Treatment Performance Assessments of Different Wetland Mesocosms

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EXECUTIVE SUMMARY

Despite their global acceptance as a sustainable and cost-efficient technology for water pollution control including urban wastewater contaminated with hydrocarbons, treatment performance of vertical-flow constructed wetlands can be hampered by clogging of the substrate media pores of the wetland filters. This clogging usually leads to blockage of filter substrate, progressive diminution of porosity and reduction of active pore volume, permeability and substrate hydraulic conductivity subsequently leading to poor water quality production by the wetland filters. This operational problem hinders the wider application and acceptability of these systems worldwide. In this study, different laboratory-scale vertical-flow constructed wetlands filled with gravel and planted with common reed were constructed and operated between June 2011 and March 2014 to assess treatment performances and their relationship with clogging, and diesel spill treatment as a function of hydraulic and organic loading rates, media size, and contact and rest time. Furthermore, to evaluate the hydrocarbon spill, approximately 130 grams of diesel fuel was poured into each of four wetland filters. This is the equivalent of a one-off inflow concentration of 20 g/l. A range of hydraulic loading rates was applied across the systems using real urban wastewater. Analysis of total petroleum hydrocarbon concentrations of outflow waters along with other water quality parameters was carried out to monitor both clogging and treatment performance variations.

Overall, all constructed wetland systems have shown relatively high removal efficiencies for the key water quality parameters regardless of filter set-up before the hydrocarbon spill and no clogging observed. The removal efficiencies dropped for those filters impacted by the diesel spill. The filter with the highest COD loading but no diesel contamination performed the best in terms of COD and BOD removal. Furthermore, filters contaminated by diesel performed worse in terms of COD and BOD, but considerably better regarding nitrate-nitrogen removal without any apparent negative impact of within bed clogging

Pertaining to seasonal variability, findings show that COD, nitrate-nitrogen and ammonia-nitrogen have shown a seasonal trend with high removal in summer compared to other seasons, while BOD removal was efficient in winter compared to summer and turbidity was greatly removed in autumn compared to other seasons. However, no clear seasonal pattern of ortho-phosphate-phosphorus and SS removal were noted. Furthermore, in the hydrocarbon contamination period, all filters regardless of the pollution, design or operation had higher removal in winter than autumn for COD, BOD, ammonia-nitrogen and ortho-phosphate-phosphorus while no seasonal trend was observed for other water quality parameters.

Investigation regarding treatment performance and clogging evolution revealed that none of the systems has shown any signs of clogging after about three years of operation even with high rate Filters 7 and 8. The simulation model confirms the empirical findings that considerable filter clogging restricting the operation has not occurred. However, a small aggregate diameter, a short contact time, a long resting time and a low COD inflow concentration were most beneficial in reducing SS accumulation within the wetland filters.

Treatment of the hydrocarbon pollutants was also assessed, and the investigation revealed that all the hydrocarbon components treated in the wetland filters were highly degraded (>80% removal efficiency) in all contaminated filters with some even attenuated below the detection limit.

The overall outcome of this research may give useful information to wetland engineers and scientists to redesign and model configuration and operation of vertical-flow systems to increase performance and sustainability by maximizing contaminants removal efficiency for pollutants found in urban wastewater and preventing clogging occurrence in the systems. Consequently, this will help in saving cost for stakeholders in terms of operation and maintenance, and allow for progressive management of the wetland systems. Moreover, it will provide beneficial judgement for petroleum and related water industries to have confidence to

incorporate wetland systems in their wastewater treatment technologies with no fear of clogging, particularly for control of hydrocarbon spills that may be released in sewage discharged to the municipal treatment plants and can also be discharged with industrial wastewater.

Abbreviation

COD	Chemical Oxygen Demand
SS	Suspended Solids
CWS	Constructed Wetlands
FWSCWs	Free Water Surface Constructed Wetlands
SSF	Subsurface Flow
SF	Surface Flow
HF	Horizontal Flow
VF	Vertical-Flow
BOD5	Biochemical Oxygen Demand after five days
NTU	Nephelometric Turbidity Unit
NO3-N	Nitrate nitrogen
PO4-P	Othophosphate-phosphorus
NH4-N	Ammonia-nitrogen
U.S.D.A	United State Department of Agriculture
VFS	Vertical-Flow Systems
VOCs	Volatile Organic Compounds
TSS	Total Suspended Solids
TDS	Total Dissolved Solids
BOD	Biochemical Oxygen Demand
SOAs	Secondary Organic Aerosols
TPH	Total Petroleum Hydrocarbons
GRO	Gasoline Range Organics
DRO	Diesel Range Organics

UK	United Kingdom
ICP	Inductively Coupled Plasma
USA	United States of America
USEPA	United State Environmental Protection Agency
TVA	Tenessa Valley Authority
Pe	Person equivalent
IWA	International Water Association
TPFO	Toxicological Profile for Fuel Oils
N	Nitrogen
P	Phosphorus
PPCPs	Pharmaceutical and Personal Care Products
LAS	Linear Alkylbenzene Sulfonates
ITRC	Interstate Technology and Regulatory Council Wetlands Team
PH	Hydrogen power
HRT	Hydraulic Residence Time
TKN	Total Kjeldhal Nitrogen
TP	Total Phosphorus
OP	Organic Phosphorus
BTEX	Benzene, Toluene, Exylene and Xylene
MTBE	Methyl Tertiary Butyl Ether
OVPH	Other Volatile Petroleum Hydrocarbon
TVPH	Total Volatile Petroleum Hydrocarbon
EC	Equivalent Carbon number index

VPH	Volatile Petroleum Hydrocarbon
Al	Aluminium
As	Arsenic
Cd	Cadmium
Cr	Chromium
Cu	Copper
Fe	Iron
Pb	Lead
Mn	Manganese
Ni	Nickel
Se	Selenium
Ag	Mercury
Zn	Zinc
UV	Ultraviolet
EPE	Environmental Protection Agency
VSF	Vertical Sub surface Flow
C	Carbon
N	Nitrogen
THC	Total Hydrocarbons
PAHs	Polyaromatic Hydrocarbons
RT	Residence Time
PBDEs	Polybrominated Diphenyl Ethers
POM	Particulate Organic Matter
EDCs	Endocrine Disruptive Chemicals
PCBs	Polychlorinated Biphenyls

DDT	DichloroDiphenylTrichloroethane
TEEB	The Economics of Ecosystems and Biodiversity
TN	Total Nitrogen
M2/pe	Metre square per Person equivalent
BS	British Standard
ISO	International Standard for Standardization
COSHH	Control of Substances Hazardous to Health Regulations
PSDS	Product Safety Data Sheet
HS	Hazardous Substances
OEL	Occupational Exposure Limit
IBM SPSS	International Business Machine Statistical Package for Social Sciences
TBD	Turbidity
WW	Raw waste water
TWF	Tap Water and Fertilizer
TWW	Tap Water and Waste water
DW	Distilled Water
FAO	Food and Agricultural Organisation
Nm	Not Applicable
N/a	Cost Benefit Analysis
CBA	Mega metre per Year
Mm/yr	

CHAPTER 1

INTRODUCTION

1.1 Overview

The aim of this chapter is to ascertain the concept of wetlands including definition, background, characteristics, importance, types, processes and principle of their application in brief. Moreover, the chapter is further partitioned into sections. Section 1.2 presents the wetland background. Justification, aim and objectives are discussed in section 1.3 and thesis outline in section 1.4.

1.2 Background

The major source of global water supply is through rainfall which produces 40,000 to 45,000 km^3 annually (Kivaisi, 2001) and expected to support the whole world population which steadily increases approximately by 85 million annually (Stikker, 1998). The rapid increase in urbanization and industrialization due to the rise in world population has led to a decrease in this water supply (Al-Baldawi et al., 2013a; Almuktar & Scholz, 2015) and can cause many water conflicts (Samso, 2014). Moreover, about 80 countries and regions worldwide are encountering water stress with some suffering great water shortage part of each year (Gleick, 1993). As a result, Scheierling et al. (2011) envisaged that by 2050, the world's population living in water stressed areas will hit 44%, subsequently leading to a conclusion by some authors that wastewater should be augmented as a viable alternative option to support this increasing population and world fresh water supply shortage (Bichai, Polo-Lopez, & Ibanez, 2012; Noori, Mehdi, & Norozi, 2013, 2014; Almuktar & Scholz, 2015). Moreover, traces of petroleum hydrocarbons from diesel spills associated with urban runoff or industrial effluent are a more recent challenge (Scholz, 2010; García-Delgado et al., 2012; Almuktar et al., 2015a; Almuktar et al., 2015b).

Excessive use and pollution of freshwater resources are nowadays global environmental issues that exert pressure on the sustainability of global ecosystems. Organic and inorganic pollutants from different sources such as domestic, industrial, and agricultural (Imfeld et al., 2009; Ijeoma & Achi, 2011; Robles-Molina et al., 2014) accumulate in surface waters, ground waters, substrates and plants leading to water quality degradation, subsequently impacting negatively on the receiving ecosystem. In 2008, environmental damage, climate change, waste of potential agricultural nutrient resources, and the lives of 2.5 billion people were reported to be imperilled as a result of food and water pollution (World Health Organization and United Nations Children's Fund Joint Monitoring Program for Water Supply and Sanitation [JMP], 2008). Furthermore, population increase globally, accompanied by sharp increase in urbanization, industrial and agricultural land use has resulted in a tremendous increase in discharge of a wide diversity of these pollutants including petroleum hydrocarbons, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), total suspended solids (TSS), turbidity, nitrogen compounds, toxic metals such as Cd, Cr, Ni and Pb, and faecal coliform to receiving water courses and has caused deleterious effects on the different components of the water environment including fisheries, thus making such water unsuitable for drinking, irrigation and aquatic life. The realization by the public of the negative impacts of these pollutants on the eco system and health problems, forced governments at various levels to impose regulations and guidelines with regard to treatment of wastewater before disposal to the receiving watercourses (Doble & Kumar, 2005; Fountolakis et al., 2009; Tram Vo et al., 2014).

Presently, petroleum is the most crucial derived source of energy globally (Onifade & Abubakar, 2007). However, leaks and spills occur regularly during exploration, production, refining, transport and storage of petroleum products from the petrochemical industries which contaminate the environment. Moreover, the pollution of the environment with these petroleum

hydrocarbons, as a result of spills from the activities of these industries and pipe vandalization by saboteurs, is a phenomenon frequently occurring in oil-producing countries all over the world. This contamination gives rise to serious problems for many countries because it is increasing as petroleum hydrocarbons continue to be used as the principle source of energy and often results in huge disturbances and disastrous consequences for the biotic and abiotic components of the ecosystem (Mueller et al., 1992; Eke & Scholz, 2008; Liu et al., 2011; Viggor et al., 2013; Wang et al., 2014). Usually, these pollutants are released into the environment by anthropogenic activities such as accidental spills or leaks from underground storage tanks or pipelines, and drain into gutters, water drains, open vacant plots, farm lands, run off and lastly to receiving water courses causing a negative impact. The release of pollutants often occurs in sewage discharged to the municipal treatment plants and pollutants can also be discharged with industrial wastewater, from small factories and public utilities and with domestic sewage (Escalas et al., 2003; Fountolakis et al., 2009; Almuktar&Scholz, 2015). Petroleum hydrocarbon-contaminated wastewaters also contain pollutants such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), nitrogen and phosphorus (Knight, Clarke Jr., & Bastian, 1999; Fountolakis et al., 2009; Abou-Elela et al., 2013; Vymazal, 2014). Even release of these petroleum hydrocarbons in small quantities into water bodies can cause their concentration to exceed regulatory limits (Spence et al., 2005; Eke & Scholz, 2008; Guittonny-Philppe et al., 2015b).

An example of these petroleum hydrocarbon pollutants is diesel oil, which refers to petroleum-derived fuel composed of approximately 75% saturated hydrocarbons (primarily paraffins, including *n*-, *iso*-, and cycloparaffins) and 25% aromatic hydrocarbons (including naphthalenes and alkylbenzenes) (Toxicological Profile for Fuel Oils [TPFO], 1995). Furthermore, diesel fuel has low water solubility because of its predominant composition of hydrophobic organic compounds (Pazos et al., 2011; Al-Baldawi et al., 2013c). It also contains volatile organic

compounds (VOCs) which are usually harmful and carcinogenic and may cause serious environmental problems to the ecosystem. These VOCs may also cause adverse effects to human health, even in low concentrations (Benmaamar & Bengueddach, 2007; Chen et al., 2012; Guittonny-Philppe et al., 2015b). They are known to integrate a group of compounds that contribute most to the formation of photochemical ozone and secondary organic aerosols (SOAs), increasing global warming (Hu et al., 2008). Generally, total petroleum hydrocarbons (TPH) are divided into gasoline range organics (GRO) corresponding to small chain alkanes (C6-C10) with low boiling point (60–170°C) and diesel range organics (DRO) including longer chain alkanes (C10-C40) with high boiling point (240–340°C) (Kamath et al., 2012). Furthermore, Viggor et al. (2013) investigated and revealed that diesel fuel is comprised of hydrocarbons of 9–16 carbons in length under the aforementioned temperature and is a widespread fuel used in engines. Several studies reported that this diesel fuel is toxic to many organisms and detrimental to human health (Moreira et al., 2011; Viggor et al., 2013; Al-Baldawi et al., 2015). So, eliminating these pollutants is imperative but strenuous with traditional methods.

Continuous increase in environmental crises such as pollution as a result of water shortages, climatic changes (Hartemink, 2006; Tram VO et al., 2014), rapid population growth and several compelling reasons, such as underground tank leakages, pipe vandalization by saboteurs, industrial oil spills, etc., necessitate the need for sustainable wastewater treatment technology that could be environmental friendly, easy to operate, less energy-intensive, and cost-effective. This is because most of the traditional treatment technologies used by the petroleum and water industries such as hydro cyclones, coalescence, flotation, centrifuges and various separators are not efficient concerning the removal of dissolved organic components including diesel in the dissolved water phase (Lin & Mendelssohn, 2009). Furthermore, other technologies such as advanced oxidation, biofiltration, separation by membrane, absorption and adsorption have

been studied and developed in order to remove these organic compounds. However, it happens that many of these procedures, due to high operating costs, are unviable. Their high cost has produced economic pressures and has compelled engineers to search for creative, cost effective and environmentally sound ways to control water pollution especially in the petroleum industry. Moreover, physical, chemical, and biological technologies have been developed to treat petroleum hydrocarbon-polluted wastewater and restore environmental quality. However, their costs are high and most of them are difficult to use under field conditions (Ji, Sun, & Ni, 2007). Therefore, it remains necessary to study natural, simple, and cost-effective techniques for treating such wastewater, such as wetland mesocosoms.

The artificial wetland mesocosoms, hereafter referred to as constructed wetlands (CWs) are engineered systems used worldwide as a result of their low energy requirement, convenience, environmental friendliness, mechanical simplicity and low cost of operation qualities (Scholz, 2007; Kayranli et al., 2010; Abou-Elela et al., 2013; Wu et al., 2014) as an alternative efficient means of water pollution control to treat a variety of wastewaters including agricultural and urban runoff, industrial effluents, animal wastewaters, sludge and mine drainage (Scholz & Lee, 2005; Scholz, 2006, 2010), petroleum wastewaters (Omari et al., 2003; Eke & Scholz, 2008; Tang et al., 2010; Wallace et al., 2011; Albaldawi et al., 2013a, b, c; Albaldawi et al., 2014; Al-Isawi et al., 2014; Vymazal, 2014; Al-Isawi et al., 2015) and have recently been applied successfully to treat domestic wastewater (Scholz, 2010; Dong et al., 2011; Sani et al., 2013a; Sani, Scholz, & Bouillon, 2013b; Dzakpasu et al., 2015; Paing et al., 2015). The technique of using artificial wetlands in the treatment of these various pollutants has been gaining reputation and increasing acceptance as a tool for environmental pollution control worldwide. The functions of these constructed wetlands follow the same principle as natural wetlands and the purification process involves variegated interconnection of wetland plants,

soils, and other microbial organisms to aid in the treatment of the wastewater (Scholz, 2006, 2010; Vymazal, 2014).

However, the performance abilities of wetland systems vary according to the system arrangement, nature, wetland plants, and microbial and weather conditions of the region (Vacca et al., 2005; Picek, Cizkova, & Dusek, 2007; Ström & Christensen, 2007; Weishampel, Kolka, & King, 2009; Scholz, 2011). The concept of artificial wetlands was not advanced only to solve environmental pollution problems, but also to enhance eco-friendly values through rehabilitation of likely hidden ecological substructures such as wetlands (Scholz, 2011; Tanner et al., 2012; Stefanakis et al., 2014).

Surface flow (SF) and subsurface flow (SSF) CWs have been reported as the main two classes of CWs (Kadlec & Knight, 1996; Kadlec et al., 2000; Langergraber et al., 2009; Knowles et al., 2011; Nivala et al., 2012; Vymazal, 2013a; Wu et al., 2014). The surface flow constructed wetland (SFCW) is massively planted with macrophytes and has an exposed water surface which is different to the subsurface flow constructed wetland (SSFCW) that has no clear water surface. As a result of water movement direction in the treatment systems (Langergraber et al., 2009; Vymazal et al., 2013a; Wu et al., 2014), SSFCWs can be further divided into horizontal flow (HF) and vertical flow (VF) systems. Generally, the substrate in HFCWs is inundated with water, unlike the substrate in VFCWs that is ponded and drained as the water is being applied intermittently into the systems (Vymazal & Kröpfelová, 2008; Knowles et al., 2011; Stefanakis, Akaratos, & Tsihrintzis, 2014).

VFCWs are the state of the art in wetland technology worldwide (Tsihrintzis et al., 2007; Scholz, 2010; Sani et al., 2012; Stefanakis et al., 2014). Furthermore, many authors (Cooper, 1999; Prochaska et al., 2007; Fan et al., 2012, Fan et al., 2013; Li, Wu, & Dong, 2015) reported that these systems are very competent in achieving a high rate of oxygen transfer. Sun, Gray, and Biddlestone (1999), Zhao, Sun, and Allen (2004), Eke and Scholz (2008), Vymazal and

Kröpfelová (2008) and Stefanakis et al. (2014) reported that wastewater applied in the systems inundates the wetland surface initially and then permeates through the wetland body by gravity. As wastewater passes through the wetland media, air enters the substrate pores (Vymazal et al., 2006; Fan et al., 2012; Fan et al., 2013; Stefanakis et al., 2014) enhancing the aeration and the microbial activity. VF systems perform well in chemical and oxygen demand variables (COD and BOD), wastewater particles and in adequate phosphorus treatment as reported by Brix and Arias (2005) and (Prochaska, Zouboulis, and Eskridge, 2007; Scholz, 2010; Paing et al., 2015) because of the inadequate time to allow full interaction of the wastewater and the wetland media. Furthermore, they can achieve a satisfactory level of nitrification (Vymazal et al., 2006; Langergraber et al., 2007; Gikas & Tsihrintzis, 2012; Fan et al., 2012; Fan et al., 2013; Song et al., 2015).

However, an inevitable drawback limiting the competitiveness and efficiency of VFCWs systems is the concomitant biological clogging and physical clogging induced as a result of excessive formation of biomass from degradation of pollutants and macrophyte litter, and retention of inert suspended fine particles, respectively. This leads to inner and outer blockage of filter substrate, and progressive reduction of active pore volume, substrate hydraulic conductivity and permeability. Eventually, the substrate may become so clogged that hydraulic malfunction occurs; e.g., untreated wastewater bypassing the system (Babatunde, 2010; Hua et al., 2014). This can greatly affect the lifetime of the system subsequently leading to poor effluent water quality to receiving water courses. Furthermore, clogging is often a seasonal phenomenon and usually leads to deterioration of water quality. Temporal variations in wetland performance depend often on the corresponding macrophyte growth rates (Picard et al., 2005; Kouki et al., 2009; Sani et al., 2013b; Al-Isawi et al., 2015). However, Merlin, Pajean, and Lissolo (2002) and Vymazal (2011a) reported that the influence of temperature seems to be

weak in their studied wetlands with regard to process efficiency because there were no significant seasonal variations.

1.3 Justification, aim and objectives

Most of the previous works on SSFCW performance and clogging focused on assessing the wetland performance efficiency based on clogging occurrences, causes, mechanisms, and modelling (Langergraber et al., 2003; Knowles, Griffin, & Davies, 2010; Knowles et al., 2011; Hua et al., 2013; Hua et al., 2014; Meyer et al., 2014,; Samso, Meyer and Garcia, 2015) while in some studies, processes, phenomena, parameters, consequences, measurements and management of clogging in relation to the system performance were investigated (Nivala & Rousseau, 2009; Nivala et al., 2012; Song et al., 2015). In the UK, few studies if any gave attention on assessing performance efficiency and clogging in SSF wetland systems particularly in VF ones (Knowles et al., 2010; Knowles et al., 2011; Hill-Casey et al., 2014). Concerted efforts were also made to explore the use of SSFCWs in treating hydrocarbons (Omari et al., 2003; Eke & Scholz, 2008; Tang et al., 2009; Tang et al., 2010; Wallace et al., 2011; Wu et al., 2012; Albaldawi et al., 2013a, b, c; Albaldawi et al., 2014; Guittonny-Philippe et al., 2015a). However, a few studies (Omari et al., 2003) investigated the performance of horizontal subsurface flow (HSSF) wetland systems to treat diesel as the target peteroleum hydrocarbon while Eke & Scholz (2008), Tang et al. (2009) and Tang et al. (2010) assessed benzene in vertical subsurface flow (VSSF) systems in the UK, though a study was recently conducted on phytoremediation of DRO hydrocarbons in the sediment of Horsea Island lagoon in Southern England (Pinchin, 2012).

Despite the numerous articles published on wetlands over the past decades, there is a notable gap in the literature regarding research on the long-term treatment performance and its relationship with clogging of VFCWs treating urban waste water contaminated with diesel because most of the works reported on CW performance, clogging and hydrocarbon treatment

have been on HSSF systems with little or none that focused on VCFW systems treating domestic wastewater contaminated with diesel.

This study particularly provides the wetland modelling community with statistically validated long-term data interpretation. This will allow modellers to define long-term and seasonal removal coefficients for individual water quality parameters, and wetland managers with insight into long term and seasonal removal processes, allowing them to revise wetland management plans accordingly. Furthermore, this research may give useful information to petroleum and related water industries to incorporate wetland systems in their wastewater treatment technologies particularly for control of petroleum hydrocarbon spills that may be released in sewage discharged to the municipal treatment plants and can also be discharged with industrial wastewater, from small factories and public utilities, and with domestic sewage. The aim of the study was therefore to assess the impact of design and operational variables on treatment performance and its relationship with clogging of vertical-flow wetland mesocosoms treating domestic wastewater contaminated with diesel.The key objectives were to evaluate:

- the current literature on performance, clogging and diesel treatment relevant to vertical-flow wetlands;
- critically the overall inflow and outflow water quality of the vertical-flow wetlands with or without diesel;
- the influence of design and operational parameters on the overall treatment performances and its relationship to clogging of different wetland filters in treating domestic wastewater with or without diesel;
- a simulation model assessing the impact of sedimentation of SS on the clogging processes of experimental wetland filters;

- critically the overall seasonal inflow and outflow water quality of vertical-flow wetlands with or without diesel
- the overall and seasonal treatment performances and their relavance to clogging of different wetland filters in treating domestic wastewater with or without diesel;
- overall performance efficiency of the vertical-flow wetland filters in hydrocarbon removal in both contaminated and uncontaminated filters

1.4 Thesis outline

This dissertation report begins by reviewing the existing information on wetlands and constructed wetlands applied for treatment of different wastewaters including urban wastewater. The study then investigates treatement performances and its relationship to clogging of the experimental vertical-flow constructed wetlands applied for domestic wastewater contaminants removal. Furthermore, biodegradation and removal efficiency of diesel as the model petroleum hydrocarbon in different wetland filters were assessed and interpreted. The report is divided into the following sections below:

- Chapter one describes the background, justification, aims and objectives, and thesis outline.
- Chapter two presents the literature review on clogging and performance in terms of treatment of different types of pollutants in constructed wetland systems from previous researches. An overview is given of the constructed wetlands enumerating the role of main wetland components (macrophytes, substrate, etc.) and different classes of flow systems (surface flow, subsurface flow (vertical and horizontal) and hybrid types). A significant proportion of the chapter is devoted to the published literature on wetlands clogging and modelling, values and benefits of wetlands, preference of some classes of wetlands over the others and different removal mechanisms of pollutants.

- Chapter three describes the materials, the experimental set-up and operation methods applied for the study. The chapter explains the experimental filter design, and aggregate compositions as well as their physical arrangement. It also includes the sampling in the green house, water quality parameters determination in the laboratory, calibration of equipments used for water quality analysis and statistical method applied in analysing the data. Furthermore, materials and methods used in petroleum hydrocarbon analysis, etc. are also reported.

- Chapter four presents the overall treatment results and discussions. The chapter shows the water quality performance with and without diesel contamination in the different filters used in this research. The performance efficiency in each filter is also statistically compared to assess the role of design components and operation conditions, and the result of the key water quality variables such as COD and their significant differences are also discussed. Furthermore, results and discussion with regard to treatment performance and its relevance to clogging of different filters, and the modelling of the systems is also presented.
- Chapter five discusses the seasonal variations in the performance efficiency of the wetland systems in both diesel and none diesel filters. Furthermore, seasonal assessment of treatment performance of the wetland systems and their relationship to clogging impact on water quality variables is also described.
- Chapter six talks about diesel assessment in different wetland filters along with other water quality parameters such as COD and BOD, their removal efficiency in percentage terms and interpretation of other forms of the petroleum hydrocarbon components including diesel and gasoline range organics in both inflow and outflow water .
- Chapter seven presents the conclusion and recommendation for further research.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

In this chapter, an in-depth historical and technical review of existing information about natural and constructed wetlands is presented, showing the hydrology, components, types and removal mechanisms of contaminants in wetlands. The chapter is also categorized into specific sections as follows: 2.1 introduces the chapter, 2.2 describes historical development of wetlands, and classification of constructed wetlands is presented in section 2.3. The components of wetlands, design and operational impact of constructed wetlands on performance, clogging processes, types of clogging, problems, advantages causes and remedial measures, and numerical modelling in constructed wetlands are presented in sections 2.4, 2.5, 2.6, 2.7, 2.8 and 2.9 respectively. Lastly, removal mechanisms of pollutants in wetlands are presented in section 2.10, while values of wetlands and the choice of vertical over horizontal-flow systems are shown in sections 2.11 and 2.12 respectively.

2.2 History of constructed wetlands

Constructed treatment wetlands are engineered wastewater purification systems that encompass biological, chemical and physical processes, which are all akin to processes occurring in natural treatment wetlands (Scholz, 2006; Kayranli et al., 2010; Kayranli et al, 2010; Abou-Elela et al., 2013; Vymazal, 2014; Wu et al., 2015). For ages, natural wetlands served as a convenient means of wastewater and sewage management which subsequently resulted in many forms of wetlands, such as marshes, deteriorating as they filled up with nutrients and became seriously polluted. It has been observed (Kadlec & Knight, 1996) that natural wetlands were probably used for disposal of collected wastewater as far back as 1912. The pioneer research with wastewater

treatment wetlands planted with macrophytes was carried out by a German scientist (Kathe Seidel) in 1952 at the Max Planck Institute, Germany (Seidel, 1965a). She conducted many experiments using macrophytes on phenol, dairy and livestock wastewaters (Seidel, 1955, 1961, 1965a, 1966, 1976), as discussed by Vymazal, (2005). Furthermore, in the early 1960s, she increased her effort in exploring the use of wetland plants in wastewater, different types of sludge, and also concentrated on upgrading the treatment of provincial and decontrolled wastewater systems from low performance efficiency (Vymazal, 2005). Because septic tank systems are anaerobic and need to be improved, Seidel incorporated a mud separation system across the permeated substrate bed and an eradication set-up in the horizontal direction to improve the treatment (Seidel, 1965b) which consequently led to the origination of new types of wetlands known as “Hybrid” which were re-established at the end of the year 2000 as reviewed by Vymazal (2005, 2011a, 2014). Cooper et al. (1996) and Vymazal (2005, 2009, 2011a, 2014) reported that the original type of vertical-flow wetlands are those started by Seidel in Germany. Moreover, interest in their use began to diminish shortly after their original design, but recovered six years later due to their nitrification ability being better than that of horizontal-flow systems. Moreover, the horizontal-flow systems were discouraging operators and designers because of their low ability in oxidising ammonia to nitrate. However, Vymazal, (2005, 2014) observed that in Europe, vertical subsurface-flow constructed wetlands are not used as much as horizontal subsurface-flow constructed wetlands.

In the 1960s, Seidel and Kickuth invented new horizontal-flow wetlands which used what is known as the “Root zone method” (RZM). This new system differed from the earlier Seidel design by having sticky substrate predominantly of clay soils and is the early wetland system used at Othfresen, Germany for municipal sewage treatment in 1974 (Kickuth, 1977, 1978, 1981; Brix, 1987; Vymazal, 2005, 2009). Furthermore, Kickuth advanced with the experimental research and disseminated this concept with his colleagues in Europe and led to

the establishment of nearly 200 municipal and industrial waste treatment systems (Bastian & Hammer, 1993). This resulted in the growth of interest of these RZM systems which spread throughout Europe in the mid-1980s. However, in the United States of America (USA), land treatment alternatives were advanced with the help of convincing research and development trials financed by some agencies in the USA such as the US Army Corps of Engineers (USACE) and the US Environmental Protection Agency (USEPA) (Bastian & Hammer, 1993). Moreover, experimental research studies on the exploration of the constructed wetlands started in Europe and the USA for wastewater treatment in the 1950s and late 1960s respectively. The research was expanded in the USA between 1970 and 1980 and between 1980 and 1990 (USEPA, 2000), plus a considerable role was played by Federal agencies involving the Tennessee Valley Authority (TVA) and the US Department of Agriculture (USDA) at the end of 1980 and beginning of 1990 respectively. Nevertheless, constructed wetlands became popular and accepted in the United Kingdom (UK) in the mid-1980s when the UK Water Industry became familiar with the RZM which had then just begun to be operated in Denmark (Cooper et al., 1996). The then Water Authorities also accepted the system because of its ability to treat wastewater in small village communities with population densities of 50 to 1000 person equivalent (Pe), though later they found out that there were many problems with the system that needed to be solved (Cooper et al., 1996) leading to the choice of subsurface vertical-flow systems by designers and researchers.

Today, the application of constructed wetlands in various wastewater purification systems is popular all over the globe (Hoffman et al., 2011; Abou-Elela & Hellal, 2012; Abou-Elela et al., 2013; Vymazal, 2014; Wu et al., 2015). However, constructed wetlands were not pervasive in developing countries (particularly in warm tropical and sub-tropical climates) such as Nigeria, and Tanzania as a result of unawareness of their significant role in environmental pollution control, though a few researches have been published recently in Egypt (Abou-Elela & Hellal,

2012; Abou-Elela et al., 2013) and Kenya (Kimani, Mwangi, & Gichuki, 2012). Furthermore, there was no technical knowhow for advancing the research technology on a geographical basis (Kivaisi, 2001), despite the fact that about 50% of the wetland area (Neue et al., 1997) in the world is in the Torrid Zone. Therefore, the knowledge of the potential for the application of the technology with regard to water pollution control and ecology enhancement needs to be disseminated and fully understood there (Mohamed, 2004; Heers, 2006; Kamau, 2009; Abou-Elela et al., 2013; Al-Baldawi et al., 2014,2015). In contrast, wetland technology and its application in wastewater treatment has been practised since the 1990s and the exploration of its research keeps increasing in other developing countries such as China (Xinshan, Qin, & Denghua, 2010; Zhang et al., 2012; Meng et al., 2014; Song et al., 2015) and India (Sheoran & Sheoran, 2006; Choudhary, Kumar, & Sharma, 2011; Sharma et al., 2013).

2.3 Classification of constructed wetlands

2.3.1 Overall classification

There are three categories of constructed wetlands. Kadlec and Knight (1996), Kadlec et al. (2000), Haberl et al. (2003), Langergraber et al. (2009) and (Hoffman et al, 2011; Sharma et al., 2013; Stefanakis et al., 2014; Vymazal, 2014) reported that classifications of wetlands are based on water level on the bed which is either free water surface-flow (FWSF CWs) or subsurface-flow (SSF CWs), based on wetland plants, and based on the direction of water movement in the wetlands. Moreover, based on the water flow direction, the wetlands are also classified into vertical and horizontal systems. However, to achieve maximum removal efficiency of pollutants, horizontal and vertical-flow wetlands are combined as a single stage known as hybrid systems (Vymazal, 2014). Recently some wetland studies showed that constructed wetlands are classified based on their objectives into: constructed wetlands for habitat creation, flood control and wastewater treatment (Vymazal 2013a; Stefanakis et al.,

2014; Vymazal, 2014). These wetlands use macrophyte plants which are aquatic plants that grow in or near water.

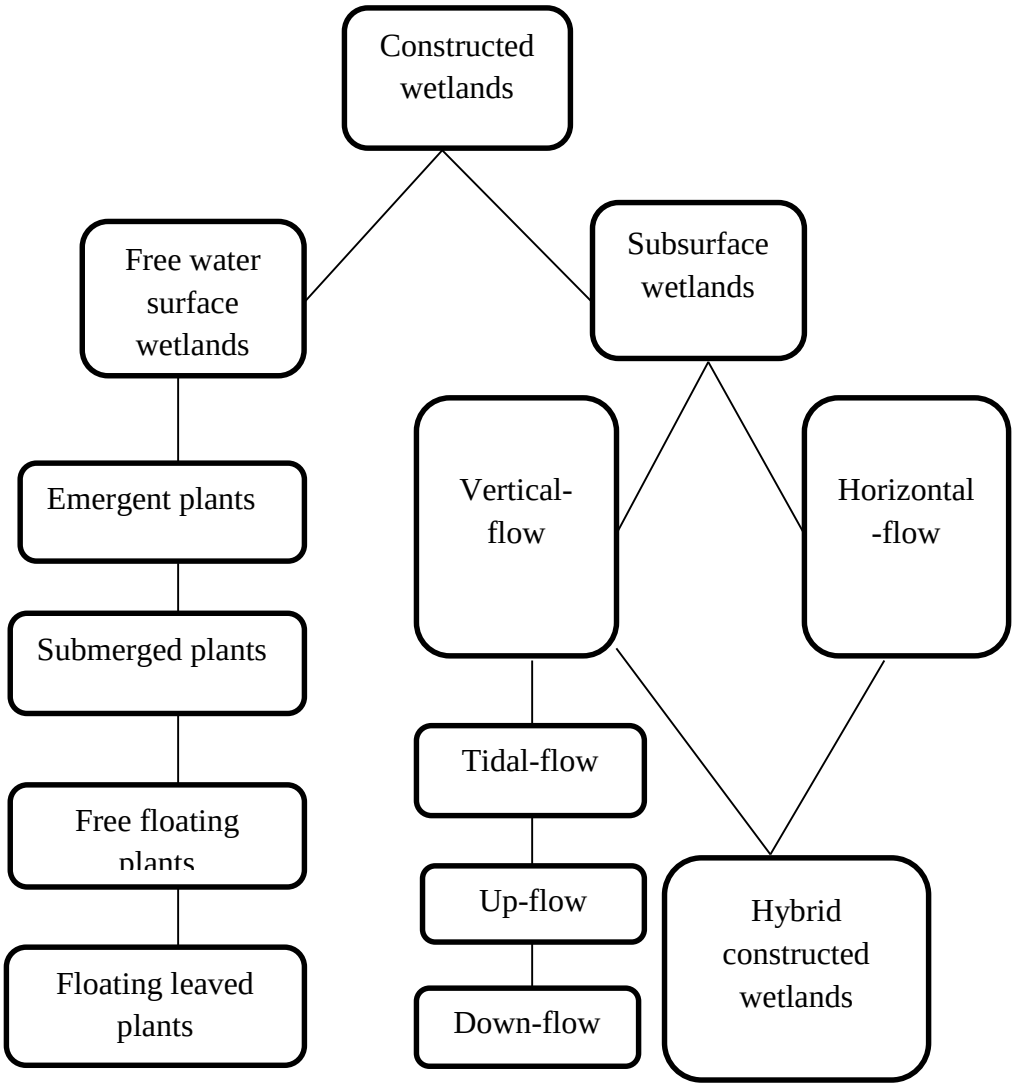

Figure 2.1 Classification of constructed wetlands

2.3.2 Free water surface-flow constructed wetlands

FWSF CWs operate like a natural wetland (Vymazal et al., 1998; Vymazal, 2006; El-Sheikh et al., 2010; Stefanakis et al., 2014; Wu et al., 2014). The wetland pool is shallow and sealed so that there is no wastewater seepage to the belowground aquifer. The wetland substrate is soil and covers up to the height of 40 cm thick, thus allowing the establishment of wetland plants (Stefanakis et al., 2014). The wetland systems are flooded from the top and water flows horizontally on top of the wetland media, developing a depth of water column of about 20 to 40 cm (Vymazal et al., 2006) or up to 80 cm (Akratos et al., 2006). The wastewater infiltrates the media or is evaporated to the atmosphere as shown in Figure 2.2.

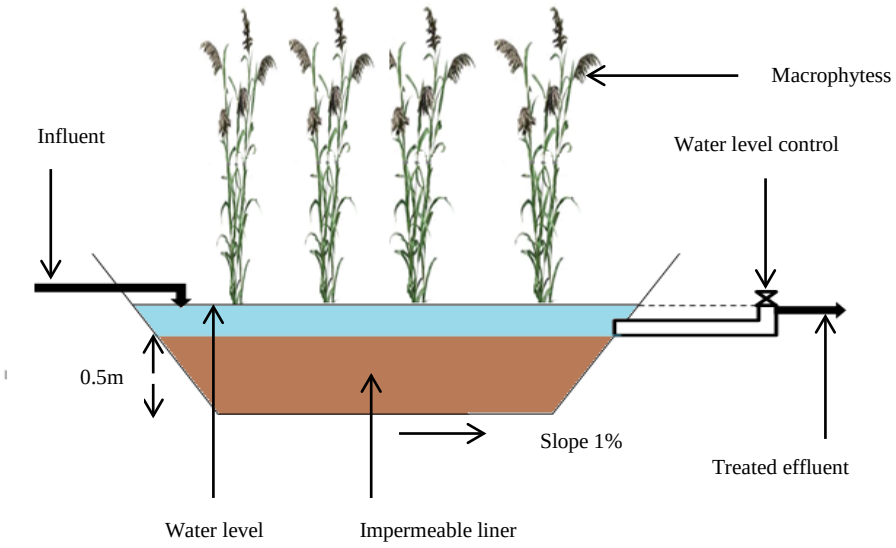

Figure 2.2: Schematic representation of free water surface-flow constructed wetlands with emergent macrophytes

The wastewater in FWSF CWs flows via the wetland bed slowly coming in contact with the soil and plants, subsequently leading to provision of a conducive environment for physical, chemical and biological removal processes to take place. These processes contribute to the attenuation of numerous wastewater contaminants (El-Sheikh et al., 2010; Stefanakis et al., 2014).

In terms of wastewater treatment, FWSF CWs are very good for removal of SS, biochemical oxygen demand (BOD_5), nitrogen, pathogens, and other contaminants such as heavy metals (Kadlec & Knight, 1996; Vymazal, 2007; Kadlec & Wallace, 2009; Kotti, Gikas, & Tsihrintzis, 2010; Tsihrintzis & Gikas, 2010) as reported by Stefanakis et al. (2014).

The application and use of these FWSF CWs has been reported to be common in North America (Kadlec & Wallace, 2009) and applied exclusively for municipal wastewater treatment. These systems can be planted with different types of macrophytes such as emergent, free floating, floating-leaved, bottom rooted or submersed macrophytes. However, despite their advantages of low cost of operation and simple technology, the FWS CWs need a large land area and the water is potentially exposed to human contact (International Water Association [IWA] Specialist Group, 2000; Stefanakis et al., 2014). Furthermore, their nearly standing water intensifies the likelihood of mosquito breeding (Stefanakis et al., 2014).

2.3.3 Subsurface-flow constructed wetlands

2.3.3.1 Vertical-flow constructed wetlands

SSF CWs are wetland systems composed of a substrate media planted with macrophytes, which wastewater passes through for quality enhancement (Knowles et al., 2011). In these systems, the arrangement set-up of sand or gravel media, allows the inundation of the wetlands with wastewater at the inlet which later, after gravitational downward movement, remains below the substrate bed. The substrate in this kind of arrangement gives a favourable avenue for the microorganisms to treat the pollutants and also buttresses processes such as filtration and adsorption (Hoffman et al., 2011). Furthermore, the authors reported that while sand beds originated in Europe and are now applied all over the world, gravel beds are used in North Africa, South Africa, New Zealand, Asia and Australia. Moreover, Fan et al. (2012), Fan et al. (2013), Nivala et al. (2013), Song et al. (2015) and Wu et al. (2015) revealed that subsurface-flow systems are very efficient in nitrogen and carbon compounds elimination due to high

oxygenation in their substrate bed and have high performance efficiency within the small area they occupy compared to SF CWs (Hoffman et al., 2011; Abou-Elela & Hellal, 2012; Abou-Elela et al., 2013; Stefanakis et al., 2014).

VF CWs systems were originally used and developed by Seidel in 1965 in Germany, when she inserted them in-between a septic tank and HSF CWs (Vymazal et al., 2006; Vymazal & Kröpfelová, 2011). The systems became pertinent in application gradually when people realized the inability of HSF systems to oxidize ammonia-nitrogen efficiently from wastewater as a result of limited oxygen in their substrate bed (Cooper, 1999; Vymazal, 2005; Stefanakis et al., 2014; Vymazal, 2014). Typically, the media in (VF) CWs goes through filling and draining cycles as the water is being dosed periodically into the systems (Vymazal & Kröpfelová, 2008; Knowles et al., 2011; Wallace, 2013; Stefanakis et al., 2014; Li et al., 2015) which makes the systems competent in achieving a high rate of oxygen transfer (Cooper, 1999; Vymazal & Kröpfelová, 2008; Knowles et al., 2011; Wallace et al., 2013; Stefanakis et al., 2014; Li et al., 2015). According to Sun et al. (1999) and Zhao et al. (2004), the wastewater is applied and inundates the wetland surface initially and then permeates through the wetland body by gravity (Figure 2.3). As the wastewater penetrates, air enters the substrate pores (Vymazal et al., 2006; Fan et al., 2012; Fan et al., 2013; Song et al., 2015) enhancing the aeration and the microbial activity.

Numerous studies were conducted to assess the performance efficiency of VF systems, and predicated that the systems are good treatment technologies with regard to water quality parameters. For instance, Brix and Arias (2005), Prochaska et al. (2007), Chang et al. (2012), and Paing et al. (2015) mentioned that VF systems perform well in the treatment of chemical oxygen demand, biochemical oxygen demand, suspended solids and limited phosphorus because of the inadequate interaction of the wastewater and the filter media. Furthermore, Vymazal et al. (2006), Langergraber et al. (2007), Gikas and Tsihrinitzis (2012) and Zhi et al.

(2015) noted that the systems can also achieve a satisfactory level of nitrification. Though some researchers referred to them as poor denitrifiers (Vymazal, 2005; Scholz, 2010; Vymazal & Kröpfelová, 2011) several studies recently showed that VFCW systems with intermittent loading regimes can denitrify well with modification (Weedon, 2003; Arias, Brix, & Marti, 2005; Gross et al., 2007; Weedon, 2010; Fan et al., 2013; Song et al., 2015).

The composition of VFCWs consists of a porous substrate bed of either gravel or sand with size gradation increment with depth (Vymazal et al., 2006). The bed arrangement is from top to bottom with depth between 45 cm and 120 cm and slope of 1–2% that facilitates easy movement, drainage, and collection of the treated wastewater effluent out of the system.

The intermittent application of VF systems allows the creation of temporary ponding of the wastewater in the range of 3–5 cm (Stefanakis et al., 2014) before it drains gravitationally downward. This application method enhances more aeration in the bed as the wastewater spreads on the wetland surface area and moves downward, subsequently sucking the fresh air into the substrate bed and removing the captured air. This type of operation enhances aeration into the bed and becomes more advanced when aeration pipes are inserted in the systems. The high bed oxygenation provides improved conditions for nitrification and organic matter decomposition in comparison to HF systems (Vymazal et al., 2006; Vymazal, 2007; Kadlec & Wallace, 2009; Stefanakis & Tsihrintzis, 2012; Stefanakis et al., 2014). Though vertical-flow systems have the advantage of occupying a small space because of their size and good treatment of high organic loading rates and nutrients, several studies have shown that clogging can be their operational problem (Cooper, Griffin, & Cooper, 2005; Knowles et al., 2011; Liu et al., 2012; Fu et al., 2013; Hua et al., 2013; Song et al., 2015). However, some studies reported that bioclogging can be mitigated when intermittent operation was applied in VF systems, because a resting operation could effectively improve porosity and the hydraulic conductivity after some days of the resting period (Hua et al., 2014; Paing et al., 2015; Wu et al., 2015).

VF systems are mainly explored in Europe, particularly in France, Denmark, Austria, Germany, UK and USA (USEPA, 1995; Kadlec & Wallace, 2009). Presently, their application is developing gradually in other parts of the world including Asia and Africa (Kivaisi, 2001; Abou-Elela & Hellal, 2012; Abou-Elela et al., 2013; Song et al., 2015; Wu et al., 2015).

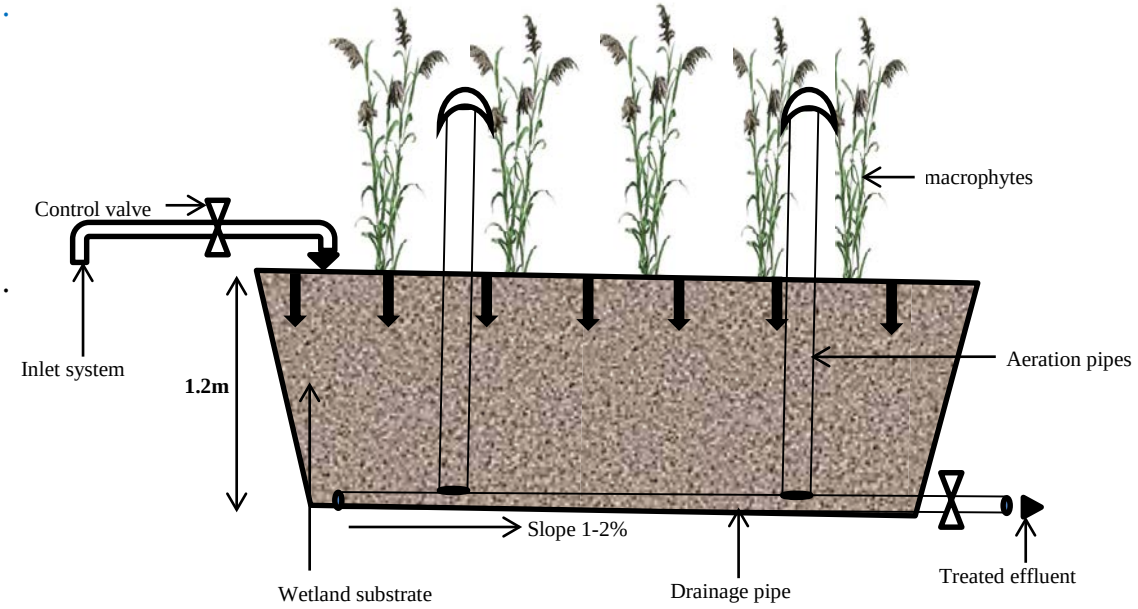

Figure 2.3 Schematic representation of vertical-flow constructed wetlands

2.3.3.2 Horizontal flow constructed wetland

Horizontal subsurface-flow constructed wetlands (HSSF CWs) are purification systems where the movement of the wastewater is in a horizontal direction and it passes gradually through the filter substrate, macrophyte roots and rhizomes till it reaches the outflow control valve where it is collected for sampling and analysis (Vymazal, 2009, 2013a, 2014). Typically, the media in (HF) CWs is permanently flooded with water, and pollutant treatment takes place through the interconnection of various microbial, physical and chemical processes (Kadlec & Knight, 1996; Vymazal, 2014). In the process of the wastewater permeation, the wastewater passes through aerobic, anoxic and anaerobic regions. Brix (1987), Cooper et al. (1996) and Vymazal, (2014) noted that oxygen availability in the substrate was provided by roots and rhizomes in the aerobic regions.

HF systems are composed of gravel, sand or their combination as a bed substrate, usually planted with reeds (Vymazal et al., 2006; Vymazal, 2014) and the wastewater passes horizontally from the inlet to the outlet beneath the porous substrate and plant roots (Figure 2.4). The substrate media provides support for the wetland plants to grow and its depth varies between 0.3 and 0.8 m (Vymazal et al., 2006; Akratos & Tsihrintzis, 2007) though the media depth depends on the type of macrophytes planted and their root depth. The slope of these systems is between 1–3% so that gravitational wastewater flow is promoted and the bottom is sealed with an impenetrable geo-membrane (Kadlec & Wallace, 2009; Stefanakis et al., 2014). Vymazal et al. (2006) stated that if these systems are properly designed, the wastewater will not be visible on the surface of the media, but will be maintained in the range of 5–15 cm below it. This leads to reduced health risk to humans and wild life habitats. Furthermore, breeding of mosquitoes is avoided (Kadlec & Wallace, 2009; Stefanakis et al., 2014).

Many researches have shown that existence of plant roots and porous media in HF systems favours the development of biofilm, which improves the removal of organic matter and SS, thus, making them good in municipal wastewater treatment, though nutrients (N and P) treatment is low (Vymazal et al., 2006; Akratos & Tsihrintzis, 2007; Kadlec & Wallace, 2009; Gikas et al., 2010; Vymazal, 2013a, 2014).

HF systems are usually used in Europe and USA (Vymazal et al., 2006; Vymazal, 2011c, 2014) and acquire a small area when compared with SFCWs systems, but have high investment costs (Tsihrintzis et al., 2007; Kadlec & Wallace, 2009).

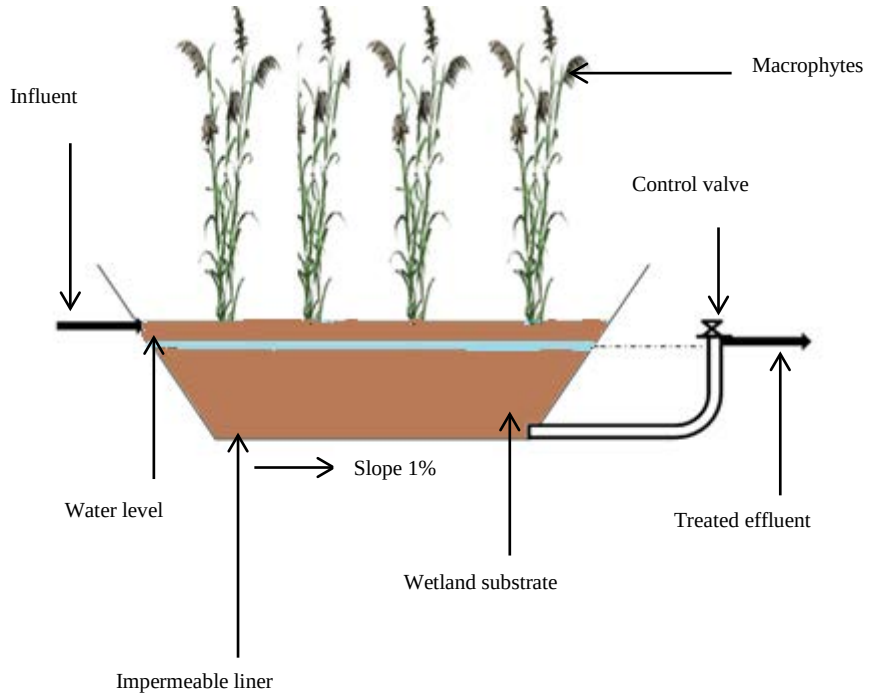

Figure 2. 4 Schematic representation of horizontal subsurface-flow constructed wetlands

2.3.3.3 Hybrid constructed wetlands

Hybrid constructed wetlands are purification systems established mainly to achieve larger nitrogen removal by exploring the operational processes of denitrification and nitrification in vertical and horizontal flow systems together, concomitantly treating the wastewater (Vymazal, 2005; Vymazal & Kröpfelová, 2011; Ayaz et al., 2012; Vymazal, 2013a, 2014). The vertical flow systems, as a result of high oxygenation in the beds, have the ability to oxidize ammonia while nitrate has been effectively treated in the horizontal systems (Vymazal & Kröpfelová, 2011; Vymazal, 2013a, 2014). Vymazal (2005, 2014) reported that the hybrid systems were originally used by Seidel between 1960 and 1969 in Germany and subsequently few full scales were constructed, e.g. in Saint Bohaire, France between 1980 and 1989 and Oaklands Park in the UK between 1990 and 1999. However, because of the need for strict discharge limits for nitrogen and more complex water treatment, their application expanded between the late 1990s and early 2000 (Vymazal, 2013a).

