# The Application of Integrated Constructed Wetlands for Contaminant Treatment and Diffusion

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# Declaration

I declare that this thesis was composed by myself and that the work contained therein is my own, except where explicitly stated otherwise in the text. The work has not been submitted in any form for any other degree or professional qualification.

Yu Dong

November 2012

*To my dearest grandpa, dad and mom.*

# Abstract

The sediment accumulation is an important characteristic in the ageing process of integrated constructed wetlands (ICW). Retained nutrient and other contaminants in wetland sediments have the potential to be remobilized and released to the overlying water column when environmental conditions change. In this study, mesocosms which filled with saturated sediments and planted with *Phragmites australis* and *Agrostis stolonifera* were set up to examine nutrient and other contaminants retention and/or release by wetland sediment and substrates. The effects of physico-chemical parameters on sediment-water contaminant exchange were also investigated through the application of multiple regression models, principal component analysis (PCA), redundancy analysis (RDA), and self-organizing map (SOM) model. The results demonstrated an average net release of chemical oxygen demand (COD), ammonia-nitrogen ($NH_3$-N), nitrate-nitrogen ($NO_3$-N) and molybdate reactive phosphorus (MRP) to the overlying water column, indicating that the ICW sediment and substrates acted as new contaminant sources. According to statistical analysis, electrical conductivity (EC) and redox potential (RP) values affected COD treatment efficiency. Chloride (Cl) concentration and RP value had an impact on $NH_3$-N treatment performance. $NO_3$-N removal was influenced by dissolved oxygen (DO) concentration and RP value. MRP treatment efficiency was related to DO concentration and EC value. The SOM model was selected as prediction tool to provide numerical estimations for the performance of ICW mesocosms. The model was validated, indicating that $NH_3$-N, $NO_3$-N, MRP, and COD treatment efficiencies

could be predicted by input variables which are quick and cost-effective to measure. The SOM model can be seen as an appropriate method for monitoring the performance of mature ICWs.

The type of vegetation played a minor role in releasing nutrients and other contaminants. However, the mesocosm planted with *Phragmites australis* outperformed the one planted with *Agrostis stolonifera*.

No water reached bottom outlet of the mesocosm suggesting that there was little potential risk to contaminate groundwater. The clay liner and the biogeochemical processes taking place within sediments proved to be effective in preventing surface water from infiltration.

Although no reduction in the overall performance has been observed for the full-scale ICW sites 7 and/or 11, this laboratory-scale study provided valuable warning signs regarding the loss of contaminant sequestration which may contribute to decline in wetland treatment performance over time.

The impacts of hydraulic loading rate (HLR) and seasonal temperature fluctuations on contaminant removal efficiencies of a new ICW system receiving domestic wastewater were also assessed. The system showed good overall treatment performance in terms of effluent quality and removal efficiency. The influence of ICW removal efficiencies of the hydraulic loading rate, which was based on overall water balance, was negligible due to large footprint and multi-cellular configuration of the studied system. Relatively low temperature in autumns and winters resulted in decreased biological activities and lower contaminant removal efficiency.

The long-term trends in nutrient removal have been investigated to five Wildfowl & Wetlands Trust constructed wetland systems. The results showed less effective removal even release of $NO_3$-N, total oxidised nitrogen (TON), ortho-phosphate-phosphorus ($PO_4$-P) and total phosphorus (TP) in many of the systems as a result of wetland aging and lack of sediment management.

# Publication List

## ***Journal articles:***

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# Chapter 1

# Introduction

## *1.1 Background of the project*

It has been widely recognized that sustainable and effective management of water resource demands a sustainable approach, linking social and economic development with protection of the environment. Wetlands in particular are achieving increasing attention for the wide range of benefits and services they provide. Wetlands, such as floodplains, marshes and reed beds, perform many significant functions including flood mitigation, contaminant removal and diffusion, and groundwater recharge.

Since 1970s, constructed wetlands (CW) have been designed and utilized worldwide to treat a variety of wastewaters including domestic sewage, dairy washings, agricultural runoff, mine drainage, urban and motorway storm runoff, and landfill leachate (Healy and Cawley, 2002; Kadlec and Wallace, 2009; Scholz, 2006). CWs employ the same structures and biogeochemical processes that exist in natural wetlands, but the operational conditions could be well controlled (Vymazal, 2010). Compared to conventional wastewater treatment processes, CWs have low capital, maintenance and energy costs, and more flexibility in contaminant loading. In addition, they may also provide wildlife habitats and recreational opportunities (Kadlec and Knight 1996; Mitsch and Gosselink, 2007).

