of construction waste for heavy metals from urban stormwater runoff. *Chinese Journal of Chemical Engineering* 23(9), pp. 1542–1550.

Wang, S., Lin, X., Yu, H., Wang, Z., Xia, H., An, J. and Fan, G. 2017. Nitrogen removal from urban stormwater runoff by stepped bioretention systems. *Ecological Engineering* 106, pp. 340–348.

Wetzel, R.G. and Hill, C. 1997. Fundamental processes within natural and constructed wetland ecosystems : short-term versus long-term objectives., pp. 1–8.

Wheater, H. and Evans, E. 2009. Land Use Policy Land use , water management and future flood risk ☆., pp. 251–264.

Wieder, R.K. 1989. A survey of constructed wetlands for acid coal mine drainage treatment in the Eastern United States. *Wetlands* 9(2), pp. 299–315.

Wiessner, A., Kappelmeyer, U., Kuschk, P. and Kästner, M. 2005. Influence of the redox condition dynamics on the removal efficiency of a laboratory-scale constructed wetland. *Water research* 39(1), pp. 248–256.

Wilson, M.A., Burt, R., Lynn, W.C., Klameth, L.C., Burt, R., Lynn, W.C. and Total, L.C.K. 1997. Total elemental analysis digestion method evaluation on soils and clays. 3624

Wittgren, H.B. and Mæhlum, T. 1997. Wastewater treatment wetlands in cold climates. *Water Science and Technology* 35(5), pp. 45–53.

Woods-Ballard, B., Kellagher, R., Woods Ballard, B., Construction Industry Research and Information Association, Great Britain, Department of Trade and Industry and Environment Agency 2007. *The SUDS manual*

Wu, H., Zhang, J., Ngo, H.H., Guo, W., Hu, Z., Liang, S., Fan, J. and Liu, H. 2015. A review on the sustainability of constructed wetlands for wastewater treatment: Design and operation. *Bioresource Technology* 175, pp. 594–601.

Yalcuk, A. 2013. Modelling different types of constructed wetlands for removing phenol from olive mill wastewater using an artificial neural network. *Ekoloji* 35(88), pp. 28–35.

Yan, Y. and Xu, J. 2014. Improving winter performance of constructed wetlands for wastewater treatment in northern china: A Review. *Wetlands* 34(2), pp. 243–253.

Zgheib, S., Moilleron, R. and Chebbo, G. 2012. Priority pollutants in urban stormwater: Part 1 - Case of separate storm sewers. *Water Research* 46(20), pp. 6683–6692.

Zhang, D.Q., Tan, S.K., Gersberg, R.M., Zhu, J., Sadreddini, S. and Li, Y. 2012. Nutrient removal in tropical subsurface flow constructed wetlands under batch and continuous flow conditions. *Journal of Environmental Management* 96(1), pp. 1–6.

Zhang, D.Q., Jinadasa, K.B.S.N., Gersberg, R.M., Liu, Y., Ng, W.J. and Tan, S.K. 2014. Application of constructed wetlands for wastewater treatment in developing countries - A review of recent developments (2000-2013). *Journal of Environmental Management* 141, pp. 116–131.

Zhang, Z., Rengel, Z., Liaghati, T., Antoniette, T. and Meney, K. 2011. Influence of plant species and submerged zone with carbon addition on nutrient removal in stormwater biofilter. *Ecological Engineering* 37(11), pp. 1833–1841.

Zhang, Z., Cui, B. and Fan, X. 2012. Removal mechanisms of heavy metal pollution from urban runoff in wetlands. *Frontiers of Earth Science* 6(4), pp. 433–444.

Zhao, Y.Q., Zhao, X.H. and Babatunde, a O. 2009. Use of dewatered alum sludge as main substrate in treatment reed bed receiving agricultural wastewater: long-term trial. *Bioresource technology* 100(2), pp. 644–8.

Zhi, W., Yuan, L., Ji, G. and He, C. 2015. Enhanced long-term nitrogen removal and its quantitative molecular mechanism in tidal flow constructed wetlands. *Environmental Science and Technology* 49(7), pp. 4575–4583.

Zhou, S. and Hosomi, M. 2008. Nitrogen transformations and balance in a constructed wetland for nutrient-polluted river water treatment using forage rice in Japan. *Ecological Engineering* 32(2), pp. 147–155.