Presently, hybrid constructed wetlands are used globally for their ability to remove ammonia, nitrate and total nitrogen from various types of wastewaters (Vymazal, 2005, 2007; Ye & Li, 2009; Xinshan et al., 2010; Vymazal & Kröpfelová, 2011; Ayaz et al., 2012; Vymazal, 2013a, 2014). Furthermore, they are also applied to treat a variety of wastewaters including winery wastewaters (Serrano et al., 2011), pharmaceuticals and personal care products (PPCPs) (Reyes-Contreras et al., 2011), oil field produced water (Alley et al., 2013), grey water (Commino, Riggio, & Rosso, 2013) and industrial effluents (Vymazal, 2014).

According to Vymazal (2013a), hybrid constructed wetlands are categorized into the following combinations: VF-HF systems, multistage VF-HF systems, VF hybrid systems, and hybrid constructed wetlands with FWSFCW systems. He however, noted that VF-HF hybrid systems are marginally more effective in ammonia treatment than the other types of the hybrid systems.

2.4 Composition of wetland

2.4.1 Macrophytes-

Wetland vegetation is a very important and prime component of a wetland ecosystem (Scholz, 2006; Lee & Scholz; 2007; Scholz, 2010; Vymazal, 2011c, 2013b; Villa et al., 2014) including constructed systems and, probably because of its presence, the systems are termed green technology (Stefanakis et al., 2014). Although these emergent plants are prominent constituents of the wetland ecosystem, purification of wastewater is carried out by the unification of various processes: chemical, physical and biological and between the macrophytes, substrate and the association of wetland microorganisms. Macrophytes are commonly used plant species in treatment wetlands (Vymazal, 2002, 2011c; Stefanakis et al., 2014) and include the following: cattail (Typha spp), common reed (Phragmites spp), rush (Juncus spp) and bulrush (Scirpus spp) Moreover, the macrophytes absorb contaminants in their tissue and furnish the microorganisms with a favourable growing environment (Vymazal, 2002, 2011c). While

growing in the filter substrate, the roots of the macrophytes dissolve organic matter and avert clogging by forming openings for the water to permeate within the substrate of an intermittent loading vertical-flow system. Furthermore, the macrophyte itself stabilizes the media in the wetland, reduces clogging build up, improves hydraulic conductivity, generates suitable avenue for the growth of bacteria, absorbs nutrients and supplies oxygen to the water (Li et al., 2008; Stefanakis et al., 2014). Conversely, some studies have shown that Phragmites australis (Cav.) Trin. ex Steud.(figure 2.5) is the universally accepted wetland plant species (IWA Specialist Group, 2000; Scholz, 2006; Vymazal, 2011c, 2014). Despite their wide use all over Europe and Northern America in treatment wetlands, the function of macrophytes plus the influence of various plant types on the treatment wetland is questionable (Scholz, 2006).

Figure 2.5: Cluster of common reeds (Phragmites australis) picture taken during autumn months

Some previous studies reported a considerable contribution of macrophytes to contaminant treatment. For example, the reduction percentage of about 89% in COD and BOD was found to be greater in planted than control systems that have a reduction percentage of about 85% (Akratos & Tsihrintzis, 2007). Karathanasis, Potter, and Coyne (2003) also found the reduction percentage of TSS and BOD to be very much lower in control systems (46%) and (63%) than

in uncontrolled systems (88–90%) and (70–75%) respectively for SSF wetlands. Fountoulakis et al. (2009) investigated removal of polycyclic aromatic hydrocarbons (PAHs) and linear alkylbenzene sulfonates (LASs) from domestic wastewater in pilot constructed wetlands and a gravel filter in Greece. The authors found that the vegetated filter recorded 79.2% and 55.5% removal efficiency of PAHs and LASs respectively compared to 73.3% and 40.9% for the gravel filter. Recently, in their review, Verlicchi and Zambello (2014) reported that high removal efficiency has been observed in planted wetlands treating pharmaceuticals including caffeine, naproxen, diclofenac and ibuprofen in comparison with unplanted ones. However, in a study to assess the removal of antibiotics from urban wastewater by constructed wetland optimization, Hijosa-Valsero et al. (2011) reported that their unvegetated SF systems exhibited higher removal of clarithromycin and trimethoprim compared to vegetated ones. However, in some studies, it was shown that, there is no significant contribution of macrophytes with regard to pollutants attenuation in planted and unplanted wetland systems. Scholz and Xu (2002) and Scholz (2006) found (BOD) removal efficiency of constructed wetlands basically the same irrespective of growing periods of the wetland plants while Balizon et al. (2002) observed insignificant removal efficiencies in their systems planted with duckweed, reed and algae.

2.4.2 Substrate

Substrate is the media used in wetland construction. The media are also called aggregates or wetland media and encompass one of the following: gravel, rock, organic materials such as compost, soil and sand. Many studies, including Stottmeister et al. (2003), Tietz et al. (2007), Dordio and Carvalho (2013), Meng et al. (2014) and Stefanakis et al. (2014), revealed that the primary support for the growth of macrophytes and microorganisms biofilm in constructed wetlands is soil. Furthermore, the origin and the soil composition have a significant impact on the hydraulic mechanisms of the system. In addition to contaminants adsorption by substrate media in constructed wetlands, the substrate also plays an important role in providing a

favourable thriving atmosphere for wetland plants and microbes to biodegrade wastewater pollutants (Tietz et al., 2007; Dordio & Carvalho, 2013; Ge et al., 2015). However, the size of the media should not be excessively large because, media with a large size does not provide an adequate surface area for biofilm establishment (Meng et al., 2014). Brix and Arias (2005) also revealed that small-sized-grain media, such as organic soil, provide a surface area for biofilm growth while media with narrow pore diameters lead to media pore blockage

Choice of pervious filter media has been reported (Hoffman et al., 2011; Meng et al., 2014; Song et al., 2015) to play a significant role with regard to hydraulic loading rate in SSFCWs because clogging of the media pores may be a problem and can affect the system performance when media porosity is not suitably selected for the corresponding organic loading application. The filtration media used in constructed wetlands depend on the objectives that need to be attained. Constructed wetlands have been designed and built with substrates ranging from fine texture soil to field stone. A coarse-grained material with high hydraulic conductivity will prevent the filter from getting clogged and close-grained material will be more efficient in reducing suspended solids and turbidity (Table 2.1). Substrate media in wetlands are regarded as hydric when they are either saturated or inundated with water. Under saturated conditions, the air in the substrate pore spaces is displaced by the water and the dissolved oxygen is utilized by the microbes. The oxygen utilized by microbes in the wetlands media is more than what will be restored through diffusion, hence the media become anoxic. However, in inundation or flooded conditions the substrate media become anaerobic (USEPA, 2000; Scholz, 2006, 2010; Stefanakis et al., 2014). A mixture of sand and gravel is recommended to improve hydraulic conditions and the removal of contaminants (IWA Specialist Group, 2000; Stottmeister et al., 2003). However, some studies suggested that smaller-sized are better than excessively large-sized media because biofilm growth is better established in the former than in the latter thus achieving a higher biodegradation ability by microbes (Dordio & Carvalho, 2013; Meng et al.,

2014), while substrates with fine pores leads to clogging of the media (Brix & Arias, 2005; Wallace & Knight, 2006; Song et al., 2015). Aggregates within wetland systems ease settling of SS and provide a surface area for the biofilms to develop and putrefy dissoluble contaminants. Multiple layers of gravel are organized in such a way that the size of the gravel increases from the top to the bottom layer. However, many studies have reported that the occurrence of clogging relates to this conventional arrangement of aggregates (Langergraber et al., 2003). Therefore, Sun, Zhao, and Allen (2007) proposed an anti-sized reed bed system, which was more effective than a conventional mono-sized reed bed with regard to the removal of several major pollutants from a high strength piggery wastewater.

Nevertheless, a recent study conducted by Song et al. (2015) expounded that an increasing-sized packing media strategy relieved clogging with high removal of COD, ammonia and nitrogen in their assessed vertical-flow wetland systems. Many studies were also conducted to assess the possibility of increasing the adsorption capacity of filter media with different substrates. For example, some publications confirmed that substrates like rice husk and

organic mulch have improved total nitrogen removal because of their organic carbon content (Saeed & Sun, 2011; Tee et al., 2012; Saeed & Sun, 2013) as reviewed by Meng et al. (2014).

Table 2. 1: Wetland media substrate characteristics (modified from Chen, Malone, & Fall, 1993; Sundaravadivel & Vigneswaran, 2009).

Media type	Grain size (mm)	Porosity (η)	Hydraulic conductivity (k_s, m s^{-1})
Coarse sand	2	0.32	1.2×10^{-2}
Gravely sand	8	0.35	5.8×10^{-2}
Fine gravel	16	0.38	8.7×10^{-2}
Medium gravel	32	0.40	11.6×10^{-2}
Coarse rock	128	0.45	115.7×10^{-2}

However, there have been contradictory views regarding the function of expensive filter media in the treatment process of constructed wetlands. Scholz and Xu (2002) in their study noted that using expensive adsorption media, like granular activated carbon, to enhance filtration performance of constructed wetlands did not improve the media adsorption capacity. Furthermore, Stefanakis and Tsihrintzis (2012) found no significant improvement in their systems performance when they used zeolite and bauxite substrates in their wetland study.

2.4.3 Microorganisms

Several studies have shown that various microbial communities exist in both aerobic and anaerobic zones of wetlands, including different forms of bacteria, fungi, algae and protozoa (Kadlec & Night, 1996; Cooper et al., 1996; Scholz, Xu, & Dodson, 2001; Paredes et al., 2007; Faulwetter et al., 2009; Shao et al., 2013; Meng et al., 2014). In wetlands, the interaction of biological, physical and chemical processes results in wastewater organic contaminants purification and transformation of nitrogen and phosphorus. The contaminants reduction is accomplished by the support of these wetland microbial communities (Figure 2.6). The microbial community in constructed wetlands plays a major role in the treatment of waste pollutants and has functional importance in the wetland environment as a result of microscopic size of the microorganisms which allows them to touch and feed the pollutants directly using their enzymes (Francis, 1996; Truu, Juhanson, & Truu, 2009). Furthermore, the microorganisms that revive, thrive and are capable of having metabolic activity in wetland systems partake in contaminants removal. The ability of constructed wetlands to remove pollutants depends on the interaction of microorganisms, wetland media and macrophytes.

Organic matter decomposition in the wetland system is also accomplished by microorganisms in aerobic and anaerobic situations. Kadlec and Wallace (2009) and Meng et al. (2014) reported that biodegradation of organic matter is generally related mostly to autotrophic and heterotrophic bacteria, certain specific protozoa, and fungi including basidiomycetes and

yeasts. The microorganisms can also adapt to transformations in the wastewater delivered to them and grow rapidly when a favourable environment and sufficient nutrients are available. Hilton (1993) and Truu et al. (2009) pointed out that the numerous microorganisms become dormant in wetlands when there is no favourable condition for their growth and survival. Moreover, they can stay dormant for many years as long as the conditions are not favourable.

Microbes perform very important activities in wetlands such as transforming numerous organic and inorganic materials from harmful to harmless ones, and changing oxidation/reduction reactions of the wetland media, and hence influence the physical, chemical and biological processes aiding in the nutrients reprocessing (USEPA, 2000; Truu et al., 2009; Ji, Zhi, & Tan, 2012; Ji, He, & Tan, 2013; Wang et al., 2015). However, the biodegradation of chemicals by microbes is a complex process that involves a series of biochemical reactions and generally differs depending on the microbes involved (Meng et al., 2014). For instance, microbes involved in nitrogen removal include some bacterial groups such as β-Proteobacteria and γ-Proteobacteria (Faulwetter et al., 2009) for ammonia oxidation. Furthermore, bacterial groups like Enterobacter and Micrococcus are involved in denitrification (Meng et al., 2014) while planctomycete-like bacteria *Candidatus Brocadia anammoxidans* are involved for anaerobic ammonium oxidation.

Microorganisms that naturally live in water, substrate, or roots of wetland macrophytes consume organic substances or nutrients thus reducing, breaking down or entirely removing a wide variety of contaminants from the wastewater. Functions of wetlands are greatly controlled by microbes and their metabolism (Wetzel, 1993; Faulwetter et al., 2009; Truu et al., 2009; Saeed & Sun, 2012; Meng et al., 2014). The association of microbes in constructed wetlands comprises of internal (indigenous) and external (foreign) microorganisms (Truu et al., 2009). Internal microorganisms are characterized by the following qualities: ability to have metabolic activity, flourish and live in wetland systems partaking in contaminants treatment, while

external microorganisms such as pathogens in the influent wastewater have no significant role to play in the wetland environment because they do not survive, as the wetland environment is hostile to non-indigenous microorganisms (Vymazal, 2005).

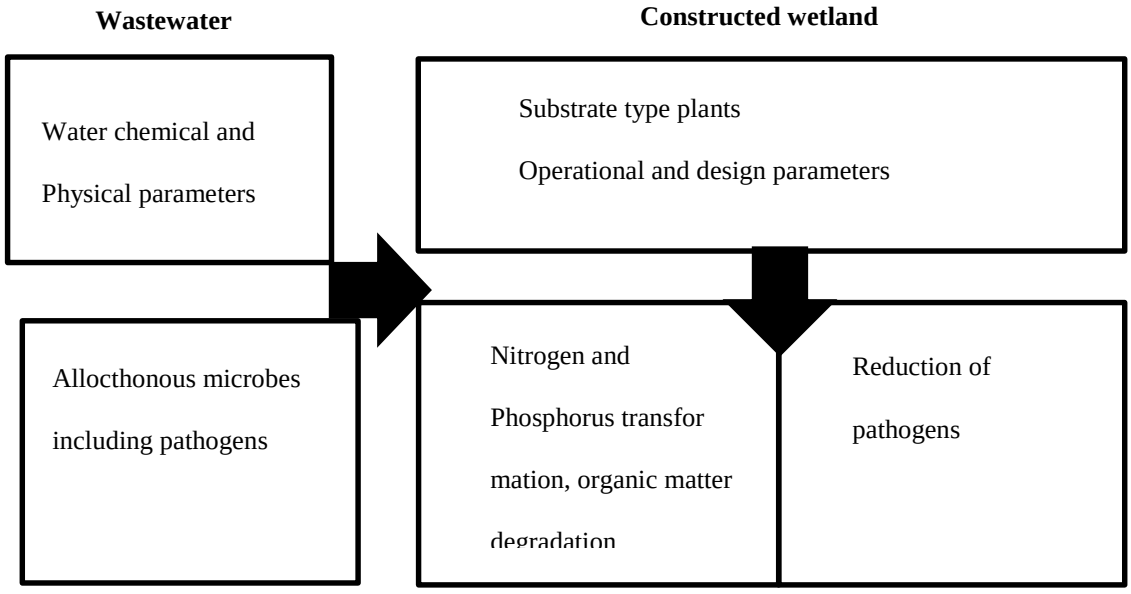

Figure 2. 6: Components that can influence microorganisms associations, anatomy and functions in constructed wetlands. Source: Truu et al. (2009).

2.4.4 Hydrology

Hydrology, which contributes to the anaerobic condition, is the constant or intermittent saturation of a substrate media in a wetland area and serves as the avenue where general biogeochemical operations take place (Sheoran & Sheoran, 2006; Eke, 2008; Scholz, 2010; Morandeira &Kandus, 2015). The operations lead to the growth of typical wetland media that provide a better environment for a predominant macrophyte society suited to existing in saturated media (Mitsch & Gosselink, 1993; Interstate Technology and Regulatory Council Wetlands Team [ITRC], 2003). In wetlands, hydrology is defined by two parameters: hydro period and depth of flooding (Gosselink & Turner, 1978). The hydro period is the time during which the soil is flooded or saturated, expressed in percentage, and is affected by numerous natural factors such as topography, geology, groundwater, subsurface soil characteristics, and weather conditions. The depth of flooding in a natural wetland varies between +2 m and –1 m

relative to the ground surface, with an average of approximately +1 m. These two parameters highly affect the characteristics (oxygen concentration, pH, nutrients, plants, etc.) and stability of the wetlands (Scholz & Lee, 2005; Scholz, 2006; Scholz, 2010).

However, In the case of constructed wetlands, the hydrological characterization of the wetland has been more complex. In wastewater treatment wetlands, the inflow is rather regular and the amount of pollutant brought in is quite constant. Furthermore, in intermittently dosed systems, the filters are flooded and drained (temporarily flooded) on a regular basis, facilitating oxygen transfer by drawing the water table down periodically to allow oxygen to penetrate into deeper levels of the filters. When the wetland is drained, the retreating water acts as a passive siphon and pulls atmospheric oxygen into the matrix as reported by Green, Friedler, and Safrai (1998), Sun et al. (2003), Vymazal and Kröpfelová (2008), Knowles et al. (2011), Wallace et al. (2013), Stefanakis et al. (2014) and Li et al., (2015).

Hydraulic retention time (HRT), is the average time that water stays in the wetland and a very significant variable in designing and evaluating treatment performance of wetland treatment systems (Hammer & Kadlec, 1983; Breen, 1997; Ghosh & Gopal, 2010). Furthermore, it is very important in designing and operating a constructed wetland and in determining the performance efficiency of settling solids, biochemical processes, and plant uptake (Kadlec & Knight, 1996; Ghosh & Gopal, 2010; Stefanakis et al., 2014).

2.5 Design and operational impact of constructed wetlands on performance

Vertical-flow constructed wetlands were reported (Kayranli et al., 2010; Scholz, 2010; Dong et al., 2011; Saeed & Sun, 2012; Abou-Elela et al., 2013; Vymazal, 2014; Paing et al., 2015) to improve several types of wastewaters with high performance efficiency. Dong et al. (2011) assessed the impact of design and operational parameters on the treatment performance and clogging processes of industrial-scale wetland systems treating domestic wastewater near Monaghan, Ireland. All wetland cells had a natural liner (compacted soil). The treatment

performance was high for most water quality variables; 98% for the biochemical oxygen demand (BOD), 94% for suspended solids (SS) 92% for chemical oxygen demand (COD), 90% for nitrate-nitrogen, 96% for total nitrogen, 97% for ammonia-nitrogen and 96% for ortho-phosphate-phosphorus. The large footprint of the system resulted in a high hydraulic retention time of approximately 92 days. The groundwater was not contaminated, possibly due to natural clogging processes and biomass development. In their study, Stefanakis and Tsihrintzis (2012) reported removal efficiency in organic matter (BOD_5 and COD) and nitrogen (TKN and NH4+-N) above 78% and 58%, respectively and 37% for phosphorus (total phosphorus [TP] and ortho-phosphate phosphorus [OP]). The authors attributed the system performance to the improved aeration in the media bed. The performance of the constructed wetland removing petroleum hydrocarbons in wastewaters containing aromatics and gasoline-range organics with 100% efficiency, with non-detectable concentrations in the effluent (Wallace et al., 2011) was also attributed to aeration of the media bed.

Tanner, Clayton, and Upsdell (1995), Rousseau et al. (2008), Gikas and Tsihrintzis (2012) and Abou-Elela et al. (2013) indicated that the pollutant removal efficiency of constructed wetlands was a function of the hydraulic loading rate and hydraulic retention time; i.e. if the hydraulic loading rate is high and the retention time is low, highly contaminated wastewater passes through the wetland quickly, which results in a corresponding relative decrease of the treatment efficiency due to insufficient time for biodegradation processes. Many researchers (Stefanakis & Tsihrintzis, 2012; Zhi et al., 2015) pointed out that water quality outflow parameters such as chemical oxygen demand (COD) are relatively unstable during the experimental setting-up phase, when the wetland is maturing. Furthermore, a long contact time results in higher removal efficiencies for ammonia-nitrogen, regardless of plant maturity. Nitrification and biodegradation in general can be promoted by relatively long resting times (artificially induced drying and aeration times). However, Stefanakis et al. (2014) noted that the biodegradation of

organic matter in VFCWs depends on the contents of the organic matter and hydraulic contact time applied during the wastewater treatment. As a result, the authors concluded that readily biodegradable organics are quickly oxidized due to high oxygenation in the wetland media bed while the recalcitrant ones are only partly degraded because of insufficient contact time. Furthermore, the organic matter decomposition was predominantly taking place in the top 10–20 cm as a result of that high oxygen availability and microbe population density in the upper wetland media bed (Tietz et al., 2007; Kadlec & Wallace, 2009; Stefanakis & Tsihrintzis, 2012).

The design of VFCWs to operate with intermittent wastewater application creates a flood on the media bed surface when the wastewater is applied before it subsequently drains gravitationally downward in a vertical direction. This type of operation provides a high amount of oxygen for aerobic microorganisms subsequently leading to high biodegradation processes (Vymazal, 2007; Stefanakis & Tsihrintzis, 2012) including aerobic decomposition of organic compounds containing nitrogen (Fan et al., 2012; Fan et al., 2013; Stefanakis et al., 2014; Zhi et al., 2015).

2.6 Processes of clogging within constructed wetlands

Clogging is defined as the developed process over operational time that leads to the blockage of substrate pores and the subsequent diminution of the corresponding hydraulic conductivity induced as a result of excessive formation of microbial biofilms build-up from pollutants degradation inside the pore space (Knowles et al., 2010, 2011; Thullner, 2010; Pedescoll et al., 2011; Nivala et al., 2012; Fu et al., 2013; Hua et al., 2014; Song et al., 2015). These pollutants come into the wetlands in the form of organic and inorganic solids from the influent stream.

Wetland scientists have recently embarked on their research on clogging as a result of its significant negative implication on the treatment efficiency of the systems (Platzer & Mauch,

1997; Zhao et al., 2004; Langergraber et al., 2009; Hua et al., 2010; Knowles et al., 2010, 2011; Le Coustumer et al., 2012; De la Varga, Díaz, & Ruiz, 2013;Hua et al., 2014; Song et al., 2015). However, clogging processes are very complex phenomena and no specific factors were stated to be the actual causes of the clogging in the systems. Some studies revealed that clogging was developed as a result of substrate pore blockage by suspended solids build up, sedimentation of biomass and growth of microorganisms (Tanner, Sukias, & Upsdell, 1998; Caselles-Osorio & Garcia, 2006; Hua et al., 2010). Conversely, Nguyen (2000) and Molle et al. (2005) attributed clogging of their systems to organic matter accumulation while Langergraber et al. (2003) and Winter and Goetz (2003) expounded that, though clogging in their systems was due to solids accumulation, biomass growth and SS loading, the latter played a significant contribution towards their systems clogging in comparison with biomass growth that has only a lesser effect compared with SS accretion. Moreover, Pedescoll et al. (2011) showed that root system development and system design were the causes of clogging while Chazarenc et al. (2009) related the problem to system operation (batch flow operation). Some studies however, revealed that in addition to the solids and the biomass growth, microorganism development has also contributed in the clogging of the media (Hua et al., 2010; Thullner, 2010; Hua et al., 2013, 2014). Yet, the factors leading to clogging are not well known (Knowles et al., 2011; Fu et al., 2013; Hua et al., 2014; Song et al., 2015).

The deposition of the organic and inorganic solids at the wetland surface leads to a clogging mat (outer blockage) and deposition of solids within pores results in substrate clogging (inner blockage). The process of clogging consists of the puncture phase for the pollutants, the formation phase of the deposition blanket-like layer, and the formation and compaction phase of the clogging layer (Scholz, 2006, 2010). Hua et al. (2010) showed that the clogging layer caused by suspended solids within vertical subsurface-flow wetlands develops gradually from the upper substrate layer to the lower substrate layer. A deposition blanket is formed on the top

of the substrate. Particulate solids are absorbed by electrostatic forces and van der Waal's forces. Larger solids are constrained into flowing through the filter, as the accumulated solids act as a sieve. A layer responsible for clogging may develop from filtered solids and from biological processes within the biomass. Clogging results in low hydraulic conductivity but it also functions as an excellent biological filter, which enhances the treatment efficiency of the system. Blazejewski and Murat-Blazejewska (1997) observed that wetlands treating sewage through filtration by sands are being clogged only shallowly (up to a few centimetres) while gravels clog much more deeply and allow solids to enter much further into the bed (Zhao, Zhu, & Tong, 2009). However, Hua et al. (2010) reported that clogging occurred in a 0-4 cm upper layer in their wetland systems. The decline of sand permeability due to SS clogging may be estimated by using equations such as the Kozeny-Carman one, which describes changes of sand porosity with time. The aggregates within wetland systems ease settling of SS and provide a surface area for the attachment of biofilms that decompose soluble pollutants. Multiple layers of gravel are organized in such a way that the size of the gravel increases from the top to the bottom layer, which has been recently reported to relieve clogging in vertical-flow constructed wetland systems (Song et al., 2015). However, many studies have reported that the occurrence of clogging relates to this conventional arrangement of aggregates (Langergraber et al., 2003), and therefore, some authors (Sun et al., 2007) proposed an anti-sized reed bed system, which was demonstrated to be more effective than a conventional mono-sized reed bed with regard to the removal of several major pollutants from a high strength piggery wastewater. The anti-sized reed bed counteracts the clogging of the bed matrix by allowing SS to be filtered and deposited more uniformly inside the bed.

One of the worst problems within subsurface-flow constructed wetlands is substrate clogging, which may only occur after a relatively long period of about five years (Geary & Moore, 1999; Scholz, 2010) or ten years (Knowles et al., 2011; Hill-Casey et al., 2014). Substrate clogging

results also in anaerobic conditions, which usually reduces the treatment performance even further (Scholz, 2010).

2.7 Types of clogging

2.7.1 Biological clogging

This is defined as the accretion and growth of microbial biomass within the substrate pores of wetland base material, leading to a reduction of the porosity of wetland media and a corresponding considerable decrease in hydraulic conductivity. Consequently, this blocks the penetration of oxygen in the wetland media leading to low treatment performance as pointed out by Thullner (2010), Knowles et al. (2011), Hua et al. (2013), Hua et al. (2014) and Song et al. (2015). Eventually, it may become so clogged (the substrate) that hydraulic malfunctions occur leading to progressive diminution of porosity and reduction of active pore volume, permeability and substrate hydraulic conductivity (Zhao et al., 2004; Davison et al., 2006; Pedescoll et al., 2011; De la varga et al., 2013; Song et al., 2015) which can greatly affect the lifetime of the system subsequently leading to poor effluent water quality to receiving watercourses.

Subsurface-flow wetlands separate and restrain biofilms (additional solids contributions from microorganisms) through transport and attachment processes (Hermansson, 1999; Tufenkji, 2007; Knowles et al., 2011). Once microbes colonize the wetland media surface, biomass further infiltrates inside the substrate media opening spaces. This will subsequently lead to clogging of the wetland media. Clogging of the media as a result of biofilm growth was reported (Caselles-Osorio & Garcia, 2006) to decrease inlet hydraulic conductivity by 64% in comparison to outlet hydraulic conductivity in their studied HSSF wetlands. However, these biofilms (Thullner, 2010) have variable impact with regard to wetland hydraulic conductivity because they are complicated naturally. For example, Mays and Hunt (2005) noted that they make assemblies with filaments under saturated conditions, establishing a thread-like net over

the media openings that may retain solids adeptly compared to homogenous biofilm layers. Tanner and Sukias (1995) also noted that majority of biofilms secrete cells and associated extra cellular polymeric substances are typically 99% water. They are a mucus-like gel, a smaller size in diameter on the nanometric scale, hence becoming nearly impenetrable (Vandevivire & Baveye, 1992) and plugging the pores between aggregates. Moreover, if these biofilms join up on another substrate fragment separately, Wallace and Knight (2006) noted that substrate clogging may eventuate and the hydraulic conductivity of the whole media can move in the direction of the hydraulic conductivity of the biofilm. Furthermore, Hua et al. (2013) found that these biofilms aggravate clogging of substrate media even if the inflow suspended solids concentration is less than 10 mg l^{-1} by enabling the solids to combine easily subsequently leading to their quick settling and interception. With this, the biofilms secrete their extracellular polysaccharide gel which adds to the stickiness of the substrate, blocking the pores and finally clogging the media. Soares et al. (1991), Winter and Goertz (2003), Zhao et al. (2009) and Hua et al. (2014) also reported that biological clogging can be noted particularly when nutrient loadings are relatively high.

Clogging of substrate media in subsurface-flow treatment wetland (SSF TW) as a result of vegetation has been controversial (Knowles et al., 2011). Some studies have the notion that vegetation counteracts media clogging while some have not. For example, with reference to the effect of vegetation counteracting clogging, Kickuth and Konemann's patent (US Patent No. 4,793,929, 1998), Fu et al. (2004) and Zhao et al. (2009) reported clogging counteracted by macrophyte root growth. The tubular structure of the roots makes channels in the substrate while growing and improves permeability, hydraulic conductivity and averts media clogging (Le Coustumer et al., 2012). Furthermore, recently, Fu et al. (2013) reported clogging abatement as result of growing macrophytes in their system. The authors attributed the abatement to penetration of the roots and rhizome of the wetland plants through the bed,

pollutants absorption, aeration improvement in the bed matrix and acceleration of microorganism growth by the plant released oxygen. Nevertheless, some studies noted that vegetation aggravates clogging. Scholz and Xu (2002) in their experiment observed that wetland plant decay may also lead to clogging of the top aggregate layer by decomposing reed litter if the top biomass is not harvested, because plant litter decays and contributes to elevated levels of SS and dissolved nutrients. Furthermore, Pedescoll et al. (2011) observed clogging in their systems as a result of macrophytes root growth with hydraulic conductivity and porosity reduction in planted wetlands compared to unplanted ones.

2.7.2 Physical clogging

This is the occurrence of clogging due to accumulation of solid particles (organic or inorganic). Inflow wastewater applied to wetlands constitutes particles of different diameters and contents. A large number of wastewater particles fall into the size of approximately 1–2 µm in diameter (Tchobanoglous, 1993) and cannot be eliminated via inactive and additional mechanical influences, and also since they are copious or large in number they cannot be affected by electrostatic forces (Zamani & Maini, 2009). However, particles in the diameter range of 0.7–2 µm have been noted by Puigagut et al. (2008) to be ultimately plentiful in the inflow and outflow of their studied wetland in Spain. Moreover, particulate solids (<100 µm) have been reported to be the cause of clogging in vertical-flow wetlands evaluated by Winter and Goertz (2003) and Hua et al. (2010).

The deposition of solids at the subsurface and at the surface of SSF TW slows down the hydraulic conductivity inside the subsurface of the wetlands and prevents water penetration of surface flow through to the subsurface of the SSF TW (Knowles et al., 2011; De la Varga et al., 2013). The mechanisms of filtration and retention of suspended solids in SSF treatment wetlands is through the principle of transport and attachment (Yao, Habibian, & O'Melia, 1971) as reviewed by Knowles et al. (2011). In the former, the solid particles collide with each

other in the transportation process and stick to themselves upon impact in the latter case (Swift & Friendlander, 1964; Knowles et al., 2011). The retention of solids on media surfaces is due to electrostatic and van der Waal's forces, and the bonding intensity (Hermansson, 1999; Hua et al., 2010) relies on the corresponding charge of the solids, gravel or soil surfaces and the entire wastewater. These retained solids are capable of stacking with each other, subsequently forming dendrites which further enter into the pore spaces of the media and increase the likelihood of solid interception (Hubbe, Chen, & Heitmann, 2009; Hua et al., 2010; Hua et al., 2014; Song et al., 2015) leading to clogging of the wetland media.

Initially, clogging of the substrate media was assumed to be due to inorganic particle contribution while organic solids would decompose sufficiently (Knowles et al., 2011). However, it has been reported by several studies that both organic and inorganic solids cause clogging of wetland media. For example, regarding clogging caused by inorganic solids, Suliman et al. (2006) attributed the clogging of their horizontal flow wetlands in Norway to blockage of the soil pores by sediment particles in the range of 6 mm diameter. In other studies, Llorens, Puigagut, and Garcia (2009) and Pedescoll et al. (2009) also revealed that more than 75% of the particles which clogged their experimental HSSF TWs in Catalonia, Spain were inorganic in nature. Furthermore, Platzer and Mauch (1997) noted in their experiment that clogging was due to accumulation of more than 90% inorganic solid materials. Regarding clogging as a result of predominantly organic solid materials, Zhao et al. (2009), Fu et al. (2013) and Song et al. (2015) have attributed clogging of their systems primarily to accumulation of organic solid materials in the wetland substrates. In terms of quantification, Tanner et al. (1998) and Nguyen (2000, 2001) noticed 80% accumulated solids in the dairy wastewater of their study contained 63–96% relatively refractory organic matter fractions composed of humic, humin and fulvic acids, originating from lignocellulosic and humic substances. The humic substances are highly colloidal and nebulous with greater potentiality and mechanical bonding

attributes which give them the ability to block media pores subsequently causing clogging of the systems (Tanner & Sukias, 1995; Nguyen, 2000). Furthermore, Fu et al. (2013) reported that labile organic solids and fulvic acid are the major contributing factors that lead to clogging of their vertical-flow wetlands in China.

2.8 Problems, advantages, causes and remedial measures of clogging

This section briefly outlines the potential problems (and some advantages) and causes associated with clogging. In summary, the key problems are as follows:

- The accumulation of solids within the media matrix favours the formation of short-circuiting and, consequently, the decrease of the hydraulic conductivity and effective volume.
- Clogging promotes the presence of water over the matrix by occlusion of interstitial spaces.
- The reduced oxygen content in the wetland due to clogging may lead to a reduction of the pollutant removal efficiency, resulting in a negative impact such as eutrophication on the receiving watercourses.

Key causes for clogging:

- Organic solids deposit on the constructed wetland surface blocking pores.
- Accumulation of SS inside the voids of the filter media.
- The initial mean void diameter is too small.
- Matrix with heterogeneous gravel (different diameters).
- Anomalies in the distribution and/or water collection systems.
- The rapid growth of microorganisms.

- Chemical precipitation and deposition within the pores.
- Obstruction of the pores caused by the growth of rhizomes and roots.

The following processes (not covered previously) usually play a minor role:

Chemical precipitation and deposition within the pores (Platzer & Mauch, 1997), chemical precipitation of metal hydroxides and sulphides (Sheoran & Sheoran, 2006), calcium carbonate (Fleming, Rowe, & Cullimore, 1999), elemental sulphur (Kadlec & Wallace, 2009)

Table 2. 2: Some literature on clogging and the representative countries

Location	Media and size	Findings	Recommendations	Title of the paper
Poland	Soil	Under sewage filtration, sand clogs shallowly up to few centimetres while gravels clog deeper into the bed more than 100 m. Decline of sand permeability due to SS application can be predicted due to Cozny Karman equation and a relationship describing changes of sand porosity with time.	Further investigations to confirm and expand the rate of validity of the developed model are needed	Blazejewski and Murat-Blazejewska (1997) Soil clogging phenomena in constructed wetlands with subsurface flow
Germany	Soil	Clogging occurs only in the upper 0-15 cm of the bed. Clogging is dependent on the height of organic mass loading.	In terms of the appropriate length of loading and recovery periods, more knowledge has to be gained	Platzer and Mauch (1997) Soil clogging in vertical-flow reed beds - Mechanisms, parameters, consequences and..... solutions?
Austria	Sand with a gravel size of 0.06/4 mm and 1/4 mm	Substrate clogging is by far the biggest operational problem of vertical flow constructed wetlands. Reasons for substrate clogging include accumulation of suspended solids, surplus sludge production, chemical precipitation and deposition in the pores, growth of plant-rhizomes and roots, generation of gas and compaction of the clogging layer		Langergraber et al. (2003) Evaluation of substrate clogging processes in vertical flow constructed wetlands

Table 2.2 (cont

Location	Media and size	Findings	Recommendations	Title of the paper
Germany	Sand based	The content of SS and especially particles > 50 µm are considered to play a key role. These particles are the same size as the pores in which seepage mainly occurs. Thus their potential for surface blocking is high. It is concluded that the construction and size of the primary settling has to ensure that the mean concentration of SS after settling does not exceed 100 mg l^{-1}. The results of this study indicate that the area of the VFCW should be designed for a maximum loading rate of 5 g m^{-2} d^{-1} and the COD load should not exceed 20 g m^{-2} d^{-1}. Choice of media including coarse fraction can abate adverse effect of clogging to some degree.		Winter and Goetz (2003) The impact of sewage composition on the soil clogging phenomena of vertical flow constructed wetlands
Norway	Sand and light weight aggregate 0.063–8 mm	It was found that a clogging layer forms at the interface between the filter and underlying soil, irrespective of the inflow regime of both water and sediment. It was also found that clogging is much slower if the water level is kept at a constant level than if it varies within the column, due to formation of a sediment plug that "shelters" the filter/soil interface. Most importantly it was shown that physical clogging is mainly caused by migration of sediment particles less than 6 mm in diameter. A simple regression model was proposed and tested for the prediction of clogging due to storm water sediment	Future research is needed to verify and test the model for other cases, and to modify the model to predict transport of particles through the filter media of at least two-dimensional systems.	Suliman et al. (2006) Change in flow and transport patterns in horizontal subsurface flow constructed wetlands as a result of biological growth.

Table 2.2 (cont)

Location	Media and size	Findings	Recommendations	Title of the paper
USA	Sand and gravel of 10.5, 6.4 and 13 mm sizes	Results showed that the growth of biofilms within the substratum pores certainly caused remarkable reduction of effective porosity, especially for the strong organic wastewater, whereas its influence on infiltration rate was negligible. It was implied that the most important contribution of biofilm growth to clogging was accelerating the occurrence of clogging.	Extend the study of operating HFCWs to other regions and incorporate heuristic knowledge acquired as a result of implementing the proposals the protocol produced.	Siriwardene, Deletic, and Fletcher (2007) Clogging of storm water gravel infiltration systems and filters: Insights from a laboratory study
China	1 mm sand and 10–20 mm gravel	The management of literature knowledge and a proposal for an operation and maintenance protocol for clogging prevention and some recommendations to improve the performance of HFCW technology		Lianfang, Wei, and Wei (2009) Clogging processes caused by biofilm growth and organic particle accumulation in lab-scale vertical flow constructed wetlands
Spain	Acquisition, analysis and integration of available data and knowledge and secondly the management of all this information	Provision of information and knowledge to be used to prevent and manage clogging problems associated with constructed wetlands	Further research needed on biomass accumulation and organics degradation on clogging.	Turon, Comas, and Poch (2009) Constructed wetland clogging: A proposal for the integration and reuse of existing knowledge
China	Perplex columns with gravel of 3, 10 and 20 mm	Clogging layer gradually develops from top of the media and the formation of deposition blanket layer on top of the substrate. The intensity of clogging reduces with depth and the SS solids were trapped in the 0-4 cm. Process of clogging is divided into 3: Puncture phase for pollutants, formation of deposition blanket layer and formation of compaction phase of the clogging layer.	Underlying mechanisms of clogging related to design, operation and maintenance should be researched further. The degree of root system impact on clogging particularly for other wetland plants is recommended.	Hua et al. (2010) Clogging pattern in vertical-flow constructed wetlands: Insight from a laboratory

Table 2.2 (cont)

Location	Media and size	Findings	Recommendations	Title of the paper
China	Perplex columns with gravel of 3, 10 and 20 mm	Clogging layer gradually develops from top of the media and the formation of deposition blanket layer on top of the substrate. The intensity of clogging reduces with depth and the SS solids were trapped in the 0-4 cm. Process of clogging is divided into 3: Puncture phase for pollutants, formation of deposition blanket layer and formation of compaction phase of the clogging layer.	Underlying mechanisms of clogging related to design, operation and maintenance should be researched further. The degree of root system impact on clogging particularly for other wetland plants is recommended.	Hua et al. (2010) Clogging pattern in vertical-flow constructed wetlands: Insight from a laboratory
UK	3–9 mm gravel, all media types and sizes	It is concluded that uneven inlet distribution, continuous surface loading and high rhizosphere resistance is responsible for the clog formation observed in this system. The average inlet hydraulic conductivity was 2 m d^{-1}, suggesting that current European design guidelines, which predict that the system will reach an equilibrium hydraulic conductivity of 86 m d^{-1}, do not adequately describe the hydrology of mature systems.	Subsequent work will compare a large cross-section of operational wetlands with a variety of ages, operating conditions and design characteristics that may help explain the clogging mechanism and allow guidelines to be stipulated which help maximize the longevity of these systems.	Knowles et al. (2010) Complementary methods to investigate the development of clogging within a horizontal sub-surface flow tertiary treatment wetland
Germany	All types of media and sizes	Bio clogging of experimental wetland columns is by far different from the field scale studies because of the complex nature of the real wetland natural porous media.	Improve understanding of microbial process relation to bio clogging in subsurface flow wetlands at the pore scale.	Thullner (2010) Comparison of bio clogging effect in saturated porous media within one and two dimensional flow systems: A review
Europe and US	All media sizes	Hydraulic and solids loading rates have to be taken into account for a design of a system to operate actively. Hydraulic overloading makes horizontal systems more easily exposed to clogging than vertical ones.	Future research should focus on elucidating the underlying mechanisms of clogging as they relate to the design, operation, and maintenance of subsurface flow treatment wetlands.	Knowles et al. (2011) Clogging in sub surface treatment wetlands: Occurrence and contributing factors

Table 2.2 (cont)

Location	Media and size	Findings	Recommendations	Title of the paper
China	8–16, 4–8 and 4 mm gravels	Results show that growing plants delayed the medium clogging process in the wetland, and for this purpose Canna indica is more effective than Cyperus alternifolius. The percentage of each component of organic matter was affected by the type of plants. C. indica promoted more strongly the accumulation of the active organic matter whereas C. alternifolius was more effective in enhancing production of fulvic acid. Both plant species led to lower humin contents in the wetland medium. Among all the components of organic matter, labile organic matter and fulvic acid were the leading factors causing wetland clogging, with the former playing the most prominent role in the process		Fu et al., (2013) Medium clogging and the dynamics of organic matter accumulation in constructed wetlands
China		Both the growth and detachment of biofilm were found to play positive roles in the clogging process under commonly used hydraulic loading in vertical constructed wetland. In addition, the existence of the biofilm enabled the suspended solids to combine much easier, which accelerated the settlement and interception of the solids.	The quantitative effects of the biofilm on clogging are still desirable to be studied	Hua et al. (2013) The role of biofilm in clogging process in vertical flow constructed wetland
China	0.12 mm coarse sand, 10 cm gravels	The results showed that the resting operation could effectively alleviate bioclogging because the hydraulic conductivity and effective porosity were improved after 3, 7 and 10 days of resting. In the upper 0–10 cm layer, the hydraulic conductivity increased 2.0, 2.6 and 3.5 times, respectively, for the three resting periods.	The optimal resting period should combine the effects of the resting time on the plants and the recovery cycle of the treatment performance in wetlands, which still require further study before putting into practice.	Hua et al. (2014) Applying a resting operation to alleviate bioclogging in vertical flow constructed wetlands: An experimental lab evaluation
China	8-9 mm, 6-7 mm, 5-6 mm, 3-4 mm gravel size	I packing is more efficient in TN removal and clogging remediation than D and U packing substrate arrangement. A formed dense biomass layer at the bottom of the reactor results in severe clogging.		Song et al. (2015) Comparative study of nitrogen removal in bio-film clogging for three filter media packing strategy in vertical-flow constructed wetlands

and growth of plant roots (Vymazal, 2002). However, a major problem is the quantification of any clogging processes. Here is a summary of the key remedial measures to combat clogging:

regular inspections using clogging tests; reduction of the water level; pre-treatment of the inflow; dosing the water intake; replacing the matrix; applying coarse gravel; cleaning the water distribution tubes.

2.9 Numerical modelling of wetland processes

Due to their enormous diversity, categories and operational strategies, proper functioning of CWs is complex and not fully understood (Meyer et al., 2014; Samso, 2014; Samso, Meyer and Garcia, 2015). Numerical models can be applied as a tool to aid in understanding the internal processes taking place in the CW systems as well as better their design (Langergraber, 2007; Langergraber et al., 2009; Hua et al., 2013; Meyer et al., 2014; Samso et al., 2015). Numerical modelling of constructed wetlands has gained popularity over the past decade. Wetlands are complex systems in which varied physical, chemical and biological processes such as sedimentation, filtration, precipitation, sorption, plant uptake, microbial decomposition and nitrogen transformations take place (Rousseau, Vanrolleghem, & De Pauw, 2004). These processes are active in parallel and mutually influence each other (Langergraber et al., 2009). Realistic descriptive models can produce reliable predictions of the performance of constructed treatment wetlands (Langergraber, 2007). Realizing the importance of modelling in designing and operation of CWs systems, recently, several concerted efforts were made to develop many numerical models as tools to aid in understanding numerous complex processes occurring in SSF wetland systems (Langergraber, 2007, 2008; Langergraber et al., 2009; Toscano et al., 2009; Giraldi, Vitturi, & Iannelli, 2010; Hua et al., 2013; Meyer et al., 2014; Samso, 2015; Samso et al., 2015). For instance, looking back to the history of numerical wetland modelling, as reviewed by Rousseau et al. (2004), the primitive first-order models by Kadlec and Knight (1996), which simply regarded wetlands as a “black box”, used a first-order rate constant to evaluate the effects of autochthonous production, sedimentation, temperature and retention time (Shepherd, Tchobanoglous, & Tchobanoglous, 2001) on the variation of the

concentrations of the contaminants in treated water. Due to oversimplification by using the first-order rate assumption, further efforts using a variable order (known as Monod-type of models) have been made to evaluate the contaminant removal rate (Kemp & George, 1997; Mitchell & McNevin, 2001). Multi-component reactive transport models were proposed to model both the transport and reactions of the main constituents of municipal wastewater in the subsurface-flow processes through wetlands (Langergraber et al., 2009). The reactive transport model highlighted the essential requirement for the description of the clogging process, which significantly influences the hydraulic conductivity of porous substrate beds and, consequently, the long-term behaviour of wetlands. Demaret et al. (2009) proposed a simple biological clogging model, which takes account of the effect of biomass growth on hydraulic conductivity (Eq. 1). The biomass growth model is assumed to account for spatial diffusion (Eq. 2). The biomass diffusion coefficient (*DM* is estimated by using a mesoscopic biofilm model (Eq. 3).

$$K = \begin{cases} K_0 \dfrac{\left(1 - \dfrac{M}{M_{clog}}\right)^b + a}{1 + a} & M < M_{clog} \\ K_0 \dfrac{a}{1 + a} & M > M_{clog} \end{cases} \quad (1)$$

Where K is the hydraulic conductivity, M is biomass density, a and b are two empirical parameters and M_{clog} is the biomass density beyond which no further reduction of hydraulic conductivity is observed.

$$\varepsilon \frac{\partial M}{\partial t} = \nabla (D_M \nabla M) + \varepsilon \left(\frac{k_3 C M}{k_2 + C} - k_4 M \right) \tag{2}$$

Where ε is the porosity of the porous substrate beds of wetlands, M is biomass density, t is time, D_M is the biomass diffusion coefficient, k_2, k_3 and k_4 are empirical parameters, and C is the concentration of the dissolved substrates (soluble reactive components) in water.

$$D_M = d \frac{\left(\frac{M}{\varepsilon M_{\max}} \right)^{\alpha}}{\left(1 - \frac{M}{\varepsilon M_{\max}} \right)^{\beta}} \tag{3}$$

Where D_M is the biomass diffusion coefficient, d, α and β are empirical parameters, M is biomass density, ε is the porosity of the porous substrate beds of wetlands, and $M_{\max}$ denotes the maximum biomass density.

Cooke, Rowe, and Rittmann (2005) discussed a rather detailed clogging model called BioClog, in which the clogging matter consists of five distinct components, each represented by a separate film layer: propionate degraders, acetate degraders, butyrate degraders, inert biomass and an inorganic layer composed of mineral precipitates and other inorganic solids. In BioClog, clogging accumulation and rates of species conversion are computed, and used to update the porosity (plus specific surface) and the source or sink terms of all species considered in the transport equation.

Recently, Giraldi et al. (2010) developed a reactive transport model for vertical-flow constructed wetlands called FITOVERT. In this model, 13 components are taken into account using the Activated Sludge Model 1 (Henze, 2000). Its transport model treats the dissolved component and particulate components separately. Clogging is described in terms of the porosity reduction due to biological growth and the filtration of particulate components using a parameter called the total volumetric specific deposit (D_{vtot}). The effect of porosity reduction on the hydraulic conductivity is then estimated according to Eq. 4, which follows the Carman-Kozeny methodology (Carman, 1956).

$$K = \frac{K_0}{\left[\left(1 + p\frac{D_{vtot}}{\varepsilon_0}\right)^x \left(1 - \frac{D_{vtot}}{\varepsilon_0}\right)^y\right]} \quad (4)$$

Where K is the hydraulic conductivity, K_0 represents K when the filter is clean during the start-up phase, p, x and y are empirical parameters, D_{vtot} is the total volumetric specific deposit, and ε_0 is the porosity of the porous substrate beds during the start-up phase of the treatment wetland.

2.10 Removal mechanisms in a wetland

2.10.1 Mechanisms of suspended solids removal

The inflow wastewater applied to wetlands contains solids particles, either organic or inorganic, of various sizes and compositions. Wetlands have the mechanical ability to eliminate suspended solids in the wastewater. In a constructed wetland, many publications confirmed that solids and particulate matter removal are achieved (Kadlec & Knight, 1996; Green et al., 1997; Leonard, 2000; ITRC, 2003; Garcia et al., 2010; Hua et al., 2013) via settling and

sedimentation, adsorption, and microbial degradation in wetland systems. However, the primary physical removal pathways in contaminant removal entail settling and sedimentation. These processes achieve effective eradication of suspended solids and particulate matter (Kadlec & Knight, 1996; ITRC, 2003; Kadlec, 2009; Abou-Elela et al., 2013). Moreover, van der Waal's forces of attraction and electric forces have been reported (Metcalf and Eddy Inc., 1991) to reduce SS concentration in constructed wetlands though the forces can repel or attract but that depends on the charges on the surface media.

In surface flow wetlands, the prevalent mechanical means (Environmental Protection Agency [EPA], 2000; Kadlec & Wallace, 2009) to eradicate suspended solids have been found to be flocculation/sedimentation and filtration. The sedimentation of SS relies upon flow discontinuation that subsequently results in settling down of the solids by force of gravity. Furthermore, SS interact and adhere to numerous contaminants like heavy metals, pathogens, organic matter and nutrients, and this helps their elimination (Sundaravadivel & Vigneswaran, 2001). Generally, treatment wetlands have been reported to efficiently reduce total suspended solids by around 80 to 90% (IWA Specialist Group, 2000). However, some recent studies have shown >90% removal efficiency in their wetland systems (Gikas & Tsihrintzis, 2012; Abou-Elela et al., 2013; Paing et al., 2015).

Manios, Stentiford, and Millner (2003) noted that the reduction of SS in vertical-flow wetlands depends on features of the filter media microorganisms and hydraulic load. VSF wetlands are very efficient in SS reduction (EPA, 1999; Tierz et al., 2007; Gikas & Tsihrintzis, 2012; Song et al., 2015) as a result of their media large surface area which allows suspended solids to settle by gravity, constrict, and adhere to media and macrophyte surfaces. However, Manios et al. (2003) observed that the main problem linked to the sedimentation and filtration of solids is the risk of media pores blockage as the wastewater permeates through subsequently causing clogging with corresponding low hydraulic conductivity resulting in water losses at the inlet of

the wetland. This clogging problem is negated by the decomposition of organic matter by microorganisms. However, the non-biodegradable mineral content of the solids, which is not disintegrated by microorganisms, contributes to the clogging of the filters.