Based on successful application of CWs, the integrated constructed wetland (ICW) concept was developed in the early 1990s to improve water quality and to provide ecological and other wetland ecosystem services by reanimating wetland infrastructure (Harrington *et al.*, 2005; Scholz *et al.*, 2007). ICW systems were originally used to treat farmyard runoff and domestic wastewater within the Anne Valley in south County Waterford. Over the past two decades, more than sixty ICW systems have been created across the Ireland.

Despite the numerous articles published on wetlands over past decades, there is a notable gap in the literature regarding research on the long-term treatment performance of CWs in contaminant removal. Sediment accumulation is an important characteristic in the ageing process of CWs. Most retained contaminants within sediments in particular nitrogen (N) and phosphorous (P) have the potential to be remobilised and released back to the overlying water when environmental conditions change (Lee *et al.*, 2011; Palmer-Felgate *et al.*, 2011). Thus, accumulated sediments might act as new contaminant sources after long-term fully operation (Lijklema *et al.*, 1993). However, the retention and/or release mechanisms and the processes are largely unknown. The relationship between physico-chemical parameters and fates of contaminant in a CW system is therefore needed to fully investigate. Furthermore, current measurement techniques of some important water quality parameters are expensive and time consuming. A model should be identified to predict those parameters (i.e. N and P) by other water quality parameters which are more cost-effective and convenient to measure.

Previous studies indicate that wetland hydrologic characteristics such as hydraulic retention time (HRT) and hydraulic loading rate (HLR) are vitally significant to determine wetland treatment performance in terms of sedimentation, aeration, biological transformations, and soil adsorption processes (Kadlec and Knight, 1996; Kadlec and Reddy, 2001; Mitsch and Gosselink, 2007). Although the application of ICW systems has been widespread in Ireland, most ICWs are semi-natural and open systems in which the flow rates are partly unknown (Mustafa *et al.*, 2009). Thus, there is a lack of information on the influence of hydrologic regime on nutrient retention and/or release by ICW systems.

In CWs, plants play several essential roles (Kong *et al.*, 2009). The presence of emergent plants encourages sedimentation of suspended solids, reduces the risk of resuspension and erosion, increases surface water retention time, and enhances nutrient reduction through uptake and storage (Brix, 1999). Furthermore, wetland plants also facilitate chemical and biological processes to eliminate water contaminants (Gottschall, 2007). However, little has been known about the long-term role and influence of wetland plants on wetland treatment efficiency.

Due to the absence of synthetic liners, groundwater contamination is a potential risk for ICW application. Long-term groundwater monitoring of a respective ICW system indicates that groundwater in vicinity of the studied system is not contaminated. The reworked subsoil associated with biogeochemical processes results in the impedance of pollutants infiltration to the groundwater (Mustafa *et al.*, 2009; Scholz, 2010). Nevertheless, since groundwater protection is legitimate concern for protecting human and environmental health (Lind and Karro, 1995), the contaminant transport from a wetland system to groundwater related to infiltration process merits further investigation.

## *1.2 Rationale, aims and objectives*

This thesis addresses above issues derived from the long-term application of ICWs to treat nutrient rich farmyard runoff and domestic wastewater. This will provide insights into long-term ICW operation and management. Through examining the data from mesocosm-scale experiment and full-scale ICW water quality monitoring, the overall aim of this project is to enhance treatment effectiveness over the lifetime of ICW by the determination of operational conditions and wetland management practice.

ICW mesocosms which filled with saturated sediments (collected from the most contaminated first cells of two 10-year-old fully operational ICW systems) and planted with *Phragmites australis* and *Agrostis stolonifera* were set up to examine contaminant retention and/or release by sediments and sub-soil pack. The application of multiple regression models, principal component analysis (PCA), redundancy analysis (RDA), and self organizing map (SOM) model provided the insights into the effects of physico-chemical parameters on these processes within sediments and substrates. The SOM model was selected as the prediction tool for estimating ICW treatment performance. In addition, the hydrologic regime is assessed through analyzing flow and meteorological monitoring data for a full-scale ICW system receiving domestic wastewater. The specific research objectives are:

1. to examine the potential of saturated ICW sediments and substrates for retaining and/or releasing contaminants;
2. to investigate the existence of relationships between physico-chemical parameters and ICW treatment performance;

3. to identify a suitable statistical model to predict treatment efficiency of ICWs by using physico-chemical parameters which are quick and inexpensive to measure;
4. to compare the performance of the helophyte common reeds (*Phragmites australis*) and widely adaptive terrestrial common bent grass (*Agrostis stolonifera*) on contaminants removal;
5. to assess the risk of groundwater contamination from the application of ICWs; and
6. to investigate annual and seasonal variations in hydraulic loading rate and contaminant removal efficiency.

## *1.3 Outline of the thesis*

The thesis is specifically arranged as follows:

Chapter 1 presents the project background, the overall aim and objectives of this study.