2.10.2 Mechanisms of organic matter removal

The elimination of COD and BOD (organic matter) in constructed wetlands was accomplished quickly via entanglement and gravity settling of coarse organic matter in the pore openings of the substrate media as noted by EPA (1993) while BOD reduction in CWs was mainly due to aerobic microbial degradation and sedimentation/filtration processes. However, some studies indicated that organic matter removal in constructed wetlands is mainly through aerobic, anaerobic, adsorption, filtration, and microbial metabolism (Karathanasis et al., 2003; Song et al., 2006; Stefanakis et al., 2014) and can be assessed by the change in COD and BOD concentrations in the wetlands. Furthermore, the removal of soluble organic substances is accomplished by the growth of microorganisms on the media, adhered on the rhizomes and roots of the macrophytes (Song et al., 2006). The function of constructed wetlands is largely dependent on organic matter accretion, dissipation and cycling. Organic matter accumulation in wetlands supplies energy to microorganisms for denitrification by providing a long-term source of carbon and sustainable source of nutrients. However, the accreted organic matter may lead to media clogging by obstructing wastewater penetration through the substrate pores thereby reducing the retention time of the wastewater and nutrient removal capacity (Nguyen, 2000). Furthermore, Tanner and Sukias (1995), Winter and Goetz (2003), Zhao et al., (2009), Hua et al. (2014) and Song et al. (2015) observed a linear relationship between clogging, COD and TSS loading rates in their studies. They indicated that an increase in COD load concentration leads to an increase in TSS concentration and severity of clogging. Constructed wetlands usually provide high BOD and COD removal (Scholz, 2010; Dong et al., 2011; Gikas & Tsihrintzis, 2012; Abou-Elela et al., 2013; Paing et al., 2015). Biochemical conversions are

crucial mechanisms to degradable organic matter in wetlands and improve water quality. This can be responsible for organic substances elimination as a result of mineralization or gasification and the formation of organic matter via synthesis of fresh biomass. DeBusk (1999), observed that organic matter has approximately 45 to 50% carbon (C), which serves as a source of energy to various microorganisms. This organic carbon is converted into carbon dioxide in the root zone by the macrophytes which supply the oxygen necessary for the conversion. Furthermore, organic matter can also be removed via adsorption/absorption processes. However, EPA (2000) reported that the ratio and strength of adsorption depend on the surface media, macrophytes, litter and organic matter properties. Bacteria and fungi are decomposers in CWs and through mineralization and gasification have been reported (Choudhary et al., 2011) to play the main role of organic matter elimination. Additionally, these microorganisms synthesize biomass and form organic metabolic by products. Moreover, it has been noted (Hong et al., 2001; Ma & Burken, 2003) that further to phytovolatilization, some wetland plants release contaminants to the atmosphere by absorbing them in their roots first and subsequently transpire them via their transpiration stream .

2.10.3 Mechanisms of nutrients removal

In wastewater treatment, removal of nitrogen and phosphorus are very important issues because of their environmental and health implications. Receiving water courses become eutrophic when they receive large amounts of nitrogen and phosphorus nutrients subsequently promoting enormous plant growth that leads to the depletion of oxygen in the water environment. Nitrogen removal within constructed wetlands is usually mainly by microbial nitrification and denitrification (Table 2.3 and Figure 2.8). In the nitrification process, ammonia is oxidized largely to nitrate. As a result of the oxidation of ammonia to nitrate, nitrate is reduced to gaseous nitrogen by the denitrification process. Nitrogen removal in many constructed wetland systems without adequate active or passive aeration is insufficient, mainly because of the lack

of available oxygen used for aerobic biological degradation (Scholz, 2010; Saeed & Sun, 2011; Fan et al., 2012; Fan et al., 2013; Vymazal, 2014; Song et al., 2015). However, some studies reported that processes involved in nitrogen elimination in constructed wetlands are nitrification, ammonia volatilization, fixation, nitrate ammonification, ammonification, denitrification, organic nitrogen burial, anammox, plant and microbial uptake and ammonia adsorption, (Choudhary et al., 2011). Nevertheless, Vymazal (2007) noted that out of the above-mentioned processes for nitrogen removal from the wastewater, denitrification, ammonia adsorption, annamox, organic nitrogen burial and ammonia volatilization are the ultimate ones for removing the nitrogen while others, like nitrification or ammonification, are actually converters of nitrogen from its different types in the wastewater. In wetlands, the conversion of organic nitrogen to ammonia for example, leads to an increase in the quantity of the ammonia as a result of the ammonification process. Furthermore, Vymazal, (2007) observed that generally nitrogen removal processes depend on the type of constructed wetlands, for example total nitrogen removal was found to be in small quantities in a single stage wetland except in a wide treatment surface area. As a result, combined systems such as hybrid constructed wetlands should be an alternative choice for complete elimination of the total nitrogen (Vymazal & Kröpfelová, 2011; Ayaz et al., 2012; Vymazal, 2013a, 2014). Nevertheless, in various constructed wetlands, the main elimination pathway is the combination of nitrification and denitrification (Vymazal, 2007; Scholz, 2010).

The denitrification/nitrification mechanisms require both aerobic and anaerobic environments. However, parameters such as pH, dissolved oxygen and temperature affect the performance of nitrifying bacteria (IWA Specialist Group, 2000). On the other hand, the enzyme needed for denitrification may be suppressed in the presence of dissolved oxygen. Nitrification/denitrification can therefore occur simultaneously only in a soil which has both aerobic and anaerobic zones (Cooper et al., 1996). Nitrification rate was reported (Neralla et

al., 2000; Vymazal, 2007) to be higher in vertical SSF wetlands, due to the good aeration of the soil through regular bed draining, than in the horizontal SSF system due to the anoxic nature of the wetlands. Therefore, many authors, (Luederitz et al. 2001; Vymazal, 2005; Vymazal & Kröpfelová, 2011; Ayaz et al., 2012; Vymazal, 2013a, 2014; Mietto et al., 2015) proposed intermittent loading as a viable option to guarantee long flowing distance and supply the organic substances necessary for denitrification to achieve high N removal.

The removal capability of N in constructed wetlands decreases (Kadlec, 1999; Werker et al., 2002; Kuschk et al., 2003; Akaratos & Tsihrintzis, 2007; Gikas & Tsihrintzis, 2010, 2012) during the winter months, implying that N removal processes are temperature dependent. This indicates that temperature can be a determinant factor in N removal, when designing constructed wetlands in cold climate regions since the higher the temperature, the higher the growth of microbes and nitrification. Nevertheless, some authors (Harbel, Perfler, & Mayer, 1995; Reed, Middlebrooks, & Crites, 1995) noted that seasonal temperature has no clear relationship with removal efficiency of nutrient. Moreover, Kadlec (1999) reported that the removal efficiencies should be affected by annual cycles of numerous parameters such as temperature, humidity, precipitation and vegetation.

Phosphorus in constructed wetlands comes as phosphate in both organic and inorganic forms in different wastewaters (Vymazal, 2007; Choudhary et al., 2011) but because of its bioavailability, macrophytes and algae utilize orthophosphate phosphorus straight. Furthermore, it is a medium between the two forms of phosphorus cycling in wetlands as reported by Vymazal (2007). In constructed wetlands, phosphorus elimination takes place through sediment retention, adsorption, desorption, fragmentation, plant or microbial uptake, mineralization and leaching (Vymazal, 2007) but predominantly removed by porous media adsorption and microbial consumption (Gikas & Tsihrintzis, 2012), mechanisms that are not directly influenced by temperature (Kadlec & Wallace, 2009). However, the quick

multiplication of the microorganisms, like algae, bacteria and fungi, and their inability to accumulate much phosphorus, means they speedily absorb it instead (Vymazal et al., 2006).

Type of wetland also determines the extent to which the phosphorus can be stored or removed. For example, Vymazal et al. (1998) reported that soil media in VSF adsorbs phosphorus but the absorption capacity depends on the media type while in FWS wetlands, the adsorption is by the emergent floating macrophytes but harvesting and returning the dead macrophytes results in the maximization of phosphorus eviction in the wetland. Phosphorus eradication in planted vertical SSF wetlands takes place through the following processes: sorption to media, biofilm absorption and macrophyte ingestion (Lantzke et al., 1999) and the eradication quantity by the three processes is in the following order: media greater than wetland plants, greater than macrophytes, greater than biofilm, in the brief-regime, while macrophyte (70%) greater than media, (20%) >> biofilm (10%), in the long-term. Furthermore, it was reported that plant harvesting eliminated additional phosphorus in the range of 10–20% (Lantzke et al., 1999).

Phosphorus removal mechanisms, like precipitation and adsorption, may cause media clogging in constructed wetlands (Knowles et al., 2011) through binding of the media substrate as a result of precipitation reaction of media chemical properties with metal hydroxides and sulphides (Sheoran & Sheoran, 2006), with calcium carbonate (Fleming et al., 1999) and with elemental sulphur (Kadlec & Wallace, 2009). In this kind of situation, media in constructed wetland systems treating wastewater containing high amounts of industrial compounds may clog if there is high biological activity and interaction with the high concentration of these compounds (Kadlec & Wallace, 2009; Dotro, Larsen, & Palazolo, 2010). Nivala et al. (2007) reported clogging in their study as a result of iron fouling of the media treating land fill leachate and attributed the problem to ferric hydroxide precipitation which under high oxidizing conditions adsorbed to media surfaces, decreased porosity, and subsequently gummed the media together. Furthermore, different cations can precipitate phosphate under certain

conditions in wetland environments such as apatite, hydroxyapatite, variscite, strengite, vivianite and wavellite (Reddy & D'Angelo, 1994).

2.10.4 Mechanisms of hydrocarbon removal

Hydrocarbons are defined as either oil, grease, crude petroleum, tars, vegetable, mineral oil, animal tars, light fuel, heavy fuel or a combination of them (Eman, 2013) which are not soluble or not well soluble in water. Imfeld et al. (2009) revealed that these hydrocarbons are evaluated usually as total petroleum hydrocarbons (TPH), total hydrocarbons (THC), volatile organic contaminants (VOCs), and diesel and gasoline range organics (DRO & GRO) in wetland studies. They further expounded that, the debilitation of organic contaminants including the hydrocarbons in wetland systems requires the combination of chemical, biological and physical processes. However, they noted that the role of a specific process changes and depends on the type of pollutant being treated, the type of wetland, type of operational design, type of macrophytes in the wetlands, environmental conditions and the type of substrate media used.

Concerted efforts were made from various researchers to remove different forms of hydrocarbons from contaminated environments in wetlands ranging from oily water (Litchfield, 1993; Ji et al., 2002, 2007), crude and chemically dispersed oil (Page et al., 2002), VOCs such as BTEX (Lu, Lin, & Chu, 2002; Wallace & Kadlec, 2005; Vymazal, 2009; Ranieri, Gikas, & Tchobanoglous, 2013), benzene (Yeom & Yoo, 1999; Eke & Scholz, 2008; Tang et al., 2009; De Biase et al., 2011), TPHs (Gessner, Kadlec, & Reaves, 2005; Lin & Mendelssohn, 2009; Zhang et al., 2014), PAHs (Zappi et al., 1996; Fountoulakis, 2009; Haritash & Kaushik, 2009, Zhang et al., 2014), gasoline range organics (Wallace & Kadlec, 2005; Vymazal, 2009), diesel range organics (Omari et al., 2003; Lin & Mendelssohn, 2009; Bergier, 2011; Liu et al., 2011; Wang et al., 2011; Albaldawi et al., 2013a, b, c; Albaldawi et al., 2014,2015) to total hydrocarbons (THC) in a mixture (Guittonny-Philippe et al., 2015a)

and these authors have attributed the abatement of these hydrocarbon pollutants to either chemical, physical or biological removal pathways individually or in combination (Table 2.3).

In constructed wetland systems, chemical sorption and adsorption processes effectively eliminate hydrocarbon pollutants in the wastewater. Sorption, a chemical attachment between wastewater particles and media surfaces, influences hydrocarbon contaminants retention in the wetland aggregates particularly during the early stages of the wetland operation when the adsorption sites are free. At this time, the wetland substrate media serves as a sink and may possess enough binding capacity to retain the contaminants due to their high adsorption capacity (Omari et al., 2003; Tang et al., 2009). For example, Cottin and Merlin (2007, 2008) and Omari et al. (2003) found out that sorption was the strong removal pathway that led to the elimination of PAHs and diesel fuel respectively in their wetland systems. However, in their review, Imfeld et al. (2009) elucidated that when the adsorption sites reach a saturation stage and can no longer adsorb hydrocarbon pollutants in the media, no further net loss occurs, rather, the pollutants are retained via a reversible sorption process. Furthermore, they noted that this retention may subsequently expose the pollutants to microorganisms and enhance their biodegradation by increasing the pollutants residence time (RT).

Table 2. 3: Hydrocarbon removal mechanisms

Hydrocarbon	Removal mechanism	Reference
Hexachlorobenzene	Mechanical settling	Pardue et al., 1993
Petroleum hydrocarbons	Mechanical settling	Thurston, 1999
Benzene	Air stripping	Yeom & Yoo, 1999
Oil: total saturated and aromatic hydrocarbons	Biodegradation and physical flushing processes	Page et al., 2002
DRO: C10-C26	Adsorption and plant uptake	Omari et al., 2003
VOCs: BTEX	Aerobic biodegradation and volatilization	Wallace & Kadlec, 2005
TPH, AHC, C7-C30	Volatilization and microbial degradation	Gessner et al., 2005
Oil	Plant uptake	Ji et al., 2007
Benzene	Volatilization	Eke & Scholz, 2008
PAH	Absorption	Fountoulakis, 2009
Diesel, PAH, TPH	Plant uptake	Lin & Mendelssohn, 2009
Benzene	Adsorption	Tang et al., 2009
DRO: C7-C30, C7-C14	Plant uptake	Bergier et al., 2011
VOCs	Volatilization and microbial degradation	De Biase et al., 2011
BTEX	Plant uptake and biodegradation	Gikas, Ranieri, & Tchobanoglous, 2011
Diesel	Plant uptake	Liu et al., 2011; Wang et al., 2011
Diesel	Plant uptake	Wang et al., 2011
Diesel	Plant uptake and biodegradation	Albaldawi et al., 2013a, b, c; Albaldawi et al., 2014, 2015
PAHs and PBDEs	Plant uptake and tidal regime	Zhang et al., 2014
PAH	Phytodegradation	Zhang et al., 2014
THC	Adsorption, aeration and microbial degradation	Guittonny-Philippe et al., 2015a

Physical sedimentation and volatilization processes are important hydrocarbon removal pathways in constructed wetlands. Sedimentation, a phenomenon, referring to physical settling down of wastewater solids to wetland aggregate occurs when hydrocarbon pollutant particles interact with particulate organic matter (POM). As a result of this interaction, the POM and the pollutants settle down or are mechanically retained (Imfeld et al., 2009). Further, the researchers claimed that in highly polluted wastewater containing large amounts of POM, the most feasible way to remove organic compounds including petroleum hydrocarbons attached to the wastewater solids is mechanical filtration. Thurston (1999) and Pardue et al. (1993)

reported mechanical settling as the removal pathway for the attenuation of petroleum hydrocarbons and hexachlorobenzene respectively in their studies. In volatilization, the contaminant is directly emitted as a vapour from the aqueous wastewater phase to the atmosphere. However, in some wetlands, the physical volatilization process is not direct but goes through a biological removal pathway. Initially, the macrophytes absorb the contaminants in their roots and then transfer them to the atmosphere via their transpiration system, a process known as phytovolatilization (Hong et al., 2001; Ma & Burken, 2003) while in other wetland plants like helophytes, Pardue (2002) disclosed that the transfer of the contaminants is via the aeranchymatous tissue. Wallace (2002), Wallace and Kadlec (2005), Vymazal (2009), De Biase et al. (2011) and Ranieri et al. (2013) have reported that volatilization was an important removal process for volatile hydrophobic compounds such as BTEX. However, Kadlec and Wallace (2009) predicated that in surface flow wetlands, the volatilization of the contaminant is expected to be more noticeable than in subsurface flow wetlands as a result of direct contact of the wastewater with the atmosphere. As a result of this direct volatilization, some authors (McCutcheon & Rock, 2001) envisaged that the volatilization may lead to air pollution and contaminant dispersal in the environment. Moreover, they argued that this, and lack of stable risk assessment, presently hinders the wide acceptance by regulatory bodies of a phytoremediation strategy for VOCs attenuation.

In the biological attenuation process, microbial degradation and plant bioremediation are very important removal mechanisms of organic compounds including petroleum hydrocarbons from wastewater in natural and constructed wetlands. In the microbial process, microorganisms eat and biodegrade the hydrocarbon contaminants as their source of energy (Al-Baldawi et al, 2013a; Al-Baldawi et al., 2014, 2015; Guittonny-Philippe et al., 2015a). However, the degradation of the contaminant depends on its physical and chemical properties, for example, the nature and number of carbon atoms constituting the contaminants or its functional groups

(Imfeld et al., 2009). Recently, some studies, (Albaldawi et al., 2013a; Albaldawi et al., 2014, 2015) assed the phytotoxicity of hydrocarbons in surface and subsurface flow wetlands using the bulrush plant. The authors revealed that the systems efficiently removed more than 80% of TPH using diesel as a hydrocarbon model and attributed the removal to degradation of the TPHs by microorganisms residing in the rhizosphere. They further concluded that the SSFW removes the hydrocarbons more efficiently than the FWSW. In addition, Bhatia and Goyal (2014) reported that the rhizosphere of macrophytes such as Phragmites, Typha, Juncus, Spartina and Scirpus provides a favourable environment for the microbial degradation of organic pollutants including PAHs. Hydrocarbon, such as diesel, remediation in wetlands is very effective because of the inborn ability of the macrophytes to aerate the rhizosphere, this leads to an increase in aerobic degradation of hydrocarbons (Hambrick, DeLaune, & Patrick Jr, 1980; Salminen et al., 2004). Furthermore, phytoremediation as a result of high root biomass from the macrophytes might produce reasonable root exudates that may advance the roots activity in the rhizosphere subsequently leading to an increase in diesel degradation (Hegde & Fletcher, 1996; Yoshitomi & Shann, 2001). In their study of subsurface flow wetlands in a green house, Li et al. (2009) and Albaldawi et al. (2013a, b, c) found that wetland plants contributed in the aeration of the rhizosphere which in turn stimulated the activity of the rhizobacteria, subsequently leading to the high removal of diesel hydrocarbon (more than 70%). However, Sun, Zhao, and Allen (2005), Leonard, Key, and Srikanthan (2003), Mander et al. (2003) and Lee and Scholz (2006) reported that organic compounds and other nutrients removal in vertical-flow constructed wetlands were good under aerobic and/or anaerobic decomposition, microbial assimilation and plant uptake. Table 2.4 shows some constructed wetland performances based on percentage in diesel treatment and their representative countries.

Table 2. 4: Average influent (in) and effluent (out) concentrations and treatment efficiency of diesel hydrocarbon in constructed wetlands in representative countries

Country	Diesel concentration mg/l		Treatment efficiency (%)	Authors/year of publication	Title of the paper
	Inflow	Outflow			
UK	n/a n/a		80.1±9.8%	Omari et al., 2003	Hydrocarbon removal in an experimental gravel bed constructed wetlands
USA	20, 40, 80, 160 n/a and 320		All in the range of 95% and above	Lin and Mendelssohn, 2009	Potential of restoration and phytoremediation with Juncus roemerianus for diesel contaminated coastal wetlands
China	1000, 5000, 15000, n/a and 20000		All in the range of 67.42±8.92%	Liu et al., 2011	Degradation of diesel-originated pollutants in wetlands by Scirpus triqueter and microorganisms
Malaysia	8,700 17, n/a 26,100 n/a	n/a 400	77.0% 91.5% 81.1%	Albaldawi et al., 2013a	Phytotoxicity test of Scirpus grossus on diesel contaminated water using a subsurface flow system comparative
Malaysia	1% 2% 3%	n/a n/a n/a	>80% for SSF & <80% for FSF >80% for SSF & <80% for FSF >80% for SSF & <80% for FSF	Albaldawi et al., 2013b	Performance of free surface and sub-surface flow systems in the phytoremediation of hydrocarbons using Scirpus Grossus
Malaysia	0.100% n/a 0.175% n/a 0.250% n/a		All 72.5%	Albaldawi et al., 2014	Optimized conditions for phytoremediation of diesel by Scirpus grossus in horizontal subsurface flow constructed wetlands (HSFCWs) using response surface methodology

n/a: not applicable

2.10.5 Mechanisms of heavy metals removal in constructed wetlands

Heavy metals elimination in wetlands occurs through various physical, chemical, and biological processes including settling, sedimentation sorption, adsorption, complexation, oxidation and reduction, cation and anion exchange, chemical precipitation and co-precipitation as insoluble salts, photodegradation, phytoaccumulation, biodegradation, microbial activity, and plant uptake (Denga, Yea, & Wonga, 2004; Sheoran & Sheoran, 2006; Galletti, Verlicchi, & Ranieri, 2010; Ranieri & Young, 2012; Guittonny-Philippe et al., 2014; Guittonny-Philippe et al., 2015a). Moreover, they tend to accumulate on the top layer (sediment and litter) in vertical-flow systems and near the inlet in horizontal-flow systems irrespective of the removal pathways (Cheng et al., 2002; Scholz & Xu, 2002). However, in their review, Sheoran and Sheoran (2006; Guittonny-Philippe et al, 2014) noted that the whole of these elimination pathways depend on each other making the entire process of the heavy metals removal mechanism very complex in wetlands. In constructed wetlands, most metals are removed from wastewater via substrate media interaction, after which the macrophytes serve as a polishing system (Matagi, Swai, & Muganbe, 1998; Denga et al., 2004; Guittonny-Philippe et al, 2014; Guittonny-Philippe et al., 2015a).

In wetland systems, physical settling and sedimentation processes effectively remove heavy metals in wastewater associated with particulate matter (ITRC, 2003; Prestes et al., 2006; Terzakis et al., 2008; Guittonny-Philippe et al, 2014) as a result of the occurrence of many dynamic transformations irrespective of whether the systems are passive or active (Johnston, 1993; Matagi et al., 1998; Sheoran & Sheoran, 2006). The metals solids can move from the wastewater to either the substrate media or microbes or in a different manner subsequently leading to their filtration and retention in the wetlands. However, in slow water, metal particles denser than water will settle down. Though it has been noted that the physical sedimentation process is the predominant pathway of heavy metal removal in both natural and artificial

wetlands, Walker and Hurl (2002) noted in their study that sedimentation only takes place after the metals have been agglomerated into bigger particles, denser than the water solids via other chemical removal processes like the physical ones, subsequently leading to the heavy metals entrapment in the wetland sediment.

Additionally, in sedimentation processes, pads of wetland floating macrophytes in surface wetlands provide an avenue for trapping of metals suspended particles as the wastewater passes slowly or eases through the wetland systems as a result of typical sheet flow and resistance exhibited by the roots of the floating macrophytes. Moreover, some authors attributed heavy metals removal predominantly to accumulation in biomass in their evaluated wetland systems (Madera-Parra et al., 2015). However, some studies revealed that metals are believed to aggregate in the wetland sediment and plant tissues including roots, shoots, stems and leaves (Guittonny-Philippe et al, 2014) because they are eliminated from the wastewater but not destroyed (Ranieri & Young, 2012).

In wetland media, one of the most important chemical removal pathways for heavy metals is sorption, a process comprising of adsorption, absorption and precipitation reactions (Marchand et al., 2010). It leads to binding and accumulation of metals to particles in the substrate media from the wastewater as the wastewater enters the wetland system. Nevertheless, Seo, Yu, and DeLaune (2008) acclaimed that the adsorption of metals to the particles is either through ion exchange or chemisorption and depends on the availability and types of elements at the adsorption sites. For instance, retention of some metals such as Pb, Cu, and Cr by adsorption is higher than Zn, Ni, and Cd (Sheoran & Sheoran, 2006). In some studies, the removal mechanism was attributed to co-precipitation and cation exchange capacity (Lizama Allende, McCarthy, & Fletcher, 2014). They have reported a removal efficiency of more than 80% of As and Fe in the zeolite and limestone and cocopeat media used in their systems. Conversely, in redox and co-precipitation processes, metals such as Fe, Al, and Mn can form insoluble

compounds via oxidation that subsequently result in the production of array of oxides, oxyhydroxides and hydroxides while sulphates are reduced to sulphides (Murray-Gulde et al., 2005) that combine with numerous elements like As, Hg, Se, and Zn to co-precipitate in comparatively insoluble forms under chemically reducing conditions as reviewed by Marchand et al. (2010).

In the biological process, microorganisms and plants interact to remove pollutants in wetland systems. The roots of wetland plants provide a suitable environmental condition for the survival of the microorganisms (rhizosphere). The root surface is also enveloped with bacteria and these growing roots may transfer the bacteria through the substrate (Trapp & Karlson, 2001). The complementary bacteria provides certain metabolic functions such as nitrogen fixation, pathogens attack prevention, and contaminants detoxification including metals to their host (Mastretta et al., 2009; Sultana et al., 2014). Furthermore, Lemanceau et al. (2009) and Mench et al. (2009) found that microbes in the wetland systems produce siderophores that inter-react with metals and lessen their toxicity or increase their labile pools and uptake by plants (Sultana et al., 2014). Plant uptake is another metal removal mechanism in wetland systems. Suspended organic matter and metals (Galletti, Verlicchi, & Ranieri, 2010; Scholz & Hedmark, 2010; Grisey et al., 2012; Guittonny-Philippe et al., 2014) are easily eliminated by macrophytes in the wetland systems through the immobilization process in the roots and the aerated rhizosphere (Ye et al., 2001; Sultana et al., 2014), subsequently colonizing and absorbing a broad species of heavy metals like Pb, Zn, Cu and Cd as noted by Denga et al. (2004) in their field study and translocating them in the below-ground biomass (Baldantoni, Lagrone, & Alfani, 2009; Zhang et al., 2010). However, the capability of the wetland plants to uptake heavy metals differs broadly and depends on the nature of the macrophyte specie, heavy metals concentration, sediment pH, organic matter content, temperature, and sediment chemistry (Sheoran, 2004; Sheoran & Sheoran, 2006; Liu et al., 2007; Marchand et al., 2010). For

example, Lizama Allende et al. (2014) noted high metals removal efficiency of more than 85% attributable to wetland media and less than 3% removal associated with macrophytes. They further expounded that the process include As co-precipitation with Fe by the substrate media in their study was due to pH adjustment and facilitated by the cation exchange capacity, while Liu et al. (2007) attributed the high removal efficiency of heavy metals of their research to macrophytes via phytoextraction and site provision for metal precipitation (Mays & Edwards, 2001).

2.10.6 Mechanisms of other contaminants removal

Apart from the well-known common pollutants treated in wetlands, such as COD, BOD, SS, nitrogen compounds, petroleum hydrocarbons, heavy metals, etc., others, such as trace elements, personal care products, pharmaceuticals, pesticides, herbicides, phenols, endocrine disruptive chemicals (EDCs) or linear alkylbenzensulfonates (LASs), polychlorinated biphenyls (PCBs), etc. were also treated by various constructed wetlands through physical, chemical, or biological processes, or the combination of them (Figure 2.8). In wetland systems, the trapping of sediment is the physical elimination mechanism of solids and organic particles in the wastewater. When the wastewater passes through the wetland substrate media, the particles settle on the media bed or plant roots as a result of the slow water movement influenced by the macrophytes and broad sheet flow subsequently enhancing the sedimentation process (DeBusk, 1999; Karathanasis et al., 2003; Chazarenc & Merlin, 2005; Gikas & Tsihrintzis, 2012; Molle, 2014; Paing et al., 2015). In their review, Imfeld et al. (2009) reported that Pardue et al. (1993), Leppich (1999) and Jackson (1999) attributed sedimentation as one of the removal pathway for chlorobenzenes and fuel (Kadlec, 1992; Wright, Weaver, & Webb, 1997; Salmon et al., 1998; Thurston, 1999; Groudeva, Groudev, & Doycheva, 2001; Boopathy, 2003) removal respectively. Contaminants including PCBs (Campanella, Bock, & Schröder, 2002), pesticides (Sherrard et al., 2004) xenobiotics derived from the pharmaceutical industry,

personal care products, hormones, etc. (Vymazal, 2009) and inorganic contaminants derived from motor way suspended on solids (Hares & Ward, 2004) have also been treated with constructed wetlands via sedimentation and filtration as removal mechanisms among other processes. However, there are some contaminants which are not removed singly in constructed wetlands, but have to be complimented with another mechanism. For example, Türker, Vymazal, and Türe (2014), reported in their review that sedimentation is complimented with plant uptake to remove boron in constructed wetlands under favourable environmental conditions. Further, the authors also reported that Türker, Böcük, and Yakar (2013a) and Türker et al. (2013b) achieved 32% and 40% removal efficiency of boron in their wetland systems via sedimentation and plant uptake processes respectively.

In chemical removal processes, sorption, photo oxidation, and volatilization are also considered as some of the major contaminant removal mechanisms (Imfeld et al., 2009). Sorption, a process referring to the chemical attachment of wastewater molecules to the surfaces of substrate media, is a very important removal mechanism in wastewater treatment in constructed wetlands. It includes the processes of adsorption and precipitation. In photo oxidation, the power of sunlight is converted to break and oxidize organic compounds such as pesticides and pathogens while volatilization is the breaking down of compounds and emission into the air as a gaseous state (DeBusk, 1999; Sundaravadivel & Vigneswaran, 2001; Imfeld et al., 2009). Organic contaminants like herbicides and phenols were reported to be treated in wetlands via the adsorption process as a chemical removal pathway (Zhang et al., 2014). Conversely, Kröpfelová et al. (2009), after 28 months of their study of inorganic contaminants removal in horizontal flow wetlands in Czech Republic, predicated that 34 trace elements were mostly removed via the adsorption process. Matamoros, Garcia, and Bayona (2005) proclaimed that pharmaceuticals such as carbamazepine are treated via sorption of the particles to the substrate media from the water phase and therefore accumulate in the sediments of the constructed

wetlands. Furthermore, (Matamoros & Bayona, 2006), explored subsurface flow wetlands in Barcelona, Spain to remove 11 pharmaceuticals and personal care products (PPCPs). The authors claimed that more than 80% removal efficiency was achieved for caffeine, salicylic acid, methyl dihydrojasmonate, and carboxy-ibuprofen. Others include 50– 80% removal for ibuprofen, hydroxy-ibuprofen, and naproxen, while more than 80% removal of Ketoprofen, diclofenac, galaxolide and tonalide was achieved in their systems and this removal was accomplished via sorption of these contaminants to the media substrate. In their study, Grove and Stein (2005) and Polprasert, Dan, and Thayalakumaran (1996) treated acetone and phenol in their constructed wetlands, and attributed the removal as a result of volatilization and phytovolatilization respectively. Furthermore, lower chlorinated benzenes (MacLeod, 1999; Keefe et al., 2004) and chlorinated ethenes (Bankston et al., 2002; Ma & Burken, 2003) were reported to be treated via the volatilization and phytovolatilization removal processes in wetland systems.

Plant uptake, phytodegradation, and phytoaccumulation are important mechanisms in biological contaminants removal processes in wetland systems. Chu, Wong, and Zhang (2006a) assed the accumulation, distribution, and transformation of DDT (dichlorodiphenyltrichloroethane) and PCBs by Phragmites australis and Oryza sativa L. in their study of constructed wetland systems; the authors found that plant uptake and accumulation were the main removal pathways for the contaminants removal. Furthermore, treatment of nutrients of agricultural importance, but harmful to plants when in excess, with constructed wetlands has been documented (Gross et al., 2007; Kröpfelová et al, 2009; Allende, Fletcher, & Sun, 2012; Türker et al., 2013a, b) and has achieved considerable removal. For example, Türker et al. (2013a) assessed the ability of macrophytes for boron removal in their wetland systems in Turkey and found that Typha latifolia and Phragmites australis absorbed a considerable amount of boron in their roots which later transferred to leaves and stems of the

wetland plants (Rees et al., 2011). Hence, the authors concluded that phytoaccumulation was the main removal mechanism. In the assessment of their subsurface-flow wetlands, (Karimi, Ehrampoush, & Jabary, 2014) also associated removal of indicator pathogens to macrophytes when they got a high removal efficiency of more than 70% of Escherichia coli and total coliform in the planted wetlands compared to the control ones. Therefore, the authors concluded that plant uptake was one of the removal mechanisms of the pathogens.

Phytodegradation, a phenomenon, referring to breaking down of organic contaminants by plant enzymes, has been found (Bankston et al., 2002; Wang et al., 2004) to occur in many wetland macrophytes such as common reed (Phragmites australis), cattail (Typha latifolia), and some poplar species (populous sp.). For example, Wang et al. (2004) predicated that phytodegradation was the removal mechanism in their study treating contaminated carbon tetrachloride wastewater by poplar plants. In addition to phytoaccumulation, plant uptake, and phytodegradation, microorganisms also play an important role in contaminants remediation in wetland systems. Braeckevelt et al. (2007) found in their research that chlorobenzenes are biodegraded by microorganisms in constructed wetland ecosystems in both aerobic and anoxic conditions. Gessner et al. (2005) investigated the potential of their pilot-scale free water surface constructed wetlands in America to remediate complex and free cyanide and associated contaminants in water from a groundwater spring. The authors concluded that the removal efficiency is over 80% for total cyanide and attributed the reduction to microbial degradation in the rhizosphere of the macrophytes. Conversely, in their study, De Biase et al. (2011) reported that biodegradation was the main removal mechanism of MTBE (methyl tert-butyl ether) contaminant in their wetland systems, though there was only 46% removal.

Overall, constructed wetlands, horizontal, vertical or their combination have been demonstrated to treat different types of contaminants in waste water with high efficiency in

different parts of the globe (Vymazal, 2014). Table 2.5 and figure 2.7 show a summary of pollutants removal processes in wetland systems.

Table 2.5: Overview of primary contaminants removal mechanisms (modified from ITRC, 2003; Imfeld et al., 2009; Choudhary et al., 2011; Abou-Elela et al., 2013; Guittonny-Philippe et al., 2015a)

Contaminants	Removal Mechanism
COD	Settling, biodegradation, plant uptake
BOD	Settling, oxidation, biodegradation
NO_3-N, NH_4-N	Settling, biodenitrification, nitrification
Organic N, NO_2	Plant uptake
PO_4-P	Settling, precipitation, microbes
Organic P	Adsorption, plant uptake
BTEX, TPHs, fuels, oil and grease	Volatilization, photochemical oxidation, biodegradation/photodegradation/phytoremediation
PAHs, chlorinated and non-chlorinated solvents	Diffusion, oxidation, photodegradation, settling, photovolatilization/evapotranspiration
Metals: Al, As, Cd, Cr, Cu, Fe, Pb, Mn, Ni, Se, Ag, Zn	Settling, precipitation, biodegradation, adsorption/ion exchange, photovolatilization, phytoremediation
Pathogens	UV radiation, microbes die off
SS and turbidity	Settling, adsorption

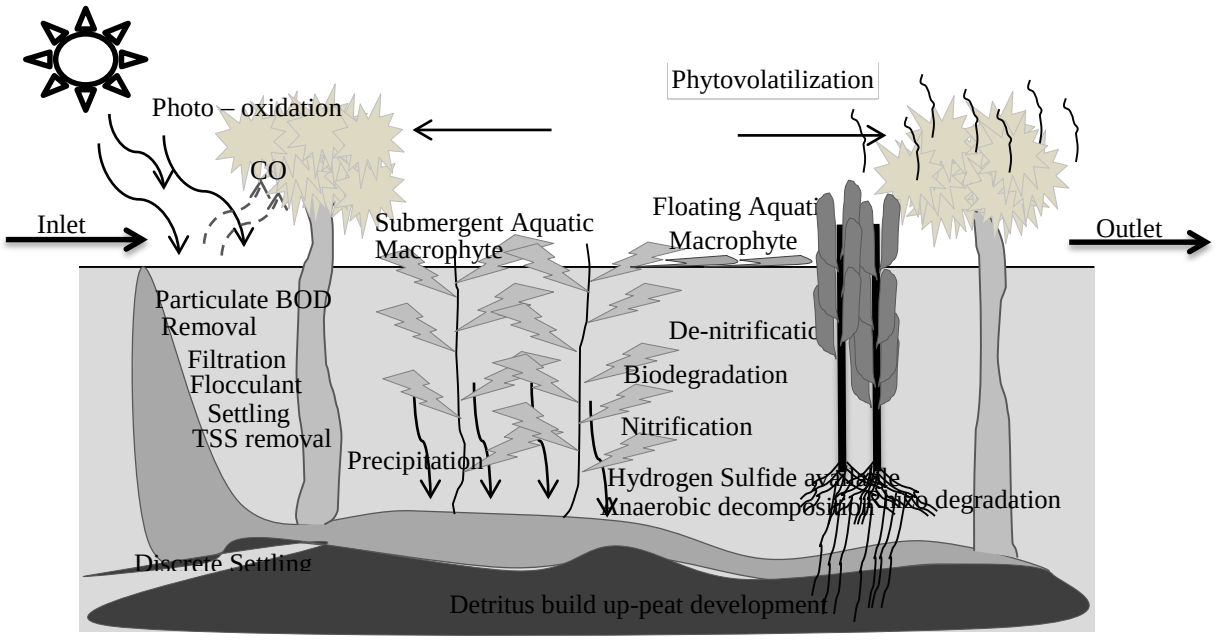

Figure 2. 7: Removal processes occurring in a wetland. Source: ITRC (2003).

2.11 Essential values of wetlands

Natural wetlands from which the ecological engineering constructed wetlands emerged, have been in existence since the time of human history. Their values are multiple, and play a vital role in the history of humanity including the prime civilizations like Egypt and Mesopotamia who used to live close to the wetland areas, that supplied an array of numerous economic and essential resources to them. However, despite all these multiple values and the historical contribution of these wetlands, it was during the last 50 years that humans realized the various positive impacts of them to their society (Stefanakis et al., 2014; Vymazal, 2014). Wetlands as a water body encompass diversity of animals and plant species. Furthermore, they give support to the lives of these flora and fauna living in the ecosystem and supply numerous important ecosystem services that help in human development such as provision of food, fuel wood, water, regulation of flood control, water quality and supply, habitat like biodiversity, and cultural services such as recreation and aesthetic enhancement (The Economics of Ecosystems and Biodiversity [TEEB], 2010). Other values include carbon dioxide absorption leading to global warming reduction, supporting the food chain indirectly by fish production and other

related edible water animals (Stefanakis et al., 2014), flood abatement, regulation of micro- and macro-climatic changes, contaminants degradation and erosion control (Minga et al., 2007). Because of their good qualities, such as water pollution control, they have been termed as “Earth’s kidneys” by some wetland scientists since they filter and retain the pollutants passing through them before they reach the receiving water courses (Kadlec & Knight, 1996; Kivaisi, 2001; USEPA, 2004: Scholz & Lee, 2005; Cui et al., 2012). Moreover, they are also referred to as biological supermarkets (Barbier, Acreman, & Knowler, 1997; Mitsch & Gosselink, 2000; Chen & Zhang, 2001; Chen & Lu, 2003) because they are among the natural environments with high natural production on Earth.

For over two decades, concerted efforts were made by several scientists to classify and summarize values of wetlands. For instance, Vymazal et al. (1998) and Cui et al. (2012) classified the values of wetlands as follows:

- Hydrological and hydraulic values which include erosion and flood control recharge of ground water aquifers, and floodplain hydrodynamics;
- Climatic effects including buffering global warming, carbon fixation and CO_2 balance, and micro-climatic influences;
- Biodiversity functions including wild life enhancement, breeding ground for water fowl, fish and invertebrates like shrimps, crabs, oysters, clams, and mussels, preservation of gene pools, and conservation of flora and fauna;
- Research studies such as training and nature studies;
- Recreational and reclamation uses which include sightseeing, aesthetic benefits, swimming and sailing;
- Energy production;
- Development of aquaculture and integrated systems, fishing and rice cultivation; and
- Mining activities.

In their studies, Millennium Ecosystem Assessment (MEA; 2005), De Groot et al. (2006), Ghermandi et al. (2010) and Cui et al, (2012) defined the values of the wetlands as groundwater aquifers embellishment, management/reformation of flood incidents (protective buffers), retaining of sediments and other materials, reduction of carbon dioxide, storage and heat release, reduction of solar radiation and relevant support to food chains. However, Stefanakis et al. (2014) noted that the values of these wetlands can be classified as ecological, socio-cultural, and economical (Figure 2.8). Furthermore, the authors suggested that the combination of these classes of values will give the overall general values of the wetlands. Schuyt and Brander (2004) and MEA (2005) in their studies, shortlisted the following values as the entire values of wetlands including ecological, socio-cultural and economical ones which include biodiversity, water supply, irrigation, fishery, livestock, water quality reclamation and flood abatement. Others are recreation, culture, CO_2 emission protection, improvement of climate, prey value, scientific value, and educational value. The authors also mentioned timber provision, source of hydroelectric power supply, salt provision, provision of sand, anti-corrosiveness, warm restoration and transportation.

From an economic perspective, concerted researches were conducted to estimate the values of wetlands on monetary bases. Costanza et al. (1997) assed the monetary value of the world's wetlands and predicated that their total estimation using American dollars reached up to a total amount of US$ 14.9 trillion. Furthermore, Schuyt and Brander (2004) reported the economic monetary value of global wetlands to be US$ 70 billion annually based on the estimated Ramsar Convention wetland area of 12.8 million km^2 including values such as biodiversity, scientific, ecological, sociocultural, and other important ones. The authors also calculated the economic value provided by US coastal wetlands in protecting storm events in monetary terms to be US$ 23.2 billion annually and a reduction from US$ 3–8 billion to US$ 1.5 billion if a new

wastewater treatment plant were to be constructed to supply the equal amount of free water supply provided by the natural wetland existing reservoirs.

Realizing the aforementioned values of wetlands by human society, including the ability to control and mitigate flood incidents from causing negative impacts to the receiving ends and wastewater purification capacity, has made them become progressively more and more recognized (Stefanakis et al., 2014; Vymazal, 2014). Today, wetlands are recognized to have the ability to remove various types of pollutants including organics, inorganics, metals, trace elements etc. from wastewater through natural physical, chemical and biological processes. This recognition stimulated the research on manmade constructed wetlands to explore the wetland potentials for different technological applications. The fundamental idea of these wetland constructions is to duplicate the numerous wetland processes in a more advantageous way to humanity under controlled environmental conditions such as flood prevention and improvement of water quality.

With regard to these man made constructed wetlands, some researchers also tried to assess their values as previously done for natural wetlands. Knight et al. (2001), in the assessment of their subsurface-flow wetlands as a habitat for wild life and humans, found that these systems provide habitat for wildlife and diversity, provision of recreational activities, such as bird-watching, water storage, and aesthetic enhancement in urban or rural environments, among others. However, while some studies revealed that both natural and artificial wetlands have the same ecological values (Campbell, Cole, & Brooks, 2002) others reported that constructed wetlands have more values than the natural ones when they did a comparative

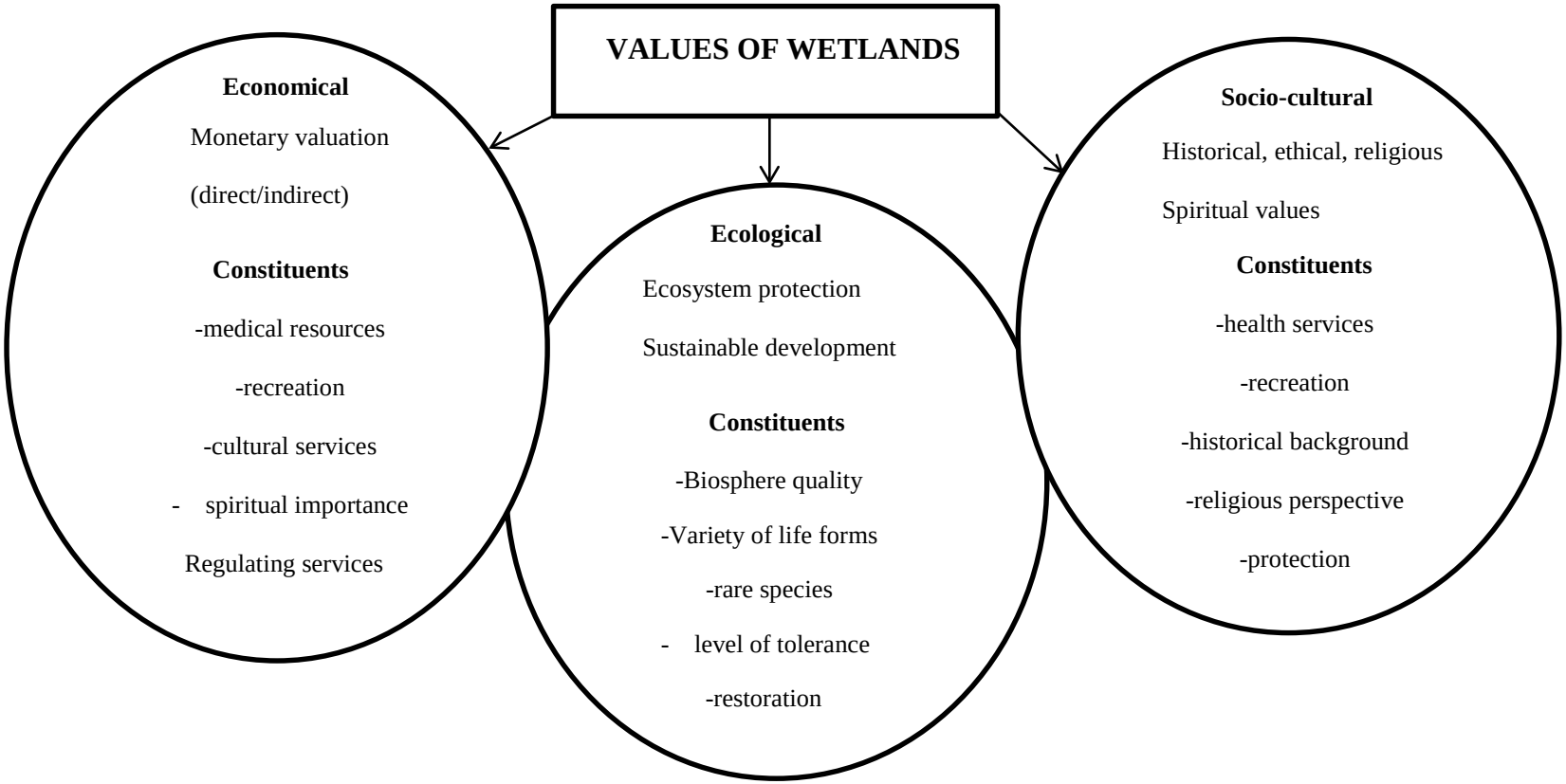

Figure 2. 8: essential values of wetlands adapted from (De Grot et al., 2006; Stefanakis et al., 2014)

research of 186 different natural and constructed wetland systems (Ghermandi et al., 2010).

2.12 Choice of vertical-flow constructed wetlands over horizontal-flow

The exploration of vertical and horizontal subsurface flow wetlands as alternative means of wastewater purification from different sources is increasing globally (Liu, Dahab, & Surampalli, 2005; Yalcuk & Ugurlu, 2009; Konnerup, Trang, & Brix, 2011; Abou-Elela et al., 2013; Kantawanichkul & Wannasri, 2013; Paing et al., 2015; Wu et al., 2015) as a result of their advantages like low cost of operation, aesthetic enhancement, easy maintenance and simple to operate (Scholz, 2006, 2010). However, despite these aforementioned qualities associated with the two types of wetlands, some research has proposed that vertical flow constructed wetlands are better than horizontal flow constructed wetlands in some water quality variables. For example, Cooper (1996) expounded that in VFCWs, draining of the substrate bed avows the reduction of BOD and ammonia nitrogen removal efficiently and provides excellent conditions for nitrification (Vymazal, 2005; Vymazal et al., 2006; Langergraber, 2007; Gikas & Tsihrintzis, 2012; Fan et al., 2012, Fan et al., 2013; Li et al., 2015; Paing et al., 2015) unlike in continuously saturated anaerobic horizontal flow wetland systems. Brix and Arias (2005) and Prochaska et al. (2007) also stated that VF systems perform satisfactorily in wastewater particle removal, and chemical and biochemical oxygen demand variables (COD and BOD). Though some researchers referred to them as poor denitrifiers (Vymazal, 2005), several studies recently showed that VFCW systems with intermittent loading regimes can denitrify well with modification. For example, Arias et al. (2005) and Gross et al. (2007) reported removal efficiency between 50% and 69% for total nitrogen (TN) and more than 90% for COD and BOD_5 after recirculating the effluent. Furthermore, Weedon (2003, 2010) found that their VFCWs systems successfully denitrified and removed 90% of SS, BOD_5, and NH4 +- N after 10 years of operation in the UK for the treatment of pre-settled urban wastewater at

typical loading rates after recirculation. The author claimed that the system was enhanced using sand as the major filter media, intermittently fed and the aeration time used was the interval between the wastewater application regimes, demonstrating that these systems are capable of achieving high treatment standards (Stefanakis et al., 2014). Furthermore, wetland systems evaluated by Shen et al. (2015) in China to enhance removal of nitrate using starch blends as solid carbon source indicated high denitrification with 98% nitrate removal efficiency. However, in their research, Li et al. (2015) have shown 95% removal of organic matter and ammonia-nitrogen without any modification.

In constructed wetland systems, VFCWs are the state of the art technologies used in water pollution control, and interest in them is increasing rapidly worldwide, probably due to the lower area demand advantage compared to HFCWs (Abou-Elela et al., 2013; Stefanakis et al., 2014; Paing et al., 2015). They require 1–2 square metres per person equivalent (m^2/pe) unlike horizontal flow that needs 5–10 m^2/pe. Many countries, including the UK, are exploring these VFCWs systems and use this unit area per person equivalent (Cooper, Smith, & Maynard, 1997; Cooper & Green, 1998; Cooper, 1999, 2005; Weedon, 2010). Other countries include Czech Republic with 1–1.5 m^2/pe (Vymazal & Kröpfelová, 2011), Germany with 1.6 m^2/pe (Olsson, 2011), Greece with 1–1.5 m^2/pe (Stefanakis & Tsihrintzis, 2012), and Canary Islands with 1.5 m^2/pe (Vera, Martel, & Márquez, 2013) as reported by Stefanakis et al. (2014).

With regard to treatment of other contaminants, apart from the traditional ones like BOD, COD, SS, etc., other pollutants found in wastewater including both organic and inorganic, have been shown to be better treated with VFCWs in comparison to HFCW systems. In their study to compare the removal efficiency between VFCWs and HFCWs in treating landfill leachate in Turkey, Yalcuk and Ugurlu (2009) revealed that vertical-flow systems removed heavy metals including Cr, Cu, Zn, Pb, and Ni present in the leachate efficiently in comparison to horizontal-flow systems. Furthermore, in Vietnam, a tropical country, Konnerup et al. (2011) assessed the

potentiality of HFCW and VFCW systems in improving the quality of the degraded river water as a result of pollution from aquaculture practices which lead to the eutrophication of the receiving water courses. The authors concluded that the vertical-flow wetland systems have a higher potential to remediate the fish pond effluents with minimal environmental negative impact than horizontal-flow wetland systems. Similarly in Vienna, Canga et al. (2011) reported that their VFCW systems were better in eliminating nitrogen than the horizontal wetland systems when they investigated the removal rates of different constructed wetland designs in Boku University after 4 years of operation.

Recently, some publications on municipal wastewater treatment studies also suggested that VFCW systems should be preferred in terms of water quality improvement over horizontal systems. For instance, Pandey et al. (2013) compared the performance of the two systems in treating municipal wastewater in Nepal to assess their treatment efficiency. They stated that vertical-flow systems did better than the horizontal-flow ones after a 7-month assessment. Furthermore, in their long-term study of 3 years, Abou-Elela et al. (2013) reported that VFCW systems were the preferred option compared to HFCWs because they were demonstrated to be more effective in removing the wastewater pollutants treated in the municipal sewage than the latter.

With regard to choice of either VFCWs or HFCWs in terms of clogging (a phenomenon referring to the blockage of substrate media pores in constructed wetland systems, leading to hydraulic conductivity reduction, substrate permeability and ponding of wastewater on the media in the worst case subsequently affecting the full performance of these systems) few studies have assessed their suitability. In their review, Knowles et al. (2011) compared the vertical and horizontal constructed wetland systems in terms of clogging susceptibility and found that horizontal-flow tertiary treatment systems in the UK are more prone to clogging issues in comparison to vertical-flow systems in France as a result of hydraulic loading rates,

hence the vertical-flow systems are the preferred choice in France. Therefore, the authors concluded that for both the systems to operate effectively, the hydraulic and solid loading rate has to be considered in their design. Comparison of these systems emphasized that both hydraulic loading rate and solids loading rate need to be considered when designing systems to operate robustly, i.e. hydraulic overloading makes horizontal-flow tertiary treatment systems in the UK more susceptible to clogging problems than vertical-flow primary treatment systems in France. Moreover, considering that absence of oxygen is prevalent in HFCWs (Vymazal, 2014) and high oxygenation in VFCWs (Hua et al., 2013, 2014; Song et al., 2015), which counteracts clogging, HFCWs, can be considered more prone to clogging than VFCWs. However, many publications have shown that clogging phenomenon is a very complex problem and not well understood in both HFCWs and VFCWs (Turon et al., 2009; Pedescoll et al., 2011; Fu et al., 2013; Hua et al., 2014; Song et al., 2015).

2.13 Summary

This chapter describes the historical development of constructed wetland systems and presents the early concepts of the technology. It also covers the discussion on wetland composition, types, removal mechanisms and numerical modelling. Furthermore, the chapter talks about petroleum hydrocarbon components and their attenuation in wetland systems. Diesel, heavy metals, and other contaminants removal are also explained. Lastly, the chapter closes with elucidation on essential values of wetlands to humans and the ecosystem environment, and preference of vertical-flow wetland systems over horizontal-flow systems.

CHAPTER 3

METHODOLOGY

3.1 Overview

The methodology used in conducting this experimental research is discussed generally in this chapter. The chapter is further divided into five sections. Sections 3.1and 3.2 introduce the chapter and layout of the experimental CWs respectively. Furthermore, composition and design of the model vertical-flow wetlands set-up used in conducting this research is explained in this section. Mode of operation of the wetland systems and the method of analysing water quality parameters is described in section 3.3 and 3.4 while the clogging test and modelling is explained in section 3.5. Petroleum hydrocarbon selection, determination, risk assessment, and completion are stated in sections 3.6, 3.7, 3.8, and 3.9 respectively. Statistical analysis used to interpret the data is described in section 3.10. The research limitations are elucidated in section 3.11 and lastly a summary of the chapter is given in section 3.12.

3.2 Experimental set-up in the greenhouse

Ten laboratory-scale vertical-flow CWs were constructed from Pyrex tubes with an inner diameter of 19.5 cm and a height of 120 cm (Figure 3.1). All filters have the same dimensions including diameter and were filled with siliceous (minimum of 30%) pea gravel up to a depth of 60 cm (Figure 3.2) and planted with Phragmites australis (Cav.) Trin. ex Steud. (Common Reed) to investigate treatment performance of different filters in terms of aggregate size, hydraulic and contaminant loading rate, contact time, resting time and the nature of wastewater and inert particles deposition on the evolution of clogging. Dead macrophyte plant material was harvested in winter and returned to the corresponding wetland filters by placing it on top of the litter zone (Sani et al., 2013a; Sani et al., 2013b). The main outlet valve was located at the bottom of each constructed wetland system.

Figure 3.1 Laboratory set-up of the vertical-flow constructed wetlands

The systems are located within a greenhouse on top of the roof of the Newton Building of The University of Salford, Greater Manchester, UK. Note that the two filters in the middle are not in operation. They are essentially controls receiving clean water.

(a) **(b)**

Figure 3. 2: substrate used for the construction of the wetland systems in the green house (a) pea gravels used for filters 3 to 10 and (b) pea gravels used for filters 1and 2

Eight further valves (used to test for clogging) were located on the sidewall of each wetland column. The sidewall valves were located at heights of 10, 20, 30, 40, 45, 50, 55 and 60 cm from the bottom of each column (Figure 3.3).

The preliminary treated urban wastewater used for the inflow water was obtained from the Davyhulme Sewage works, one of the largest wastewater treatment plants in Europe (http://en.wikipedia.org/wiki/Davyhulme), operated by the water company United Utilities in Greater Manchester. Fresh wastewater was collected approximately once per week, and was stored and aerated by standard aquarium air pumps in a cold room before use. The wastewater quality was highly variable, and comprised domestic and a small amount of industrial wastewater as well as surface water runoff. Furthermore, Aqua Medic Titan chillers (Aquacadabra, Barnehurst Road, Bexleyheath, UK) were used to keep the temperature of the below-ground part of the wetland systems at about 12°C. This temperature simulates the temperature of the upper earth layer where the root system of the wetland plants of a real treatment system would be.In order to simulate a one-off diesel fuel (100% pure; no additives) spill, 130 g (equivalent to an inflow concentration of 20 g/l) of diesel fuel (100% pure; no additives) was poured into Filters 1, 3and 7, and into one of the two control column (Control A) on 26 September 2013 (Table 3.1). The fuel was obtained from a petrol station operated by Tesco Extra (Pendleton Way, Salford, UK).

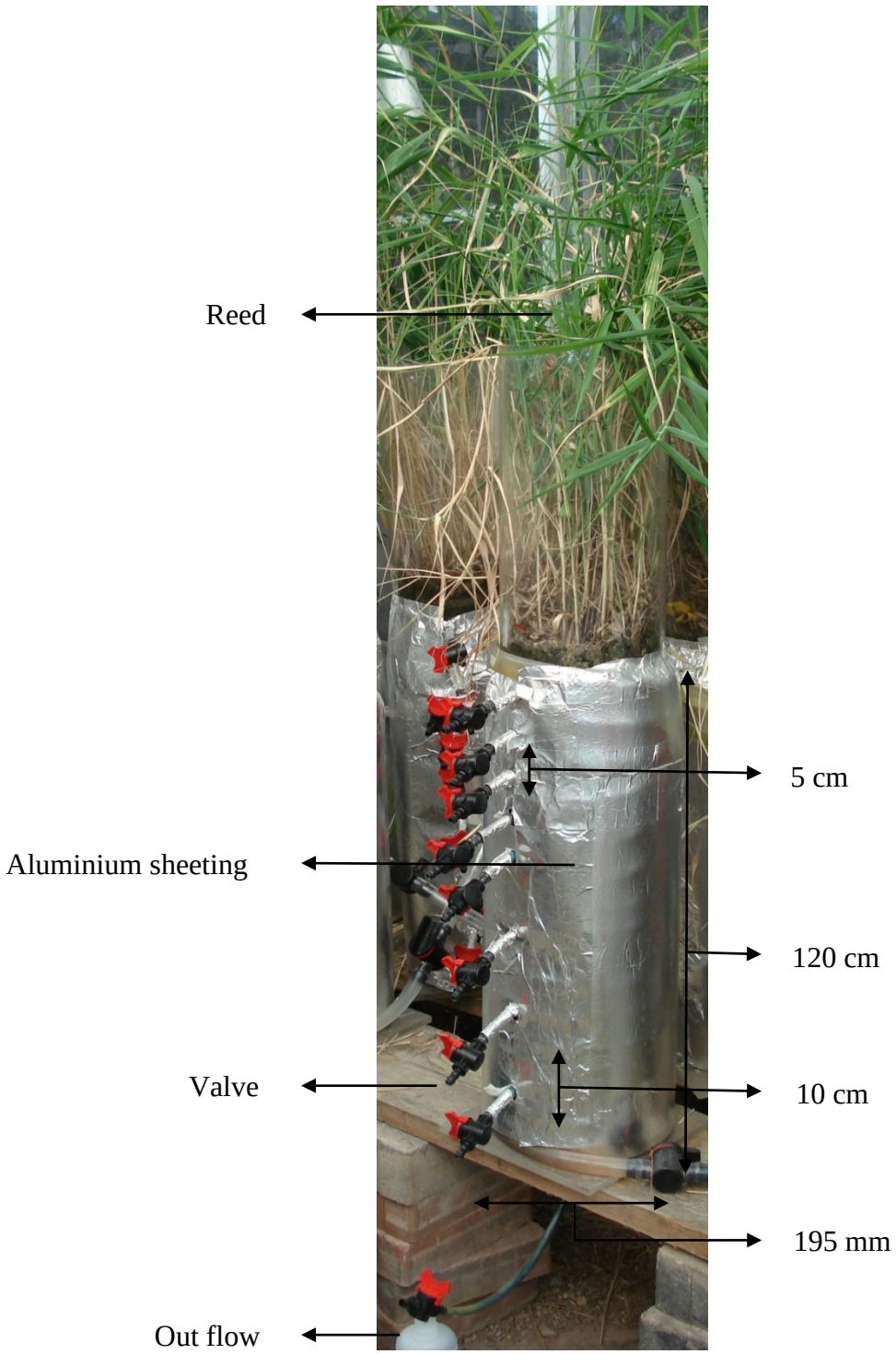

Figure 3.3: A picture of constructed wetland filter in the green house

Table 3.1 indicates an overview of the experimental set-up used in the study to test the impact of four variables. Filters 1 and 2 compared to Filters 3 and 4 test the influence of a larger aggregate diameter.

Table 3.1: Experimental set-up used in the study

Wetland filters	Design and/or operational variable			
	Aggregate diameter	Contact time	Resting time	Chemical oxygen demand
	(mm)	(h)	(h)	(mg/l)
Filters 1 and 2	20	72	48	138.9
Filters 3 and 4	10	72	48	138.9
Filters 7 and 8	10	72	48	272.9
Filter 9	10	36	48	138.9
Filter 10	10	36	24	138.9
Control A	10	72	48	2.1
Control B	10	72	48	2.1

Filters 7 and 8 compared to Filters 3 and 4 check the impact of a higher loading rate. The application of a lower contact rate is tested if Filter 9 is compared with Filters 3 and 4. Finally, a lower resting time is the difference between Filters 9 and 10. Undiluted wastewater was introduced to wetlands with a high loading rate (Filters 7 and 8). The remaining Filters 1 to 4 and Filters 9 and 10 received wastewater diluted with de-chlorinated tap water. All wetland columns received 6.5 l of inflow wastewater during the feeding mode (Table 3.1) Furthermore, all columns except 9 and 10 have replicates until the date when petroleum hydrocarbon was introduced (only the second replicates received diesel) because of lack of enough resurces and space to accommodate them.

Note: Annually treated approximate volumes of wastewater: Filters 1 to 8, 470 l/a (except 5 and 6, which receive tap water); Filter 9, 624 l/a; Filter 8, 858 l/a. Filters 2, 4 and 8 are replicates

for the most common operational scenarios. On 26 September 2013, 130 g of diesel was added to Filters 1, 3, 7 and Control A (formally Filter 5). Furthermore, the COD was used as the criterion to differentiate between low and high loads (Table 3.1). An inflow target COD of about 273 mg/l (usually between 122 and 620 mg/l) was set for wetlands with a high loading rate (Filters 7 and 8). The remaining Filters 1, 2, 3, 4, 9 and 10 received wastewater diluted with de-chlorinated tap water. The target inflow COD for these filters was approximately 139 mg/l (usually between 43 and 350 mg/l).

3.3 Mode of operation

The wetland system was designed to operate in batch flow mode. Two types of water were used for the study as the influent: raw wastewater and raw waste water mixed with tap water. Wetlands 7 and 8 are fed with raw wastewater without dilution while other filters are fed with raw waste water diluted with tap water except for controls that receive only tap water. The application is intermittent, as a batch through the surface of the filter, and then gradually percolates downward through the gravel drainage network to the bottom of the wetlands. Wetland columns received 6.5 L of inflow water during the feeding mode, which was different between several filters (Table 3.1). Columns 1–6 were sampled after 72 h contact time and then left to rest for 48 h, while columns 7 and 8 were sampled after 36 h contact time and left to rest for 48 and 24 h, respectively. This resting allows air to refill the wetland systems, and the next dose traps this air – leading to much improved oxygen transfer. The treatment technology generally relies on processes similar to those used extensively in gravel "filter beds", enhanced by the extensive rhizomatous root system of the reed plants (*Phragmites australis*) which can transfer limited quantities of oxygen into the surrounding media, stimulating bacterial communities.

3.4 Water quality analyses

During over 2-years of operation, water samples were collected from the wetland systems and routine obstruction observations, and water quality sampling were carried out according to American Public Health Association (APHA; 2005) unless stated otherwise to monitor clogging evolution and treatment performance, respectively. The spectrophotometer DR 2800 Hach Lange (www.hach.com) was used for standard water quality analysis for variables including chemical oxygen demand (COD), ammonia-nitrogen (NH_4-N), nitrate-nitrogen (NO_3-N), orthophosphate-phosphorus (PO_4-P) and suspended solids (SS). All of these parameters were tested using standard laboratory procedures and methods, and all analyses were completed within 24 h of sample collection.

COD and BOD_5 were measured by the potassium dichromate-boiling method and incubation method, respectively. The BOD_5 in this research was determined in all water samples with the OxiTop IS 12-6 system, a manometric measurement device, supplied by the Wissenschaftlich-Technische Werkstatten (WTW), Weilheim, Germany. The measurement principle is based on measuring pressure differences estimated by piezoresistive electronic pressure sensors. Nitrification was suppressed by adding 0.05 ml of 5 g^{-L} N-Allylthiourea (WTW Chemical Solution No. NTH 600) solution per 50 ml of sample water. COD analysis was performed with Palintest Tubetest with product code LCK 314. In the Palintest COD method, the water sample is oxidized by digesting in a sealed reaction tube with sulphuric acid and potassium dichromate in the presence of a silver sulphate catalyst. This reaction takes place in Palintest pre-prepared tubetest that contain the above required reagents. The amount of dichromate reduced is proportional to the COD. The absorbance of the COD samples was read with the Palintest Spectrophotometer model instrument. COD values were recorded as this model is a direct reading user-friendly photometer pre-programmed for Palintest water tests.

Nutrients were determined by automated precision colorimetry methods using a Palintest Tubetest with product code LCK 339 for nitrate, LCK 303 for ammonia and LCK 049 for otho-phosphate phosphorus. Nitrate was reduced to nitrite by cadmium and determined as an azo dye at 540 nm (using a Perstorp Analytical EnviroFlow 3000 flow injection analyzer) following diazotisation with sulfanilamide and subsequent coupling with N-1-naphthylethylendiamine dihydrocloride (Allen, 1974). Ammonia-N and ortho-phosphate-P were determined by automated precision colorimetry in all water samples from reaction with hypochlorite and salicylate ions in solution in the presence of sodium nitrosopentacyanoferrate (nitroprusside), and reaction with acidic molybdate to form a phosphomolybdenum blue complex, respectively (Allen, 1974). The coloured complexes formed were measured spectrometrically at 655 and 882 nm, respectively.

Turbidity, pH and SS were measured with a Turbicheck Turbidity Meter (Lovibond Water Testing, Tintometer Group, www.lovibond.com), sensION+Benchtop Multi-Parameter Meter (Hach Lange, Düsseldorf, Germany) and spectrophotometer DR 2800 respectively by placing composite water samples directly in to the instruments. These handy, easy to use, robust and waterproof instruments perform with low costs the most important parameters for wastewater monitoring. These meters come complete with sensors, calibration and maintenance solutions for measurement.

Temperature data for the first year of operation were recorded outside and in the shade at an official weather station in Woodford located south-east of Salford. The raw data were supplied by the UK Met Office (www.metoffice.gov.uk). Concerning the second and third year of operation, inside temperature measurements were performed by research group team members inside and outside the greenhouse.

For all the above parameters analysed above, calibration of the equipments used in their measurement was performed at and when necessary as instructed in their user manual. For

example, calibration is done with water before SS determination was conducted as prescribed in Hach Lange (www.hach.com) user manual, while turbidity and pH instruments are calibrated when the digital screen on their measuring equipments indicated the need for the calibration, and is also carried out in accordance with their user manual book (www.lovibond.com) and (Hach Lange, Düsseldorf, Germany) respectively.

3.5 Clogging tests and modelling

Overall hydraulic conductivity measurements to assess the severity of clogging were performed. The columns were regularly filled with wastewater to the top of the debris layer and subsequently emptied after a resting time of two hours to allow for air bubbles to escape from the media. The time taken to drain each column and the associated water volume captured were noted. The average hydraulic conductivity can be calculated by using Darcy's Law as shown in Eq. 5. Darcy's law is generally used to describe the water flow through porous media. For a constant flow rate, the hydraulic gradient between an upstream and downstream point must increase as clogging reduces the hydraulic conductivity. For the case of vertical-flow constructed wetlands, Darcy's law can be expressed as shown in E

$$K = \frac{Q \times L}{A_W \times (h_1 - h_2)} \tag{5}$$

Where K (m/d) is the saturated hydraulic conductivity of the media; Aw (m^2) is the wetted cross-sectional area of the reactor in the axial flow direction; Q (m^3/d) is the flow rate; L (m) is the distance between an upstream and a downstream point in the axial flow direction; h_1 (m) is the water depth at the upstream point; and h_2 (m) is the water depth at the downstream point.

$$u = -K \frac{\partial H}{\partial z} \tag{6}$$

Where u is the velocity of the flowing solution, K is the hydraulic conductivity, H is the water head, and z is the elevation.

As an indirect measure of clogging, SS samples were taken from the inflow wastewaters, the layer of debris on top of each filter, the eight sampling ports of each column and the outflows. The results were used as input data for the mathematical model, which was developed to analyse the major influences and sub-mechanisms involved in the clogging processes.

A project-specific model was used to simulate the evolution of the liquid-solid mixture consisting of light particles within the filter column. Three major mechanisms that affect the particle transport in the filter were taken into consideration, namely, diffusion, sedimentation and adsorption of particles. A one-dimensional model was created because of the linear structure of the filter column. The mathematical model describes mass transport of SS and associated sedimentation through the wetland column. Solutions to the model are obtained by using the finite element analysis performed for different time periods. Initial coefficients were chosen for sedimentation, damping, adsorption and diffusion. The model output was compared with the experimental data to get a better insight into the particle transport processes.

Meyer et al. (2014) undertook a comparative review of the scope and aims of a wide range of constructed wetland models. The Wang-Scholz model was the most suitable model for this case study, because it is the only suitable model concerned with solid deposition in vertical-flow wetlands treating urban wastewater. Furthermore, the model has already been previously calibrated for the same wetland system (Sani et al., 2013b) using earlier data.

The Wang-Scholz model (Eq. 7; Massoudieh et al., 2008) was applied to simulate both settling and aggregation mechanisms. By neglecting the effect of the varied sizes of SS and the lateral flow along the walls of the filters, Eq. 7 can be simplified to Eq. 8. The mechanical dispersion of SS can be described with Eq. 9.

$$\frac{\partial \varphi_i}{\partial t} = D\frac{\partial^2 \varphi_i}{\partial z^2} - (u - v_i)\frac{\partial \varphi_i}{\partial z} \pm \psi_i + \frac{q(z)}{A}\varphi_{i,in} \quad (7)$$

Where φ_i is the concentration of SS with particle sizes of range *i*, *t* is time, *D* is the dispersion coefficient, *z* is the vertical elevation position, *u* is the vertically flowing water velocity (positive upward), v_i is the fall velocity or settling velocity of the SS of particle size *i*, ψ_i is the source or sink term of the SS of particle size *I* and is used to take account of the effect of the aggregation or break-up of particles, *q*(*z*) is the lateral inflow to the wetland, *A* is the wetland area, and $\varphi_{i,in}$ is the concentration of the SS of size *i* in the lateral flow.

Applying the model described by Eq. 7 for vertical-flow constructed wetland systems, the particles sizes and the lateral flow are not accounted for. As a result, the effects of aggregation and break-up of SS particles will be reflected by the dispersion coefficient and the settling velocity. A modified mass conservation governing model is expressed in Eq. 8, which requires four sub-models for the dispersion coefficient *D*, the vertically flowing water velocity *u*, the fall velocity *v* and the source or sink term *R*.

$$\frac{\partial \varphi}{\partial t} = D\frac{\partial^2 \varphi}{\partial z^2} - (u - v)\frac{\partial \varphi}{\partial z} + \dot{R} \quad (8)$$

Where φ is the concentration of SS particles of all sizes within the treated wastewater, *t* is time, *D* is the dispersion coefficient, *z* is the vertical elevation position, *u* is the vertically flowing water velocity (positive upward), *v* is the fall velocity or settling velocity of the SS, and *R* is the source or sink term of suspended solids particles due to the physical adsorption on the surface of the pebbles within the constructed wetland bed.

$$D_{md} = \alpha \cdot u \quad (9)$$

Where D_{md} is the mechanical dispersion, α is the dispersivity, and u is the velocity of the flowing solution, which for continuous flow, may be estimated using Darcy's law (Eq. 6).

A relatively simple model for the settling velocity v of the SS is shown in Eq. 10. This model uses the hindered settling function described by Davis and Gecol (1994). A popular hindered settling function is shown in Eq. 11 (Richardson & Zaki, 1954). The empirical parameter n in Eq. 11 may have the value 5.1 (Rowe & Babcock, 2007).

$$v_i = w_0^i f_i \tag{10}$$

Where v is the settling velocity of a particle with size i, w^i_0 is the terminal settling velocity of an isolated particle of size i, and f_i is the hindered settling velocity.

$$f_i = (1-\varphi)^n \tag{11}$$

Where f_i is the hindered settling velocity, φ is the total particle fraction or concentration, and n is an empirical parameter. To solve Eq. 8, the value of R must be calculated. Suspended solids within wastewater provide surface area to adsorb dissolved substances. Adsorbed biomass located on aggregates promotes the aggregation of particles. A particle adsorbed onto a pebble surface may provide the nucleus site for subsequent biomass growth. The growth of biomass will provide further surface area for more particle adsorption. The Monod reaction kinetic rate has been widely used to model the biomass growth in wetlands (Langergraber, 2007; Soleimani et al., 2009). In this work, Eq. 12 relates the particle absorption to biomass growth. Using Eq. 2 to describe biomass growth, Eq. 12 can be written as:

$$\dot{R} = -M_T q_m \frac{\varphi}{\varphi_s + \varphi} \tag{12}$$

Where *R* is the source or sink term of suspended solids due to the physical adsorption on the surface of the pebbles within the constructed wetland bed, *MT* is the biomass concentration, q_m is the maximum growth rate, φ is the total particle fraction or concentration, and φ_s is a constant, the particle concentration in wastewater when the growth rate is the half of the maximum value q_m.

The model introduced above has been applied to simulate the SS sedimentation processes within the experimental wetland filters. Values obtained from the above literature have been used for parameters where no measurements were available. Moreover, appropriate assumptions regarding the boundary conditions, which are subject to underlying mechanisms and the operation of the filters, have been made.

3.6 Petroleum hydrocarbon selection

Diesel was used as a model petroleum hydrocarbon to assess the removal of low water solubility hydrophobic organic compounds and was chosen for the following reasons:

- It is a fuel used everywhere in the world, particularly in industry and has turned into one of the most frequent organic pollutants in the environment as a result of the increase in technological development (Albaldawi et al., 2013a), and is toxic and detrimental to human health (Moreira et al., 2011). Therefore, diesel is of major concern owing to its toxicity and carcinogenicity effects.
- It is part of a group of compounds that contribute the most to the formation of photochemical ozone and secondary organic aerosols (SOAs), increasing global warming (Hu et al., 2008).
- It is a known carcinogen and harmful organic compound, and may cause serious environmental problems to the ecosystems even in small concentrations (Benmaamar & Bengueddach, 2007).

- It has a lower rate of volatilization than other types of fuels such as kerosene and gasoline (Truax, Britto, & Sherrard, 1996), thus assessment of microorganisms could be explored correctly.
- Traditional treatment technologies used by the petroleum and water industries such as hydro cyclones, coalescence, flotation, centrifuges and various separators are not efficient concerning the removal of dissolved organic components of hydrocarbons including diesel in the dissolved water phase (Lin & Mendelssohn, 2009) but are effective in heavy hydrocarbons removal (Eke & Scholz, 2008).

3.7 Petroleum hydrocarbon analysis

TPHs were determined by gas chromatography and flame ionization by Exova Health Sciences (Hillington park, Glasgow, UK) according to their own accredited "TPH in Waters (with Aliphatic/Aromatic Splitting) Method" (Exova Health Sciences, 2014), which is accredited to the British Standard (BS) method BS EN ISO IEC 17025 by the United Kingdom Accreditation Service and compatible with the International Organization for Standardization (ISO) standards (e.g., ISO17025), BS method BS DD 220 1994, and American Standard methods (United States Environmental Protection Agency (USEPA) Method 3510C and USEPA SW846 Method 8015).

In order to assess the natural volatilization process in the wetland filters, 500 ml of pure diesel was poured into an open round container of 10 cm diameter, and kept in the greenhouse to mimic the natural volatilization process of the simulated diesel spill wetland filters. Another container with 500 ml diesel was kept in a laboratory fume cupboard for comparison.

3.8 Risk assessment

Diesel fuel, a hydrocarbon containing different forms of organic compounds such as aromatic and saturated, is usually harmful and carcinogenic. Considering this, a risk assessment was required before the beginning of the experiment. The risk assessment was carried out using the

University of Salford's Control of Substances Hazardous to Health Regulations (COSHH) and Product Safety Data Sheet (PSDS) forms. These forms document the risk assessment and safe work systems information related to the hazardous properties of the substances used in the research. The procedures governing the application of the hazardous substances (diesel) in the experimental research were listed in order to ensure that the research was carried out with minimum risk to health of the research students or other people that may be affected. Furthermore, directives were stated to ensure safety in each step of the research including the types of materials which needed to be used such as clothes to be worn in the laboratory or greenhouse. The research student was also trained and advised with regard to the health risks associated with possible exposure routes such as inhalation, absorption via the skin and oral ingestion when working with hazardous substances like diesel.

3.9 Risk assessment completion for activities involving hazardous substances

After reading the COSHH assessment code of practice, the risk assessment forms were completed and their content delivered to the users of the hazardous substances and their acceptance was obtained and recorded in the appropriate declaration section. A brief description of the work was addressed in the assessment as shown below:

- Safe storage of the hydrocarbon (diesel) in a secure and suitable storage place, such as in a laboratory cupboard, when not in use.
- Preparation of the petroleum hydrocarbon (diesel) in a fume cupboard.
- Transportation of the prepared solution from the fume cupboard to the wetland filters in the greenhouse in an air tight container that is securely sealed.
- Pouring of the diesel from the container into the different experimental filters.
- Analysis of treated wastewater effluent.
- Removal and disposal of treated wastewater through the recognized chemical waste stream.

In addition to above assessment, we ensured that Chemical Safety Information Sheet (CSIS) was obtained from the supplier. Furthermore, we made sure that where the substance (diesel) is spilled out as a result of the activity, its hazardous properties and exposure routes were checked with special caution regarding the following:

- The substance or group of substances to be used, or produced, in the above activity were named and listed in the Hazardous substances (HS) form. Where the substance presents an inhalation hazard and has been assigned an Occupational Exposure Limit (OEL), caution was taken and the OEL stated.
- Each of the substances was classified according to one, or both, of the following categories: toxic or harmful.

The risk assessment was carried out at the Peel building of the School of Environmental and Life Sciences (Public Health Department).

3.10 Data analysis

After data collection, data were subjected to a normality test before validation and subsequent analysis. Because of high variability, the data were not normally distributed even after transformations with transformers such as arc sine, square root, log, etc. and as a result, easy statistical tools that will fit the abnormal distributed data such as non-parametric tools were sought and applied. Microsoft Excel (www.microsoft.com) was used for the general data analysis. The non-parametric Mann-Whitney U-test was computed using IBM SPSS Statistics Version 20 and used to compare the medians of two (unmatched) samples since virtually all sample data (even after data transformation) were not normally distributed, so that an analysis of variance could not be applied.

3.11 Limitations of the experimental research

In this study, despite the fact that the experimental constructed wetlands used are not comparable to large scale systems used in industries, some studies performed based on similar

wetland columns (Babatunde et al., 2011; Sani et al., 2013a; Sani et al., 2013b; Al-Isawi et al., 2014; Almuktar et al., 2015a) were reported to demonstrate results applicable to field scale and therefore accepted by the scientific community.

The wetlands assessed in this experimental study are in the greenhouse under semi-controlled environments and cannot be compared with other wetlands in real field situations. However, the results of the research can serve as a model to be used in the design and up-scaling of new wetlands to be operated in different climates. Furthermore, considering that wetlands in real life situations utilize a large land area coupled with abundant natural energy inputs to build-up a self-maintaining structure, which will provide favourable environment for various types of microorganisms as a result of its diverse microenvironments, the wetland set-up used in this study could not represent the actual requirement of the enormous land area involved in actual field scale. Moreover, actual large constructed wetlands may serve as a home to many types of different animals which will have an effect on the processes occurring in the wetland which are not considered in these small wetlands.

As a result of lack of enough resources and space to accommodate the required number of replicates needed for this experimental research, some of the wetland filters like filters 1 and 2, 3 and 4, 5 and 6, and 7 and 8 are replicated while filters 9 and 10 are not. Furthermore, one out of these each replicates received petroleum hydrocarbon 2 years after the start of the experiment in the former filters. As a result, the wetland systems used in this experiment could not represent the actual wetland set-ups with full replication though many studies were conducted using the same wetland columns (Sani et al., 2012; Almuktar and Scholz, 2015) and accepted by scientific community.

Direct clogging assessment could not also be possible within the small experimental vertical-flow wetlands because doing so could destroy the systems. Furthermore, the experimental wetlands are being used continuously by both under and post graduate researchers for their projects. As a result, we used indirect means of measuring clogging such as hydraulic

conductivity and suspended solids concentration in different side pots of the wetland filters and the outflow waters to estimate clogging evolution.

3.12 Summary

This chapter explains the wetlands set-up used for the experimental research including their design and operation. It also describes the different types of analyses carried out for various water quality parameters, clogging and modelling. Furthermore, petroleum hydrocarbon selection is elucidated in addition to risk assessment undertaken while conducting the research. Finally, the method of data analysis used to interpret the results and limitations of the research are explained.

CHAPTER 4

ASSESSMENT OF OVERALL TREATMENT PERFORMANCE

4.1 Overview

This chapter explains overall summary results and discussion of the key water quality parameters and its relation to clogging for the period of study. Section 4.1 introduces the chapter itself while 4.2 discusses the overall treatment performance of the wetland filters including influent and effluent water quality. Furthermore, in this section, statistical differences between the variables are also presented. Assessment of clogging based on water quality variables and the simulation model are interpreted in 4.3 and 4.4 sections respectively while summary of the chapter is shown in section 4.5.

4.2 Overall performance of wetland filters and their relationship with clogging

4.2.1 Inflow water quality

Average mean inflow concentrations of water quality parameters monitored in a wetland operation for about three years of operation were analysed in this section. The raw domestic waste water quality was examined, tabled and interpreted. Table 4.1 shows the overall inflow water quality before dilution for the four experimental periods. The wastewater quality was highly variable, and was comprised mainly of domestic wastewater and surface water runoff. The industrial wastewater component was minimal. The data variability was relatively high, reflecting the use of real urban wastewater (Sani et al., 2013b; Al-Isawi et al., 2014; Al-Isawi et al 2015). The COD was used as the criterion to differentiate between low and high loads. An inflow target COD of about 273 mg/l (usually between 122 and 620 mg/l) was set for wetlands with a high loading rate (Filters 7 and 8). The remaining Filters 1 to 4 and Filters 9 and 10 received wastewater diluted with de-chlorinated tap water. The target inflow COD for these filters was approximately139 mg/l (usually between 43 and 350 mg/l).

Table 4.1: Overall inflow water quality of the raw domestic waste water mixed with urban runoff (before dilution) from 27/06/11 to 30/04/14

Parameter	Unit	Number	Mean	Minimum	Maximum	Standard deviation
First experimental phase 27/06/11 to 25/09/11						
COD	mg/l	34	356.5	90.0	620.0	185.88
NH_4-N	mg/l	15	21.6	3.0	36.1	9.78
NO_3-N	mg/l	10	0.9	0.2	1.7	0.56
PO_4-P	mg/l	20	9.0	5.7	13.6	2.61
SS	mg/l	18	209.6	54.0	400	138.01
Second experimental phase 26/09/11 to 25/09/12						
COD	mg/l	116	267.7	125.0	620.0	118.25
BOD	mg/l	28	103.3	42.0	150.0	32.60
NH_4-N	mg/l	84	45.2	14.9	86.0	22.66
NO_3-N	mg/l	72	3.4	0.3	14.4	3.86
PO_4-P	mg/l	80	17.0	2.4	40.0	10.88
SS	mg/l	98	77.0	2.4	294.8	68.73
TBD	mg/l	36	303.4	90.0	450.0	103.54
Third experimental phase 26/09/12 to 25/09/13						
COD	mg/l	58	239.8	122.0	390.0	91.39
BOD	mg/l	117	151.2	40.0	330.0	67.83
NH_4-N	mg/l	60	59.1	0.1	131.8	23.44
NO_3-N	mg/l	54	7.7	0.3	20.9	5.94
PO_4-P	mg/l	50	13.0	2.9	32.1	9.11
SS	mg/l	132	232.25	18.0	760.0	177.47
TBD	mg/l	98	120.7	6.7	457.0	94.43

Table 4.1 (cont)

Fourth experimental phase 26/09/13 to 30/04/14						
Parameter	Unit	Number	Mean	Minimum	Maximum	Standard deviation
COD	mg/l	16	246.1	112.0	360.0	93.02
BOD	mg/l	68	133.3	10.0	360.0	98.45
NH_4-N	mg/l	22	32.4	3.1	70.0	24.06
NO_3-N	mg/l	20	3.7	0.4	14.0	4.32
PO_4-P	mg/l	18	16.3	9.3	27.6	5.77
SS	mg/l	70	143.9	27.0	474.0	113.13
TBD	mg/l	65	89.5	12.3	391.0	86.30

Note: only filters 7 and 8 received the above water characteristics. The remaining filters received diluted waste water (i.e. 1 part de-chlorinated tap water and 1 part wastewater).

The undiluted influent concentrations for COD, BOD, ammonia-nitrogen, nitrate-nitrogen, ortho-phosphate-phosphorus, SS and turbidity were 278 mg/l, 129 mg/l, 40 mg/l, 16 mg/l, 14 mg/l, 166 mg/l and 171 NTU (nephelometric turbidity units), respectively.

4.2.2. Comparison of outflow water qualities

4.2.2.1 Comparison of oxygen demand variables (COD and BOD)

COD and BOD are used to evaluate organic matter concentration in constructed wetlands. Their removal mechanisms include aerobic, anaerobic, adsorption, filtration, and microbial metabolism (Karathanasis et al., 2003; Song et al., 2006; Stefanakis et al., 2014). Overall performance with regard to water quality parameters is shown in Tables 4.2, 4.3, 4.4 and 4.5 including the chemical and biochemical oxygen demand variables. The result shows that all filters demonstrated relatively good COD removal (excluding the time close to the start-up and period of petroleum hydrocarbon contamination) as depicted in Figure 4.1. This can be explained by the fact that, close to the start-up period, the biological activity necessary for microbial degradation takes time to develop and as such, the treatment efficiency can be

expected to improve after microbial acclimatization (Scholz, 2006, 2010; Sani et al., 2012; Sani et al., 2013a; Sani et al., 2013b, Al-Isawi et al., 2014; Al-Isawi et al 2015; Almuktar et al., 2015a) while during the period of petroleum hydrocarbon contamination, the sharp decline in COD removal efficiency (Table 4.5 and Figure 4.1) could be attributed to the artificial contribution of petroleum hydrocarbon to the COD of the inflow water poured in the wetland filters. This has been confirmed by Al-Isawi et al. (2014) and Al-Isawi et al. (2015) who in their recent study, reported a sharp increase in COD outflow concentrations of their wetland filters when subjected to diesel spill as a result of the indirect increase of the COD in the inflow wastewater.

Table 4.2: Comparison of outflow water quality and air temperature for first experimental phase (27/06/11 to 25/09/11)

Parameter	Unit	Number	Mean	Rem (%)	Minimum	Maximum	Stdev
Filter 1 and 2							
COD	mg/l	11	81.0	55.1	34.8	135.0	33.07
NH_4-N	mg/l	7	7.9	44.6	0.8	21.8	6.83
NO_3-N	mg/l	5	0.6	-17.4	0.4	1.3	0.26
PO_4-P	mg/l	10	2.0	58.1	0.2	3.3	0.88
SS	mg/l	9	25.7	75.1	6.0	85.0	23.02
Filter 3 and 4							
COD	mg/l	10	75.6	58.1	36.4	120.0	29.45
NH_4-N	mg/l	7	11.1	22.0	3.8	30.9	8.06
NO_3-N	mg/l	5	0.4	12.2	0.3	0.6	0.10
PO_4-P	mg/l	10	2.0	56.7	1.0	3.2	0.75
SS	mg/l	9	27.2	73.7	7.0	120.0	33.31
Filter 7 and 8							
COD	mg/l	11	167.9	53.0	84.2	452.0	104.66
NH_4-N	mg/l	7	28.0	-29.7	12.9	62.8	17.58
NO_3-N	mg/l	5	0.7	20.0	0.5	0.9	0.19

Table 4.2 (cont)

Parameter	Unit	Number	Mean	Rem (%)	Minimum	Maximum	Stdev
PO_4-P	mg/l	10	4.6	48.5	2.4	7.4	1.75
SS	mg/l	8	35.6	83.0	9.0	75.0	18.29
Filter 9							
COD	mg/l	11	102.3	43.4	58.2	255.0	55.55
NH_4-N	mg/l	7	18.2	-27.9	8.2	35.8	9.60
NO_3-N	mg/l	4	0.5	0.8	0.4	0.6	0.12
PO_4-P	mg/l	11	2.5	45.6	1.8	3.3	0.56
SS	mg/l	10	33.6	67.5	9.0	85.0	27.73
Filter 10							
COD	mg/l	13	345.5	54.2	90.0	620.0	185.88
NH_4-N	mg/l	9	11.7	18.0	6.5	18.7	4.35
NO_3-N	mg/l	6	0.3	29.7	0.2	0.5	0.09
PO_4-P	mg/l	13	2.2	53.1	1.4	3.9	0.66
SS	mg/l	14	18.6	81.8	7.0	45.0	10.97
AT	^oC	28	14.9	n/a	11.1	18.1	2.10

n/a, not applicable.

Table 4.3: Comparison of outflow water quality and air temperature for second experimental phase (26/09/11 to 25/09/12)

Parameter	Unit	Number	Mean	Rem (%)	Minimum	Maximum	Stdev
Filter 1 and 2							
COD	mg/l	52	56.7	57.5	5.0	135.0	29.22
BOD	mg/l	13	36.2	30.5	15.0	70.0	18.11
NH_4-N	mg/l	37	9.1	75.4	0.3	25.3	5.90
NO_3-N	mg/l	34	1.1	14.4	0.0	7.8	1.81
PO_4-P	mg/l	40	3.0	69.7	0.0	6.0	1.36
SS	mg/l	49	7.3	83.8	0.2	52.0	10.16
TBD	NTU	15	1.7	99.0	0.0	5.1	1.87
Filter 3 and 4							
COD	mg/l	50	56.6	59.9	6.0	165.0	33.73
BOD	mg/l	13	32.2	38.1	10.0	65.0	19.96

Table 4.3 (cont)

Parameter	Unit	Number	Mean	Rem (%)	Minimum	Maximum	Stdev
NH_4-N	mg/l	37	6.9	81.3	0.1	31.2	5.68
NO_3-N	mg/l	34	1.6	-28.1	0.0	11.9	2.64
PO_4-P	mg/l	40	2.6	73.1	0.0	6.5	1.25
SS	mg/l	49	6.1	86.4	0.0	60.0	11.01
TBD	NTU	15	1.2	99.3	0.0	3.9	1.28
Filter 7 and 8							
COD	mg/l	50	89.9	66.4	20.5	240.0	48.95
BOD	mg/l	13	41.5	59.8	0.0	130.0	37.44
NH_4-N	mg/l	41	15.7	65.3	0.9	35.8	8.65
NO_3-N	mg/l	37	3.1	9.9	0.0	21.2	4.53
PO_4-P	mg/l	40	4.5	73.5	0.0	8.2	2.25
SS	mg/l	47	11.1	85.6	1.4	84.0	15.95
TBD	NTU	15	4.9	98.4	0.0	12.1	3.57
Filter 9							
COD	mg/l	57	59.1	56.2	10.9	158.0	31.04
BOD	mg/l	14	23.2	55.4	0.0	70.0	17.05
NH_4-N	mg/l	44	5.6	84.9	0.0	14.8	3.61
NO_3-N	mg/l	47	4.2	-232.8	0.0	14.6	4.00
PO_4-P	mg/l	47	2.5	74.3	0.0	4.9	1.16
SS	mg/l	55	7.2	84.2	0.0	50.0	9.85
TBD	NTU	19	2.5	98.6	0.0	9.1	2.77
Filter 10							
COD	mg/l	59	54.8	59.3	11.8	128.0	27.29
BOD	mg/l	14	16.1	69.1	0.0	55.0	14.03
NH_4-N	mg/l	46	5.5	85.1	0.2	13.7	3.41
NO_3-N	mg/l	45	3.3	-164.7	0.0	12.7	3.47
PO_4-P	mg/l	48	2.3	76.2	0.0	4.8	1.17

Table 4.3 (cont)

Parameter	Unit	Number	Mean	Rem (%)	Minimum	Maximum	Stdev
SS	mg/l	60	6.0	86.8	0.0	40.0	8.51
TBD	NTU	19	2.1	98.8	0.0	6.8	2.18
AT	°C	141	12.7	n/a	0.8	28.0	4.20

AT, air temperature, ^{O}C, degrees celcius, n/a not applicable.

The BOD removal efficiencies generally improved over time (Tables 4.2, 4.3, 4.4 and 4.5). This improvement can be attributed to the development of a mature biomass adjusted to the environmental boundary conditions of the wetland system (Sani et al., 2013a; Sani et al., 2013b; Al-Isawi et al., 2014; Al-Isawi et al., 2015; Almuktar et al., 2015a).

With regard to clogging of the wetland systems due to organic matter particles within the period of this research, none of the filters have shown any sign of clogging (Tables 4.7 and 5.6 of chapter 5) restricting their treatment performance efficiency even before and during the period of petroleum hydrocarbon pollution (Tables 4.2, 4.3, 4.4 and 4.5) despite the fact that numerous studies have revealed that accreted organic matter (COD and BOD) in form of solids overtime may lead to media clogging by obstructing wastewater penetration through the substrate pores thereby reducing the retention time of the wastewater and pollutants removal capacity (Tanner &Sukias, 1995; Nguyen, 2000). The plausible reason for this good performance observed in the current study, could be attributed to gradual microorganism's ability to biodegrade the accumulated organic matter particles overtime in addition to the intermittent aeration that might have enhanced the biodegradation of the pollutants and averting aggregation of the organic particles in the substrate media, subsequently leading to within bed clogging abatement of the wetland systems. This phenomenon has been confirmed by Al-Isawi et al. (2015) and Almuktar et al. (2015a) lately in their research. However, there was a prescence of litter zone formed on top of each filter (Table 5.6 of chapter 5) which was partly due to both the high

strength and SS load of the wastewater, but mainly due to the dead macrophyte plant material that was harvested in winter and returned to the corresponding wetland filters confirming data by Sani et al. (2013a), Sani et al. (2013b) and Al-Isawi et al. (2014).

The overall mean COD and BOD removal efficiencies for Filters 7 and 8 (both with high loading rate) were higher than those for Filters 3 and 4 (both with low loading rate). This difference was statistically significant as shown in Table 4.6, which summarizes an assessment of the statistically significant differences between outflow water quality variables of different filters using the non-parametric Mann-Whitney U-test. The opposite is the case for the equivalent COD loads. A comparison of Filters 3 and 4 with Filter 9 gives insight into the effect of contact time on the treatment performance. The overall removal efficiencies were rather similar. The COD and BOD removals for Filters 1 to 4 were also similar, indicating that aggregate size may not matter.

Table 4.4: Comparison of outflow water quality and air temperature for third experimental phase (26/09/12 to 25/09/13)

Parameter	Unit	Number	Mean	Rem (%)	Minimum	Maximum	Stdev
Filter 1 and 2							
COD	mg/l	29	64.4	49.3	39.1	117.0	17.07
BOD	mg/l	61	37.2	51.2	0.0	105.0	21.70
NH_4-N	mg/l	29	11.6	69.4	0.4	31.2	9.90
NO_3-N	mg/l	27	2.1	47.8	0.1	9.7	2.83
PO_4-P	mg/l	25	3.0	56.7	1.4	6.2	1.27
SS	mg/l	65	7.8	93.3	0.0	46.0	8.80
TBD	NTU	50	6.9	89.5	0.0	44.0	8.35
Filter 3 and 4							
COD	mg/l	29	57.9	54.4	23.2	95.1	13.82
BOD	mg/l	61	33.8	55.6	0.0	150.0	25.72
NH_4-N	mg/l	29	8.4	77.8	0.2	28.0	8.21

Table 4.4 (cont)

Parameter	Unit	Number	Mean	Rem (%)	Minimum	Maximum	Stdev
NO_3-N	mg/l	27	3.0	26.4	0.1	10.5	3.15
PO_4-P	mg/l	25	2.5	62.8	1.3	6.0	0.97
SS	mg/l	65	5.8	95.0	0.0	26.0	5.28
TBD	NTU	50	6.5	90.1	0.0	63.4	8.53
Filter 7 and 8							
COD	mg/l	29	81.3	66.0	32.1	126.0	20.92
BOD	mg/l	60	48.6	67.9	5.0	245.0	35.59
NH_4-N	mg/l	29	25.0	57.7	1.2	62.2	20.06
NO_3-N	mg/l	28	6.0	9.9	0.1	24.8	6.15
PO_4-P	mg/l	25	4.2	68.0	1.0	7.8	1.72
SS	mg/l	65	8.6	96.3	0.0	48.0	9.04
TBD	NTU	50	10.9	90.9	0.0	65.4	13.36
Filter 9							
COD	mg/l	26	55.8	56.1	16.8	78.3	15.37
BOD	mg/l	65	28.28	63.0	0.0	75.0	16.13
NH_4-N	mg/l	32	8.0	79.0	0.4	27.2	6.69
NO_3-N	mg/l	30	5.6	-37.1	0.3	17.5	4.40
PO_4-P	mg/l	26	3.0	56.5	1.7	6.8	0.94
SS	mg/l	69	7.3	93.8	0.0	49.0	9.56
TBD	NTU	56	6.9	89.5	0.0	30.9	7.93
Filter 10							
COD	mg/l	27	62.4	50.9	24.9	88.2	12.73
BOD	mg/l	73	27.9	63.4	0.0	68.0	17.30
NO_3-N	mg/l	29	4.9	-18.8	0.1	17.5	4.69
PO_4-P	mg/l	24	3.1	54.1	1.7	8.4	1.32
SS	mg/l	87	8.8	92.4	0.0	39.0	10.03
TBD	NTU	61	8.6	87.0	0.0	53.1	10.93
AT	°C	306	13.1	n/a	1.0	29.0	3.5

AT, air temperature, ^{O}C, degrees celcius, n/a not applicable.

During the period of petroleum hydrocarbon contamination, the overall mean COD and BOD removal efficiencies for Filter 7 with high loading rate were higher than those of Filter 3 with low loading rate (though both have low efficiencies). The statistical difference was insignificant, implying that the loading rate may also not matter (Table 4.6).

Figure 4.2 shows the distribution of the biochemical oxygen demand variable, BOD. The traditional UK standard for BOD removal from secondary wastewater is 20 mg/l and 25 mg/l for sensitive and less sensitive (e.g., many coastal discharges) areas, respectively (Royal Commission on Sewage Disposal, 1915). Regarding sensitive watercourses, Filters 1, 3 and 7 Regarding sensitive watercourses, Filters 1, 3 and 7 before hydrocarbon contamination were 63, 60, and 61 times non-compliant, while after the contamination, they were 16, 17 and 16 times respectively.

Table 4.5: Comparison of outflow water quality and air temperature for last experimental phase (26/09/13 to 30/04/14)

Parameter	Unit	Number	Mean	Rem (%)	Minimum	Maximum	Stdev
Filter 1							
COD	mg/l	9	108.0	12.3	36.7	346.0	94.44
BOD	mg/l	34	22.4	66.2	0.0	70.0	16.34
NH_4-N	mg/l	11	6.6	63.8	1.1	29.0	7.99
NO_3-N	mg/l	10	0.5	76.2	0.2	0.9	0.26
PO_4-P	mg/l	8	3.3	61.2	1.1	10.8	3.09
SS	mg/l	36	12.4	81.8	0.0	52.0	11.59
TBD	NTU	36	10.3	81.4	3.5	28.4	6.23
Filter 2							
COD	mg/l	5	48.2	61.0	18.4	93.2	35.28
BOD	mg/l	33	13.9	79.0	0.0	36.0	8.82
NH_4-N	mg/l	11	6.2	65.7	0.5	18.6	6.21
NO_3-N	mg/l	9	3.4	-68.5	0.3	8.6	3.24

Table 4.5 (cont)

Parameter	Unit	Number	Mean	Rem (%)	Minimum	Maximum	Stdev
PO_4-P	mg/l	8	3.1	63.7	1.9	5.2	1.34
SS	mg/l	36	7.1	89.6	0.0	49.0	11.38
TBD	NTU	36	6.4	88.4	2.0	46.1	6.84
Filter 3							
COD	mg/l	9	115.2	6.7	53.2	332.0	87.18
BOD	mg/l	34	25.7	61.4	0.0	98.0	19.31
NH_4-N	mg/l	11	4.3	76.6	0.7	16.9	4.82
NO_3-N	mg/l	10	0.5	77.7	0.1	1.1	0.36
PO_4-P	mg/l	8	3.0	64.7	0.9	9.5	2.80
SS	mg/l	36	13.0	81.0	0.0	54.0	11.21
TBD	NTU	36	11.0	80.2	2.9	30.7	6.39
Filter 4							
COD	mg/l	5	42.1	65.9	10.4	90.6	36.72
BOD	mg/l	31	13.0	80.5	0.0	40.0	10.33
NH_4-N	mg/l	10	4.9	73.2	0.1	15.2	4.81
NO_3-N	mg/l	9	0.6	-73.4	0.1	1.0	0.41
PO_4-P	mg/l	8	3.1	63.2	1.7	5.7	1.39
SS	mg/l	36	8.0	88.4	0.0	50.0	12.55
TBD	NTU	36	6.6	88.1	1.9	27.3	6.25
Filter 7							
COD	mg/l	9	160.7	34.7	60.5	356.0	113.06
BOD	mg/l	32	25.7	80.7	0.0	78.0	19.98
NH_4-N	mg/l	11	14.1	56.5	5.7	61.5	15.89
NO_3-N	mg/l	10	1.1	71.6	0.2	2.8	0.81
PO_4-P	mg/l	8	4.6	71.6	1.0	13.6	4.19
SS	mg/l	37	14.8	89.7	0.0	68.0	15.25
TBD	NTU	36	11.4	87.2	4.1	35.8	7.84
Filter 8							
COD	mg/l	5	61.7	75.0	27.8	139.0	47.47

Table 4.5 (cont)

Parameter	Unit	Number	Mean	Rem (%)	Minimum	Maximum	Stdev
BOD	mg/l	33	18.0	86.5	0.0	44.0	13.60
NH_4-N	mg/l	10	12.9	60.1	0.5	54.2	15.62
NO_3-N	mg/l	9	3.5	6.9	0.2	17.9	5.57
PO4-P	mg/l	8	4.2	74.3	2.0	13.5	3.86
SS	mg/l	37	8.4	94.2	0.0	41.0	10.31
TBD	NTU	36	7.0	92.2	2.1	27.0	6.34
Filter 9							
COD	mg/l	6	39.5	68.0	14.1	106.0	36.56
BOD	mg/l	39	13.9	79.0	0.0	42.0	9.80
NH_4-N	mg/l	11	4.8	73.4	0.1	20.7	7.96
NO_3-N	mg/l	9	4.3	-114.8	0.4	10.4	3.47
PO_4-P	mg/l	8	3.2	61.8	1.8	7.8	2.05
SS	mg/l	40	2.2	96.8	0.0	13.1	3.23
TBD	NTU	39	3.3	94.1	1.8	13.3	1.98
Filter 10							
COD	mg/l	6	47.6	61.5	18.3	102.0	34.2
BOD	mg/l	46	14.7	77.8	0.0	36.0	8.71
NH_4-N	mg/l	10	2.8	84.42	0.09	17.4	5.2
NO_3-N	mg/l	9	3.7	-88.2	0.4	10.8	4.38
PO_4-P	mg/l	7	3.5	58.3	1.8	7.5	2.28
SS	mg/l	49	2.6	96.1	0.0	16.0	3.58
TBD	NTU	51	3.9	92.8	1.8	12.7	2.14
Control A							
COD	mg/l	8	72.1	ned	6.9	312.0	99.31
BOD	mg/l	33	13.0	ned	0.0	42.0	10.58
NH_4-N	mg/l	11	1.8	ned	0.0	4.6	1.71
NO_3-N	mg/l	10	0.6	ned	0.0	2.0	0.61

Table 4.5 cont)

Parameter	Unit	Number	Mean	Rem (%)	Minimum	Maximum	Stdev
PO_4-P	mg/l	8	3.2	ned	1.8	7.8	2.05
SS	mg/l	36	6.5	ned	0.0	39.0	9.70
TBD	NTU	36	4.9	ned	2.2	21.3	4.46
Control B							
COD	mg/l	5	35.1	ned	3.5	90.3	36.80
BOD	mg/l	34	8.1	ned	0.0	34.0	8.59
NH_4-N	mg/l	10	2.0	ned	0.1	6.9	1.95
NO_3-N	mg/l	9	0.6	ned	0.1	1.0	0.41
PO_4-P	mg/l	7	3.5	ned	1.9	7.6	2.28
SS	mg/l	36	2.7	ned	0.0	16.0	3.58
TBD	NTU	36	5.3	ned	1.2	27.5	5.58
AT	°C	158	11.3	n/a	2.0	20.0	3.8

AT, air temperature, ^{O}C, degrees celcius ned not enough data, n/a not applicable

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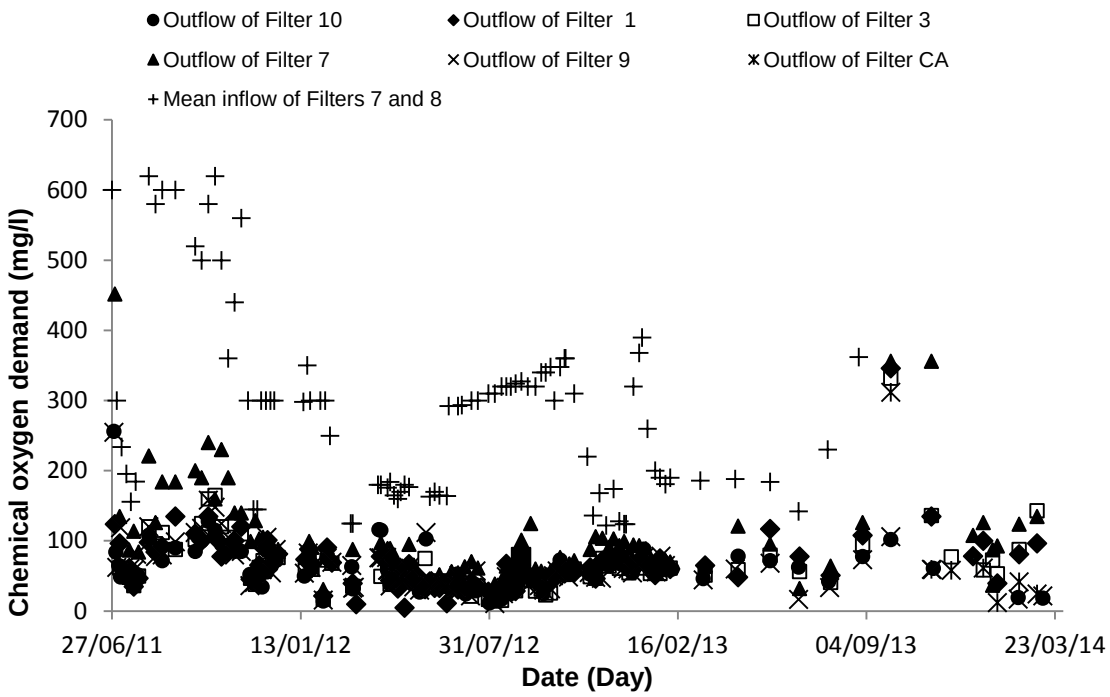


Figure 4. 1: Overall variations in COD for inflow and outflow

With regard to Filters 2, 4, 8, 9 and 10, they were 65, 66, 75, 64 and 68 times non-compliant respectively. In comparison, Filters 1, 3 and 7 before and after petroleum hydrocarbon contamination, were 51, 44, 42 and 13, 12 and 10 times non-compliant for less sensitive areas, respectively. The relative poor performance of Filters 7 and 8 can be explained by the high inflow loading rates. However, Filters 9 and 10 perform relatively well due to a low loading rate.