Chapter 2 reviews CW technology for wastewater treatment. Details of their applications are given. In addition, this review also describes the principal treatment mechanisms of water quality contaminants in CWs.

Chapter 3 describes the concept of integrated constructed wetland (ICW). Special emphasis is given to the potential infiltration of contaminated water to groundwater. The ICW treatment efficiencies of nutrients and other contaminants in farmyard runoff and domestic wastewater is further confounded by the interpretations of data presented in published journal articles.

Chapter 4 describes experimental setup and the study sites along with data collection, monitoring scheme and subsequent analysis. Statistical and artificial neural network models are also introduced.

Chapter 5 presents the laboratory-scale research on the potential of nutrient retention and/or release by saturated sediments and subsoil pack. The effects of physico-chemical parameters on contaminant treatment are discussed. In addition, the effects of two wetland plants in removing contaminants from wastewater are also compared.

Chapter 6 focus on the impacts of HLR and seasonal temperature on contaminant removal efficiencies within an integrated constructed wetland system treating domestic wastewater.

Chapter 7 assesses long-term treatment performance of five Wildfowl and Wetlands Trust (WWT) constructed wetlands. The design and characteristics of the study sites, monitoring scheme are also described.

Chapter 8 concludes the project by summarising main findings from this study and makes recommendation for the potential further research opportunities.

# Chapter 2

# Constructed Wetlands

## 2.1 Introduction

Compared to conventional treatment processes, constructed wetland (CW) is an effective and economical alternative to wastewater treatment technology for the control of nutrients (i.e. nitrogen and phosphorus) and other contaminants (Scholz, 2010; Vymazal, 2011). Over the past five decades CWs have been used increasingly to treat various types of wastewaters, such as agricultural runoff, domestic wastewater, urban and motorway storm runoff, and landfill leachate, particularly in Europe and North America (Kadlec and Wallace, 2009).

This review mainly presents contaminant removal mechanisms in CWs by focusing on recent international research. There has been much debate regarding the long-term performance of wetlands in removing or releasing nutrients to any extent, and the processes by which the nutrient is released. In general, the issues addressed in this chapter are:

- removal mechanisms of nutrient and other contaminants in CWs;
- the application of CWs in wastewater treatment;
- long-term treatment performance and operational problems of CWs;
- management recommendations for CWs specific to wetland sediments.

## *2.2 Definition and types of constructed wetlands*

Constructed wetlands are engineered systems, designed and constructed to treatment wastewater simulating the natural processes of natural wetlands which include the interaction and combination of substrates, wetland vegetation, and their associate microbial communities.

CWs have been widely used to improve water quality (Scholz and Lee, 2005; Vymazal, 2011). Research data obtained for these systems have generally been variable, but on the whole it has shown that contaminants such as biochemical oxygen demand (BOD), total suspended solids (TSS) and bacterial matter can be effectively removed from the influent (Kadlec *et al.*, 2000; Mitsch *et al.*, 2009). In contrast to natural systems, CWs can be designed as the defined flow pattern over a specifically selected substrate and vegetation type for a controlled hydraulic pathway and retention time (Brix, 1994).

CWs can be classified according to three important design parameters, hydrology (free surface flow and subsurface flow), the dominant form of macrophytes (free-floating, emergent, and submerged) and flow path (horizontal and vertical). Considering wastewater characteristics, the treatment requirements, the climate and the amount of available land, a system design may also combine different types of CWs (i.e. hybrid or multi-stage systems) (Vymazal, 2001a; Vymazal *et al.*, 1998).

CWs with free water surface flow (FWS) represent the oldest type of artificial wetland design. In a FWS-CW system, water flows above ground and plants are rooted in the sediment layer or floating on the water surface. The bottom of the cell or channel is generally lined with impermeable layers (clay or geotextile) to prevent wastewater leaking to groundwater. The substrate consists of rocks, gravel and soil.

The FWS-CWs are successfully used to treat municipal wastewater, stormwater runoff and mine drainage waters (Kadlec and Knight, 1996; Kadlec and Wallace, 2009; Vymazal and Kröpfelová, 2008). In addition, data on the performance of FWS-CWs treating wastewater from livestock facilities indicated they can be valuable for treating wastewater from confined animal feeding facilities as well (Knight *et al.*, 2000).

There are two basic types of subsurface flow (SSF) CWs: horizontal flow (HF or HSF) CWs and vertical flow (VF) CWs. HF-CWs were pioneered in Germany by Seidel in the 1950 and developed further in 1970 (Brix, 1994). A HF-CW system typically consists of a bed filled with filter material (soil and/or gravel of varying size fractions) and is planted with emergent vegetation. The water is distributed at the inlet and flows horizontally through the porous medium just below the surface of the bed. Contaminant removal is mostly based on anoxic/anaerobic conditions. The aerobic zones only locate around rhizosphere where oxygen is supplied by a plant pathway (Brix, 1987).

VF-CWs are fed intermittently and only the top layer is flooded. Then, the wastewater gradually percolates down through the permeable soil filter media and is collected by drainage pipes at the bottom. Since 1990s, the upflow VF-CWs have been developed and used as household treatment systems, especially for phosphorus removal (Breen and Chick, 1995; Farahbakhshazad and Morrisson, 2003). A comparison between three CW systems is present in Table 2-1.

Table 2-1 Advantages and disadvantages of surface flow and subsurface flow constructed wetlands (Scholz and Lee, 2005; Vymazal, 2007; Vymazal *et al.*, 2006).

| Constructed wetland types | Advantages | Disadvantages |
|---|---|---|
| Surface flow constructed wetlands | • Inexpensive and simple to construct and operate, and easy to maintain<br>• Greater aesthetic appeal and provides wildlife habitats<br>• Recreational opportunities availability<br>• Less energy required | • Larger land area requirement<br>• Long start-up time to reach full working capacity<br>• Pest and odour problems. |
| Horizontal flow constructed wetlands | • Long flowing distance, and contaminant gradients can be established<br>• Denitrification of nitrogenous compounds<br>• Reduced risk of exposing humans or wildlife to toxics<br>• Efficient in organic matter and total suspended solids<br>• Greater cold tolerance | • Relative larger land area use<br>• Only used for small flow<br>• Limited aerobic zones for ammonium oxidation and other oxygen-dependent processes<br>• Careful hydraulic calculation and monitoring are necessary to maintain water level and passage of wastewater |
| Vertical flow constructed wetlands | • Decreased land area use<br>• Good oxygen transfer and supply<br>• Enhanced nitrification<br>• Simple hydraulics<br>• Efficient in organic matter and total suspended solids<br>• Greater cold tolerance | • Shorter retention time<br>• Poor denitrification<br>• Less effective in phosphorus and nitrate reduction |

Hybrid CWs are considered as the most favourable design to optimise the performance in wastewater treatment (Vymazal, 2011). They have the capacity to remove a wider range of contaminants (in particular nitrogen), as well as to allow for more effective removal of the same contaminant, such as particulate and organic forms. The VF-HF and HF-VF systems are the most dominant hybrid options. However, any type of CW could be combined in order to achieve higher removal efficiency (Vymazal, 2005).

In general, the design of CWs is mainly based on the premise, or previous successful examples. Recent studies have attempted to improve understanding of the treatment processes within a CW system. However, it is not possible to assume that an outcome of efficient contaminant removal in a certain system can be successfully achieved in all cases. Therefore, where wetland systems are proven effective in removing contaminants, they have to be assessed and their processes should be fully understood so that further systems can be constructed based on the similar design criteria.

## *2.3 Wetland plants*

Wetland plants (vegetations) are the most significant component in a constructed wetland system. The primary roles and functions of wetlands physical components of wetland vegetation are listed in Table 2-2. Numerous studies have reported that planted CW systems performed better compared to systems without any plants. However, most of studies were only carried out in a short term when the vegetations were newly planted with adequate capacity to uptake nutrients and to produce large amount of biomass.

The vegetations used in constructed wetlands can be categorized into three main groups – emergent aquatic macrophytes, floating-leaved macrophytes, and submerged aquatic macrophytes (Brix and Schierup, 1990; Wetzel, 2001; Williams, 1964). The detailed description and common species of three groups of macrophytes are summarised in Table 2-3.

Table 2-2 The roles of physical components of wetland vegetations (Brix, 1997).

| Component of wetland vegetation | Role in wetland performance |
|---|---|
| Aerial tissue | • Light attenuation to reduce growth of phytoplankton<br>• Reduce the risk of resuspension<br>• Develop aesthetic appearance<br>• Storage of nutrients<br>• Provide a suitable habitat for wildlife |
| Submerged tissue | • Filtering and screening effect to separate large debris out<br>• Reduce water current velocity to enhance rate of sedimentation and to reduce resuspension<br>• Provide surface area for attached biofilms<br>• Excretion of photosynthetic oxygen to increases aerobic degradation<br>• Uptake of nutrients |
| Vegetation roots and rhizomes | • Provide surface for attached bacteria and other micro-organisms<br>• Control erosion<br>• Prevents the medium from clogging<br>• Release of oxygen<br>• Uptake of nutrients<br>• Release of antibiotics |

## *2.4 Supporting media or substrate*

Substrates cannot only physically support the growth of vegetation, but also act vital roles in contaminant removal processes such as sedimentation, filtration and sorption

(Wang and Zhang, 2012). The substrate media also provides attachment surfaces for micro-organisms and sources for microbial processes (Saeed and Sun, 2012). Most engineered wetlands are constructed with coarse sand, coarse gravel and fine gravel (Sundaravadivel and Vigneswaran, 2009).