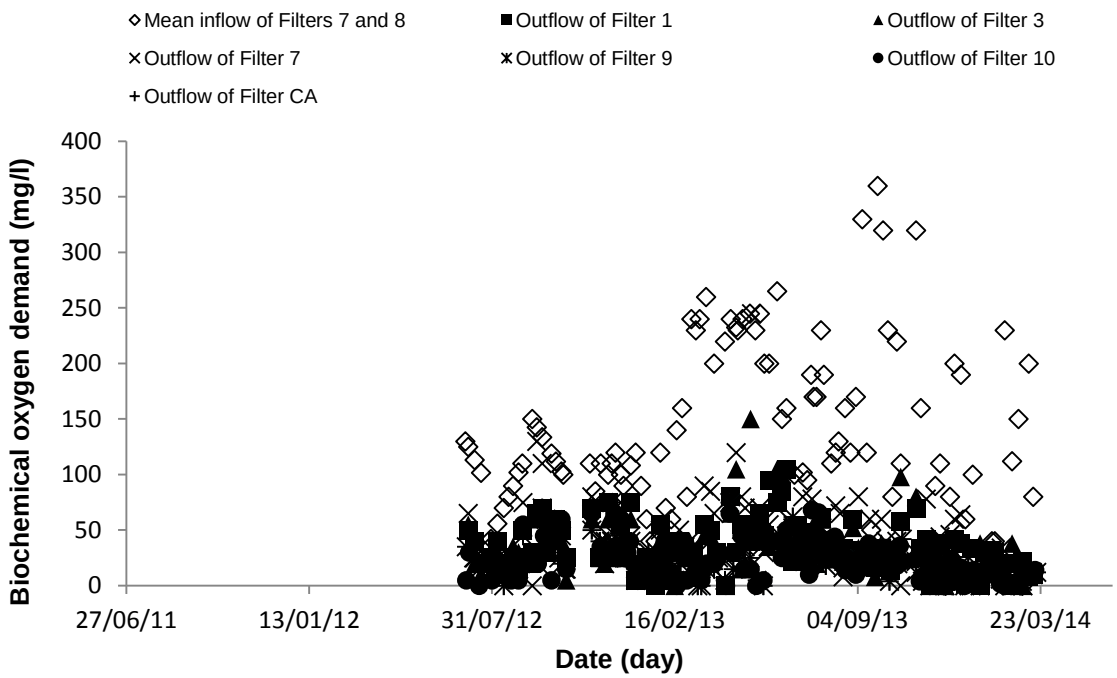


Figure 4.2: Overall variations in BOD5 for inflow and outflow

4.2.2.2 Comparison of nutrients variables

Removal of nutrients in constructed wetlands is imperative because of their environmental and health implications. Receiving water courses become eutrophic when they receive large amounts of these nutrients subsequently promoting enormous plant growth that leads to the depletion of oxygen in the receiving water environment. Nitrogen removal in constructed wetlands is primarily by microbial nitrification and denitrification.

In the nitrification process, ammonia is oxidized largely to nitrate. As a result of the oxidation of ammonia to nitrate, nitrate is reduced to gaseous nitrogen by the denitrification process However, the removal is insufficient without active and passive aeration, mainly because of inadequate oxygen available for aerobic biodegradation (Scholz, 2010; Saeed & Sun, 2011; Fan et al., 2012; Fan et al., 2013; Vymazal, 2014; Song et al., 2015).

Removal of ammonia in constructed wetlands is a complex process (Vymazal, 2007) and involves series of chemical, physical and biological reactions within the wetland media.

However, several publications have demonstrated that high aeration (Fan et al., 2012; Fan et al., 2013; Liu et al., 2014), which promotes the build-up of ammonia oxidizing bacteria leads to high ammonia nitrification (Zhi et al., 2015).

In this research, Tables 4.2, 4.3, 4.4 and 4.5 above show comparisons of the overall nutrients outflow water quality in different experimental phases, while Table 4.6 summarizes an assessment of the statistically significant differences between outflow water quality variables of different filters using the non-parametric Mann-Whitney U-test.

The overall reduction rates of ammonia-nitrogen were relatively high, partially due to temperatures usually being above 15°C during the warm seasons (Tsihrintzis et al., 2007) and aeration (Fan et al., 2012; Fan et al., 2013; Liu et al., 2014; Zhi et al., 2015). The removal efficiencies were low if undiluted wastewater was used. Table 4.6 indicates that inflow water high in COD results in a statistically significant (P<0.05) difference between the mean daily values of Filters 7 and 8 in comparison to the mean daily values of Filters 3 and 4. However, aggregate size, resting time and contact time were not important for the overall ammonia-nitrogen removal.

A typical standard by UK regulations (UK Government, 1994) was not set for ammonia-nitrogen that would relate to the treatment system used in this experiment. However, a realistic guideline threshold value concerning secondary wastewater treatment in this experiment would be 20 mg/l (Sani et al., 2013b). Filters 1 to 8 were 9, 10, 5, 5, 64, 33, 6 and 6 times non-compliant, respectively before petroleum hydrocarbon contamination. After the contamination however, Filters 1 and 7 were one-times non-compliant while Filter 3 complied (Figure 4.3). In comparison, a common standard set by environment agencies for the second nitrogen variable, nitrate-nitrogen, concerning secondary treatment of wastewater is 50 mg/l (Sani et al., 2013b). All filters were compliant.

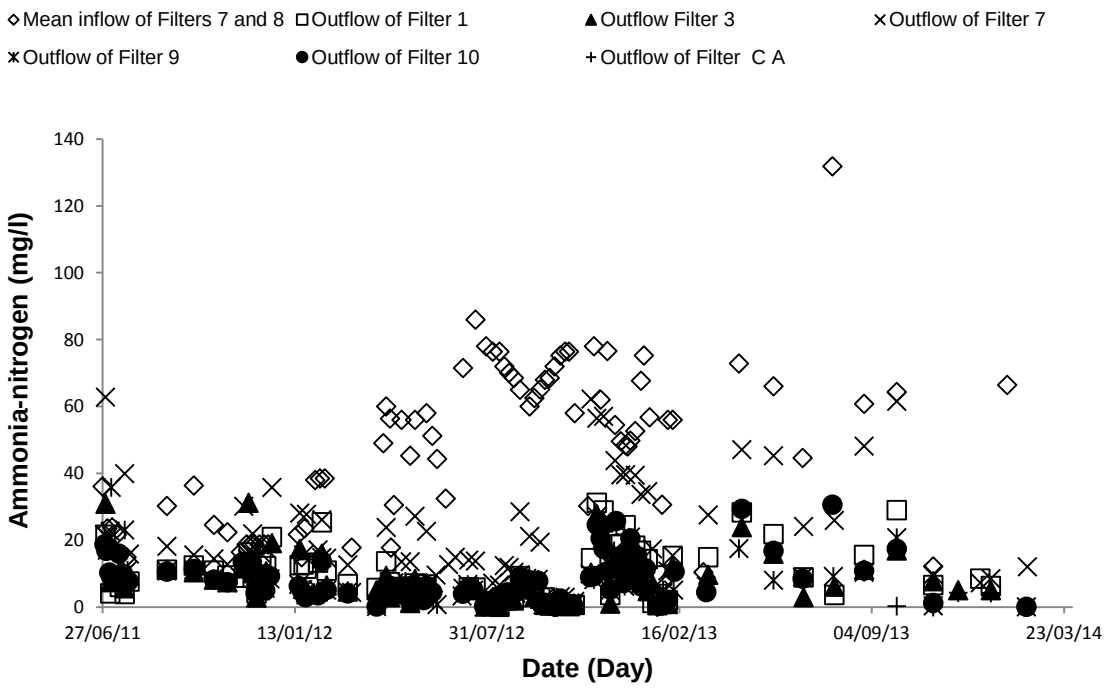


Figure 4.3: Overall variations for ammonia-nitrogen in the inflow and outflow

Denitrification in wetlands has been reported in many publications (Scholz, 2010; Ji et al., 2012; Ji et al., 2013) and positively correlated with organic carbon supply from macrophytes (Bastviken et al., 2005; Souza et al., 2008; Shen et al., 2015) and temperature (Stefanakis & Tsihrintzis, 2012; Mietto et al., 2015). Although the nitrate-nitrogen concentration in the inflow was relatively low (Table 4.1), the outflow concentrations were relatively high for all filters (Tables 4.2, 4.3, 4.4 and 4.5). Only Filters 3, 4, 7, 8, 9 and 10 had positive removal efficiencies (though very small). In contrast, other filters functioned as sources for nitrate-nitrogen in the first experimental phase. In the second and third experimental phases, however, Filters 1, 2, 7, 8 and Filters 1, 2, 3, 4, 7 and 8 had low positive removal efficiencies respectively. In contrast, the outflow concentration of other filters served as a source for nitrate-nitrogen. The negative removal efficiencies for nitrate-nitrogen indicated that denitrification was likely to be only a minor removal mechanism (Kayranli et al., 2010; Sani et al., 2013a; Sani et al., 2013b; Al-Isawi et al., 2014). However, the necessary conditions for denitrification to occur (e.g., anoxic

environment and presence of easily bio-degradable organic carbon) were not directly monitored within the entire small wetlands, because this would have been too destructive (Sani et al., 2013b).

The nitrate-nitrogen reduction was higher for smaller compared to larger aggregate sizes. Long contact and resting times, and a low COD loading were also positive (Table 4.2). The mean overall daily nitrate-nitrogen values of Filters 3 and 4 compared to Filter 9 were statistically significantly different from each other (Table 4.6).

Overall performance of wetland filters regarding the nutrients variables shows that all the nutrients were relatively removed from all filters though removal was better in filters without petroleum hydrocarbons compared to those filters contaminated with except for nitrate-nitrogen which showed better removal in the latter. The overall removal efficiency was relatively high with no significant difference between the filters (Table 4.6). The nitrogen removal could be attributed to biodegradation processes of diesel spills in Filters 1, 3 and 5 which reduced the availability of nutrients to microorganisms and *P. australis*. However, as the biodegradation of diesel progresses, small amounts of remaining petroleum hydrocarbon promote the growth of some microorganisms, which increase the degradation rate (Al-Isawi et al., 2014; Al-Isawi et al., 2015).

Literature has shown that there is a direct relation ship between accumulated total nitrogen and total carbon inform of organic matter accumulation overtime in CWs and leads to a significant media clogging and declined treatment performance (Tanner, 1994; Nguyen, 2000). However, in this research, though direct measurement of clogg matter (organic and inorganic solids) was not conducted because doing that will destroy the experimental wetlands, indirect measurement of clogging by measuring SS outflow concentration from the wetland's main outlet and side wall valves, and hydraulic conductivity (Tables 4.7 and 5.6 of chapter 5) was performed. The result from the wetland's performance efficiency in both pre and post petroleum hydrocarbon

pollution (Tables 4.2, 4.3, 4.4 and 4.5) of this research, indicated that none of the wetland systems was negatively affected with regard to within bed filter pore clogging as a result of high nitrogen compounds removal, improved permeability and low outflow SS concentration recorded from the wetland filters (Tables 4.7 and 5.6 of chapter 5). The explanation behind this could be due to high biodegradation activity by nitogen oxidizing bacteria stimulated by bed oxygenation during resting times of the wetland induced by the intermittent operation mode. Several authors have indicated that a resting operation could effectively improve porosity and the hydraulic conductivity after some days of the resting period and improve treatment performance efficiency (Hua et al., 2014; Paing et al., 2015; Wu et al., 2015). However, the litter zone observed on top of each filter was partly due to both the high strength and SS load of the wastewater, but mainly due to the dead macrophyte plant material that was harvested in winter and returned to the corresponding wetland filters (Sani et al., 2013a; Sani et al., 2013b; Al-Isawi et al., 2014). Furthermore, petroleum hydrocarbon has been reported to supply energy for rhizomicrobes, thus increasing nitrogen degradation in the wetland systems leading to the observed high removal of the nitrogen compouds (Al-Baldawi et al., 2015; Al-Isawi et al., 2015) without filter clogging and negative impact on the systems porosity and hydraulic permeability (Al-Isawi et al., 2015; Song et al., 2015) confirming the data of the current study.

Removal mechanisms of phosphorus in constructed wetland systems have been reported to include plant uptake (Vymazal, 2011c, 2013a), microbial uptake and accretions in wetland media (Gikas & Tsihrintis, 2012), retention by wetland substrate and precipitation in water column (Gikas et al., 2007). Furthermore, several publications have shown that phosphorus is one of the most difficult pollutants to remove by constructed wetlands (Pant, Reddy, & Lemon, 2001; Fia et al., 2014; Vera et al., 2014).

In this study, the ortho-phosphate-phosphorus removal efficiencies ranged between 46 and 58%, 70 and 76%, 54 and 68% and 58 and 72% for all filters regardless of the loading rate in

first, second, third and fourth experimental phases respectively (Tables 4.2, 4.3, 4.4 and 4.5), which is surprising, considering that an overall statistically significant difference for COD has been noted (Table 4.6). Furthermore, aggregate size and resting time were not crucial parameters in terms of overall ortho-phosphate-phosphorus removal. This can be explained by the fact that phosphorus is usually present in particulate form, and does not dissolve well in filters that are not yet saturated by phosphorus or other compounds competing for adsorption sites (Scholz, 2006, 2010).

In CWs, phosphorus particles are attached to suspended solids and are removed due to settlement, adsorption and microbial consumption (Gikas & Tsihrintzis, 2012). However, the accumulation of these suspended solids via the adhesion of biofilms due to microorganism growth contributes to clogging (Hua et al., 2010; Zhao et al., 2009) consequently limiting the competitiveness and efficiency of the wetland systems. In this research, the overall wetland performance in removing the phosphorus after and before petroleum hydrocarbon pollution was relatively good in all filters without any negative sign of clogging and hydraulic conductivity (Tables 4.2, 4.3, 4.4, 4.5, 4.7 and 5.6 in chapter 5). This has been confirmed by Al-Isawi et al. (2014) and Al-muktar and Scholz (2015) who noted high phosphorus removal efficiency in their wetland systems without any within bed clogging of the filter media and attributed the better performance as a result of high aeration and microbial activity that promoted the high phosphorus biodegradation, porosity and hydraulic conductivity improvement. Nevertheless, as a result of both high strength and SS load of the wastewater, and dead macrophyte plant material that was harvested in winter and returned to the corresponding wetland filters, a litter zone accumulation on top of each filter was evident.

All filters performed insufficiently in terms of phosphorus removal compared to other key parameters such as COD and ammonia-nitrogen. Findings confirm those by several studies (Smith et al., 2006; Sani et al., 2013a; Al-Isawi et al., 2014) indicating that constructed

wetlands were not efficient in removing phosphate in Nordic countries, especially during prolonged high loading periods. The regulations (UK Government, 1994) set a value of 2 mg/l for total phosphorus for communities between 10,000 and 100,000 inhabitants. A threshold for ortho-phosphate-phosphorus that would relate to the treatment system discussed in this thesis does not exist. However, a realistic guideline threshold value for ortho-phosphate-phosphorus could be 1 mg/l (Sani et al., 2013b). Filters 1 to 8 were 71, 74, 71, 73, 72, 75, 83 and 82 times non-compliant, respectively from first to third experimental phases while petroleum hydrocarbon contaminated filters 1, 3 and 5 were all non-compliant after the contamination (Figure 4.4).

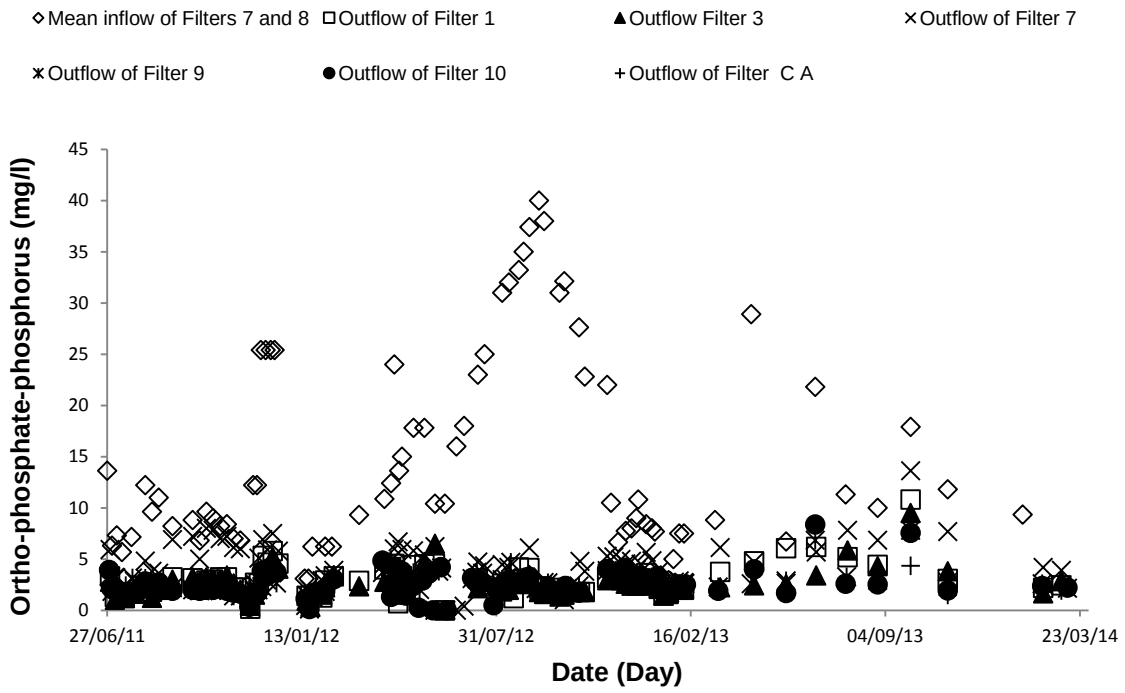


Figure 4.4: Overall variations for ortho-phosphate-phosphorus in the inflow and outflow

4.2.2.3 Comparison of particles

Although, a publication by Vymazal (2014) revealed that sedimentation, filtration, aggregation and surface adhesion are the primary removal mechanisms for suspended solids, several studies confirmed that solids and particulate matter removal are achieved (Kadlec & Knight, 1996;

Green et al., 1997; Leonard, 2000; ITRC, 2003; Garcia et al., 2010; Hua et al., 2013) via settling and sedimentation, adsorption, and microbial degradation in wetland systems.

The overall removal efficiencies for SS were high (Tables 4.2, 4.3, 4.4 and 4.5). A higher loading rate had a significantly (P<0.05) negative impact on the overall treatment performance before petroleum hydrocarbon contamination (Table 4.6). Suspended solids accumulated in the top part of the filters as a result of litter layer formation two years later, confirming findings by Hua et al. (2010), Scholz (2010) and Sani et al. (2013b). The presence of different aggregates did not seem to have an influence on solids retention, at least in the early stages of operation. Despite numerous publications relating clogging with SS accumulation in the wetland media and poor treatment performance of wetland systems, the current study result indicated that there was no evident of within bed clogging as a result of high SS removal efficiency of more than 80% observed in all filters even in the period after the systems are polluted with petroleum hydrocarbons (Tables 4.2, 4.3, 4.4, 4.5 and 4.7). This indicates that the observed SS concentration and hydraulic conductivity values were relatively low (Table 5.6 of chapter 5) and have not impacted negatively and restricted porosity, permeability and the overall treatment performance of the wetland systems,. The plausible reason for this could be, high solids biodegradation achieved as a result of high intermittent aeration during the operation mode that might have stimulated and enhanced the activity of the rhizomicrobes in the contaminants removal, confirming findings by Hua et al.(2014), Paing et al.(2015) and Song et al.(2015).

The traditional UK standard for SS removal from secondary wastewater is 30 mg/l (Royal Commission on Sewage Disposal, 1915). Overall, uncontaminated filters 1 to 8 were 8, 12, 4, 7, 14, 10, 9 and 13 times non-compliant, respectively. However, contaminated filters 1, 3 and 5 were 3, 4 and 5 times non-compliant accordingly after the contamination. More recently, the regulations (UK Government, 1994) have set a value of 35 mg/l. Uncontaminated filters 1 to 8

were 5, 9, 4, 7, 11, 10, 8 and 8 times non-compliant, respectively (Figure 4.5). However, authorities try to comply with the more stringent traditional guideline.

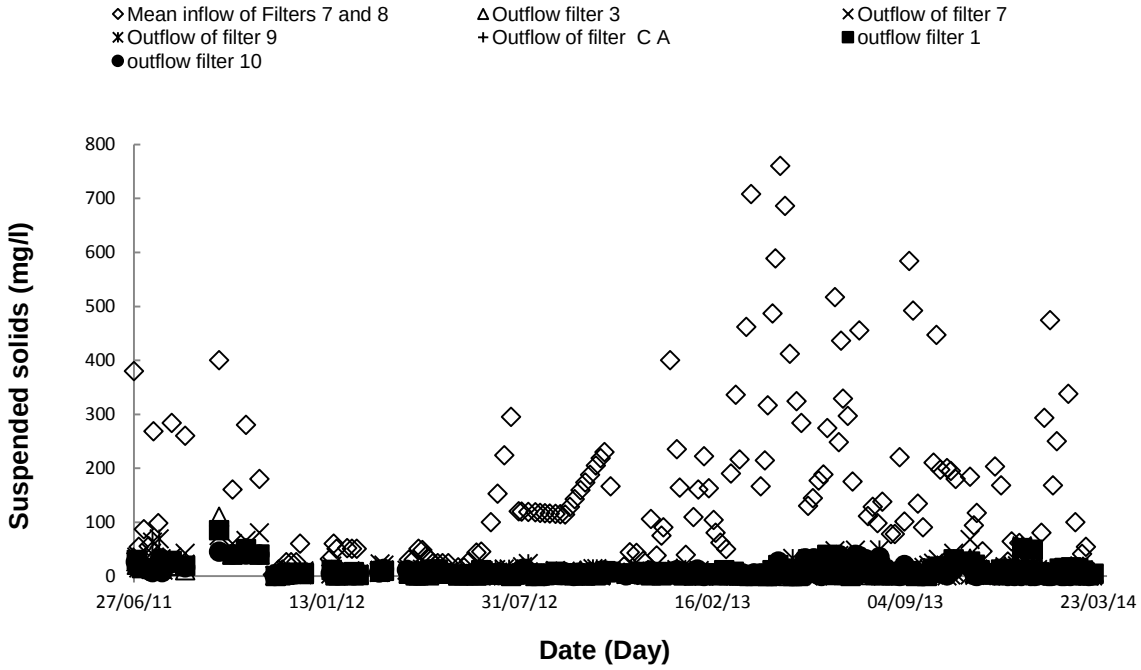


Figure 4.5: Overall variations for suspended solids in the inflow and outflow

Table 4.6: Overview of the statistically significant differences between outflow water quality variables of different wetland filters using the non-parametric Mann-Whitney U-test (27/06/11-30/04/14)

Parameter	Unit	Statistics	Aggregate diameter[a]	Contact time[b]	Resting time[c]	Chemical oxygen demand[d]
First to third experimental phase (27/06/11-25/09/13)						
Chemical oxygen demand	mg/l	*P-value*	0.355	0.526	0.804	<0.000
		h	0	0	0	1
Biochemical oxygen demand	mg/l	*P-value*	0.183	0.068	0.476	0.011
		h	0	0	0	1
Ammonia-nitrogen	mg/l	*P-value*	0.079	0.856	0.676	<0.000
		h	0	0	0	1
Nitrate-nitrogen	mg/l	*P-value*	0.237	<0.000	0.095	0.025
		h	0	1	0	1
Ortho-phosphate-phosphorus	mg/l	*P-value*	0.080	0.134	0.241	<0.000
		h	0	0	0	1
Suspended solids	mg/l	*P-value*	0.025	0.483	0.519	<0.000
		h	1	0	0	1
Turbidity	mg/l	*P-value*	0.832	0.983	0.543	0.031
		h	0	0	0	1
Parameter	Unit	*Statistics*	Aggregate diameter[e]	Contact time[f]	Resting time[g]	Chemical oxygen demand[h]
Fourth experimental phase (26/09/13-30/04/2014)						
Chemical oxygen demand	mg/l	*P-value*	0.895	0.025	0.423	0.200
		h	0	1	0	0
Biochemical oxygen demand	mg/l	*P-value*	0.554	0.001	0.472	0.520
		h	0	1	0	0
Ammonia-nitrogen	mg/l	*P-value*	0.200	0.224	0.972	0.002
		h	0	0	0	1
Nitrate-nitrogen	mg/l	*P-value*	0.406	0.001	0.691	0.049
		h	0	1	0	1
Ortho-phosphate-phosphorus	mg/l	*P-value*	0.462	0.345	0.817	0.294
		h	0	0	0	0
Suspended solids	mg/l	*P-value*	0.505	<0.000	0.184	0.978
		h	0	1	0	0
Turbidity	mg/l	*P-value*	0.454	<0.000	0.005	0.640
		h	0	1	1	0
Parameter	Unit	*Statistics*	Aggregate diameter[i]	Contact time[j]	Resting time[k]	Chemical oxygen demand[l]
Fourth experimental phase (26/09/13-30/04/2014)						
Chemical oxygen demand	mg/l	*P-value*	0.347	1.000	0.423	0.251
		h	0	0	0	0
Biochemical oxygen demand	mg/l	*P-value*	0.272	0.281	0.472	0.129
		h	0	0	0	0
Ammonia-nitrogen	mg/l	*P-value*	0.496	0.418	0.972	0.121
		h	0	0	0	0
Nitrate-nitrogen	mg/l	*P-value*	0.627	0.480	0.691	0.895
		h	0	0	0	0
Ortho-phosphate-phosphorus	mg/l	*P-value*	0.753	0.600	0.817	0.638
		h	0	0	0	0
Suspended solids	mg/l	*P-value*	0.991	0.001	0.184	0.649
		h	0	1	0	0
Turbidity	mg/l	*P-value*	0.275	<0.000	0.005	0.937
		h	0	1	1	0

[a]Comparison between the mean daily values of Filters 1 and 2, and the mean daily values of Filters 3 and 4
[b]Comparison between the mean daily values of Filters 3 and 4, and Filter 9
[c]Comparison between Filters 9 and 10
[d]Comparison between mean daily values of Filters 3 and 4, and mean daily values of Filters 7 and 8
[e]Comparison between the mean daily values of Filters 1 and 3
[f]Comparison between the mean daily values of Filters 3 and 9

[g]Comparison between Filters 9 and 10
[h]Comparison between mean daily values of Filters 3 and 7
[i]Comparison between the mean daily values of Filters 2 and 4
[j]Comparison between the mean daily values of Filters 4 and 9
[k]Comparison between Filters 9 and 10
[l]Comparison between mean daily values of Filters 4 and 8
Note: *P-value*, probability of obtaining a test statistic at least as extreme as the one that was actually observed, assuming that the null hypothesis is true; *h*, response indicator; if *h*=1, filters are statistically significantly different (*P-value* < 0.05) for the corresponding water quality parameter; if *h*=0, the difference is not significant

4.3 Performance assessment of filter clogging based on water quality variables

A review discussing clogging of vertical-flow wetland systems has been published by Knowles et al. (2011). The key operational parameters in terms of clogging were hydraulic and solids loading rate. With respect to this work, no significant differences in hydraulic conductivity were usually recorded for all filters. For water quality variables with high (i.e. above 100 mg/l; Table 4.2) overall mean inflow concentrations, Table 4.6 indicates that an elevated COD inflow load and a smaller aggregate size makes a significant difference in terms of overall COD and SS outflow concentrations in the first to third experimental phases while only a significant difference in contact time was noticed in the fourth phase (Table 4.6). The development of a litter zone on top of each filter was observed after over two years of operation in spring 2013. This was partly due to both the high strength and SS load of the wastewater, but mainly due to the dead macrophyte plant material that was harvested in winter and returned to the corresponding wetland filters. Most SS accumulated in the litter zone of all filters. These findings confirm results from previous studies (Hua et al, 2010; Scholz, 2010; Sani et al., 2013a; Sani et al., 2013b; Al-Isawi et al., 2014). Furthermore, the effluents were usually below the threshold value of 30 mg/l (traditional UK standard) for SS removal from secondary wastewater (Royal Commission on Sewage Disposal 1915). The removal efficiencies for SS were generally relatively high, particularly for the first three phases (Tables 4.2, 4.3 and 4.4) before the diesel spill. However, some effluent values during the set-up phase, where the filter biomass was immature, were far above 30 mg/l due to the release of fines associated with the aggregates and the in ability of the weak biofilm to retain solids originating from the

wastewater (Sani et al., 2013a; Al-Isawi et al., 2014). Table 4.6 indicates clearly that filters with petroleum hydrocarbon contamination showed elevated SS concentrations compared to those without. Furthermore, depending on the stage of biodegradation overtime, initially dying contaminated biomass and later on degraded diesel contributed to elevated SS and turbidity values within the filters (Table 4.5) as confirmed by Al-Isawi et al. (2014) and Al-Isawi et al. (2015). Concerning filter bed clogging evolution measured in terms of SS accumulation, none of the systems have shown any signs of serious within-bed clogging after over two years of operation even for the high rate Filters 7 and 8, which contrasts with the expectation of noticing clogging phenomena for this system by Sani et al. (2013a) and Al-Isawi et al. (2014). This justified the overall good treatment performance of the wetland systems in about 30 month period of operation in the current study without any serious substrate media clogging, reduced hydraulic conductivity and porosity. However, a very modest but statistically significant breakthrough of turbidity has been noticed for high rate filters (Tables 4.2, 4.3, 4.4 and 4.5).

4.4 Performance assessment of filter clogging using the simulation model

A comparison between the experimental mean seasonal SS accumulation profiles and the modelled profiles for the experimental wetlands is shown in Figures 4.7, 4.8, 4.9, 4.10 and 4.11. Serious clogging was neither observed nor modelled. Modelling performance was rather poor for the set-up period, adequate for the first 2 years after the set-up period, and very variable after the petroleum hydrocarbon spill. Overall, the modelling results of the SS sedimentation show that the clogging model was suitable particularly for Filters 1-8 after the set-up period and are in broad agreement with the experimental findings (Sani et al., 2013a) except for the litter zone that could not be modelled. The model referred to as the Wang-Scholz model was used to compare between measured and predicted values. This clogging model was particularly appropriate after the first experimental phase (Figures 4.7b, 4.7c, 4.8b, 4.8c, 4.9b and 4.9c) and before the introduction of petroleum hydrocarbon. However, the original model was not

designed to deal with petroleum hydrocarbon spills resulting in unforeseen SS contributions in the first place. Furthermore, in his review, Meyer et al. (2014) demonstrates that there are currently no specific models addressing this challenge.

Figure 4.6

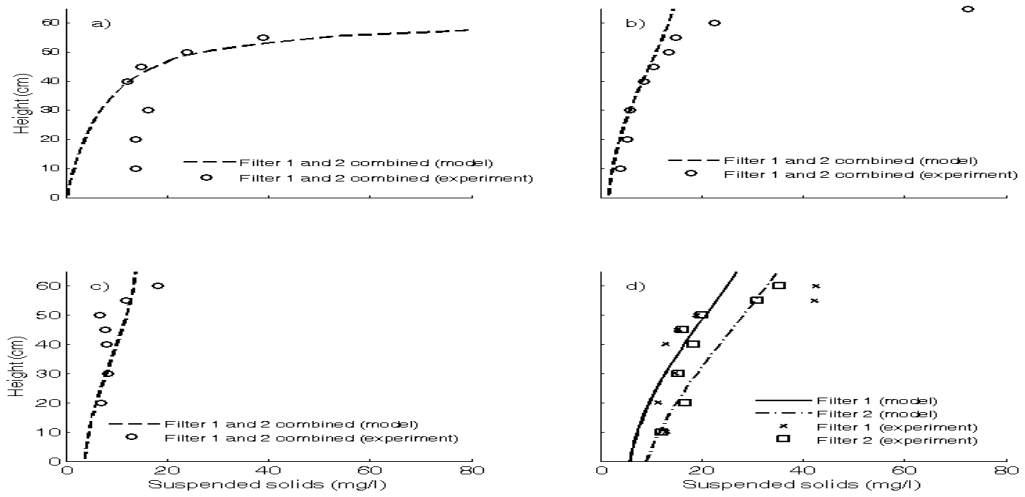
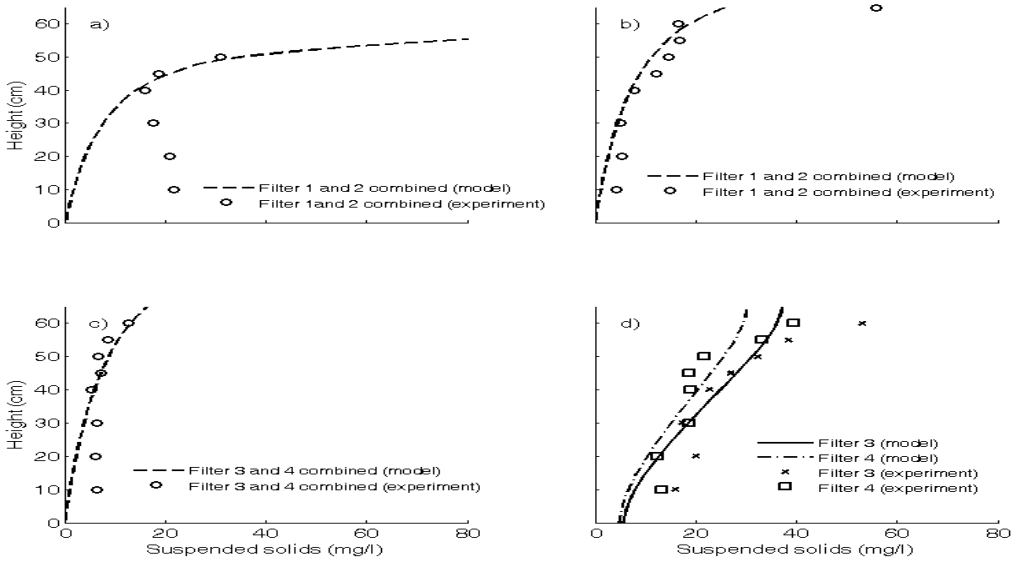


Figure 4.7



*Note that figures 4.6 to 4.10 have been published in Al-Isawi, R., Scholz, M., Wang, Y., & Sani, A. (2014). Clogging of vertical-flow constructed wetlands treating urban waste water contaminated with diesel spill. *Environmental Science Pollution Research*. doi: 10.1007/s11356-014-3732-8

Figure 4.6: Comparison between the measured and modelled distribution of suspended solids (SS) with depth within Filter 1 combined with Filter 2 after (a) set-up period, (b) first year after

set-up and (c) second year after the set-up, as well as at (d) the end of experiment for Filters 1 and 2 separately. Note that the value 86 mg/l for (a) has not been displayed. In Figure 4.7, (a) is a set-up period for Filters 3 and 4 combined, (b) first year after set-up and (c) second year after set-up, while at (d) the end of the experiment for Filters 3 and 4 separately.

From the beginning of the experiment in 2011, the litter layer was absent and the model explained reality well by simulating the mechanical dispersion of SS below the litter zone. In comparison, a litter layer associated with elevated SS values was formed later. A clear SS profile that decreases from the top to the bottom of all filters was evident. The profile can be explained by the maturation of the filter biomass retaining SS and not by a gradual increase in clogging of filter pores (Sani et al., 2013a; Sani et al., 2013b; Al-Isawi et al., 2014). The SS particle sedimentation process and its effect on clogging can be modelled for all wetland filters using equations introduced in sections 2.7 and 3.4 of chapters 2 and 3 respectively. A simulation model was applied to assess filter clogging predominantly based on SS accumulation within the wetland filters. Solids entrapment is classified as physical or mechanical clogging. Suspended solids are filtered and therefore retained by wetland media, debris and roots via attachment processes. Wastewater contains waste particles of different size and composition. As these particles build up within the filters, the efficiency of subsequent removal is reduced due to the decrease in pore space. Some particles are electro-statically attracted and stack onto each other, often forming dendrites. These dendrites block the pore space, thus increasing particle interception.

Figure 4.8

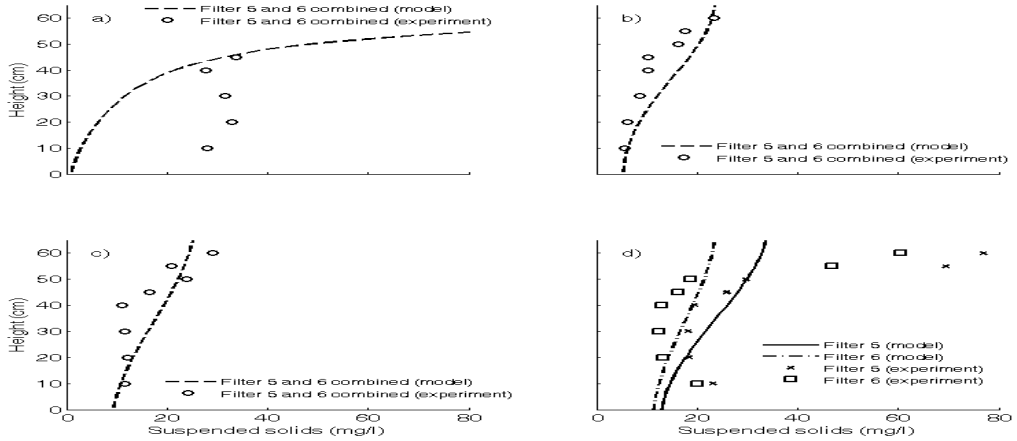


Figure 4.9

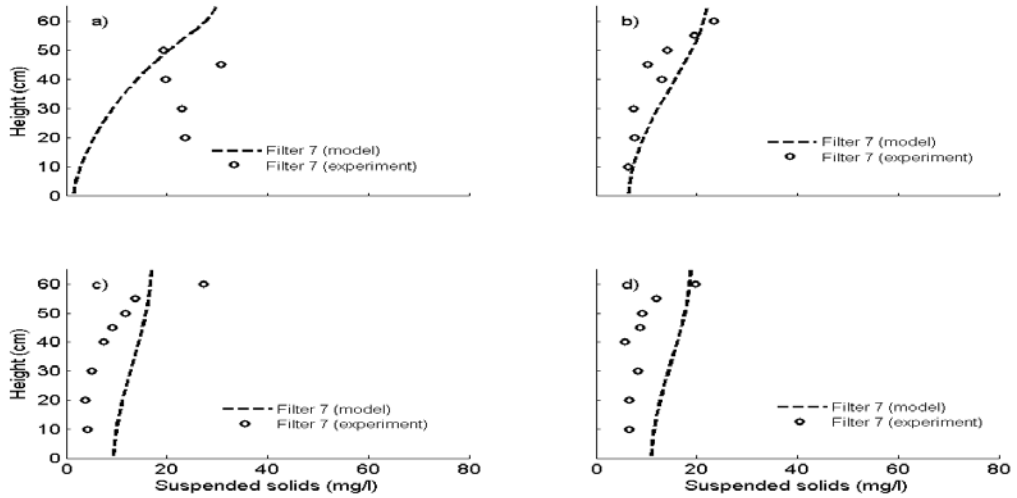


Figure 4.10

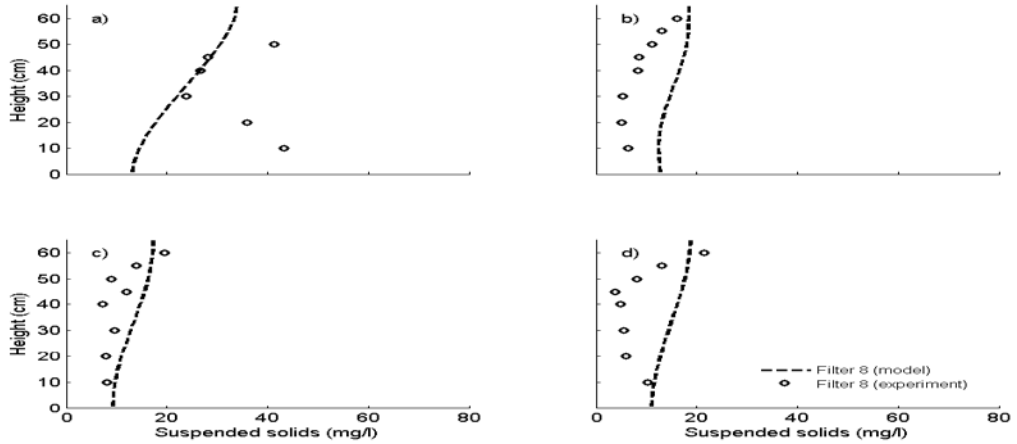


Figure 4. 8: Comparison between the measured and modelled distribution of suspended solids (SS) with depth within Filter 7 combined with Filter 8 after (a) set-up period, (b) first year after the set-up period and (c) second year after the set-up period, as well as at (d) the end of the

experiment for Filters 7 and 8 separately. **In Figures 4.9 and 4.10**, (a) is a set-up period, (b) first year after set-up, (c) second year after set-up, while (d) is separately the end of the experiment for Filters 9 and 10.

Ponding, which occurs in heavily clogged filter systems, was not observed, because the hydraulic conductivity was not sufficiently low to stop inflow water from infiltrating. However, a higher loading rate led to the accumulation of more biomass. Overall, Table 4.7 shows that there is no clear indication of imminent clogging for any wetland filter. This observation has been confirmed by several studies (Sani et al., 2013a; Sani et al., 2013b; Al-Isawi et al., 2014) implying that vertical-flow constructed wetlands do not clog and restrict the hydraulic conductivity of the wetland filters even with petroleum hydrocarbon spill over a long-term, subsequently, leading to the overall good treatment performance efficiency of the wetland systems observed in the present study. The values obtained with Darcy's Law (Eq. 1) represent the average media hydraulic conductivity of the cross-sectional area in the axial flow direction, but do not reveal whether clogging is more severe at specific vertical locations within that cross section. The application of Darcy's Law only provides an approximation of the media hydraulic conductivity as it cannot take into account the varying thickness of the water table resulting from the porous media flow energy balance (i.e., *Aw* varies between the upstream and downstream point (Bear, 1979) for horizontal flow systems as discussed by Nivala et al. (2012)). Therefore, the SS profile was obtained to assess where the flow restriction is likely to be the greatest. However, all SS values within the filter are rather small.

Table 4.7: Hydraulic conductivity performance of the wetland filters measured as the mean volume (l) of drained outflow per second

Second experimental phase (26/09/11 to 25/09/2012); n=5								
Draining time (s)	60	120	180	240	300	360	420	480
Filters 1 and 2	2.31	1.88	1.34	1.30				
Filters 3 and 4	2.07	1.76	1.37	0.84	0.40	0.40	0.28	
Filters 7 and 8	1.60	1.41	1.24	0.93	0.83	0.40		
Filter 9	2.53	2.08	1.67	0.67				
Filter 10	2.32	2.07	1.76	1.81	0.06			
Filters A and B	2.04	1.93	1.62	0.63	0.54			
Third experimental phase (26/09/12 to 25/09/2013); n=24								
Filters 1 and 2	2.10	1.77	1.37	0.88	0.51	0.41	0.42	0.24
Filters 3 and 4	2.17	1.82	1.48	0.85	0.55	0.54	0.24	0.19
Filters 7 and 8	1.69	1.48	1.29	1.03	0.64	0.29	0.37	0.16
Filter 9	2.32	2.05	1.56	0.83	0.41			
Filter 10	2.45	2.04	1.59	0.73	0.49	0.13		
Fourth experimental phase (26/09/13 to 30/04/2014); n=9								
Filter 1	1.98	1.77	1.40	0.77	0.23			
Filter 2	2.58	2.11	1.46	0.44				
Filter 3	2.38	1.97	1.52	0.29				
Filter 4	2.04	1.83	1.45	0.91	0.55	0.18		
Filter 7	1.58	1.38	1.22	1.01	0.60	0.35		
Filter 8	2.19	1.74	1.53	0.87	0.91	0.22		
Filter 9	2.16	1.81	1.51	0.86	0.44			
Filter 10	2.14	1.86	1.38	0.89	0.55	0.36		
Filter A	2.42	2.01	1.74	0.92	0.44			
Filter B	1.85	1.53	1.36	1.17	0.69	0.32	0.33	

4.5 Summary

This chapter discussed the overall treatment performance and its relationship with clogging of the wetland filters for the period of study. This includes quality of the inflow water, comparison of the outflow water quality variables including the oxygen demand variables, nutrients and particles both during and before the period of petroleum hydrocarbon contamination. Furthermore, elucidation of overall statistical differences between the variables, and assessment of clogging based on water quality variables and modelling was also described in this chapter.

CHAPTER 5

ASSESSMENT OF SEASONAL TREATMENT PERFORMANCE

5.1 Overview

The seasonal performance and its relation to clogging of the wetland systems are discussed in this chapter in different sections. Moreover, the chapter explains the summary of the overall seasonal results and discussions of the key water quality parameters, and seasonal assessment of SS accumulation in the wetland filters as index of clogging for the period of study. Section 5.1 discusses the seasonal treatment performances of the wetland filters including influent water quality of all the variables while effluent water quality and statistical differences between the variables are presented in section 5.2. Assessment of clogging based on water quality variables is interpreted in section 5.3.

5.2 Seasonal performance of wetland filters and their relationship with clogging

5.2.1 Seasonal inflow water quality

Average seasonal inflow performance data of over 30 months of wetland operation were analysed. Furthermore, the study monitored seasonal changes recorded over time in an attempt to understand the inflow water quality variables and their relationship in the system. Table 5.1 shows the seasonal inflow water quality of the undiluted wastewater used for the study period from June 2011 to March 2014. The mean inflow concentrations for COD, ammonia-nitrogen, nitrate-nitrogen, ortho-phosphate-phosphorus and SS were relatively high and variable. In 2011, the COD concentrations in summer were higher than in autumn. Similarly, the COD values in summer 2012 were higher than in autumn and spring. In contrast, BOD_5 concentrations in 2012 were lower in summer when compared to autumn. However, in 2013, autumn and summer COD concentrations were higher than those of winter and spring respectively, unlike high BOD inflow concentrations recorded in spring and summer compared

Table 5.1: Seasonal inflow water quality parameters (value and sample number in brackets, and standard deviation) of domestic wastewater mixed with urban runoff before dilution

Parameter	Summer 2011[a]	Autumn 2011[b]	Winter 2011/12[c]	Spring 2012[d]	Summer 2012[e]	Autumn 2012[f]
Chemical oxygen demand	407(10) ± 207.0	391.3(15) ±151.87	256.0(8) ±85.16	183.4(14) ±33.02	312.1(13) ±12.05	261.0(14) ±96.75
Biochemical oxygen demand	nm[l]	nm[l]	nm[l]	nm[l]	101.0 (13) ±32.68	108.6 (12) ±12.44
Ammonia-nitrogen	20.4(8) ±8.8	21.2(10) ±5.82	27.9(7) ±10.45	49.1(12) ±13.6	71.5(11) ±7.53	65.0(14) ±13.5
Nitrate-nitrogen	0.8(5) ±0.56	0.8(10) ±0.35	0.3(4) ±0.06	5.5(10) ±4.27	3.5(11) ±3.36	6.7(14) ±4.00
Ortho-phosphate-phosphorus	9.0(9) ±2.77	12.9(15) ±8.15	5.0(6) ±2.34	14.7(9) ±4.53	29.9(11) ±8.20	20.9(9) ±10.52
Suspended solids	185.8(8) ±126.2	145.3(11) ±132.9	49.1(6) ±9.32	27.5(16) ±12.90	132.0(16) ±55.54	125.7(14) ±77.28
Turbidity	nm[l]	nm[l]	nm[l]	nm[l]	297.4(18) ±108.81	115.9(14) ±91.43

Parameter	Winter 2012/13[g]	Spring 2013[h]	Summer 2013[i]	Autumn 2013[j]	Winter 2013/14[k]	Spring 2014
Chemical oxygen demand	230.3(11) ±91.94	186.0(2) ±2.83	244.7(3) ±110.73	352.5(2) ±10.61	200.7(3)±73.22	nm[l]
Biochemical oxygen demand	118.0(16) ±67.76	221.2(15) ±33.50	150.4(17) ±64.1	167.1(14) ±110.0	104.3(12) ±72.56	nm[l]
Ammonia-nitrogen	46.0(12) ±21.99	69.4(2) ±4.81	79.07(3) ±46.4	32.2(3) ±28.10	41.4(5) ±25.04	nm[l]
Nitrate-nitrogen	11.8(9) ±6.51	5.2(2) ±5.61	0.5(3) ±0.21	0.8(2) ±0.12	5.7(5) ±5.48	nm[l]
Ortho-phosphate-phosphorus	7.2(11) ±2.43	17.8(2) ±15.68	14.36(3) ±6.48	14.9(2) ±4.31	16.4(4) ±5.04	nm[l]
Suspended solids	158.5(17)±100.83	379.9(18) ±206.44	232.9(18) ±162.11	166.6(14) ±102.83	147.5(14) ±138.50	nm[l]
Turbidity	85.2(4) ±32.49	166.3(14) ±125.60	108.6(17) ±75.02	71.37(16) ±34.04	118.03(12) ±133.14	nm[l]

[a]21/06/11 to 22/09/11; [b]23/09/11 to 21/12/11; [c]22/12/11 to 19/03/12; [d]20/03/12 to 19/06/12; [e]20/06/12 to 21/09/12; [f]22/09/12 to 20/12/12; [g]21/12/12 to 19/03/13; [h]20/03/13 to 20/06/13; [i]21/06/13 to 21/09/13; [j]22/09/13 to 20/12/14; [k]21/12/14 to 19/03/14; and [l]not measured

with other seasons. Only mean inflow data of winter season are recorded in 2014, as a result, no trend in seasonal variability.