Table 2-3 The description of wetland vegetations and common species (Saeed and Sun, 2012).

| Group | Life form description | Common species |
|---|---|---|
| Emergent macrophytes | These are typically life form in wetlands, and can grow within a water table range from 0.5 m below the soil surface to a water depth of 1.5 m or more. They usually produce aerial stems, leaves and an extensive root and rhizome system. Due to plenty of internal air space for oxygen transportation to lower sediments and substrates, the vegetations are to adapted to growing in a water-logged or submersed substrate. | *Phragmites australis* (Common Reed), *Glyceria* spp. (Mannagrasses), *Eleocharis* spp. (Spikerushes), *Typha* spp. (Cattails), *Scirpus* spp.(Bulrushes), *Iris* spp. (Blue and Yellow Flags) and *Zizania aquatica* (Wild Rice). |
| Floating-leaved macrophytes | These species can range from large plants with aerial and /or floating leaves and well-developed roots, to surface-flowting plants with few or no roots. | *Nymphaea* spp. and *Nuphar* spp. (Waterlilies), *Potamogeton natans* (Pondweed), *Hydrocotyle vulgaris* (Pennyworth), *Eichhornia crassipes* (Water Hyacinth), *Pistia stratiotes* (Water Lettuce), Lemna spp. And Spirodella spp. (Duckweed) |
| Submerged macrophytes | The photosynthetic tissue for these plants is entirely submerged by water. They normally grow well in oxygenated water. | Elodeid type (i.e. *Elodea*, *Myriophyllum*, *Ceratophyllum*) Isoetid (rosette) type (i.e. *Isoetes*, *Littorella*, *Lobelia*) |

The physical-chemical properties of substrate play significant roles in wastewater treatment processes. Many studies have suggested that hydraulic conductivity is one of the most important factors to be considered when selecting suitable media. Typically, CW systems constructed with fine and soil-based substrates have low hydraulic conductivity, while higher conductivity can be observed for coarse sand and gravel-based medium based CWs. Table 2-4 presents the hydraulic conductivity of representative wetland media.

As to improve contaminant treatment performance of CWs, alternative substrates have been widely used to replace conventional wetland media (Akratos and Tsihrintzis, 2007). These potential substrates include organic wood-mulch, rice husk, zeolite, light weight aggregates, alum slag, peat, maerl, compost and shale (Saeed and Sun, 2012). According to pervious studies, however, every unconventional substrate has its advantages and limitations. It is important to select a suitable substrate according to operation conditions and wastewater characteristics.

Table 2-4 Wetland substrate characteristics (Chen *et al.*, 1993, Sundaravadivel and Vigneswaran, 2009).

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

Several studies with gravel-based CWs have reported the problems of substrate clogging. This might be the biggest operational problems of CW by far. The rate of clogging in wetland media largely depends on organic and suspended solids loading rates. Theoretical estimation on the service life span of a hypothetical gravel-bed wetland subjects to clogging by organic and inorganic wastewater solids and microbial detritus indicated that the system could be used for 100 years (Sundaravadivel and Vigneswaran, 2009). In addition, microbial organisms are able to grow attached to the media. After the long-term operation, micro-organisms may accumulate as thick biofilm layers and result in clogging the surface of substrates. The impacts of substrate clogging on contaminant removal can therefore be considered as a research goal in the long-term application of CWs.

## *2.5 Hydrology and hydraulics of constructed wetlands*

### 2.5.1 Wetland hydrology

Wetland hydrology is an essential factor in the establishment and maintenance of CWs. A minor change in wetland hydrology may have a significant impact on the chemical and physical conditions in a wetland system (Mitsch and Gosselink, 1993). In addition, most contaminant removal and retention processes are time dependent, and an alternation of wetland hydrology may reduce retention time and result in saturation and decline of wetland treatment efficiency (Bowmer, 1987; Dierberg *et al.*, 2002; Sanford *et al.*, 1995). Furthermore, knowledge of hydraulic conditions is essential for modelling and predicting the removal efficiency of CWs and leads to a better optimization of the size and geometry of CWs. A vital design parameter for CWs is the potential or, as often called, the nominal hydraulic retention time (HRT) of water (Kadlec and Bastiaens, 1992; Persson *et al.*, 1999; Shilton & Prasad, 1996).