With regard to nutrients variables, the mean inflow concentrations of nitrogen compounds have shown an unsteady seasonal trend (Table 5.1) for the period of study. However, ortho-phosphate-phosphorus has shown a clear seasonal trend throughout the study period. Ammonia and nitrate-nitrogen inflow concentrations showed no clear seasonal trend in 2011. In 2012 however, ammonia recorded high values in summer and autumn compared to spring and winter while nitrate nitrogen concentrations were higher in autumn and spring than in summer and winter. In contrast, high ammonia inflow concentrations were recorded in summer and spring 2013 while autumn and winter recorded low concentrations. Nitrate-nitrogen indicates a seasonal variability in 2013 with high values in winter and spring, and low values in summer and autumn (Table 5.1). The mean inflow seasonal variations for ortho-phosphate-phosphorus show that values in autumn were higher than values in summer in 2011. In contrast, higher values were recorded in summer and autumn 2012 compared with spring and winter which recorded lower values. In 2013, however, spring recorded the highest ortho-phosphate-phosphorus concentrations and winter recorded the lowest (Table 5.1), while no clear seasonal trend can be identified in 2014 because only mean inflow concentrations of the winter season are evident.

Seasonal variability with mean inflow solid particles data has demonstrated a clear trend (Table 5.1) throughout the over-two-year wetland operation. The results indicated that suspended solids and turbidity have shown a seasonal trend in 2011 and 2012 with high values in summer and autumn respectively, and low values in winter and spring for the former in 2012. Furthermore, in 2013, they both recorded high values in spring and summer compared with autumn and winter which recorded low values for SS. In contrast, turbidity recorded low values in winter and autumn in 2013. However, in 2014, a clear seasonal trend was absent since only

average inflow concentrations of solid particles in the winter season are recorded. Overall, the seasonal inflow water quality parameters (Table 5.1) show relatively high variability with seasons.

5.2.2 Seasonal comparison of outflow water qualities

5.2.2.1 Comparison of oxygen demand variables

Organic matter removal in constructed wetlands is mainly through aerobic, anaerobic, adsorption, filtration, and microbial metabolism (Karathanasis et al., 2003; Song et al., 2006) and can be assessed by the change in COD and BOD concentrations in the wetlands. Overall seasonal mean effluent concentrations of the organic matter for the wetland filters operated for the entire study period were analysed and are presented in Tables 5.2 and 5.3. Assessment of statistically seasonal significant differences between effluent water quality variables is accordingly shown in Tables 5.4 and 5.5. The result shows that all filters demonstrated relatively good seasonal COD removal (with the exception of the time close to the start-up period and period of hydrocarbon contamination). This good removal can be attributed to the development of biological activity necessary for microbial degradation that took place over time and as such, the treatment efficiency can be expected to improve after microbial acclimatization (Scholz, 2006, 2010; Babatunde et al., 2011; Sani et al., 2012; Sani et al., 2013a; Sani et al., 2013b; Al-Isawi et al., 2014; Al-Isawi et al., 2015). Furthermore, the tables show a clear seasonal trend with high COD values in autumn and low COD values in summer, which confirms previous findings (Song et al., 2006; Sani et al., 2013b), but contradicts data by Merlin et al. (2002) and Vymazal (2011b) who reported no significant seasonal COD variations in their study However, the possible reason for this contradiction could be due to the fact that the wetlands reported in the contradicting literature are fully matured (6years old and bove) and operated in many treatment stages (more than one stage).

Table 5.2: Comparison of seasonal mean quarterly outflow water quality and mean quarterly air temperature for the period of first to third experimental phase (27/06/11 to 25/09/13 all in mg/l (except turbidity in NTU))

Filters 1 and 2 combined					Parameters					
Seasons	Year	Temp (in)	Temp (out)	COD	BOD	NH_4-N	NO_3-N	PO_4-P	SS	TBD
Summer	2011[a]	nm	14.9	73.5	nm	7.9	0.5	1.6	19.6	nm
Autumn	2011[b]	nm	7.8	89.8	nm	13.0	0.3	3.2	31.4	nm
Winter	11/12[c]	nm	3.7	58.4	nm	13.7	1.1	2.5	6.0	nm
Spring	2012[d]	nm	9.2	63.7	nm	7.0	2.5	3.2	5.2	nm
Summer	2012[e]	21.6	18.9	39.3	32.9	3.9	0.2	2.7	4.3	1.6
Autumn	2012[f]	11.8	10.1	57.3	23.1	9.4	1.1	2.4	5.0	2.5
Winter	12/13[g]	9.0	7.0	64.4	10.3	11.9	4.0	2.5	4.0	1.0
Spring	2013[h]	17.9	14.3	82.5	23.0	25.1	0.6	5.4	11.4	11.3
Summer	2013[i]	24.1	20.8	77.1	33.5	0.3	0.01	4.1	10.0	10.2
Filters 3 and 4 combined										
Summer	2011[a]	nm	14.9	72.2	nm	11.1	0.4	1.6	16.8	nm
Autumn	2011[b]	nm	7.8	93.3	nm	11.7	0.3	2.9	31.5	nm
Winter	11/12[c]	nm	3.7	53.8	nm	7.8	1.1	2.1	4.9	nm
Spring	2012[d]	nm	9.2	58.6	nm	5.3	2.5	2.9	3.4	nm
Summer	2012[e]	21.6	18.9	32.0	29.2	3.2	0.2	2.4	3.3	1.2
Autumn	2012[f]	11.8	10.1	51.6	19.6	7.0	1.1	2.0	4.6	0.8
Winter	12/13[g]	9.0	7.0	59.5	8.4	8.1	4.0	2.2	3.7	6.3
Spring	2013[h]	17.9	14.3	69.2	23.3	20.0	0.6	2.5	6.8	9.7
Summer	2013[i]	24.1	20.8	64.9	30.1	0.2	0.01	4.0	8.94	10.2
Filters 7 and 8 combined										
Summer	2011[a]	nm	14.9	164.6	nm	28.0	0.6	4.0	30.2	nm
Autumn	2011[b]	nm	7.8	149.8	nm	18.3	0.3	6.0	40.9	nm
Winter	11/12[c]	nm	3.7	87.5	nm	22.0	1.1	3.2	10.7	nm
Spring	2012[d]	nm	9.2	86.8	nm	13.4	2.5	4.9	7.1	nm
Summer	2012[e]	21.6	18.9	61.8	37.5	11.6	0.2	3.1	6.9	4.9

Table 5.2 (cont.)

Seasons	Year	Temp (in)	Temp (out)	COD	BOD	NH_4-N	NO_3-N	PO_4-P	SS	TBD
Autumn	2012[f]	11.8	10.1	78.0	25.8	21.4	1.1	3.9	5.1	0.9
Winter	12/13[g]	9.0	7.0	80.1	10.7	22.7	4.0	7.1	3.7	7.6
Spring	2013[h]	17.9	14.3	108.4	30.3	46.2	0.6	6.9	11.9	19.7
Summer	2013[i]	24.1	20.8	76.7	46.6	1.0	0.01	6.77	14.2	14.5
Filter 9										
Summer	2011[a]	nm	14.9	101.3	nm	18.2	0.5	2.6	27.9	nm
Autumn	2011[b]	nm	7.8	90.6	nm	8.8	0.3	2.1	28.3	nm
Winter	11/12[c]	nm	3.7	54.6	nm	6.3	1.1	1.4	5.8	nm
Spring	2012[d]	nm	9.2	59.0	nm	4.4	2.5	3.0	4.4	nm
Summer	2012[e]	21.6	18.9	40.3	19.6	4.1	0.2	3.0	6.6	2.7
Autumn	2012[f]	11.8	10.1	52.4	21.7	7.8	1.1	2.9	6.3	2.4
Winter	12/13[g]	9.0	7.0	62.6	7.8	7.0	4.0	2.7	4.8	8.9
Spring	2013[h]	17.9	14.3	64.2	11.3	12.8	0.6	2.7	5.6	8.0
Summer	2013[i]	24.1	20.8	41.2	28.9	9.5	3.3	4.3	10.9	9.1
Filter 10										
Summer	2011[a]	nm	14.9	82.5	nm	11.7	0.3	2.2	29.1	nm
Autumn	2011[b]	nm	7.8	76.2	nm	9.2	0.3	2.3	23.7	nm
Winter	11/12[c]	nm	3.7	52.5	nm	5.7	1.1	1.5	6.1	nm
Spring	2012[d]	nm	9.2	62.3	nm	4.7	2.5	2.8	4.1	nm
Summer	2012[e]	21.6	18.9	35.3	16.1	3.9	0.2	2.6	3.6	2.2
Autumn	2012[f]	11.8	10.1	60.0	18.3	9.4	1.1	3.0	5.0	2.0
Winter	12/13[g]	9.0	7.0	62.7	7.1	8.6	4.0	2.7	4.8	10.0
Spring	2013[h]	17.9	14.3	75.0	11.1	23.1	0.6	2.8	7.9	10.3
Summer	2013[i]	24.1	20.8	60.9	30.7	16.7	0.8	4.5	16.0	12.2

[a]21/06/11 to 22/09/11(data collection started on 01/07/11); [b]23/09/11 to 21/12/11; [c]22/12/11 to 19/03/12; [d]20/03/12 to 19/06/12; [e]20/06/12 to 21/09/12; [f]22/09/12 to 20/12/12; [g]21/12/12 to 19/03/13; [h]20/03/13 to 20/06/13; and [i]21/06/13 to 22/09/13. Note: nm, not measured and NTU nephelometric turbidity unit.

Furthermore, the wetland systems have a well-developed and established microbial population, and are planted with many species of macrophytes compared to the current experimental lab-scale wetlands which are smaller in size, planted with only common reed and have just over two years in operation. Several studies have shown that mature and large-scale wetlands remove organic matter well, including COD, due to higher biological degradation rates (Piccard et al., 2005; Kayranli et al., 2010). The high biodegradation of organic matter was attributed to high microbial population activity of the aerobic and anaerobic bacteria, which are temperature independent and function even at low temperatures of about 5°C (Vymazal, 2002; Vymazal, 2011a; Gikas & Tsihrintzis, 2012). Furthermore, the organic matter removal capacity is very high due to the large wetland size providing high mean retention times. There are also references which indicated that wetlands planted with different types of macrophytes, as in the case of reported contrasting studies, could be more effective in performance compared to wetlands planted with only one species of macrophyte as in the case of the present wetlands. For instance, Karathanasis et al. (2003) and Abou-Elela et al. (2013) have reported that the presence of various species of wetland plants provide a more effective distribution of roots and favourable environment, which stimulate the development of a great diversity of microbial communities. This root diversity delays the waste water movement in the wetlands which in turn increases the detention time, subsequently leading to higher removal efficiencies throughout the seasons (Prochaska et al., 2007; Abou-Elela et al., 2013). In this research, the observed low COD outflow concentrations in summer can be attributed to increased biodegradation and decomposition of organic compounds by microorganisms as a result of an increase in temperature in the wetland systems during warm summer months (Kayser & Kunst, 2005; Prochaska et al., 2007). There was a statistically significant seasonal variation for COD noted when filters with a low loading rate are compared to those with high ones (Table 5.4)

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Table 5.3: Comparison of seasonal outflow water quality and air temperature for the period of fourth experimental phase, a period after petroleum hydrocarbon spill (25/09/13 to 19/03/14 all in mg/l) except turbidity in NTU

Seasons				Parameters						
Filter 1	Year	Temp (in)	Temp (out)	COD	BOD	NH_4-N	NO_3-N	PO_4-P	SS	TBD
Autumn	2013	14.9	12.7	240.5	28.3	14.9	0.4	6.93	12.9	10.6
Winter	13/14	10.7	8.8	72.0	18.3	4.5	0.5	1.92	14.7	11.3
Filter 2										
Autumn	2013	14.9	12.7	86.4	18.3	12.0	3.6	4.10	6.1	5.7
Winter	13/14	10.7	8.8	24.9	9.4	3.9	2.9	3.08	9.6	8.4
Filter 3										
Autumn	2013	14.9	12.7	181.7	33.6	9.9	0.37	6.65	12.3	10.1
Winter	13/14	10.7	8.8	83.1	22.3	2.9	0.42	1.79	16.0	13.0
Filter 4										
Autumn	2013	14.9	12.7	81.4	18.9	8.9	4.3	3.76	8.1	6.2
Winter	13/14	10.7	8.8	81.6	8.0	3.5	3.2	3.36	9.2	7.5
Filter 7										
Autumn	2013	14.9	12.7	356.0	37.9	26.87	0.7	10.65	19.2	14.5
Winter	13/14	10.7	8.8	112.2	19.5	8.12	1.0	3.01	14.8	11.1
Filter 8										
Autumn	2013	14.9	12.7	107.6	27.6	23.0	9.3	8.12	10.0	9.0
Winter	13/14	10.7	8.8	29.5	8.7	11.7	2.2	3.07	7.8	6.2
Filter 9										
Autumn	2013	14.9	12.7	82.5	18.1	7.3	2.5	5.26	5.2	4.6
Winter	13/14	10.7	8.8	19.4	10.1	1.4	4.2	2.86	1.0	2.6
Filter 10										
Autumn	2013	14.9	12.7	174.4	19.6	6.5	5.6	4.74	4.5	5.0
Winter	13/14	10.7	8.8	18.85	9.8	1.2	3.1	3.32	1.1	3.1

This can be explained by the fact that high rate filters are likely to be overloaded in summer and autumn 2011, winter, spring, summer and autumn 2012 and winter 2013. However, after hydrocarbon contamination in the fourth experimental phase, the period after some selected filters were contaminated with diesel, the result shows that all filters contaminated with diesel demonstrated poor COD removal compared to those without diesel in all seasons (Table 5.3). This difference can be explained by the increase of the inflow COD as a result of diesel application which might have resulted in the sharp increase of the outflow COD values recorded by the affected filters (Al-Isawi et al., 2014; Al-Isawi et al., 2015). However, aggregate diameter, resting time, contact time and loading rates showed no clear statistical difference on seasonal COD removal trends (Table 5.5).

Figures 5.1 and 5.2 show the seasonal variations of COD and BOD variables from summer 2011 to winter 2014 respectively. Table 5.2 indicates a seasonal trend with high BOD values in summer and low BOD values in winter, which confirms previous findings (Scholz, 2011; Sani et al., 2013b; Amteghy, 2014) but contradicts some studies reported elsewhere (Song et al., 2006; Vymazal, 2011a) which found low BOD values in summer and high BOD values in winter. This contradiction could be attributed to the fact that in addition to the small size of the experimental wetlands used in the conduction of this research compared to that of the contrasting authors, the high temperature of 22°C observed in the current study, could have stimulated evaporation rates to be high in the summer, consequently causing the outflow concentration of the BOD to increase. Papaevangelou, Gikas, and Tsihrintzis (2012) explained that the effect of evapotranspiration starts being significant at temperatures above 15°C which is in agreement with the current study temperature. However, in the case of the contradicting literature, their wetlands are larger in size with high microbial activity and optimal plant function due to higher temperature observed in summer, subsequently leading

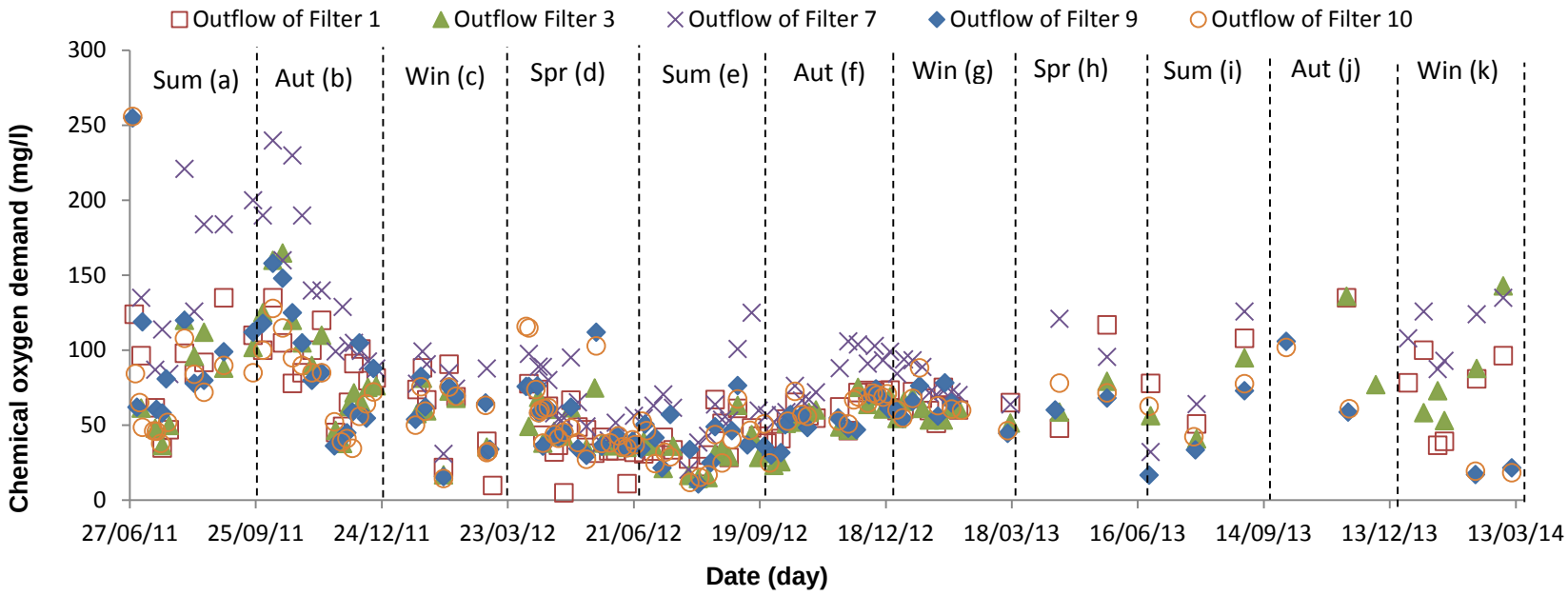

Figure 5.1: Overall seasonal variations in chemical oxygen demand

a 21/06/11 to 22/09/11; b 23/09/11 to 21/12/11; c 22/12/11 to 19/03/12; d 20/03/12 to 19/06/12; e 20/06/12 to 21/09/12; f 22/09/12 to 20/12/12; g 21/12/12 to 19/03/13; h 20/03/13 to 20/06/13; i 21/06/13 to 22/09/13; j 23/09/13 to 21/12/13; k 22/12/13 to 19/03/14. Diesel was applied on 26/09/13 and data collection started on 27/06/11 and stopped on 19/03/14. Note that the following sampling points have not been displayed: a) 452 (Filter 7) in summer 2011; b) 346 (Filter 1) in autumn 2013; c) 332 (Filter 3) in autumn 2013; and d) 356 (Filter 7) in autumn 2013

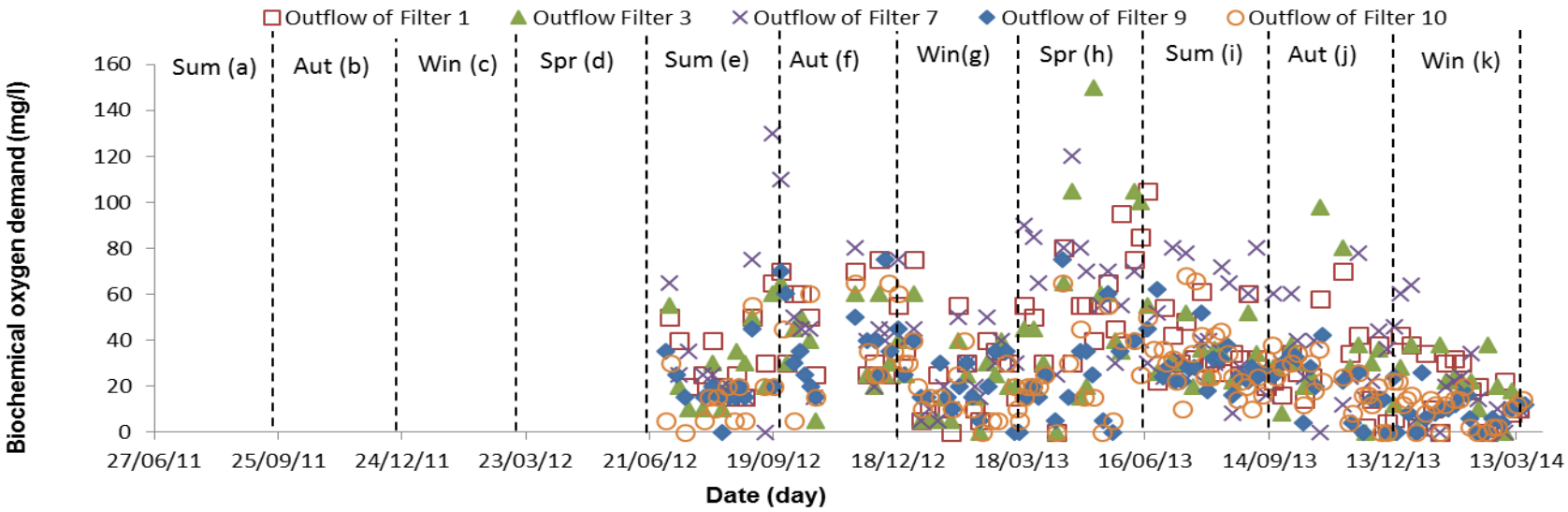

Figure 5.2: Overall seasonal variations in biochemical oxygen demand

a 21/06/11 to 22/09/11; b 23/09/11 to 21/12/11; c 22/12/11 to 19/03/12; d 20/03/12 to 19/06/12; e 20/06/12 to 21/09/12; f 22/09/12 to 20/12/12; g 21/12/12 to 19/03/13; h 20/03/13 to 20/06/13; i 21/06/13 to 22/09/13; j 23/09/13 to 21/12/13; k 22/12/13 to 19/03/14. Diesel was applied on 26/09/13 and data collection started on 27/06/11 and stopped on 19/03/14

to higher removal efficiency of the BOD concentration in comparison to the current study wetlands. Furthermore, in the current study, the return of the harvested biomass into the wetland systems during the previous season might have contributed to the increase of the outflow BOD concentration after decomposition by the activity of microorganisms due to increase of temperature in the summer period, in contrast to the reference literature in which there was no report of returning harvested biomass in the wetland systems. In their studies, Thomas, Glover, and Kalaroopan (1995), Hunt and Poach (2001) and Karathanasis et al. (2003) expounded that constructed wetland plants gradually add carbon and other compounds, including the BOD, in the wetland systems as a result of plant litter production, thus, the systems cannot remove the compounds entirely. On the other hand, the relative low seasonal BOD outflow observed in winter in this research, could be attributed to microbial degradation and decomposition by aerobic and anaerobic bacteria that are temperature independent (Vymazal, 2002; Vymazal, 2011a; Gikas & Tsihrintzis, 2012) which can biodegrade organic matter efficiently even in low temperatures.

Organic matter particles in CWs accumulate in media pores and if not biodegraded, cause gradual substrate clogging. However, overall seasonal treatment performance of the wetland filters in this study indicated that, these wetland systems are robust and relatively efficient in organic matter removal as a result of high biodegradation of the organic matter solids in form of COD and BOD regardless of the seasonal variation, which is attributed to the development of biological activity and aeration that took place over time in the wetland systems, and as such, the treatment efficiency was gradually improved leading to clogging abatement with maintained hydraulic conductivity and porosity (Tables 5.2 and 5.3) even after petroleum hydrocarbon contamination confirming data elsewhere (Al-Isawi et al., 2015).

A statistically significant seasonal variation for BOD was only recorded in summer 2013 when filters with low loading rates are compared with high ones. This could be explained by the fact

that high rate filters are probably overloaded during the season. However, aggregate diameter, resting time and contact time had no clear influence on seasonal BOD removal trends (Table 5.3).

In the petroleum hydrocarbon contamination period, BOD removal shows a clear seasonal trend with low values in winter and high values in autumn for contaminated and uncontaminated filters respectively, though contaminated filters recorded higher values compared to uncontaminated ones confirming data by Al-Isawi et al. (2015) but in disagreement with Eke (2008) who reported no clear trend with BOD outflow concentrations in his study with petroleum hydrocarbon contaminated filters. This might be due to the fact that in the current research, the assessment of seasonal petroleum hydrocarbon treatment is based on only two seasons (autumn and winter), which is probably insufficient to give a clear conclusion compared to the referenced reported literature where seasonal assessment of the water quality parameters including BOD was consistently monitored for over 30 months of operation. Furthermore, the high dose of petroleum hydrocarbon applied in the current research wetland systems is based on a one-off spill application of 130 grams (equivalent to an inflow concentration of 20 g/l) in the selected wetland filters compared to only 1 g/l of petroleum hydrocarbon used as inflow reported in the referenced literature. However, the low and high effluent BOD concentrations observed in winter and autumn seasons could probably be attributed to biodegradation of petroleum hydrocarbon compounds, which might have contributed to the high elevated concentration of BOD in autumn when a large amount of diesel was applied in the selected filers. Several studies confirmed that petroleum hydrocarbon residual and its biodegradation products were the significant source of carbon contributing to high concentration of organic matter including BOD in the wetland systems (Tang et al., 2010; Al-Isawi et al., 2015).

Table 5.4: Assessment of the statistically significant differences between seasonal outflow water quality variables (only shown if seasonally measured) of different filters using the non-parametric Mann-Whitney U-test

Parameters	Unit	Statistic	Aggregate diameter[a]	Contact time[b]	Resting time[c]	Chemical oxygen demand[d]
First to third experimental phase (27/06/11 to 25/09/13)						
Summer 2011[e]						
COD	mg/l	*P-value*	0.713	0.191	0.210	0.006
		h	0	0	0	1
BOD	mg/l	nm	nm	nm	nm	nm
NH_4-N	mg/l	*P-value*	0.225	0.110	0.064	0.013
		h	0	0	0	1
NO_3-N	mg/l	*P-value*	0.463	0.805	0.107	0.028
		h	0	0	0	1
PO_4-P	mg/l	*P-value*	0.705	0.010	0.075	0.001
		h	0	1	0	1
SS	mg/l	*P-value*	0.916	0.385	0.402	0.011
		h	0	0	0	1
TBD	NTU	nm	nm	nm	nm	nm
Autumn 2011[f]						
COD	mg/l	*P-value*	0.983	0.772	0.299	0.004
		h	0	0	0	1
BOD	mg/l	nm	nm	nm	nm	nm
NH_4-N	mg/l	*P-value*	0.130	0.449	0.762	0.028
		h	0	0	0	1
NO_3-N	mg/l	*P-value*	0.570	0.173	0.623	0.130
		h	0	0	0	0
PO_4-P	mg/l	*P-value*	0.740	0.556	1.000	0.000
		h	0	0	0	1
SS	mg/l	*P-value*	0.793	0.511	0.921	0.250
		h	0	0	0	0
TBD	NTU	nm	nm	nm	nm	nm
Winter 2011/12[g]						
COD	mg/l	*P-value*	0.418	0.874	0.627	0.018
		h	0	0	0	1
BOD	mg/l	nm	nm	nm	nm	nm
NH_4-N	mg/l	h	0.025	0.643	0.269	0.006
		0	1	0	0	1
NO_3-N	mg/l	*P-value*	0.209	0.675	0.916	0.917
		h	0	0	0	0
PO_4-P	mg/l	*P-value*	0.522	0.465	0.916	0.144
		h	0	0	0	0
SS	mg/l	*P-value*	0.248	0.230	0.880	0.059
		h	0	0	0	0
TBD	NTU	nm	nm	nm	nm	nm
Spring 2012[h]						

Table 5.4(cont.)

Parameters	Unit	Statistic	Aggregate diameter[a]	Contact time[b]	Resting time[c]	Chemical oxygen demand[d]
		h	0	0	0	1
COD	mg/l	*P*-value	0.371	0.700	0.925	0.031
		h	0	0	0	1
BOD	mg/l	nm	nm	nm	nm	nm
NH_4-N	mg/l	*P-value*	0.102	0.270	0.563	0.052
		h	0	0	0	0
NO_3-N	mg/l	*P-value*	0.718	0.059	0.262	0.105
		h	0	0	0	0
PO_4-P	mg/l	*P-value*	0.377	0.947	0.504	0.077
		h	0	0	0	0
SS	mg/l	*P-value*	0.212	0.061	0.680	0.002
		h	0	0	0	1
TBD	NTU	nm	nm	nm	nm	nm
Summer 2012[i]						
COD	mg/l	*P-value*	0.334	0.138	0.461	0.001
		h	0	0	0	1
BOD	mg/l	*P-value*	0.542	0.204	0.333	0.749
		h	0	0	0	0
NH_4-N	mg/l	*P-value*	0.450	0.602	0.948	0.002
		h	0	0	0	1
NO_3-N	mg/l	*P-value*	0.895	0.001	0.870	0.066
		h	0	1	0	0
PO_4-P	mg/l	*P-value*	0.450	0.040	0.247	0.166
		h	0	1	0	0
SS	mg/l	*P-value*	0.019	0.111	0.144	0.002
		h	1	0	0	1
TBD	NTU	*P-value*	0.201	0.138	0.871	0.003
		h	0	0	0	1
Autumn 2012[j]						
COD	mg/l	*P-value*	0.383	0.963	0.097	0.002
		h	0	0	0	1
BOD	mg/l	*P-value*	0.456	0.827	0.891	0.382
		h	0	0	0	0
NH_4-N	mg/l	*P-value*	0.250	0.438	0.448	0.018
		h	0	0	0	1
NO_3-N	mg/l	*P-value*	0.613	0.011	0.906	0.098
		h	0	1	0	0
PO_4-P	mg/l	*P-value*	0.130	0.010	0.771	0.001
		h	0	1	0	1
SS	mg/l	*P-value*	0.695	0.148	0.345	0.693
		h	0	0	0	0
TBD	NTU	*P-value*	0.976	0.840	0.840	0.976
		h	0	0	0	0
Winter 2012/13[k]						
COD	mg/l	*P-value*	0.158	0.433	0.958	0.000

Table 5.4 (cont)

Parameters	Unit	Statistic	Aggregate diameter[a]	Contact time[b]	Resting time[c]	Chemical oxygen demand[d]
		h	0	0	0	1
BOD	mg/l	*P-value*	0.472	0.970	0.626	0.178
		h	0	0	0	0
NH_4-N	mg/l	*P-value*	0.140	0.577	0.805	0.008
		h	0	0	0	1
NO_3-N	mg/l	*P-value*	0.450	0.405	0.734	0.241
		h	0	0	0	0
PO_4-P	mg/l	*P-value*	0.693	0.014	0.761	0.000
		h	0	1	0	1
SS	mg/l	*P-value*	0.283	0.291	0.819	0.316
		h	0	0	0	0
TBD	NTU	*P-value*	0.538	0.379	0.871	0.538
		h	0	0	0	0
Spring 2013[l]						
COD	mg/l	*P-value*	1.000	1.000	0.121	0.121
		h	0	0	0	0
BOD	mg/l	*P-value*	0.624	0.015	0.942	0.097
		h	0	1	0	0
NH_4-N	mg/l	*P-value*	0.439	0.439	0.439	0.121
		h	0	0	0	0
NO_3-N	mg/l	*P-value*	0.121	0.121	0.121	0.439
		h	0	0	0	0
PO_4-P	mg/l	*P-value*	0.121	0.121	1.000	0.121
		h	0	0	0	0
SS	mg/l	*P-value*	0.121	0.156	0.496	0.309
		h	0	0	0	0
TBD	NTU	*P-value*	0.089	0.182	0.713	0.007
		h	0	0	0	1
Summer 2013[m]						
COD	Mg/l	*P-value*	0.153	0.275	0.275	0.827
		h	0	0	0	0
BOD	mg/l	*P-value*	0.335	0.454	0.625	0.018
		h	0	0	0	1
NH_4-N	mg/l	*P-value*	0.513	0.513	0.513	0.05
		h	0	0	0	1
NO_3-N	mg/l	*P-value*	1.000	0.127	0.275	0.376
		h	0	0	0	0
PO_4-P	mg/l	*P-value*	0.827	0.827	0.513	0.127
		h	0	0	0	0
SS	mg/l	*P-value*	0.653	0.233	0.071	0.062
		h	0	0	0	0
TBD	NTU	*P-value*	0.547	0.446	0.178	0.249
		h	0	0	0	0

[a]Comparison between the mean daily values of Filters 1 and 2, and the mean daily values of Filters 3 and 4; [b]Comparison between the mean daily values of Filters 3 and 4, and Filter 9; [c]Comparison between Filters 9 and 10; [d]Comparison between mean daily values of Filters 3 and 4, and mean daily values of Filters 7 and 8; [e]21/06/11 to 22/09/11 (data collection started on 01/07/11); [f]23/09/11 to 21/12/11; [g]22/12/11 to 19/03/12; [h]20/03/12 to 19/06/12; [i]20/06/12 to 21/09/12; [j]22/09/12 to 20/12/12; [k]21/12/12 to 19/03/13; [l]20/03/13 to 20/06/13; [m]21/06/13 to 22/09/13. Note: *P-value*, probability of obtaining a test statistic at least as extreme as the one that was actually observed, assuming that the null hypothesis is true; h, response indicator; if h=1, filters are statistically significantly different (*P-value* < 0.05) for the corresponding water quality parameter; if h=0, the difference is not significant.

However, after subsequent consumption of the organic matter by the wetland microbes, which are active even in low temperatures, the BOD concentration is reduced in the winter season (Table 5.3). Significant statistical difference in contact time was noted in winter when a longer contact time was compared with a shorter one which led to greater removal of BOD. This could be attributed to the fact that the longer contact time provides enough duration for pollutants to be biodegraded by microorganisms in the wetland systems (Song et al., 2006; Prochaska et al., 2007; Gikas & Tsihrintzis, 2012).

5.2.2.2 Comparison of nutrients variables

Nitrogen removal within constructed wetlands is usually mainly by microbial nitrification and denitrification. In the nitrification process, ammonia is oxidized largely to nitrate. As a result of oxidation of ammonia to nitrate, nitrate is reduced to gaseous nitrogen by the denitrification process. Nitrogen removal in many constructed wetland systems without adequate active or passive aeration is insufficient, mainly because of the lack of available oxygen used for aerobic biological degradation (Scholz, 2010).

Table 5.2 shows the seasonal trend of nitrate-nitrogen, ammonia-nitrogen and ortho-phosphate-phosphorus. With regard to nitrate-nitrogen, the result indicates high values in winter and low values in summer confirming previous findings (Werker et al., 2002; Kuschk et al., 2003; Gikas et al., 2007; Sani et al., 2013b) but contradicting data by Kayranli et al. (2010) who reported high values in summer compared to low values in winter. This contradiction could be attributed to the large wetland size and their exposure to high temperature because the systems are open,

as a result, the effluent nitrate-nitrogen concentration could be higher due to increase in evapotranspiration, indicating a considerably higher nitrification rate in summer than in winter due to high microbial activity, and the presence of easily available organic carbon leading to greater removal of nitrate-nitrogen in winter than in summer in comparison to the higher removal achieved in summer than in winter with regard to small size wetlands used in the present study. Some studies revealed that the consumption of organic carbon by heterotrophs which is supplied by macrophytes leads to an increase in the heterotrophic activity, subsequently leading to oxygen consumption by the heterotrophs (Souza, Araujo, & Coelho, 2008).

Table 5.5: Assessment of the statistically significant differences between seasonal outflow water quality variables (only if seasonally measured) of different filters using the non-parametric Mann-Whitney U-test

Parameters	Unit	Statistics	Aggregate diameter[n]	Contact time[o]	Resting time[p]	Chemical oxygen demand[q]
Fourth experimental phase (26/09/13 to 19/03/14)						
Autumn 2013[r]						
COD	mg/l	*P-value*	0.564	0.248	0.564	0.076
		h	0	0	0	0
BOD	mg/l	*P-value*	0.967	0.145	0.854	0.152
		h	0	0	0	0
NH_4-N	mg/l	*P-value*	0.564	1.000	1.000	0.248
		h	0	0	0	0
NO_3-N	mg/l	*P-value*	0.439	0.439	0.439	0.121
		h	0	0	0	0
PO_4-N	mg/l	*P-value*	1.000	0.439	0.439	0.439
		h	0	0	0	0
SS	mg/l	*P-value*	0.624	0.002	0.888	0.085
		h	0	1	0	0
TBD	NTU	*P-value*	0.663	0.002	0.443	1.66
		h	0	1	0	0
Winter 2013/2014[s]						
COD	mg/l	P-value	0.855	0.053	1.000	0.144
		h	0	0	0	0
BOD	mg/l	P-value	0.418	0.006	0.736	0.136
		h	0	1	0	0
NH_4-N	mg/l	P-value	0.221	0.317	0.317	0.180
		h	0	0	0	0
NO_3-N	mg/l	P-value	1.000	0.317	0.317	0.317
		h	0	0	0	0
PO_4-N	mg/l	P-value	1.000	1.000	1.000	0.121

Table 5.5 (cont)

Parameters	Unit	Statistics	Aggregate diameter[n]	Contact time[o]	Resting time[p]	Chemical oxygen demand[q]
		h	0	0	0	0
SS	mg/l	P-value	0.382	0.000	0.429	0.428
		h	0	1	0	0
TBD	NTU	P-value	0.419	0.000	0.095	0.254
		h	0	1	0	0
Autumn 2013[x]						
COD	mg/l	*P-value*	0.439	1.000	0.564	0.439
		h	0	0	0	0
BOD	mg/l	*P-value*	0.950	0.820	0.854	0.058
		h	0	0	0	0
NH_4-N	mg/l	*P-value*	0.121	1.000	1.000	1.000
		h	0	0	0	0
NO_3-N	mg/l	*P-value*	1.000	1.000	0.439	0.439
		h	0	0	0	0
		h	0	0	0	0
SS	mg/l	*P-value*	0.643	0.256	0.888	0.208
		h	0	0	0	0
TBD	NTU	*P-value*	0.182	0.086	0.443	0.412
		h	0	0	0	0
Winter 2013/2014[y]						
TBD	NTU	*P-value*	0.182	0.086	0.443	0.412
		h	0	0	0	0
COD	mg/l	*P-value*	0.121	1.000	1.000	0.121
		h	0	0	0	0
BOD	mg/l	*P-value*	0.341	0.234	0.736	0.907
		h	0	0	0	0
N H_4-N	mg/l	*P-value*	n/a	n/a	n/a	n/a
		h	-	-	-	-
NO_3-N	mg/l	*P-value*	0.221	0.317	0.317	0.317
		h	0	0	0	0
PO_4-N	mg/l	*P-value*	0.121	1.000	1.000	0.683
		h	0	0	0	0
SS	mg/l	*P-value*	0.259	0.034	0.429	0.428
		h	0	1	0	0
TBD	NTU	*P-value*	0.852	0.012	0.095	0.885
		h	0	1	0	0

[n]Comparison between the mean daily values of Filters 1 and 3; [o]Comparison between the mean daily values of Filters 3 and 9; [p]Comparison between the mean daily values Filters 9 and 10; [q]Comparison between mean daily values of Filters 3 and 7; [r]23/09/13 to 21/12/13; [s]22/12/13 to 19/03/14; [t]Comparison between mean daily values of Filters 2 and 4; [u]Comparison between mean daily values of Filters 4 and 9; [v]Comparison between mean daily values of Filters 9 and 10; [w]Comparison between mean daily values of Filters 4 and 8; [x]23/09/13 to 21/12/13; and [y]22/12/13 to 19/03/14. Note: *P-value*, probability of obtaining a test statistic at least as extreme as the one that was actually observed, assuming that the null hypothesis is true; h, response indicator; if h=1, filters are statistically significantly different (*P-value* < 0.05) for the corresponding water quality parameter; if h=0, the difference is not significant.

As a result, Bastviken et al. (2005) reported that the oxygen concentration in the wetlands reduced and contributed to the increase in denitrification. However, the high removal of nitrate-nitrogen observed in summer in comparison to low removal observed in winter reported in the current research, could be attributed to lower temperatures and lack of easily available carbon, which negatively affects the activity of microorganisms to denitrify in winter (Gikas et al., 2007; Sani et al., 2013b). Differences in contact time are significant during warm months. A longer contact time leads to greater removal of nitrate-nitrogen. In comparison, differences in loading rate only result in significant variations of nitrate-nitrogen during warm months (Table 5.4). This can be explained by the fact that high rate filters are likely to be overloaded during summer 2011. However, during the period of petroleum hydrocarbon contamination, Table 5.3 shows no clear trend in terms of nitrate-nitrogen seasonal variations which has been confirmed by previous findings (Tang et al., 2010). Furthermore, aggregate diameter, contact time, resting time and loading rate show no significant differences on seasonal nitrate-nitrogen removal (Table 5.5).

With regard to ammonia-nitrogen seasonal removal, Table 5.2 shows a clear seasonal trend with high values in spring and low values in summer, which confirms the findings by Song et al. (2006), Gikas and Tsihrintzis (2012) and Sani et al. (2013b) but contradicts data by Kayranli et al. (2010) who noted higher effluent values in winter compared to other seasons. The probable reason for this contradiction could be low microbial activity as a result of low temperatures and lack of oxygen, which might have reduced the nitrification process within the wetland systems, consequently leading to the observed high values. A study conducted by Werker et al. (2002) has shown that, at temperatures of about 10°C, nitrification rates in constructed wetland systems are impeded and quickly drop at 6°C. However, in comparison, aerobic and anaerobic bacteria which are temperature independent are probably responsible for the effective removal of ammonia-nitrogen in the winter period of the present study. Kuschk

et al. (2003) and Gikas et al. (2007) reported that at temperatures below 15°C, bacteria responsible for nitrogen elimination do not work proficiently, and plant growth stops which is in agreement with current research.

The high removal efficiency of ammonia-nitrogen obtained in summer compared to other seasons in this study could be attributed to high temperature and plant growth with elevated microbial activity, oxygen and carbon for the high nitrification process in the wetland systems. Akratos and Tsihrintzis (2007), Gikas and Tsihrintzis (2010), Kotti et al. (2010), and Gikas and Tsihrintzis (2012) expounded that nitrogen compounds such as ammonia are effectively removed at temperatures above 15°C. Effect of loading rate has shown significant differences for ammonia-nitrogen when filters with low loading rate are compared to those with high ones (Table 5.4). This could be explained by the fact that, it is likely that high rate filters are overloaded at least during colder months.

In the Petroleum hydrocarbon contamination period, contaminated filters recorded high values of ammonia-nitrogen in autumn compared to low values in winter and higher values than those recorded in uncontaminated wetland filters (Table 5.3). The high removal efficiency of ammonia-nitrogen noted in winter could be attributed to progressive biodegradation of the petroleum hydrocarbon compounds by microorganisms after the contamination in autumn which led to a high nitrogen concentration. Recently, Al-Isawi et al. (2014) and Al-Isawi et al. (2015) have shown that after a hydrocarbon spill in their constructed wetlands in autumn, the spill-contaminated filters recorded high values of ammonia-nitrogen at the beginning but after subsequent degradation by microorganisms, the concentration became low in winter which is in agreement with the current findings. However, aggregate diameter, contact time, resting time and loading rate have no significant influence on the seasonal removal of ammonia-nitrogen during the period of petroleum hydrocarbon contamination (Table 5.5).

Nutrients solid particles accumulate in wetland media and cause gradual clogging of the substrate in CW systems by blocking the media pores. However, as a result of relatively high treatment performance and removal efficiency of nitrogen compounds in all seasons from the wetland systems observed in this research in both pre and post petroleum hydrocarbon contamination, which was attributed to progressive microbial degradation and aeration of the media bed, has lead to opening of the substrate pores from solids blockage, mitigating clogging development, and maintaining hydraulic conductivity and porosity in the wetland filters confirming data by Hua et al.(2014) and Song et al.(2015).

Figures 5.3, 5.4 and 5.5 show the seasonal variations of outflow nitrate-nitrogen, ammonia nitrogen and ortho-phosphate-phosphorus for the entire study period.

In constructed wetlands, phosphorus elimination takes place through sediment retention, adsorption, desorption, fragmentation, plant or microbial uptake, mineralization and leaching (Pant et al., 2001; Vymazal, 2007). However, the quick multiplication of the microorganisms like algae, bacteria and fungi and their inability to accumulate much quantity of phosphorus, means they speedily absorb it instead (Vymazal, 2006).Table 5.2 indicates no clear seasonal trend for phosphorus removal confirming previous findings (Sani et al., 2013b) but contradicting data by Merlin et al. (2002) who noted low values for summer and high values for winter in their study. This contradiction could be due to high storage of phosphorus in the organic matter accumulated over time in the mature wetlands (over 6 years old) which could be higher in the summer as a result of elevated microbial activity and optimal growth of macrophytes. Wallace and Knight (2006) stated that detritus serves as a source of carbon to wetland microbes for denitrification and helps with long-term phosphorus accumulation. In comparison to the present study, the possible reason for not observing a seasonal trend could be the fact that the wetland systems have been in operation for less than three years old with free adsorption sites that are not saturated, thus leading to phosphorus sequestration in all

seasons without differences. A study by Tanner, Sukias, and Upsdell (1999) found that constructed wetlands remove phosphorus effectively in the initial years of operation but removal starts to diminish after five years of operation. High COD inflow concentrations (Table 5.1) had a significantly positive influence on the treatment efficiency for ortho-phosphate-phosphorus. Ortho-phosphate-phosphorus removal seems to be independent of temperature if contact time and loading rate vary. This could be explained by the dominant physical and not biological removal processes (Scholz, 2010). In the period of petroleum hydrocarbon contamination however, Table 5.3 shows that all filters show a seasonal trend for phosphorus removal with high values in autumn and low values in winter but aggregate diameter, contact time, resting time and loading rate have no significant influence on the seasonal removal trends. The high concentration of phosphorus observed in autumn could be attributed to initial dying contaminated biomass and later on degraded diesel depending on the stage of biodegradation over time whichsubsequently reduces in winter by microbial degradation (Al-Isawi et al., 2014; Al-Isawi et al., 2015).

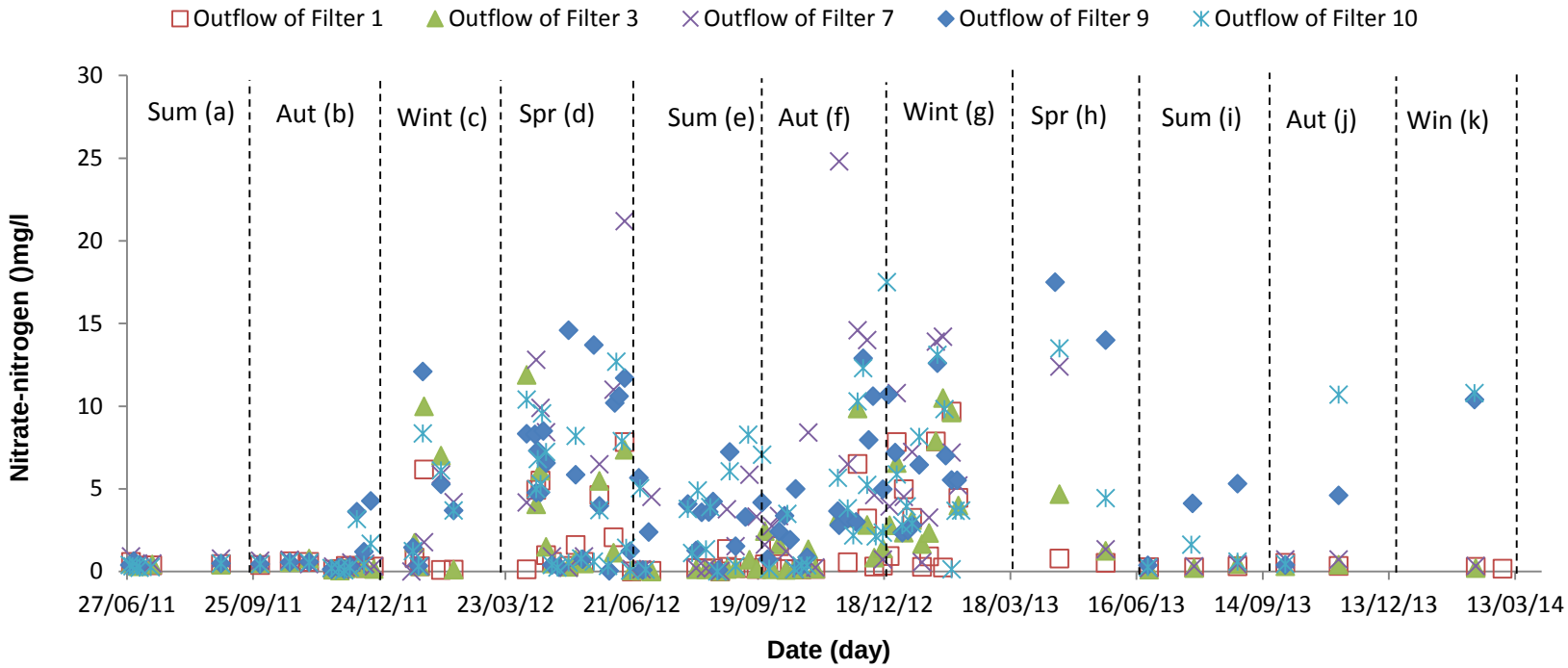

Figure 5.2: Overall seasonal variations in outflow nitrate-nitrogen

a 21/06/11 to 22/09/11; b 23/09/11 to 21/12/11; c 22/12/11 to 19/03/12; d 20/03/12 to 19/06/12; e 20/06/12 to 21/09/12; f 22/09/12 to 20/12/12; g 21/12/12 to 19/03/13;h 20/03/13 to 20/06/13;I 21/06/13 to 22/09/13 j 23/09/13 to 21/12/13; k 22/12/13 to 19/03/14. Diesel was applied on 26/09/13and.data.collection.started.on.27/06/11.and.stopped.on.19/03/14

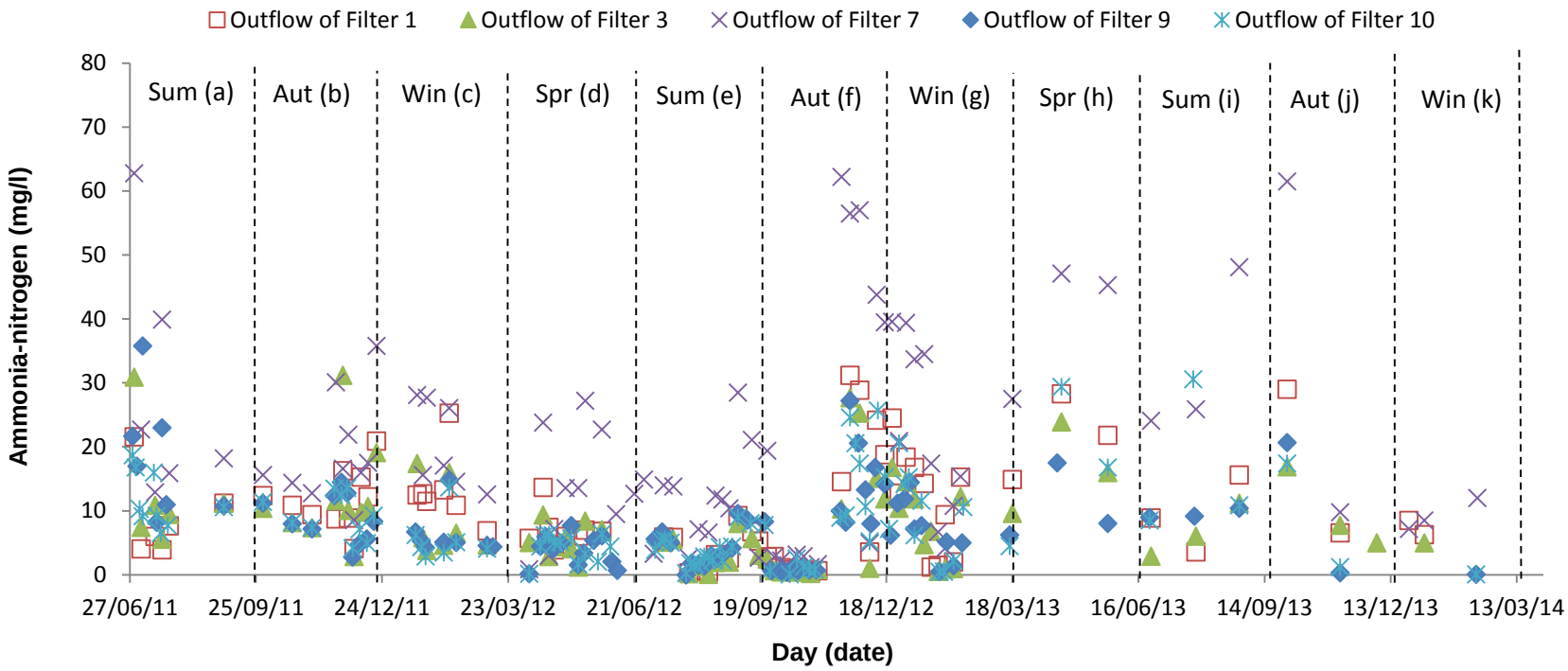

Figure 5. 3: Overall seasonal variations in outflow ammonia-nitrogen

a 21/06/11 to 22/09/11; b 23/09/11 to 21/12/11; c 22/12/11 to 19/03/12; d 20/03/12 to 19/06/12; e 20/06/12 to 21/09/12; f 22/09/12 to 20/12/12; g 21/12/12 to 19/03/13; h 20/03/13 to 20/06/13; i 21/06/13 to 22/09/13; j 23/09/13 to 21/12/13; k 22/12/13 to 19/03/14. Diesel was applied on 26/09/13 and data collection started on 27/06/11 and stopped on 19/03/14 .

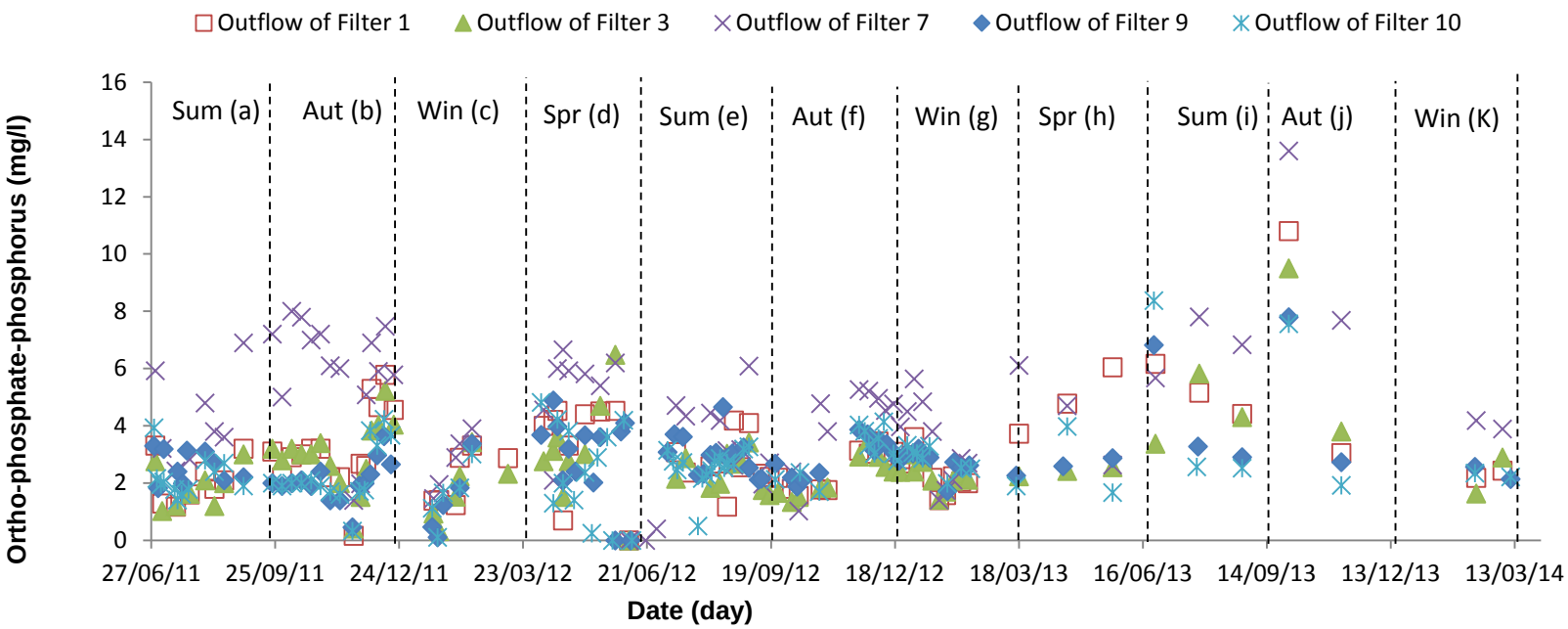

Figure 5. 4: Overall seasonal variations in outflow ortho-phosphate-phosphorus

a 21/06/11 to 22/09/11; b 23/09/11 to 21/12/11; c 22/12/11 to 19/03/12; d 20/03/12 to 19/06/12; e 20/06/12 to 21/09/12; f 22/09/12 to 20/12/12; g 21/12/12 to 19/03/13; h 20/03/13 to 20/06/13; i 21/06/13 to 22/09/13; j 23/09/13 to 21/12/13; k 22/12/13 to 19/03/14. Diesel was applied on 26/09/13 and data collection started on 27/06/11 and stopped on 19/03/14

5.2.2.3 Comparison of particles variables

The primary removal pathways for suspended solids and particulate matter in wetland systems are settling and sedimentation, adsorption, and microbial metabolism (Kadlec & Knight, 1996; Green et al., 1997; Leonard, 2000; ITRC, 2003). Figures 5.6 and 5.7 indicate seasonal SS and turbidity outflow concentrations for the entire study period. Table 5.2 indicates no clear seasonal trend for SS in the outflow of all filters confirming previous findings (Gikas & Tsihrintzis, 2012; Sani et al., 2013b) but contradicting data by Song et al. (2006) who found higher outflow concentration of SS in autumn compared to other seasons. The possible reason for this contradiction can probably be attributed to composition of the SS particles. The authors of the referenced contradicting literature claimed reed harvesting as the contributing factor to the high effluent SS concentration observed in the autumn period since the SS removal was due to sedimentation and filtration and was not biological indicating that the SS particles are inorganic in nature. In comparison, the high removal of SS throughout all seasons in this research could be attributed to both physical and biological removal processes. Karathanasis et al. (2003) reported that rooted biomass of the planted wetland systems gives more efficient filtration of the SS load and provides complimentary treatment of the organic portion of the SS load via microbial degradation processes which is in agreement with this study. However, significant seasonal variation for SS was noted when filters with small size aggregates were compared to filters with large size aggregates in summer 2012. Furthermore, when filters with a low loading rate were compared to those with a high one in summer 2011, spring 2012 and summer 2012, statistical significant difference was also evident (Table 5.4), probably because the high loading rate filters are likely overloaded in summer and spring of 2011 and 2012 while lack of adequate surface area for biofilm establishment in the larger aggregates compared to smaller ones might have been the possible reason for the observed

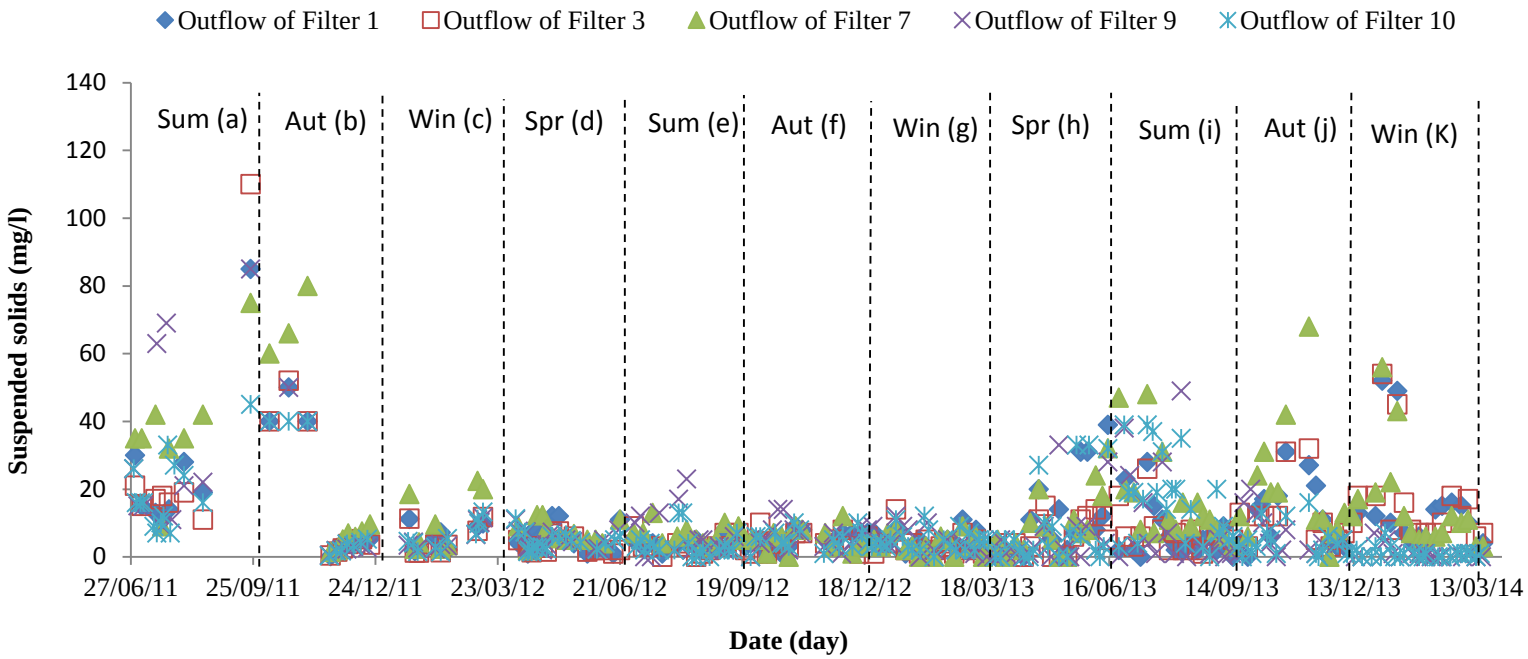

Figure 5. 5: Overall seasonal variations in outflow suspended solidsa 21/06/11 to 22/09/11; b 23/09/11 to 21/12/11; c 22/12/11 to 19/03/12; d 20/03/12 to 19/06/12; e 20/06/12 to 21/09/12; f 22/09/12 to 20/12/12; g 21/12/12 to 19/03/13; h 20/03/13 to 20/06/13; i 21/06/13 to 22/09/13; j 23/09/13 to 21/12/13; k 22/12/13 to 19/03/14. Diesel was applied on 26/09/13 and data collected started on 27/06/11and stopped on 19/03/14.

Difference (Meng etal. 2014) in summer2012.

With regard to turbidity, Table 5.2 indicates that high turbidity values are recorded in spring while low values are recorded in autumn. There are no internationally recognized outflow compliance values for turbidity. Statistical significant differences in loading rate were noted for turbidity removal in summer 2012 and spring 2013 (Table 5.4). Results reflect those for SS during warm months, indicating a good relationship between turbidity and microbial activity leading to organic matter degradation and subsequently to an increase in particles (Karathanasis et al., 2003; Sani et al., 2013b). However, in the period of petroleum hydrocarbon contamination, a seasonal statistical significant difference was recorded for contact time in autumn 2013 and winter 2014 for SS and turbidity respectively (Table 5.5). This difference could be attributed to insufficient time for microbial degradation in autumn and winter seasons. Clogging of the wetland media has been attributed to the blockage of substrate pores by SS particles leading to poor treatment performance efficiency and the subsequent diminution of the corresponding hydraulic conductivity. However, in this study, even in the perod of petroleum hydrocarbon pollution, there was no apparent sign of media clogging observed as the SS concentration values were below the threshold value of 30mg/l in all seasons except at the start up period and on top of the litter zone for all filters. The gradual development of the wetland biomass and microbial activity as the wetland systems mature overtime might have enhanced the high biodegradation of the SS particles leading to the observed good treatment performance of the wetland filters with no apparent sign of within bed clogging while immature biomass and the in ability of the weak biofilm to detain SS originating from the influent, and both the high strength and SS load of the wastewater and diesel degradation components and initial dying biomass depending on the stage of biodegradation were the cause for the high SS concentration during the set-up period and on top of the litter zone respectively .

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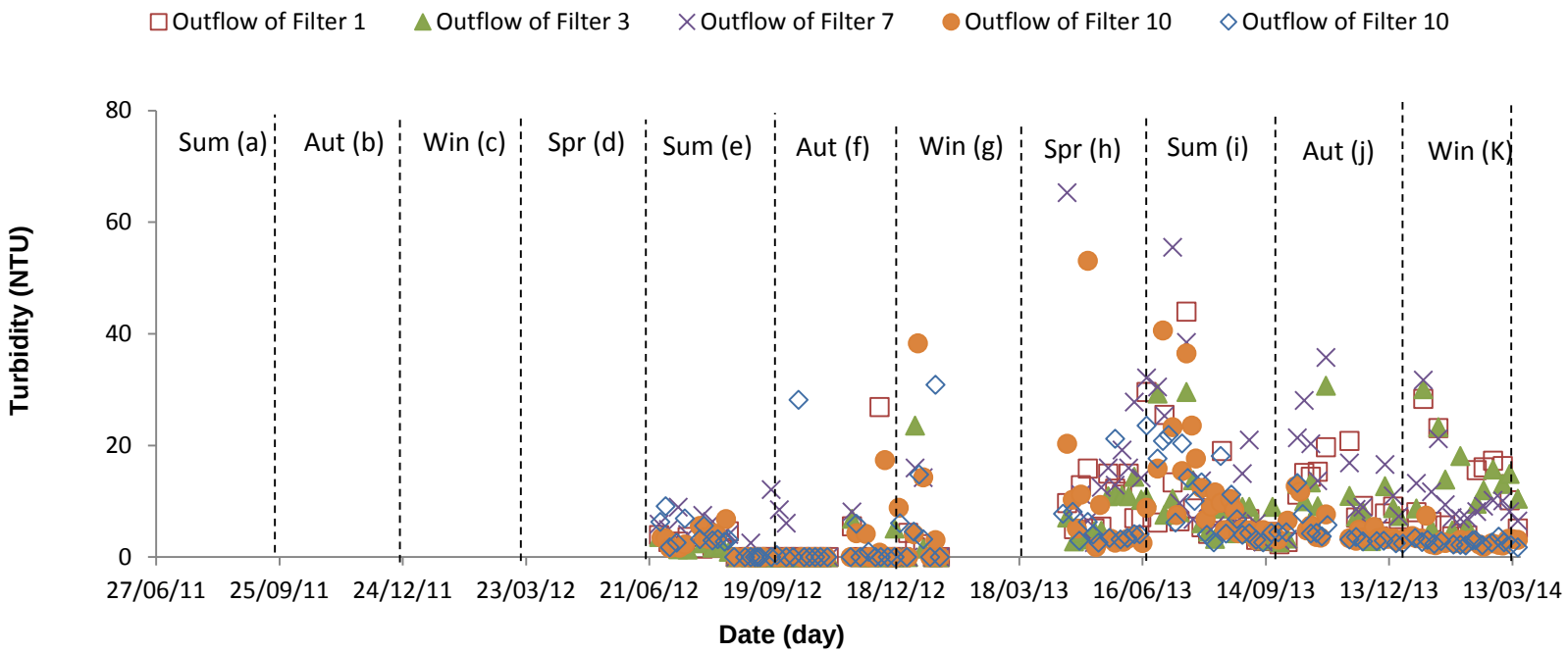

Figure 5. 6: Overall seasonal variations in outflow turbidity

a 21/06/11 to 22/09/11; b 23/09/11 to 21/12/11; c 22/12/11 to 19/03/12; d 20/03/12 to 19/06/12; e 20/06/12 to 21/09/12; f 22/09/12 to 20/12/12; g 21/12/12 to 19/03/13; h 20/03/13 to 20/06/13; i 21/06/13 to 22/09/13; j 23/09/13 to 21/12/13; k 22/12/13 to 19/03/14. Diesel was applied on 26/09/13 and data collected started on 27/06/11 and stopped on 19/03/14.

5.3 Seasonal assessment of filter performance based on SS accumulation in the substrate bed and its relationship to clogging

Tables 5.6 and 5.7 show the overall seasonal assessment of SS accumulation in the wetland filters and its relationship to clogging. For water quality variables with high (i.e. above 100 mg/l; Table 5.4 above) seasonal mean inflow concentrations, Table 5.4 indicates that only an elevated COD inflow load makes a significant difference in terms of seasonal COD concentrations in all seasons and SS outflow concentrations in summer 2011, spring 2012 and summer 2012. The development of a litter zone on top of each filter was observed after the first year of operation from summer 2012 to summer 2013 (Table 5.6). This was partly due to both the high strength and SS load of the wastewater (Sani et al., 2013a). However, concerning filter bed clogging evolution, measured in terms of SS accumulation, none of the systems have shown any signs of serious within-bed clogging after more than two years of operation (Sani et al., 2013b; Al-Isawi et al., 2014; Al-Isawi et al., 2015) even for the high rate Filters 7 and 8 in all seasons including the period of petroleum hydrocarbon contamination (Tables 5.6 and 5.7). However, a very modest but statistically significant breakthrough of turbidity was noticed for high rate filters in summer 2012 and spring 2013 (Table 5.4) indicating a good treatment efficiency by the wetland systems which was achieved as a result of gradual microbial acclimation and biomass development as the wetlands mature and intermittent aeration during the feeding mode operation subsequently, leading to high solids degradation, opening the blocked media pores, improving the hydraulic conductivity and the corresponding porosity of the substrate pores with observed low SS concentration. In the period after petroleum hydrocarbon application, Table 5.7 shows that all filters particularly those contaminated with diesel recorded high values of SS concentration within and on top of the litter zone compared to the pre-petroleum hydrocarbon application period. This increase in SS concentration can be attributed to diesel degradation components and initial dying biomass depending on the stage

of biodegradation that might have, over time, accumulated in the contaminated filters (Al-Isawi et al., 2014; Al-Isawi et al., 2015). Furthermore, some diesel components are recalcitrant in nature (Al-Baldawi et al., 2013a; Al-Baldawi et al, 2014), and might have led to the high concentration observed within the bed and on top of the litter zone.

Table 5.6: Mean suspended solids (SS) concentration within the filters (27/06/11 to 25/09/13; first to third experimental phase) all in mg/l

Sampling location	Filters 1 and 2	Filters 3 and 4	Filters 7and 8	Filter 9	Filter 10
Summer 2011 (21/06/11 to 22/09/11)					
Litter layer of filter	-	-	-	-	-
60 cm above outlet	-	-	-	-	-
55 cm above outlet	14.0	7.0	15.0	-	-
50 cm above outlet	14.8	10.0	25.5	7.0	15.0
45 cm above outlet	11.0	15.6	23.9	27.0	17.3
40 cm above outlet	8.6	13.3	19.9	12.0	17.3
30 cm above outlet	14.2	14.3	22.4	15.5	16.5
20 cm above outlet	11.7	15.2	24.0	15.5	27.8
10 cm above outlet	11.8	15.0	22.1	16.5	35.3
Outflow water	22.6	20.9	40.7	32.8	19.5
Summer 2012 (20/06/12 to 21/09/12)					
Litter layer of filter	81.9	63.5	114.8	82.8	68.0
60 cm above outlet	25.0	19.0	26.8	23.3	16.1
55 cm above outlet	14.9	19.3	21.1	19.6	13.0
50 cm above outlet	14.8	17.0	19.0	14.1	11.1
45 cm above outlet	11.9	13.9	11.9	10.3	8.5
40 cm above outlet	9.8	9.0	12.1	13.1	8.3
30 cm above outlet	6.8	5.9	10.0	7.4	5.3
20 cm above outlet	6.2	5.5	7.1	7.6	5.1
10 cm above outlet	4.3	5.1	6.6	6.3	6.3
Outflow water	5.1	3.3	6.6	6.6	3.6
Autumn 2012 (22/09/12 to 20/12/12)					
Litter layer of filter	42.7	29.1	34.7	54.4	29.0
60 cm above outlet	11.6	6.2	10.4	9.6	13.2
55 cm above outlet	7.1	10.6	8.3	13.2	9.0
50 cm above outlet	4.7	3.2	6.4	5.8	7.0
45 cm above outlet	4.4	3.7	6.9	3.4	4.0
40 cm above outlet	4.3	3.2	6.3	3.2	3.8
30 cm above outlet	4.3	2.5	6.1	3.6	3.4
20 cm above outlet	3.1	4.5	4.7	2.8	1.8
10 cm above outlet	3.4	2.2	5.6	2.2	3.2
Outflow water	4.5	4.3	5.2	6.3	5.0
Winter 2012/13 (21/12/12 to 19/03/13)					

Table 5.6 (cont)

Sampling location	Filters 1 and 2	Filters 3 and 4	Filters 7and 8	Filter 9	Filter 10
Litter layer of filter	65.2	48.4	69.8	40.3	35.2
60 cm above outlet	13.0	12.1	19.9	11.6	8.2
55 cm above outlet	6.4	8.3	16.8	9.0	5.8
50 cm above outlet	4.3	5.1	8.4	6.7	3.3
45 cm above outlet	3.2	4.1	6.9	3.6	4.0
40 cm above outlet	3.7	3.1	6.4	2.4	1.3
30 cm above outlet	2.9	3.5	5.8	3.6	2.2
20 cm above outlet	2.5	2.8	5.1	3.0	3.7
10 cm above outlet	2.7	2.2	3.8	2.1	1.3
Outflow water	4.2	3.7	4.8	4.8	4.8
Spring 2013 (20/03/13 to 20/06/13)					
Litter layer of filter	245.0	257.3	401.2	260.8	289.3
60 cm above outlet	29.2	40.9	47.9	49.7	38.8
55 cm above outlet	18.4	11.6	30.0	25.2	21.2
50 cm above outlet	11.3	9.0	26.3	15.3	14.5
45 cm above outlet	14.4	7.0	15.3	13.0	11.2
40 cm above outlet	12.2	7.1	12.9	8.3	8.8
30 cm above outlet	12.6	13.0	15.3	5.7	5.0
20 cm above outlet	12.6	8.3	11.2	3.7	4.3
10 cm above outlet	14.4	8.6	12.1	2.7	4.7
Outflow water	12.1	6.0	9.6	5.6	7.9
Summer 2013 (21/06/13 to 22/09/13)					
Litter layer of filter	143.6	133.9	244.9	149.1	197.3
60 cm above outlet	18.1	10.1	33.6	35.6	17.5
55 cm above outlet	15.8	7.5	23.8	9.8	17.4
50 cm above outlet	6.7	8.5	49.0	17.3	10.3
45 cm above outlet	9.0	12.7	33.4	15.0	23.4
40 cm above outlet	12.4	7.1	16.7	13.9	12.5
30 cm above outlet	12.8	5.8	17.3	6.5	22.8
20 cm above outlet	9.4	9.6	24.3	5.1	17.6
10 cm above outlet	11.7	11.9	22.6	8.4	19.0
Outflow water	10.0	8.94	14.2	10.9	16.0

However, there was no significant sign of within bed noted in terms of measured SS accumulation in all filters including high loading rate Filters including high loading rate Filters 7 and 8 (Table 5.7)

Table 5.7: Seasonal mean suspended solids (SS) accumulation within the wetland filters (26/09/13 to 20/12/13; data collection started on 22/09/13) after hydrocarbon application on 26/09/13 all measured in mg/l

Autumn 2013 (22/09/13 to 20/12/13)								
Sampling location	Filter 1	Filter 2	Filter 3	Filter 4	Filter 7	Filter 8	Filter 9	Filter 10
Litter layer of filter	451.8	395.3	479.3	333.8	249.3	134.8	194.0	234.2
60 cm above outlet	62.3	52.3	66.0	32.3	34.25	35.8	20.8	18.6
55 cm above outlet	35.5	38.0	44.0	25.0	28.3	34.0	15.5	12.8
50 cm above outlet	24.8	25.5	37.3	14.5	26.5	30.0	9.8	9.2
45 cm above outlet	20.3	25.8	33.3	17.0	22.3	25.8	7.5	4.4
40 cm above outlet	20.3	34.3	26.5	13.0	18.5	22.3	5.7	4.8
30 cm above outlet	23.3	22.3	21.5	18.5	22.8	22.0	8.3	4.8
20 cm above outlet	14.8	22.0	25.3	16.0	20.8	19.0	5.5	5.6
10 cm above outlet	14.5	17.8	19.5	18.8	25.0	205	8.0	7.8
Outflow water	12.9	6.1	12.3	8.1	19.2	10.0	5.2	4.5

5.4 Summary

This chapter discussed overall seasonal performance and clogging of different filter wetlands in both pre- and post-petroleum hydrocarbon periods in addition to seasonal inflow variability. The impact of different seasons on the key water quality parameters in various wetland systems was evaluated and discussed in detail. Moreover, seasonal trends were noted and their possible reasons were also interpreted in both petroleum hydrocarbon and non-petroleum hydrocarbon contaminated filters during and after the petroleum hydrocarbon pollution. Suspended solids concentration as the index of clogging has been also assessed in all the filters. Furthermore, they are evaluated based on seasonal variability and probable rationale of any variation observed has been elucidated and described.

CHAPTER 6

PETROLEUM HYDROCARBON REMOVAL IN DIFFERENT WETLAND FILTERS

6.1 Overview

In this chapter, section 7.1 introduces the summary of the overall performance of the wetland filters in post hydrocarbon period. The chapter is also divided into sections 7.2, 7.3 and 7.4. Section 7.2 discusses the inflow water quality and performance of the wetland filters after hydrocarbon pollution including the oxygen demand variables, nutrients and the particles. Treatment of different hydrocarbon components in various filters was also assessed and is interpreted in section 7.3, while a summary of the chapter is discussed in section 7.4.

6.2 Performance evaluation of water quality parameters in petroleum hydrocarbon contaminated wetland filters

6.2.1 Inflow water quality

Average mean inflow concentrations of water quality parameters monitored in a wetland operation for about one year of petroleum hydrocarbon contamination are analysed in this section. The raw domestic wastewater quality was examined, tabled and interpreted. Table 7.1 shows the overall inflow water quality before dilution for the period when some filters were selected and subjected to a one-off diesel spill as a target hydrocarbon to assess their performance efficiency with regard to petroleum hydrocarbon. The undiluted influent concentrations for COD, BOD, ammonia-nitrogen, nitrate-nitrogen, ortho-phosphate-phosphorus, SS and turbidity were 246 mg/l, 133 mg/l, 32 mg/l, 4 mg/l, 16 mg/l, 144 mg/l and 90 NTU, respectively.

Table 6.1: Inflow water quality: (raw (i.e. before dilution) domestic wastewater mixed with urban runoff) from 26/09/13 to April 2014 when some selected filters were subjected to a one-off diesel spill.

Parameters	Unit	Number	Mean	Minimum	Maximum	Standard deviation
COD	mg/l	16	246.1	112.0	360.0	93.02
BOD	mg/l	68	133.3	10.0	360.0	98.45
NH_4-N	mg/l	22	32.4	3.1	70.0	24.06
NO_3-N	mg/l	20	3.7	0.4	14.0	4.32
PO_4-P	mg/l	18	16.3	9.3	27.6	113.13
SS	mg/l	70	143.9	27.0	474.0	86.30
TBD	NTU	65	89.5	12.3	391.0	0.32

Note: only Filters 7 and 8 received the above water characteristics. The remaining filters received diluted wastewater (i.e. 1 part dechlorinated tap water and 1 part wastewater)

6.2.2 Comparison of petroleum hydrocarbon outflow water qualities

6.2.2.1 Comparison of oxygen demand variables (COD and BOD)

Organic matter expressed in the form of COD and BOD is removed via aerobic, anaerobic, adsorption, filtration, and microbial metabolism (Karathanasis et al., 2003; Song et al., 2006; Stefanakis et al., 2014) in wetlands. Furthermore, its concentration in urban wastewater is enormous (Stefanakis et al., 2014) and particularly COD can reach up to values of between 100,000 and 1,000,000,000 mg/l in hydrocarbon spill contamination (Scholz, 2010). Average performance data for about one year of wetland operation during the period of petroleum hydrocarbon pollution were monitored and are analysed in this section. The study examined changes over time in the wetland filters with or without petroleum hydrocarbon contamination regarding the water quality variables.

Overall performance with regard to water quality parameters is shown in Table 7.2 including the chemical and biochemical oxygen demand variables. The operation of the wetland filters without petroleum hydrocarbon spill was relatively good for key water quality parameters except nitrate-nitrogen (Table 7.2). However, the result with reference to COD shows that, all filters with hydrocarbon spill (1, 3, 7 and control A) showed poor COD removal efficiencies (less than 35%) and relatively lower BOD removal efficiencies (66–81%) compared to their corresponding filters without petroleum hydrocarbons (78–87% of BOD) and (35–75% of

COD). This demonstrates that diesel spills resulted in a sharp decline of the removal efficiency of the COD in petroleum hydrocarbon spill wetland filters probably because of the indirect artificial contribution of the COD in the inflow water, which might have elevated the outflow COD values observed (Chavan & Mukherji, 2008; Lohi et al., 2008; Al-Isawi et al., 2014; Al-Isawi et al., 2015) since it has been reported that petroleum hydrocarbons such as diesel are associated with high COD values (Scholz, 2010). However, in this study, note that the calculated removal efficiencies do not take account of the additional COD and BOD associated with the diesel spill. On the other hand, the relatively high COD and BOD removal efficiencies observed in the uncontaminated wetland filters could be attributed to the gradual improvement in macrophytes growth and wetland microbe's acclimation as the wetland systems mature, subsequently leading to high pollutants biodegradation (Scholz, 2006, 2010; Babatunde et al., 2011; Sani et al., 2012; Sani et al., 2013a; Sani et al., 2013b).

Pollution of urban wastewater with a petroleum hydrocarbon spill adversely affects organic matter treatment in constructed wetlands (Al-Isawi et al., 2014; Al-Isawi et al., 2015) because of the associated high amount of different petroleum hydrocarbon compounds in the spill. Furthermore, as a result of their recalcitrant nature, these petroleum hydrocarbon components (Sun et al., 2010; Al-Baldawi et al., 2014) perturb the physical, chemical and biological properties in the wetland systems (Sutton et al., 2013; Ying et al., 2013) subsequently leading to low organic matter depuration. In this research, the overall mean COD and BOD removal efficiencies for Filter 8 without petroleum hydrocarbon are higher than those of Filter 7 with petroleum hydrocarbon (both with high loading rate). This difference was not statistically significant as shown in Table 7.3, which summarizes an assessment of the statistically significant differences between outflow water quality variables of different filters using the non-parametric Mann-Whitney U-test. A comparison of Filter 1 with Filter 2, and Filter 3 with Filter 4 gives an insight into the effect of low loading rate on the treatment performance with

and without petroleum hydrocarbon. The overall removal efficiencies were also higher for filters without hydrocarbon than those with, though the difference is not great with regard to BOD (Table 7.2). A comparison between Filters 3 and 4 has shown a statistical significant difference in petroleum hydrocarbon impact. The relatively poor performance of the contaminated filters can be explained by the high inflow loading rates, which could also contribute to the influence of the high applied petroleum hydrocarbon in the influent wastewater as mentioned previously (Al-Isawi et al., 2014; Al-Isawi et al., 2015). Nevertheless, there were no significant differences with all filters observed when the period of contamination was compared with the uncontaminated one (Table 7.3).

With respect to COD however, there was a significant difference in all filters contaminated with petroleum hydrocarbons during the contamination period if compared with the corresponding period before they were polluted (Table 7.3) which could probably be due to the indirect artificial contribution of the COD in the inflow water, which might have elevated the outflow COD values observed (Chavan & Mukherji, 2008; Lohi et al., 2008; Al-Isawi et al., 2014; Al-Isawi et al., 2015).

Regulatory agencies for environmental pollution control set standard threshold values for wastewater contaminants like COD and BOD in secondary wastewater treatment. For example, the common standard set by environment agencies like The Urban Waste Water Treatment (England and Wales) Regulations (UK Government, 1994), which implements the Council Directive 91/271/EEC Concerning Urban Waste Water Treatment (European Community, 1991), sets a threshold value of 125 mg/l for COD removal in secondary wastewater treatment. Filters 1, 3 and 7 were 2, 2 and 4 times non-compliant with this standard, respectively (Figure 7.1). With regard to BOD however, 20 mg/l and 25 mg/l were set for sensitive and less sensitive (e.g., many coastal discharges) areas, by the traditional UK

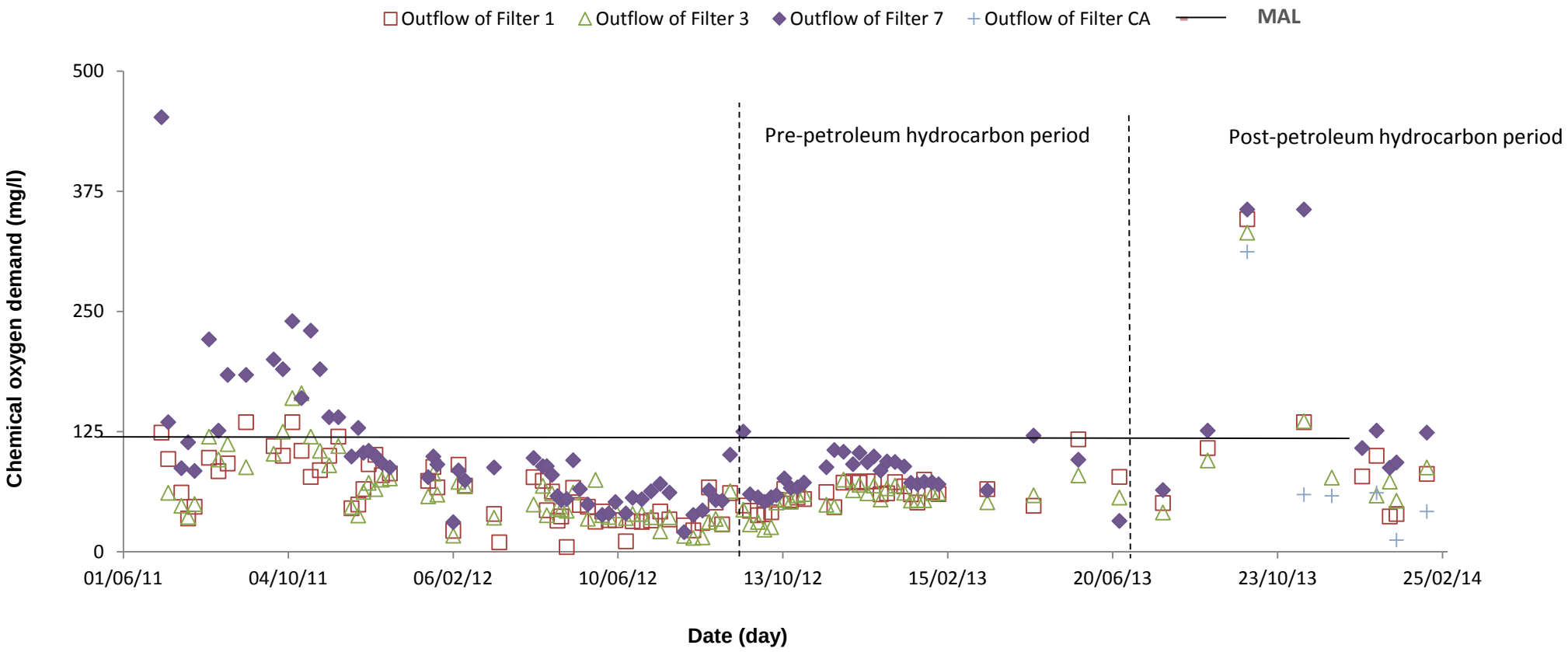

Figure 6. 1: Temporal variations of chemical oxygen demand for the effluent of filters with diesel contamination. The diesel was applied in the filters on 26/09/13. Data collection started from 27/06/11 and stopped on 19/03/13. MAL, maximum allowable limit

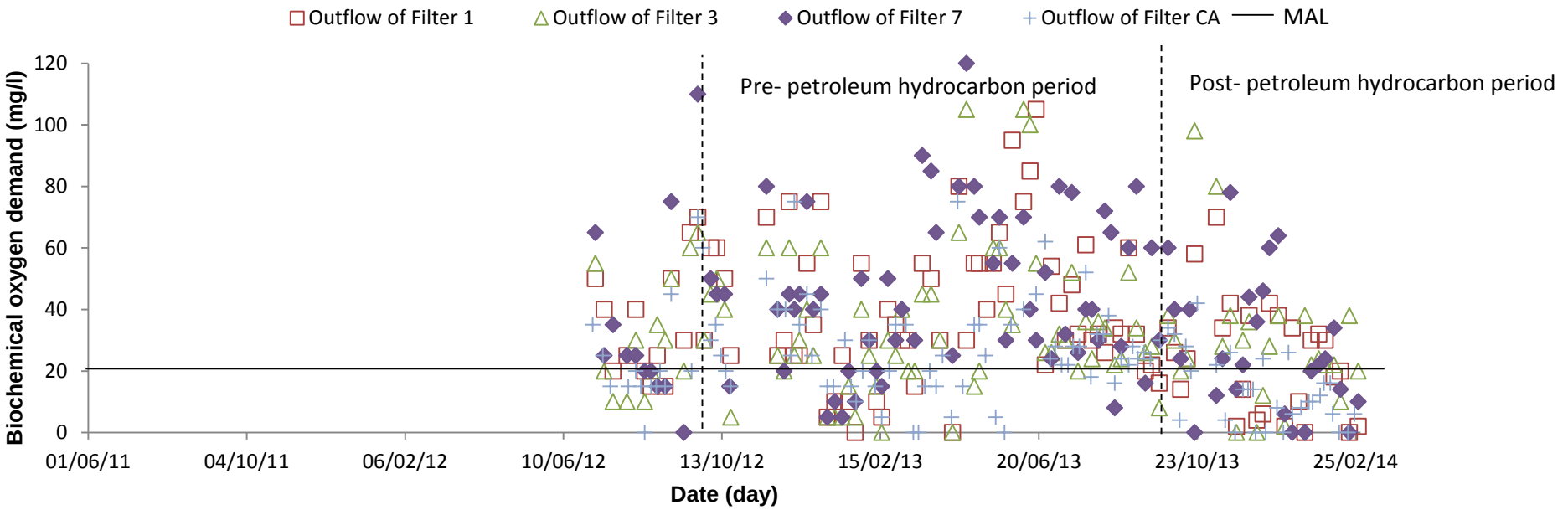

Figure 6. 2: Temporal variations of biochemical oxygen demand for the effluent of filters with diesel contamination

The diesel fuel was applied in the filters on 26/09/2013. Data collection started from 27/06/11 and stopped on 19/03/14. MAL – maximum allowable limit

standard for BOD removal from secondary wastewater (Royal Commission on Sewage Disposal, 1915). With respect to sensitive watercourses, Filters 1, 3 and 7 were 16, 17 and 16 times non-compliant, while in less sensitive areas, they were 13, 12 and 10 times non-compliant, respectively (Figure 7.2).

6.2.2.2 Comparison of nutrient variables (P and N)

In constructed wetlands, removal of nitrogen is predominantly by microbial nitrification and denitrification. However, the removal is insufficient without active and passive aeration, mainly because of inadequate oxygen available for aerobic biodegradation (Scholz, 2010; Saeed & Sun, 2011; Fan et al., 2012; Fan et al., 2013; Vymazal, 2014). Overall performance of wetland filters regarding the nutrient variables shows that all the nutrients were relatively removed from all filters, though removal was better in filters without petroleum hydrocarbon compared to those filters contaminated with it, except for nitrate-nitrogen which shows better removal in the latter.

Ammonia removal in constructed wetlands is intricate (Vymazal, 2007) and involves series of chemical, physical and biological reactions within the wetland media. However, numerous studies have shown that high aeration (Fan et al., 2012; Fan et al., 2013; Liu et al., 2014), which promotes the build-up of ammonia oxidizing bacteria, leads to high ammonia nitrification (Zhi et al., 2015). Overall reduction rates of ammonia-nitrogen in this study were relatively high ranging from 57% to 84% in all filters (Table 7.2) regardless of petroleum hydrocarbon contamination (though better in low loading rate filters than high loading ones) confirming findings by Eke and Scholz (2007) and De Biase et al. (2011) who reported 83% and 73–76% ammonia-nitrogen removal respectively in their hydrocarbon treatment wetlands but contradicting data elsewhere (Wu et al., 2012). The high removal of ammonia-nitrogen observed in this study could be attributed to the fact that intermittent aeration, increase in aerobic bacteria and established macrophytes growth as a result of improved wetland

maturation that took place over time, might have promoted the nitrification process leading to high ammonia removal (Fan et al., 2013; Al-Isawi et al., 2014; Al-Isawi et al., 2015). However, the possible reason why contrasting findings reported are in disagreement with the current study data could be due to the fact that despite the assessed wetlands in the reported literature being mature (over 6 years), the combined effect of sulphate and other inorganic compounds present in the wetland might have hindered the nitrification process, hence leading to the observed dropped value of ammonia removal from 75 to 42%. Previous studies have reported on the effect of sulphate on ammonia oxidation in constructed wetlands. Aesoy, Odegaard, and Bentzen (1998) and Wiessner et al. (2008) have shown that the high sulphide concentration effect on sulphate in their wetland systems impacts negatively on the oxidation and nitrification process of ammonia-nitrogen. The authors attributed the inhibition to sulphide toxicity and an increase in the reduction rate of sulphate which inhibit the growth and activity of wetland microbes leading to a high concentration of ammonia in the outflow (Van der Welle et al., 2007). Moreover, low aeration due to continuous loading in the reference literature could also be another reason for the lower removal values. Fan et al. (2012) and Fan et al. (2013) have stated that intermittent aeration leads to an increase in the growth of ammonia oxidizing bacteria with high nitrification activity.

Table 7.3 indicates an overview of statistically significant differences between outflow water quality variables of different wetland filters in the pre- and post-petroleum hydrocarbon period and with or without petroleum hydrocarbon contamination using the non-parametric Mann-Whitney U-test. With regard to ammonia, all filters, regardless of petroleum hydrocarbon contamination period and whether or not contaminated, have shown no statistical significant differences between the water quality parameters (Table 7.3).

Regarding a threshold value for ammonia removal in secondary wastewater treatment, the Urban Waste Water Treatment (England and Wales) Regulations (UK Government, 1994), did

not set a common standard typical for ammonia-nitrogen that would relate to the treatment system used in this experiment. However, a realistic guideline threshold value concerning secondary wastewater treatment in this study would be 20 mg/l (Sani et al., 2013b). After the hydrocarbon contamination, Filters 1 and 7 were one-time non-compliant while Filter 3 complied (Figure 7.3).

Nitrate-nitrogen removal in constructed wetlands is by denitrification (Scholz, 2010; Ji et al., 2012; Ji, He, & Tan, 2013). Several studies have reported positive correlation between denitrification of nitrate and supply of organic carbon, by macrophytes, to heterotrophs (Bastviken et al., 2005; Souza et al., 2008; Shen et al., 2015), and temperature (Stefanakis & Tsihrintzis, 2012; Mietto et al., 2015), subsequently leading to an increase in the heterotrophic activity and oxygen consumption, and hence higher denitrification. However, an inadequate denitrification process has been noted in some tidal flow constructed wetland studies as a result of insufficient carbon supply to allow the denitrification process to occur, which is reliant on the degradation preference of organic matter, and elevated nitrate concentration in the wetland outflow caused by aerobic environment in the wetland media bed. This situation impedes the activity and growth of the denitrifying microbes (Li et al., 2015). In this study, despite the fact that nitrate-nitrogen concentration in the inflow was relatively low, the outflow concentrations were relatively high for all filters. Only Filters 1, 3, 7 and 8 had positive removal efficiencies. In contrast, all other filters functioned as sources for nitrate-nitrogen because of the observed negative efficiency values in the outflow. The negative removal efficiencies for nitrate-nitrogen indicated that denitrification was likely to be only a minor removal mechanism (Kayranli et al., 2010; Sani et al., 2013a; Sani et al., 2013b; Al-Isawi et al., 2014). However, the necessary conditions for denitrification to occur were not directly investigated because these conditions (e.g. anoxic environment and presence of easily bio-degradable organic carbon) were not directly monitored within the entire small wetlands as this would have been too destructive

(Sani et al., 2013b). The overall nitrate-nitrogen removal efficiency observed in the present research is relatively high with little difference between the filters (Table 7.2). The nitrogen removal could be attributed to the high biodegradation processes of diesel spills in the contaminated filters, which over time promoted the growth of some microorganisms, providing a high source of carbon and energy (Chavan & Mukherji, 2008; Tang et al., 2010), and subsequently stimulating the nitrogen reduction via petroleum hydrocarbon degradation by, the wetland microbes (Scholz, 2010; Al-Isawi et al., 2014; Al-Isawi et al., 2015). Several hydrocarbon treatment studies have indicated that established macrophytes growth greatly absorbs nitrogen which elevates microbial activity in the wetland systems, resulting in high total nitrogen reduction (Ji et al., 2007) as a result of hydrocarbon degradation processes (Tang et al., 2010), confirming the data of the present study. The mean overall daily nitrate-nitrogen values of all filters with or without petroleum hydrocarbon and during the pre- and post-petroleum hydrocarbon period were not statistically significantly different from each other (Table 7.3). A common standard set by environment agencies for the nitrate-nitrogen variable disposal concerning secondary treatment of wastewater is 50 mg/l (Sani et al., 2013b) and all filters were compliant (Figure 7.4). Removal mechanisms of phosphorus in constructed wetland systems have been reported to include plant uptake (Vymazal, 2011c, 2013a), microbial uptake and accretions in wetland media (Gikas & Tsihrintzis, 2012), and retention by wetland substrate and precipitation in water column (Gikas et al., 2007). However, some studies have shown that it is one of the most difficult pollutants to remove by constructed wetlands (Pant et al., 2001; Prochaska & Zouboulis, 2006; Fia et al., 2014; Vera et al., 2014) The ortho-phosphate-phosphorus removal efficiencies in this study ranged between 58 and 74% for all filters regardless of the loadin rate and petroleum hydrocarbon contamination (Table7.2), confirming findings within the range reported in literature (Eke & Scholz, 2007;

Chavan & Mukherji, 2008; Al-Isawi et al., 2014; Al-Isawi et al., 2015) for petroleum hydrocarbon treatment wetlands. The relatively high ortho-phosphate-phosphorus removal can be attributed to gradual maturity and improvement of the wetland systems, established biomass as a result of macrophytes growth, high aeration due to intermittent feeding mode, and microbial acclimatization, which might have enhanced the high phosphorus reduction. Furthermore,petroleum hydrocarbon applied in the selected filters might have influenced the activity of the system microbes via the provision of carbon as the source of energy from its biodegradation processes (Chavan & Mukherji, 2008; Lohi et al., 2008; Al-Isawi et al., 2014; Al-Isawi et al., 2015) leading to subsequent microbial consumption. Phosphorus removal has been reported as the function of porous media adsorption and microbial uptake, processes not affected directly by temperature (Gikas & Tsihrintzis, 2010; Kadlec & Wallace, 2009; Stefanakis et al., 2009) and plant consumption (Vymazal, 2011b; Gikas & Tsihrintzis, 2012; Vymazal, 2013a).

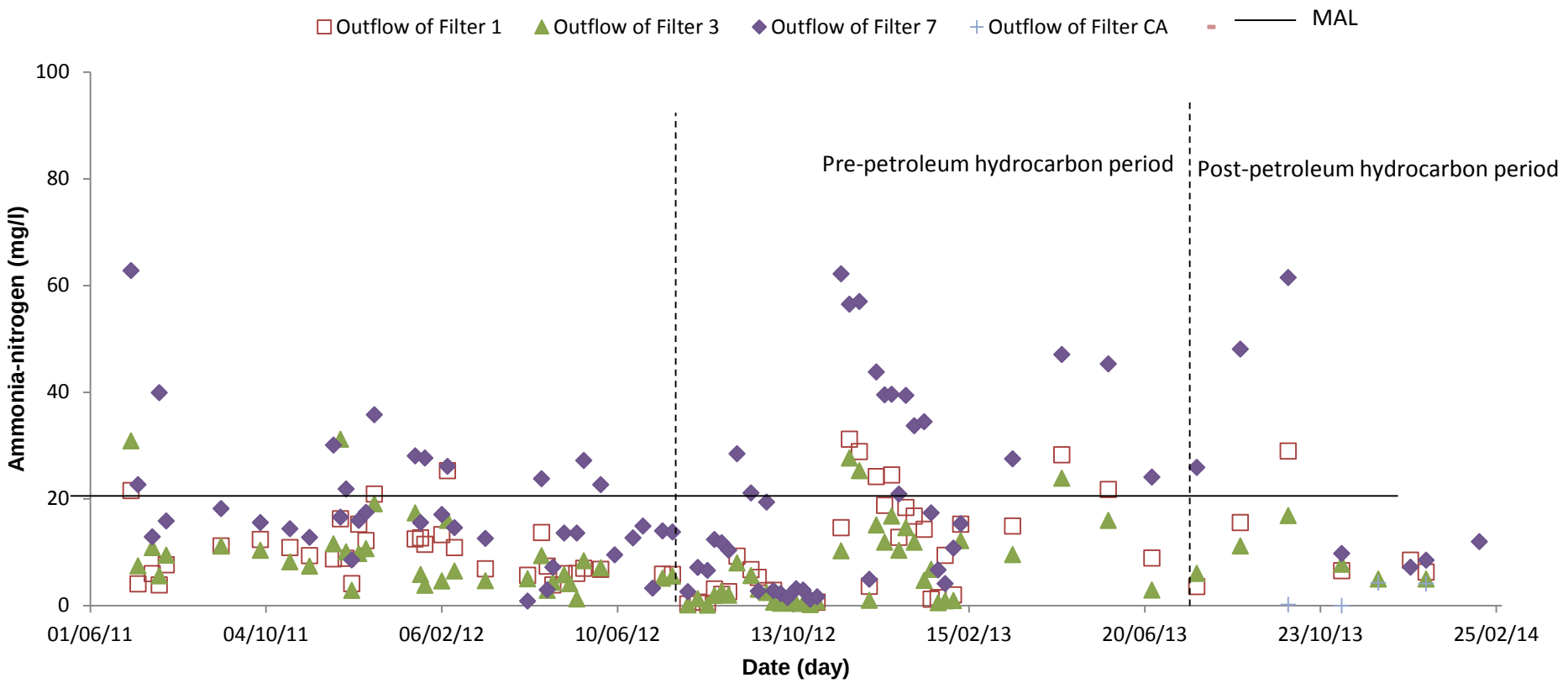

Figure 6. 3: Temporal variations of ammonia-nitrogen for the effluent of filters with diesel contamination

The diesel fuel was applied in the filters on 26/09/2013. Data collection started from 27/06/11 and stopped on 19/03/14. MAL – maximum allowable limit

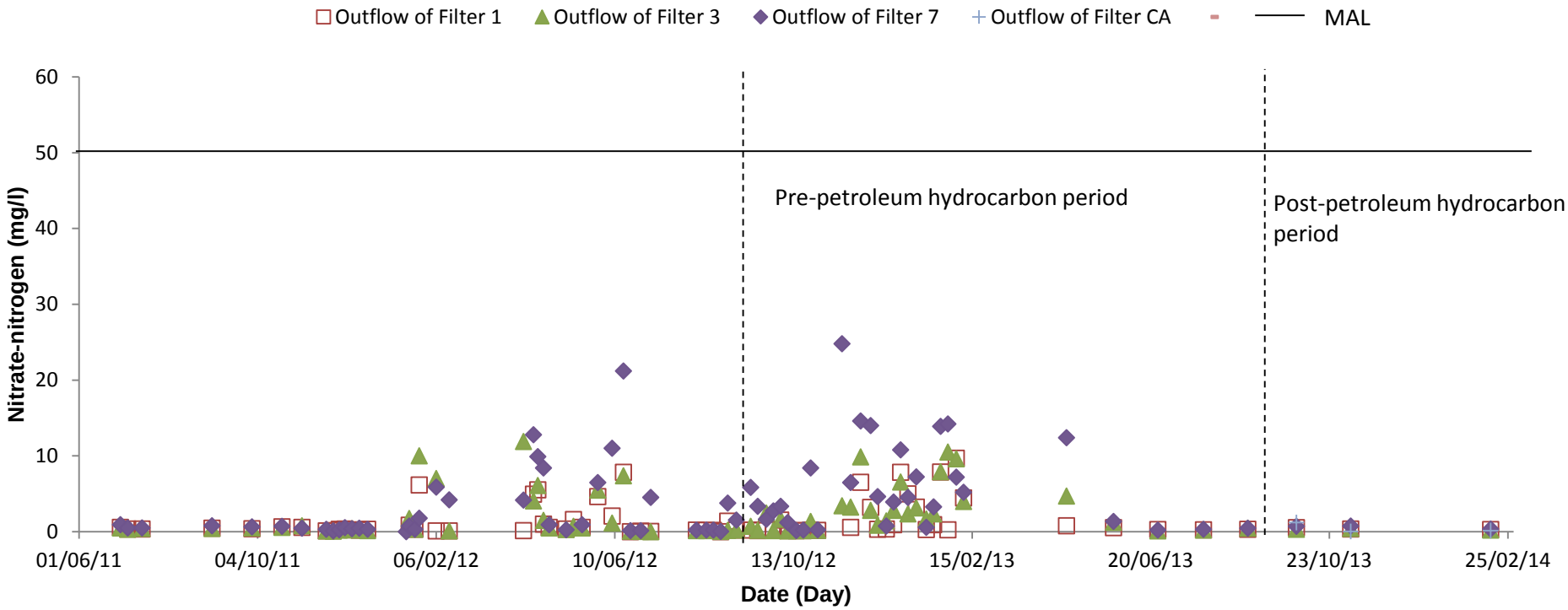

Figure 6. 4: Temporal variations of nitrate-nitrogen for the effluent of filters with diesel contamination

The diesel fuel was applied in the filters on 26/09/2013. Data collection started from 27/06/11 and stopped on 19/03/14. MAL – maximum allowable limit.