## 2.5.2 Water balance

The water balance study is a key quantitative test of hydrological understanding of a wetland system. In general, the water balance is performed by comparing the total quantity of water transferred into a wetland with the total quantity of water transferred out. The water balance can be summarised by a simple addition of inputs to and outputs from the wetland system as expressed in Eq. 2-1:

$$\Delta V = (Q_{in} + P + R + L + OB + PU_i + S + GD + GS) - (E + D + Q_{out} + PU_o + GR) \quad [2\text{-}1]$$

Where, $\Delta V$ is the net difference between inputs and outputs; $Q_{in}$ is inflow, $P$ is precipitation; $R$ is runoff; $L$ is lateral inflow; $OB$ is over-bank flow; $PU_i$ is water pumped into the wetland; $S$ is spring; $GD$ is groundwater discharge; $GS$ is groundwater seepage; $E$ is evapotranspiration; $D$ is drainage; $Q_{out}$ is outflow; $PU_o$ is water pumped out of the wetland; $GR$ is groundwater recharge (i.e. infiltration).

Some water transfer mechanisms mentioned above may not occur in any particular wetland and thus will have a zero value in the water balance calculation. It should be noted that if the total inputs of are not approximately equal to the total outputs of a water balance, then this may imply that a potentially significant water transfer mechanisms either has been ignored or measured inaccurately. Hence the water balance can help to identify particular components where additional or more detailed investigations are required.

### 2.5.3 Flood control and stormflow modification

Wetlands are able to store the runoff from heavy rainfall or snow-melt events. They function as transition and buffer zones that reduce the possibility of flooding in downstream or moderate the magnitude of flooding. Scholz and Sadowski (2009), who initiated the concept of sustainable flood retention basins (SFRB), identified wetlands as four subclasses – sustainable flood retention wetland, aesthetic flood retention wetland, integrated flood retention wetland and natural flood retention wetland. While the effectiveness of wetlands for flood retention and abatement may vary, depending on the size of wetland system, the saturation of soils, water level fluctuations, plant community, habitat elements, ground water hydrology, and downstream conditions (USEPA, 2006).

## *2.6 Removal processes and fate of contaminants*

### 2.6.1 Introduction

Many processes and mechanisms are involved in the removal of wastewater contaminants within CW systems. In general, the principal removal mechanisms are based on physical, chemical, and biological processes (Kadlec and Knight, 1996; Vymazal, 2005).

Physical removal processes include sediment trapping, where TSS and organic particles either settle on the bed floor of wetlands or are trapped in plant roots. Wastewater generally moves rather slowly through wetlands because of the resistance provided by aquatic macrophytes and the characteristic of broad sheet flow. Consequently, sedimentation can be enhanced (DeBusk, 1999). On the other hand, resuspension of settled particulate matter may occur due to increased flow velocities, wind-driven turbulence, disturbance by animals and humans, and gas lift (i.e. oxygen generated by algae and submerged plants; nitrogen oxides and nitrogen gas from denitrification; or methane formed in anaerobic processes) (Greenway and Jenkins, 2004).

Biological processes play a major role in the removal of contaminant within CWs. The principal biological processes include plant uptake and microbial metabolic activity. Wastewater contaminants such as nitrate, ammonium and phosphate can be seen as the form of essential plant nutrients. Plants assimilate these nutrients and other contaminants (i.e. cadmium and lead) and convert them into additional plant biomass. The biological removal rate is dependent on the plant growth rate and concentration of contaminant in plant tissue. Moreover, microorganisms present in wetland systems including bacteria, fungi, coagulate colloid material, may also provide short-term storage of nutrients (Sundaravadivel and Vigneswaran, 2001). Furthermore, the metabolic processes play a significant role in removal of a wide variety of organic compounds (DeBusk, 1999).

In addition to physical and biological processes, a wide range of chemical processes such as sorption, photo oxidation, and volatilization are also considered as one of the major contaminant removal mechanisms. Sorption is the significant chemical process for transferring ion charges from aqueous phases (water) to solid phases (soil). Sorption includes the processes adsorption and precipitation. Adsorption refers to the attachment of ions to soil particles and precipitation which can lead to precipitation of metal from the water column as insoluble forms. Photo oxidation utilizes the power of sunlight to break down and oxidize compounds such as pesticides and pathogens. Volatilization can break down the compound and expelling it into the air as a gaseous state (DeBusk, 1999; Sundaravadivel and Vigneswaran, 2001).

### 2.6.2 Suspended solids

Physical processes such as gravitational settling play an important role in the removal of total suspended solids (TSS). In a FWS-CW, TSS is primarily removed by flocculation/sedimentation and filtration/interception. These processes are influenced by several factors including particle size, shape, specific gravity and properties of substrates. Interception and attachment to plant surfaces can also be seen as another important process in TSS removal. The surfaces of plants in wetlands are coated with active layer of biofilm called periphyton which can absorb colloidal and soluble matter. These solids may then be metabolized and converted to gases or biomass (USEPA, 1999).