Table 6. 1: **Comparison of outflow water quality and air temperature for the period of one-off petroleum hydrocarbon spill (26/09/2013 to 30/04/2014)**

Parameter	Unit	Number	Mean	Removal %	Minimum	Maximum	Standard deviation
Filter 1							
COD	mg/l	9	108.0	12.3	36.7	346.0	94.44
BOD	mg/l	34	22.4	66.2	0.0	70.0	16.34
NH_4-N	mg/l	11	6.6	63.8	1.1	29.0	7.99
NO_3-N	mg/l	10	0.5	76.2	0.2	0.9	0.26
PO_4-P	mg/l	8	3.3	61.2	1.1	10.8	3.09
SS	mg/l	36	12.4	81.8	0.0	52.0	11.59
TBD	NTU	36	10.3	81.4	3.5	28.4	6.23
Filter 2							
COD	mg/l	5	48.2	61.0	18.4	93.2	35.28
BOD	mg/l	33	13.9	79.0	0.0	36.0	8.82
NH_4-N	mg/l	11	6.2	65.7	0.5	18.6	6.21
NO_3-N	mg/l	9	3.4	-68.5	0.3	8.6	3.24
PO_4-P	mg/l	8	3.1	63.7	1.9	5.2	1.34
SS	mg/l	36	7.1	89.6	0.0	49.0	11.38
TBD	NTU	36	6.4	88.4	2.0	46.1	6.84
Filter 3							
COD	mg/l	9	115.2	6.7	53.2	332.0	87.18
BOD	mg/l	34	25.7	61.4	0.0	98.0	19.31
NH_4-N	mg/l	11	4.3	76.6	0.7	16.9	4.82
NO_3-N	mg/l	10	0.5	77.7	0.1	1.1	0.36
PO_4-P	mg/l	8	3.0	64.7	0.9	9.5	2.80
SS	mg/l	36	13.0	81.0	0.0	54.0	11.21
TBD	NTU	36	11.0	80.3	0.9	30.7	6.39
Filter 4							
COD	mg/l	5	42.1	65.9	10.4	90.6	36.72
BOD	mg/l	31	13.0	80.5	0.0	40.0	10.33
NH_4-N	mg/l	10	4.9	73.2	0.1	15.2	4.81
NO_3-N	mg/l	9	0.6	-73.4	0.1	1.0	0.41
PO_4-P	mg/l	8	3.1	63.2	1.7	5.7	1.39
SS	mg/l	36	8.0	88.4	0.0	50.0	12.55
TBD	NTU	36	6.6	88.1	1.9	27.3	6.25
Filter 7							
COD	mg/l	9	160.7	34.7	60.5	356.0	113.06
BOD	mg/l	32	25.7	80.7	0.0	78.0	19.98
NH_4-N	mg/l	11	14.1	56.5	5.7	61.5	15.89
NO_3-N	mg/l	10	1.1	71.6	0.2	2.8	0.81
PO_4-P	mg/l	8	4.6	71.6	1.0	13.6	4.19
SS	mg/l	37	14.8	89.7	0.0	68.0	15.25
TBD	NTU	36	11.4	87.2	4.1	35.8	7.84
Filter 8							
COD	mg/l	5	61.7	75.0	27.8	139.0	47.47
BOD	mg/l	33	18.0	86.5	0.0	44.0	13.60
NH_4-N	mg/l	10	12.9	60.1	0.5	54.2	15.62
NO_3-N	mg/l	9	3.5	6.9	0.2	17.9	5.57
PO_4-P	mg/l	8	4.2	74.3	2.0	13.5	3.86

[a] not enough data; na, not applicable

Table 6.2 cont.

Parameter	Unit	Number	Mean	Removal %	Minimum	Maximum	Standard deviation
SS	mg/l	37	8.4	92.2	0.0	41.0	10.31
TBD	NTU	36	7.0	92.2	2.1	27.0	6.34
Filter 9							
COD	mg/l	6	39.5	68.0	14.1	106.0	36.56
BOD	mg/l	39	13.9	79.0	0.0	42.0	9.80
NH_4-N	mg/l	11	4.8	73.4	0.1	20.7	7.96
NO_3-N	mg/l	9	4.3	-114.8	0.4	10.4	3.47
PO_4-P	mg/l	8	3.2	61.8	1.8	7.8	2.05
SS	mg/l	40	2.2	96.8	0.0	13.1	3.23
TBD	NTU	39	3.3	94.1	1.8	13.3	1.98
Filter 10							
COD	mg/l	6	47.6	61.5	18.3	102.2	34.2
BOD	mg/l	46	14.7	77.8	0.0	36.0	8.71
NH_4-N	mg/l	10	2.8	84.2	0.09	17.4	5.2
NO_3-N	mg/l	9	3.7	-88.2	0.4	10.8	4.38
PO_4-P	mg/l	7	3.5	58.3	1.8	7.5	2.28
SS	mg/l	49	2.6	96.1	0.0	16.0	3.58
TBD	NTU	51	3.9	92.8	1.8	12.7	2.14
Filter A							
COD	mg/l	8	35.1	ned[a]	6.9	312.0	99.31
BOD	mg/l	33	8.1	ned[a]	0.0	42.0	10.58
NH_4-N	mg/l	11	2.0	ned[a]	0.0	4.6	1.71
NO_3-N	mg/l	10	0.6	ned[a]	0.0	2.0	0.61
PO_4-P	mg/l	8	3.5	ned[a]	1.8	7.8	2.05
SS	mg/l	36	2.7	ned[a]	0.0	39.0	9.7
TBD	NTU	36	5.3	ned[a]	2.2	21.3	4.46
Filter B							
COD	mg/l	5	35.1	ned[a]	3.5	90.3	36.80
BOD	mg/l	34	8.1	ned[a]	0.0	34.0	8.49
NH_4-N	mg/l	10	2.0	ned[a]	0.1	6.9	1.95
NO_3-N	mg/l	9	0.6	ned[a]	0.1	1.0	0.41
PO_4-P	mg/l	7	3.5	ned[a]	1.9	7.6	2.28
SS	mg/l	36	2.7	ned[a]	0.0	16.0	3.58
TBD	NTU	36	5.3	ned[a]	1.2	27.5	5.58
Air T^o	^OC	158	113	na	2.0	2.0	3.8

However, there are some studies of treatment wetlands treating wastewater contaminated with petroleum hydrocarbons and other organic compounds which reported more than 90% phosphorus removal efficiency, though the efficiency declined to 10% after a certain period of operation (Wu et al., 2012). These findings are in disagreement with the present study. The possible reason for this can be explained by the fact that despite the wetlands in the reported literature being more mature than the current ones of this study (6 years of operation), the inflow phosphorus concentration is low (5 mg/l) compared to the one used in this study (16

mg/l). Furthermore, the wetlands are larger in size with a larger foot print and surface area which might have elevated the high removal efficiency reported. Nevertheless, the authors attributed the decrease in the removal efficiency to sulphate toxicity, as a result of high sulphide concentration in the contaminated wastewater which negatively affected the phosphorus outflow concentration observed.

Petroleum hydrocarbon contamination of the wetland filters and the effect of the pre- and post-pollution period on water quality parameters were not statistically significantly different in terms of overall ortho-phosphate-phosphorus treatment (Table 7.3). The regulations (UK Government, 1994) set a value of 2 mg/l for total phosphorus for communities between 10,000 and 100,000 inhabitants. A threshold for ortho-phosphate-phosphorus that would relate to the treatment system discussed in this research does not exist. However, a realistic guideline threshold value for ortho-phosphate-phosphorus could be 1 mg/l. Filters 1, 3 and 7 were all 4 times non-compliant, after the pollution (Figure 7.5).

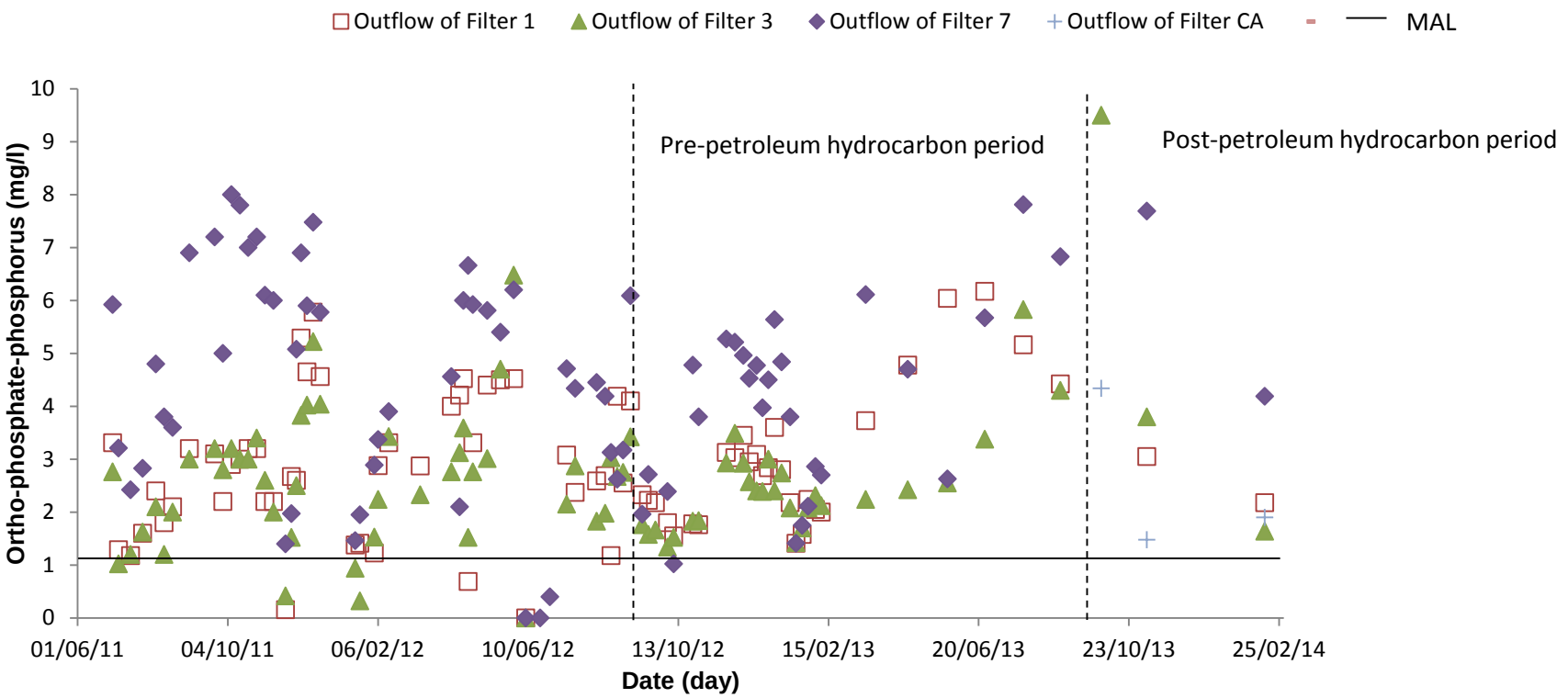

Figure 6. 5: Temporal variations of ortho-phosphate-phosphorus for the effluent of filters with diesel contamination.

The diesel fuel was applied in the filters on 26/09/2013. Data collection started from 27/06/11 and stopped on 19/03/14.MAL – maximum allowable limit.

6.2.2.3 Comparison of particles (SS and TBD)

Elimination of solids and particulate matter has been reported to be achieved (Kadlec & Knight, 1996; Green et al., 1997; Leonard, 2000; ITRC, 2003; Garcia et al., 2010; Hua et al., 2013) via settling and sedimentation, adsorption, and microbial degradation in wetland systems. However, Vymazal (2014) revealed that sedimentation, filtration, aggregation and surface adhesion are the primary removal mechanisms for suspended solids.

The results in this study regarding SS and turbidity, show that all filters, including those contaminated with petroleum hydrocarbons, demonstrated high removal efficiency (more than 80%) though filters with petroleum hydrocarbon contamination showed elevated SS concentrations compared to those without petroleum hydrocarbons immediately after the pollution, confirming findings by Al-Isawi et al. (2014) and Al-Isawi et al. (2015) (Table 7.2). This could be attributed to biodegradation process products of diesel spills in the affected filters that reduced the availability of nutrients to microorganisms and *P. australis*, thus reducing the biodegradation of the solids which might have led to the elevation of the SS and turbidity concentration particularly in the upper layers of wetland filters (Eke & Scholz, 2008). Furthermore, depending on the stage of biodegradation over time, initially dying contaminated biomass and later on degraded diesel might have contributed to the elevated values of SS within the filters. However, as the biodegradation of diesel progresses, small amounts of remaining hydrocarbon promote the growth of some microorganisms, which might have increased the degradation rate, subsequently leading to lower SS and turbidity concentration again (Al-Isawi et al., 2014; Al-Isawi et al., 2015). The high removal efficiency observed in suspended solids and turbidity could be due to sedimentation, plant uptake and microbial degradation as a result of improved macrophytes growth and high microbial activity as the wetland matures (Babatunde et al., 2011; Sani et al., 2012; Sani et al., 2013a; Sani et al., 2013b; Al-Isawi et al., 2014; Al-Isawi et al., 2015).

Several studies have shown a high positive correlation between wetland systems maturity and TSS removal (Karathanasis et al., 2003; Gikas & Tsihrintzis, 2012; Paing et al., 2015).

Nevertheless, a study conducted by Lohi et al. (2008) to assess diesel contaminated wastewater in a laboratory bioreactor has shown a suspended solids removal of 99% which is apparently a little higher than the current experimental highest value of 90% and 97% in diesel and non-diesel contaminated filters respectively. A possible reason for this difference might be due to the fact that, despite high inflow TSS concentration of 900 mg/l reported in the referenced literature compared with 144 mg/l in the current research, the relatively high influent diesel concentration of 20,000 mg/l in this study might have been the cause of the lower concentration-based removal efficiency of 90% SS. While the 1200 mg/l diesel fuel concentration reported in the referenced literature was probably enough to provide sufficient carbon as the source of energy to the reactor microorganisms, thus resulting in higher degradation of the TSS with very low outflow concentration. Tang et al. (2010), Al-Isawi et al. (2014), and Al-Isawi et al. (2015) reported that petroleum hydrocarbon residual and its degradation materials were the essential source of carbon as a source of energy that promotes the growth of some microorganisms, which increase the degradation rate. Moreover, a high amount of petroleum hydrocarbon degraded materials combined with initial and accumulated over time dying biomass from constructed wetlands contribute to increase in SS and turbidity concentrations (Al-Isawi et al., 2014; Al-Isawi et al., 2015), which might also be another reason for the lower 90% SS removal efficiency observed in this study compared to the one of the referenced literature. The impact of petroleum hydrocarbon pollution on suspended solids and turbidity in the pre- and post-petroleum hydrocarbon periods has shown a significant statistical difference (Table 7.3). This difference can be explained by the fact that diesel fuel artificially applied in the wetland filters might have led to the increased observed value.

Table 6. 3: Overview of the statistically significant differences between P-values regarding outflow water quality variables (mg/l) of different wetland filters using the non-parametric Mann-Whitney U-test (26/09/13 to 19/03/14)

Parameter	Impact of petroleum hydrocarbon[a]	Impact of petroleum hydrocarbon[b]	Impact of petroleum hydrocarbon[c]
Chemical oxygen demand	0.126	0.126	0.089
Biochemical oxygen demand	0.054	0.003	0.146
Ammonia-nitrogen	0.355	0.348	0.297
Nitrate-nitrogen	0.149	0.275	0.275
Ortho-phosphate-phosphorus	0.564	0.564	0.149
Suspended solids	0.001	0.001	0.008
Turbidity	0.001	0.000	0.001
Parameter	Impact of petroleum hydrocarbon[d]	Impact of petroleum hydrocarbon[e]	Impact of petroleum hydrocarbon[f]
Chemical oxygen demand	0.028	0.002	0.000
Biochemical oxygen demand	0.052	0.411	0.049
Ammonia-nitrogen	0.527	0.411	0.484
Nitrate-nitrogen	0.322	0.105	0.054
Ortho-phosphate-phosphorus	0.266	0.138	0.141
Suspended solids	0.000	0.000	0.000
Turbidity	0.000	0.000	0.000

[a]Comparison between Filters 1 and 2; [b]Comparison between Filters 3 and 4; [c]Comparison between Filters 7 and 8; [d]Comparison between Filter 1 pre- and post-hydrocarbon; [e]Comparison between Filter 3 pre- and post-hydrocarbon; and [f]Comparison between Filter 7 pre- and post-hydrocarbon. Note *P*-value is a probability of getting a test statistic at least as extreme as the one that was actually observed. Filters are statistically significantly different only if the *P*-value is <0.05 for the corresponding water quality parameter.

6.3 Petroleum hydrocarbon treatment in the wetland filters

Organic compounds degradation in constructed wetlands has been documented in numerous researches (Imfeld et al., 2009; Scholz, 2010; Tang et al., 2010; De Biase et al., 2011; Ranieri et al., 2013; Al-Isawi et al., 2014; Al-Isawi et al., 2015). In vertical-flow constructed wetlands, attenuation of petroleum hydrocarbon compounds has been attributed to volatilization and biodegradation (De Biase et al., 2011; Al-Isawi et al., 2014; Al-Isawi et al., 2015) and adsorption, aeration and microbial degradation (Al-Isawi et al., 2014; Al-Isawi et al., 2015; Zhang et al., 2014; Guittonny-Philippe et al., 2015a). Table 7.4 shows diesel fuel as the model petroleum hydrocarbon evaluated in this study and its constituents with their corresponding concentration values in the diesel before and after their treatment in the wetland filters. The analysed constituents are aliphatic, aromatic, total petroleum hydrocarbon (TPH), methyl tertiary butyl ether (MTBE), benzene, toluene, ethylene, xylene (BTEX), o-xylene, m-p xylene and volatile petroleum hydrocarbon (VPH). However, all these diesel compounds were found to be below the 10 µg/l detection limit in Filters 2, 4, 8, 9, 10 and control B outflow concentrations indicating very little or none of the pollutant compounds in the background inflow wastewater of these low loading filters since they are not contaminated with the petroleum hydrocarbons. Despite their high concentration in the diesel fuel, aliphatic and aromatic hydrocarbons with equivalent carbon (EC) index numbers 5-7 and 7-8 respectively were also below the 10 µg/l detection limit in all uncontaminated filters and less than 1 µg/l in the contaminated ones (Table 7.4). Furthermore, MTBE, BTEX, m-p xylene, o-xylene, other volatile petroleum hydrocarbon (OVPH) and total volatile petroleum hydrocarbon (TVPH) have also shown to be in the range of less than 10 µg/l in both polluted and unpolluted filters in spite of their high concentration in the diesel fuel except the MTBE (which even in the diesel and the inflow wastewater has a value below 10 µg/l). However, an aromatic with EC index number 35-44 has very low diesel concentration, but below 10 µg/l in all uncontaminated filters compared to the contaminated ones which are below 1 µg/l with the exception of Filter 10 that

recorded the concentration of 10 µg/l. Overall, results of the petroleum hydrocarbon removal efficiencies for each petroleum hydrocarbon component in different wetland filters, including natural background concentrations of diesel species in the raw wastewater which were low after the analysis, are depicted in Table 7.5. However, the findings are based only on a one-off sample. The overall removal efficiency is relatively very high for all petroleum hydrocarbon components with little difference between the filters except in controls (Table 7.5). The observed good performance in the different wetland filters could be explained by the fact that high aeration, as a result of the intermittent operation mode applied to the wetland systems, established reed growth and biomass achieved over time due to wetland maturity, and high microbial activity could have enhanced the biodegradation and removal of the petroleum hydrocarbon efficiently. Several studies have confirmed the above findings by showing a positive correlation between petroleum hydrocarbon removal and the aforementioned factors. For example, De Biase et al. (2011), Al-Baldawi et al. (2014), and Guittonny-Philippe et al. (2015a) have shown that an increase in aeration in the wetland systems stimulates the activity of petroleum hydrocarbon degradation bacteria leading to high removal efficiency of the organic compounds in the rhizosphere (Imfeld et al., 2009; Gikas, Ranieri, & Tchobanoglous, 2013). Furthermore, enzymatic and organic acid secretions (Zhang et al., 2011) from the wetland plant high root biomass, as a result of established reed growth achieved from the mature wetlands over time, increases the density, diversity, and activity of particular wetland microbes, which subsequently, degrade the petroleum hydrocarbons (Hedge & Fletcher, 1996; Yoshitomi & Shann, 2001; Li et al., 2009; Al-Baldawi et al., 2013a; Al-Baldawi et al., 2013b; Al-Baldawi et al., 2013c). In their study, Omari et al. (2003), Salminen et al. (2004), Al Mahruki, Alloway, and Patzelt (2006), and Bhatia and Goyal (2014) have indicated that common reed plants have the ability to enhance petroleum hydrocarbon degradation in wetland systems.

Table 6. 2: Overall overview of the analysis of petroleum hydrocarbon and its constituents in different wetland filters for 10 March 2014.

Analyte (µg/l)		Wetland filters											
Aliphatics	Method	Filter 1	Filter 2	Filter 3	Filter 4	Filter 7	Filter 8	Filter 9	Filter 10	Control A	Control B	Inflow	Diesel
EC5-7	AN15-1	<1*	<10	<1*	<10	<1*	<10	<10	<1*	<1*	<10	<1*	71900
EC>7-8	AN15-1	<1*	<10	<1*	<10	<1*	<10	<10	<1*	<1*	<10	<1*	538000
EC>8-10	SOPO5	<1*	<10	<1*	<10	<1*	<10	<10	99	<1*	<10	185	19465
EC>10-12	SOPO5	<1*	<10	<1*	<10	<1*	<10	<10	<1*	73	<10	76	1180882
EC>12-16	SOPO5	28	<10	14	<10	<1*	<10	<10	<1*	124	<10	16	273642
EC>16-35	SOPO5	72	<10	55	<10	14	<10	<10	<1*	70	<10	31	246575
EC>35-44	SOPO5	<1*	<10	<1*	<10	<1*	<10	<10	<1*	<1*	<10	<1*	419
TEC5-44 I	SOPO5	100	<10	69	<10	<1*	<10	<10	99	267	<10	309	2330883
Aromatics													
EC5-7	AN15-1	<1*	<10	<1*	<10	<1*	<10	<10	<1*	<1*	<10	<1*	366000
EC>7-8	AN15-1	<1*	<10	<1*	<10	<1*	<10	<10	<1*	<1*	<10	<1*	63000
EC>8-10	SOPO5	<1*	<10	<1*	<10	<1*	<10	<10	17	<1*	<10	19	572

Table 6.4 (cont.)

Aliphatics	Method	Filter 1	Filter 2	Filter 3	Filter 4	Filter 7	Filter 8	Filter 9	Filter 10	Control A	Control B	Inflow	Diesel
EC>10-12	SOPO5	<1*	<10	<1*	<10	<1*	<10	<10	<1*	41	<10	54	3296
EC>12-16	SOPO5	<1*	<10	<1*	<10	<1*	<10	<10	<1*	37	<10	215	8672
EC>16-21	SOPO5	<1*	<10	<1*	<10	<1*	<10	<10	<1*	<1*	<10	157	6672
EC>21-35	SOPO5	<1*	<10	<1*	<10	<1*	<10	<10	<1*	<1*	<10	27	7866
EC>35-44	SOPO5	<1*	<10	<1*	<10	<1*	<10	<10	<1*	<1*	<10	<1*	36
TEC5-44	SOPO5	<1*	<10	<1*	<10	<1*	<10	<10	17	79	<10	473	456114
TTPH[a] I and II	SOPO5	100	<10	69	<10	14	<10	<10	116	346	<10	782	2786997
MTBE[b] III	AN15a	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Benzene IV	AN15a	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	65120
Toluene V	AN15a	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	302300
E benzene VI	AN15a	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	9405
m-p Xylene VII	AN15a	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	34890

Table 6.4 (cont.)

Aliphatics	Method	Filter 1	Filter 2	Filter 3	Filter 4	Filter 7	Filter 8	Filter 9	Filter 10	Control A	Control B	Inflow	Diesel
o-Xylene VIII	AN15a	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	17570
Other VPH[c] IX	AN15a	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	1038900
Total VPH[d]	AN15	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	1467185

Note: The detection limit was 10 µg/l. Figures indicated by a * were less than the detection limit. The equivalent carbon number index is indicated by EC. [a]total petroleum hydrocarbon, [b]methyl tertiary butyl ether, other [c]volatile petroleum hydrocarbon, [d]total volatile petroleum hydrocarbon.

via atmospheric oxygen transfer to their roots and support the microbial population and their activity by deriving carbon as their energy source from the petroleum hydrocarbon (Chen et al., 2012), hence the higher removal efficiency of the organic compounds.

6.3.1 Petroleum hydrocarbon components degradation and removal in the wetland filters

Investigations have shown (Imfeld et al., 2009) that removal of petroleum hydrocarbons in wetland systems requires either a chemical, biological or physical process, or a combination of these, which are evaluated as TPH, total hydrocarbons (THC), VOCs, diesel range organics (DRO) and gasoline range organics (GRO). The DRO are composed of aromatics and aliphatics (Lin & Mendelson, 2009; Liu et al., 2011; Zhang et al., 2014) in addition to other petroleum hydrocarbon components. In this study, diesel, as the model petroleum hydrocarbon, is analysed into its various species, their concentration in inflow and outflow, and associated removal efficiency in different wetland filters. Figures 7.1, 7.2 and 7.3 show the removal efficiencies of TPH, total aromatcs and aliphatics of contaminated filters. The removal efficiencies of total aliphatics and total aromatics with all petroleum hydrocarbon fractions (C8 to C35) are shown in Table 7.5. All filters without petroleum hydrocarbon (2, 4, 8, 9, 10 and control B) have shown very high removal efficiencies for all hydrocarbon fractions (>96%, Table 7.4 (though data for percentage removal are not shown)). However, in the contaminated filters, except for the control A, the total aliphatics are within the range of 68 to 78% for low loading rate filters and 97% for the high loading one (Figure 7.1), while in the total aromatics, all filters and control A have shown high removal efficiencies of more than 96% and 83% respectively (Figure 7.2), irrespective of loading rate or contamination indicating that the removal efficiency of Filter 7 with high loading rate in total aliphatics was better than that of Filters 1 and 3 with low loading rate (Table 7.5). This can be explained by high degradation activity as a result of high microbial population in Filter 7 due to the high amount of nutrients from the undiluted wastewater received over time by the high loading rate filter in addition to

that from the petroleum hydrocarbon compound as a source of carbon and energy (Awe et al., 2008), thus the better removal observed in Filter 7 compared to the corresponding Filters 1 and 3. Furthermore, the high removal efficiency removal of 83% in the control can be attributed to the influence of the inherent microorganisms capable of degrading petroleum hydrocarbons in the filter (Liu et al., 2011), while lack of mature biomass, as a result of low nutrients concentration to boost the growth and activity of the indigenous microbes, could be the possible reason for the observed lower value of 83% efficiency compared to other filters. Moreover, the experimental findings indicated that total aromatics are more biodegraded than total aliphatics in all filters, confirming data by Lin and Mendelson (2009) who in their pot study to evaluate the potential of restoration and phytoremediation with *Juncus roemerianus* for diesel-contaminated coastal wetlands, found high removal efficiency in the range of 85 to 99.8% in the aliphatic hydrocarbons, while the aromatic hydrocarbons recorded efficiency in the range of 84 to 100%, with phytoremediation being more effective in degrading aromatics than aliphatic components.Nevertheless, investigation by Liu et al. (2011) in their research to evaluate degradation of diesel-originated pollutants in wetlands by *Scirpus triqueter* and microorganisms, recorded high removal efficiency of different diesel components in the fractions of C16-C24 in the range of 57 to 67% with aliphatic hydrocarbons being more degraded than aromatics by the degradation microbes in the roots rhizosphere, which is in disagreement with the current study data (68 to 97%). The possible reason for the difference observed between the present experimental data and that of contradicting literature could be the combined impact of improved and well matured macrophytes and microorganisms in the relative long-term operated wetland systems (about three years) in the present research, which resulted in high microbial degradation of the petroleum hydrocarbon components, with the corresponding high removal.

Table 6. 3: Overview of the analysis of the petroleum hydrocarbon components in the diesel fuel (value and petroleum hydrocarbon removal efficiency in brackets) for 10th March, 2014. Filters 1, 3, 5 and Control A were contaminated with diesel. The detection limit was 10 µg/l. Figures indicated by a * were actually returned as less than the detection limit.

Analyte (µg/l)	Filter 1	Filter 3	Filter 7	Filter 8	Filter 9	Filter 10	Control A	Inflow	Diesel
Aliphatic >EC8-10	<1*	<1*	<1*	<10	<10	99	<1*	185	19465
	(99.5)	(99.5)	(99.5)	(94.6)	(94.6)	(46.5)	(99.5)		
Aliphatic >EC10-12	<1*	<1*	<1*	<10	<10	<1*	73	76	1180882
	(98.7)	(98.7)	(98.7)	(86.8)	(86.8)	(98.7)	(3.9)		
Aliphatic >EC12-16	28	14	<1*	<10	<10	<1*	124	16	273642
	(-75.0)	(12.5)	(93.8)	(37.5)	(37.5)	(93.8)	(-675.0)		
Aliphatic >EC16-35	72	55	14	<10	<10	<1*	70	31	246575
	(-132)	(-77)	(54.8)	(67.7)	(67.7)	(96.8)	(-125.8)		
Total Aliphatics EC5-44 (I)	100	69	14	<10	<10	99	267	309	2330883
	(67.6)	(77.7)	(95.5)	(96.8)	(96.8)	(68.0)	(13.6)		
Aromatic >EC8-10	<1*	<1*	<1*	<10	<10	17	<1*	19	572
	(94.7)	(94.7)	(94.7)	(47.4)	(47.4)	(10.5)	(94.7)		
Aromatic >EC10-12	<1*	<1*	<1*	<10	<10	<1*	41	54	3296
	(98.1)	(98.1)	(98.1)	(81.5)	(81.5)	(98.1)	(24.1)		
Aromatic >EC12-16	<1*	<1*	<1*	<10	<10	<1*	37	215	8672
	(99.5)	(99.5)	(99.5)	(95.3)	(95.3)	(99.5)	(82.8)		
Aromatic >EC16-21	<1*	<1*	<1*	<10	<10	<1*	<1*	157	6672
	(99.4)	(99.4)	(99.4)	(93.6)	(93.6)	(99.4)	(99.4)		
Aromatic >E21-35	<1*	<1*	<1*	<10	<10	<1*	<1*	27	7866
	(96.3)	(96.3)	(96.3)	(63.0)	(63.0)	(96.3)	(96.3)		

Table 6.5 (cont.)

Analyte (µg/l)	Filter 1	Filter 3	Filter 7	Filter 8	Filter 9	Filter 10	Control A	Inflow	Diesel
Total Aromatics EC5-44 (II)	<1*	<1*	<1*	<10	<10	17	79	473	456114
	(99.8)	(99.8)	(99.8)	(97.9)	(97.9)	(96.4)	(83.3)		
Total TPH (=I+II)	100	69	14	<10	<10	116	346	782	2786997
	(87.2)	(91.2)	(98.2)	(98.7)	(98.7)	(85.2)	(55.8)		

EC, equivalent carbon number index; TPH, total petroleum hydrocarbon.

efficiencies, compared to the two-month short-term experimental findings reported in the referenced literature.

With regard to the observed biodegradation of aliphatics being greater than that of aromatics in the referenced literature, which is the reverse of the present findings, data could be attributed to type of macrophyte plants, and nature and selectivity differences of the consortium bacteria involved in the degradation process (Greenwood et al., 2008; Binazadeh, Karimi, & Li, 2009), since debilitation of petroleum hydrocarbon in the plants rhizosphere is a function of the degrading microbes (Greenwood et al., 2008; Al-Baldawi et al., 2014; Al-Isawi et al., 2014; Al-Isawi et al., 2015).

Findings from this research (Table 7.5) also indicate that aliphatics EC12-16 and EC16-35 have negative removal efficiencies in Filters 1, 3 and control A suggesting that these filters functioned as sources of these organic compounds in their outflow concentrations rather than as sinks (Al-Isawi et al., 2015). The plausible reason for this could be the accumulation over time of the background aliphatics received from the inflow domestic water that might have become resistant to degradation by the wetland consortium of the microbes, leading to an increase in the observed effluents concentration, higher than the inflow with negative values. Aliphatic hydrocarbon compounds are reported to be more biodegradation resistant than aromatics because of their high number of molecular weight, and their resistance increases with increase in molecular weight (Agency for Toxic Substances and Disease Registry [ATSDR], 2004; Greenwood et al., 2008; Liu et al., 2011). Furthermore, low microbes as a result of low concentration of nutrients in the diluted wastewater received by the affected Filters 1, 3 and control A could not biodegrade the aliphatics efficiently compared to the high loading rate Filter 7 with high nutrient concentration that has enough microbes to degrade the aliphatics effectively without the negative values (Awe et al., 2008).

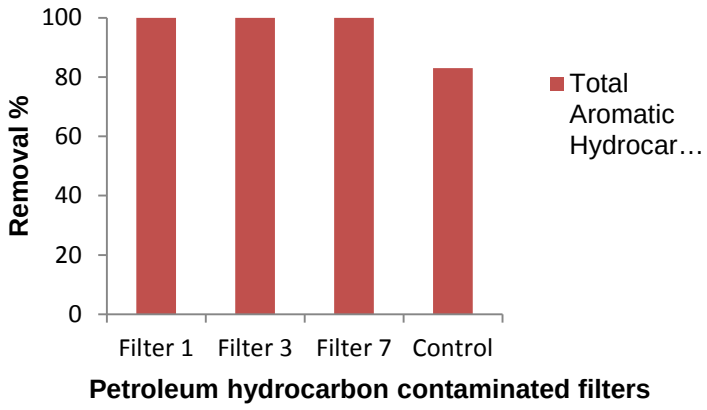

Figure 6. 6: Total aromatic removal efficiency (%) in different wetland filters

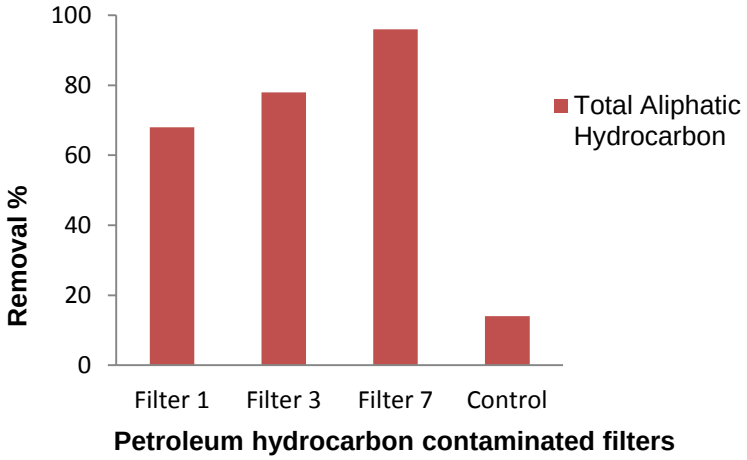

Figure 6. 7: Total aliphatic removal efficiency (%) in different wetland filters

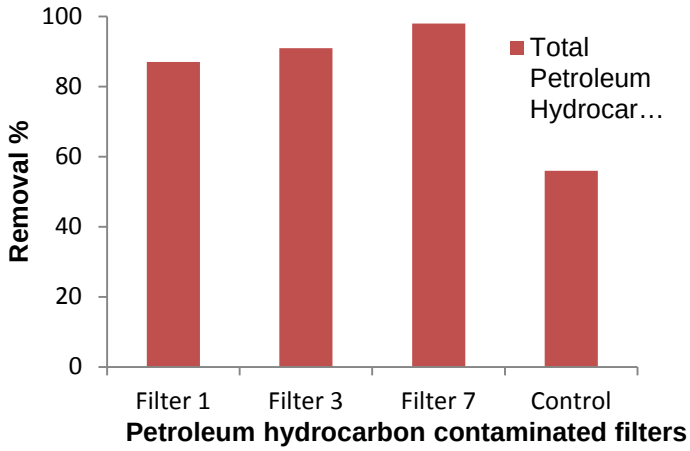

Figure 6. 8: Total petroleum removal efficiency (%) in different wetland filters

With respect to other petroleum hydrocarbon components, TPH compounds were virtually entirely removed from all filters with 87% as the lowest and 99% as the highest depuration

efficiency in all contaminated filters except for control (Figure 7.3), probably due to high aeration supported by the intermittent operation regime in the wetland systems (Scholz, 2010; Al-Baldawi et al., 2014; Al-Isawi et al., 2014; Al-Isawi et al., 2015), which stimulated and elevated microbial degradation of the organic compounds. Several studies have reported similar results to the current research findings. For example, Chavan and Mukherji (2008), Al-Baldawi et al. (2013a) and Guittonny-Philippe et al. (2015a) recorded a removal efficiency of TPH as the index hydrocarbon in the range of 90 to 100% in their treatment systems and attributed the elimination to microbial degradation. However, note that all other diesel components like MTBE, VPH, BTEX, etc., whose removal efficiencies are not shown, were below 10 μg/l in all filters including control regardless of contamination or operation (Table 7.4) indicating their complete removal (>99%). This could be attributable to the combined effect of volatilization and phytovolatilization in addition to biodegradation since they are volatile in nature (Imfeld et al., 2009). Moreover, based on the evaporation experiments, about 30% of the diesel had evaporated after a month, and no further evaporation was noticed on visual inspection after that, suggesting that volatilization and phytovolatilization are the main removal mechanisms during the first few days of petroleum hydrocarbon application. This has been confirmed recently by Al-Isawi et al. (2014) and Al-Isawi et al. (2015) who noted total elimination of volatile organic compounds including MBTE, VPH and BTEX with outflow concentration below the detection limit from their wetland systems.

Environmental regulatory agencies for water pollution control have set a limit for disposal of hydrocarbon compound pollutants in wastewater for secondary wastewater treatment. For example, a common standard set by these agencies for aliphatics in the range of C8-C35 hydrocarbon fractions concerning secondary treatment of wastewater is 300 μg/l (WHO, 2005) and all filters were compliant (Table 7.6). Also, aromatics in the class of C10-C16 and total aromatics with C5-44 hydrocarbon compounds should not exceed the threshold values of 100

μg/l and 300 μg/l respectively. The standard for TPH however, is set at 5000 μg/l by the environmental agencies (EPA, 2005). All filters complied.

In order to evaluate the performance of the present wetland filters in terms of petroleum hydrocarbon treatment, findings of the present research was compared with studies conducted and reported in literature regarding treatment wetlands treating urban wastewater contaminated with, specifically, petroleum hydrocarbons like aromatics, aliphatics and TPH (Table 7.6). Overall results indicated that all the effluent concentrations of the contaminated filters in this study are below the outflow values reported in the reference literature except for the control and the non-polluted filters with respect to aliphatics and aromatics, which may be due to lack of mature biomass and nutrients in the former, and insufficient microorganisms in the latter to achieve the hydrocarbon degradation. However, TPH values were higher than the reported values in the contaminated filters, probably due to high inflow petroleum hydrocarbon concentration in comparison with the reported literature (Table7.6). Investigations regarding treatment wetlands treating domestic wastewater contaminated with petroleum hydrocarbons are limited (Giraud et al., 2001; Fountoulakis et al., 2009; Al-Isawi et al., 2014; Al-Isawi et al., 2015). In this research, aromatic hydrocarbon fractions of EC12-16 with total aromatics of EC5-44, and TPH, have outflow concentration in the contaminated filters below the detection limit, and in the region of 14 μg/l and 100 μg/l, except in control, for the former and latter respectively. .

Table 6. 4: Overview of references summarizing typical petroleum hydrocarbon concentrations in wetlands and associated standard thresholds measured in µg/l

Analyte	Unit	Typical outflow of wetlands treating domestic wastewater	Secondary wastewater treatment standards for petroleum hydrocarbon	Typical outflow of wetlands treating specifically petroleum hydrocarbons
Aliphatic >EC8-10	µg/l	–	300[a]	25[g]
Aliphatic >EC10-12	µg/l	–	300[a]	55[g]
Aliphatic >EC12-16	µg/l	–	300[a]	210[g]
Aliphatic >EC16-35	µg/l	–	300[a]	73[g]
Total Aliphatics EC5-44	µg/l	–	–	101[g]
Aromatic >EC8-10	µg/l	–	20[c]	0.6[j]
Aromatic >EC10-12	µg/l	–	100[a]	0.5[j]
Aromatic >EC12-16	µg/l	Non detect[k]	100[a]	Non detect[h]
Total Aromatics EC5-44	µg/l	0.17)[i]	300[a]	0.17[i]
TPH	µg/l	25000[h]	5000[b]	0.12 -0.28[d,e,f]

EC, equivalent carbon number index; TPH, total petroleum hydrocarbons; [a]WHO (2005); [b]EPA (2005); [c]Scottish Environmental Protection Agency (2004); [d]Kadlec and Knight (1996); [e]Moshiri (1993); [f]Tchobanoglous and Burton (1991); [g]Bergier (2011); [h]Al-Baldawi (2013a); [i]Fountoulakis et al.(2009); [j] Wallace et al. (2011); and [k]Giraud et al. (2001).

The outflow TPH values reported by Al-Baldawi et al. (2013a) were even above the values noted in the contaminated filters of this study (Tables 7.5 and 7.6) probably because of the integrated effect of established matured biomass, high microbial activity and high aerobic environment in the wetland systems that was achieved over time (about 3 years), which resulted in high biodegradation of the petroleum hydrocarbon in the present study compared to the short-term experiment undertaken in the reference literature (72 days). However, the results of Giraud et al. (2001) and Fountoulakis et al. (2009) are in agreement with the present findings data with respect to aromatic EC12-16 and total aromatic EC5-44 outflow concentration (Table 7.6).

6.4 Summary

This chapter discussed the inflow water quality and overall treatment of petroleum hydrocarbon and its associated compounds in the wetland filters, alongside water quality parameters. It also addressed the impact of petroleum hydrocarbon on the performance of different wetlands in treating the wastewater contaminants. Furthermore, removal efficiency of both organic and inorganic pollutants recorded in both contaminated and uncontaminated wetland filters were evaluated and interpreted. Biodegradation and removal of diesel components alongside treatment efficiency were also appraised and discussed.

CHAPTER 7

CONCLUSION AND RECOMMENDATION FOR FURTHER RESEARCH

7.1 Conclusion

Experimental vertical-flow constructed wetland rigs were operated and used to evaluate the internal processes and efficacy of the wetlands and impact of design and operational variables on treatment performance and its relationship on clogging evolution of the systems. Furthermore, the wetlands were also explored for treating petroleum hydrocarbon spill in shock loading (one-off dose) alongside clogging and other water quality parameters. The overall results show that none of the laboratory scale vertical-flow constructed wetlands showed any signs of clogging after about three years of operation. Moreover, the systems were shown to be highly efficient for the treatment of petroleum hydrocarbon and other water quality variables.

The main conclusions emanating from this research are summarized as follows:

- Overall, all constructed wetland systems have shown relatively high removal efficiencies for the key water quality parameters regardless of filter set-up before the petroleum hydrocarbon spill, which impeded plant development and led to poor water quality (except for nitrate-nitrogen used for biodegradation of diesel) (chapters 4, 5 and 7).
- In the first experimental phase, the start-up period, relatively high removal efficiencies of COD, ortho-phosphate-phosphorus, and SS were noted. The removal efficiencies exceeded 43, 46, and 68% respectively in all filters irrespective of loading or aggregate size. Greater removal efficiencies of COD, BOD, ammonia-nitrogen, ortho-phosphate-phosphorus, turbidity and SS were also recorded in the second experimental phase, a period after start-up; the reduction efficiencies observed in all filters were above 56, 30, 69, 65, 98 and 83%, respectively, regardless of operational and design parameters. Findings in the third experimental period indicated that a minimum reduction of 49,

51, 57, 54, 92 and 87% of COD, BOD, ammonia-nitrogen, ortho-phosphate phosphorus, SS and turbidity was noted in all wetland filters.

- However, in the period after petroleum hydrocarbon pollution of some selected filters, the filter with the highest COD loading but no diesel contamination performed the best in terms of COD and BOD removal. Furthermore, filters contaminated by diesel performed worse in terms of COD and BOD, but considerably better regarding nitrate-nitrogen removal. In this period, the key water quality parameters, COD, BOD, ammonia-nitrogen, nitrate-nitrogen, ortho-phosphate-phosphorus, SS and turbidity have removal efficiency of more than 12, 6 and 34% , 66, 61 and 80% , 63, 61 and 56%, 76, 77 and 71%, 61, 64 and 71%, 80, 80 and 89%, and 81, 80 and 87% in hydrocarbon contaminated Filters 1, 3 and 7 respectively, while 60, 65, 74, 67 and 61%, 78, 80, 86, 78 and 77%, 65, 73, 60, 73 and 84%, 63, 63, 74, 61 and 58%, 89, 88, 94, 96 and 96%, and 88, 88, 92, 94 and 92% for COD, BOD, ammonia-nitrogen, ortho-phosphate-phosphorus, SS and turbidity in non-contaminated Filters 2, 4, 8, 9 and 10 respectively. However, some filters, including both contaminated and non-contaminated, recorded negative values in their outflow concentration for nitrate-nitrogen indicating that the filters served as a source for the nitrate-nitrogen (chapters 4 and 7).
- With regard to modelling, the proposed Wang-Scholz model developed to assess the filter clogging is simple, transparent and delivers good estimations for less complex filter operations. Furthermore, the model performed well with respect to the prediction of SS within the filters. The modelling results were generally poor for the set-up period, adequate for the first two years after the set-up period and variable after the diesel spill. However, the model runs consistently under-predicted the SS concentrations within the litter zones and the model does not account for biological growth, decay of plant matter, degrading leaves and stems, and diesel spills. All these contribute to SS accumulation on top of the filter and the model was never designed to deal with them.

- Pertaining to the clogging evolution however, the results show that none of the systems has shown any signs of clogging after about three years of operation, and serious clogging phenomena impacting negatively on the treatment performance and the hydraulic conductivity were also not observed, which is surprising considering that the wastewater load is high and the filters can be regarded as mature. The simulation model confirms the observation based on the water quality analysis of all filters that considerable filter clogging restricting the operation has not occurred after these years of operation indicating that vertical-flow wetlands under intermittent operation mode can effectively treat inorganic and organic contaminants in about three years without clogging. However, a small aggregate diameter, a short contact time, a long resting time and a low COD inflow concentration were most beneficial in reducing SS accumulation within the wetland filters.
- The result of investigation of seasonal influence on the performance and its relationship to evolution of clogging of the wetland systems revealed that all constructed wetlands have high removal of key water quality variables COD, BOD, ammonia-nitrogen, nitrate-nitrogen, ortho-phosphate-phosphorus, turbidity and SS without any sign of within bed clogging except at the period of start-up and petroleum hydrocarbon contamination, though high inflow seasonal variability was noted. Findings also indicate that some variables showed a seasonal removal trend while some have no pattern. For instance, COD, nitrate-nitrogen and ammonia-nitrogen have shown a seasonal trend with high removal in summer compared to other seasons, while BOD removal was efficient in winter compared to summer and turbidity was greatly removed in autumn compared to other seasons. However, no clear seasonal pattern of ortho-phosphate-phosphorus and SS removal were noted. With regard to the petroleum hydrocarbon contamination period, all filters, regardless of the pollution, design or operation, had higher removal in winter than autumn for COD, BOD, ammonia-

nitrogen and ortho-phosphate-phosphorus while no seasonal trend was observed for other water quality parameters. These data indicate that intermittent vertical-flow systems are dynamic, robust and reliable eco-technologies that can efficiently treat both traditional and petroleum hydrocarbon pollutants even in low temperature seasons without being clogged.

- Degradation of the petroleum hydrocarbon pollutants was also assessed, and the investigation revealed that all the petroleum hydrocarbon components treated in the wetland filters were highly degraded (>80% removal efficiency) in all contaminated filters with some even attenuated below the detection limit. For example, non-detect values were recorded for TVPH, MTBE, BTEX, etc. in all filters. However, with regard to water quality parameters, the filter with the highest COD loading but no diesel contamination performed the best in terms of COD and BOD removal. Filters contaminated by diesel performed worse in terms of COD and BOD, but considerably better regarding nitrate-nitrogen removal. Furthermore, the findings demonstrate that even with the high dose of the hydrocarbon spill in the wetland filters, clogging and low hydraulic conductivity to restrict the system performance were not observed. This result has shown the robustness of vertical-flow wetlands under intermittent operation mode in eliminating various types of contaminants including organic compounds in urban wastewater, even in shock loading, without being clogged. The successful removal of the aromatic and aliphatic hydrocarbon components and other pollutants will make constructed treatment wetland a very attractive and sustainable technology capable of meeting a zero discharge goal without clogging in the production, storage, refining and transportation sectors of the oil and gas industry.

- Considering the result of a separate evaporative study, findings suggest that volatilization, phytovolatilization and biodegradation are likely to be the major petroleum hydrocarbon removal mechanisms in the wetland systems

7.2. Recommendations for future work

Though clogging was not observed, its effect on the treatment performance of vertical-flow wetlands in terms of petroleum hydrocarbon removal in a long-term controlled experiment is recommended for further investigation. Moreover, research under controlled laboratory conditions or field scale should be undertaken to find out more about the microbial removal processes responsible for ammonia-nitrogen, nitrate-nitrogen and plant-originating SS reduction. The investigation of a real wetland becoming more mature until it requires decommissioning, which might, however, take as long as 20 years, will be an additional advantage.

Although this research has demonstrated the potential for future use of CWs for treatment of petroleum hydrocarbon and other traditional contaminants without clogging, there is an obvious need for numerical process modelling and long-term process assessments of water quality parameters in vertical-flow CWs treating wastewater subjected to different hydrocarbon one-off and regular dosages of diesel. This could form the data base for an improved Wang-Scholz model. Furthermore, the long-term monitoring of wetland plants to evaluate their tolerance to different petroleum hydrocarbon species and concentrations should be considered.

With regard to volatilization, phytovolatilization and biodegradation, as the possible removal mechanisms of petroleum hydrocarbon treatment in constructed wetlands, further research should focus on the specification of biodegradation products and quantification of the proportion of petroleum hydrocarbons being lost through volatilization and phytovolatilization to the atmosphere under varying temperatures and other environmental conditions in field-scale wetland systems.

The potential causes of treatment efficiency decline of some water quality parameters, particularly COD removal in the petroleum hydrocarbon pollution period, need to be assessed further more preferably in field-scale wetlands in a long-term study for about five to ten years.

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