VF wetlands provide a great reduction of suspended solids due to low velocity and large contact surface areas of substrates. However, as wastewater passes through the soil media, TSS might clog pores and reduce the hydraulic conductivity of the substrates producing head losses at the entrance of the wetlands (Manios *et al.*, 2003). By using different types of media, clogging may significantly be minimized and TSS removal can be consequently achieved.

Resuspension of settled solids may take place due primarily to turbulence created by animals, high inflows or winds. In addition, the oxygen generated by algae and submerged plants, nitrogen oxides and nitrogen gas from denitrification, or methane produced in anaerobic process may cause flotation of particulates (Kadlec and Knight, 1996). Resuspension can also occur because of the formation of biomass by primary production or through the metabolism of influent wastewater constituents (EPA, 1999).

### 2.6.3 Organic matter degradation

Organic matter is basically degraded by microorganisms through fermentation and aerobic or anaerobic respiration, and mineralized a source of energy or assimilated into biomass (Polprasert *et al.*, 1998). Other removal mechanisms for organic matter include sedimentation, sorption and volatilization (Vymazal *et al.*, 1998). During the microbiological degradation, aerobic heterotrophic bacteria consume oxygen and break down organic matter. Therefore, insufficient oxygen supply will significantly reduce the performance of this biological oxidation. Anaerobic breakdown of organic matter occurs in the absence of dissolved oxygen and yields methane as end-product (Cooper *et al.*, 1996). Additionally, wetland plants can also store organic carbon in plant biomass thus making the plant sinks for organic carbon (DeBusk, 1999).

## 2.6.4 Mechanisms for nitrogen removal in constructed wetlands

### 2.6.4.1 Introduction

There are several processes for the removal of nitrogen from wastewater in a wetland environment. In general, the ultimate pathways of nitrogen reduction are nitrification followed by denitrification (Spieles and Mitsh, 1999; Vymazal, 2007), plant uptake (Gersberg *et al.*, 1984; Kadlec and Knight, 1996) and accumulation in soil (Dong and Lin, 1994). Fig. 2-1 shows nitrogen transformation in a wetland system. USEPA (1998) reported that nitrogen removal efficiencies range from 25 to 85% depends on the type of CWs.

### 2.6.4.2 Forms of nitrogen within wetland systems

Nitrogen entering wetlands is present in particulate and dissolved organic and inorganic N forms. The relative proportions of the nitrogen composition largely depend on the source of wastewater and the type of pre-treatment (Reddy and D'Angelo, 1997). The major forms of inorganic nitrogen are: nitrate ($NO_3^-$) and nitrite ($NO_2^-$), coupled with ammonia ($NH_3$) and ammonium ($NH_4^+$) (Gale *et al.*, 1993; Kadlec, 1999c; Taylor *et al.*, 2005). The organic nitrogen forms are dominated by amino acids, urea, uric acid, amines, purine, and pyrimidines (Stevenson and Cole, 1999).

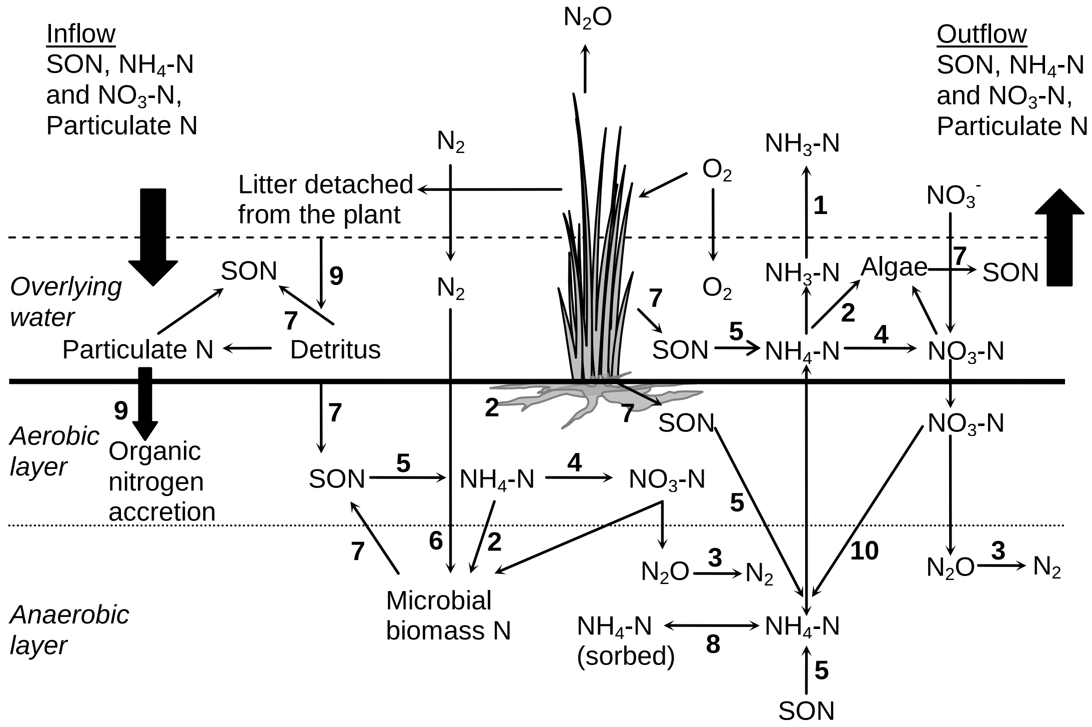



Figure 2-1 Nitrogen transformations in soil and water column of wetlands (modified from Mitsch and Grosselink, 2007). N, nitrogen; SON, soluble organic nitrogen; $NH_3$-N, ammonia-nitrogen; $NH_4$-N, ammonium; $NO_3$-N, nitrate-nitrogen; $O_2$, oxygen; $N_2$, nitrogen gas; $N_2O$, nitrous oxide; $NO_3^-$, nitrate ion. 1 = volatilization; 2 = plant and microbial uptake; 3 = denitrification; 4 = nitrification; 5 = mineralization; 6 = nitrogen fixation; 7 = fragmentation and leaching; 8 = sorption and desorption; 9 = burial; 10 = nitrate reduction to ammonium.

### 2.6.4.3 Ammonification

Ammonification is the process where the bacterial breakdown of organic nitrogen into inorganic nitrogen such as ammonia, which is also known as mineralization. Kinetically, ammonification proceeds more rapidly than nitrification (Kadlec and Knight, 1996; Lee *et al.*, 2009; Vymazal, 2007). Reedy and Patrick (1984) indicated that ammonification processes are highly influenced by temperature, pH, C/N ratio, available nutrients, and soil condition (texture and structure). Ammonification rates are fastest in the oxygenated zone and decrease in the anaerobic zone. The optimum pH for ammonification is between 6.5 and 8.5 (Vymazal, 1995). In addition, Bowmer (1987) indicated the summer and winter differences in nitrogen removal are attributed to the effect of temperature on ammonification rate. The optimal temperature for ammonification is 40–60 ℃ (Hammer and Knight, 1994; Vymazal, 1995). From the reported literature data, it could be found that ammonification rate by double with a temperature increase of 10 ℃ (Hershkowitz, 1986).

#### 2.6.4.4 Nitrogen fixation

Nitrogen fixation is the conversion of atmospheric nitrogen ($N_2$) to ammonia by a wide variety of symbiotic actinomycetes and asymbiotic heterotrophic bacteria and blue-green algae (Johnston, 1991). However, fixed nitrogen is an essentially negligible loading contribution to CWs receiving wastewater with high nitrogen loading. Furthermore, the presence of high concentrations of ammonium inhibits nitrogen fixation rates (Kadlec and Knight, 1996).

#### 2.6.4.5 Ammonia volatilization

Ammonia volatilization is a physicochemical process where unionized ammonia is removed from the solution to the atmosphere. Ammonia volatilization can be appreciable if the pH is above 8.0 (Freney *et al.*, 1985; Reddy and Patrick, 1984). Ammonia volatilization may become a significant nitrogen removal mechanism under higher ammonia concentration (>20 mg $l^{-1}$), pH values, and water temperature conditions. Vymazal (2007) present that at pH of 9.3 the ratio between ammonia and ammonium ions was 1:1, the losses of $NH_3$ via volatilization were significant. Atmospheric parameters above CWs such as wind velocity, air temperature, and ammonia concentration in the air may significantly impact the amount of ammonia volatilized from wetlands (Poach *et al.*, 2002).

#### 2.6.4.6 Nitrification

The major pathway for ammonia removal CWs is governed by microbial nitrification and denitrification (Kadlec and Knight, 1996). Biological nitrification is performed by identified nitrifiers (including ammonia-oxidizing bacteria and nitrate-oxidizing bacteria) such as *Nitrosomonas*, *Nitrosopira*, *Nitrosococcus*, *Nitrobacter*, *Nitrospina*, and *Nitrosolobus* (Kadlec and Knight, 1996; Vymazal, 2007). In the nitrification process, ammonia that may either be present in influent, or be produced during ammonification of organic nitrogen in the influent, is first oxidized to nitrite (ammonia oxidation). Nitrite is subsequently oxidized to nitrate (nitrite oxidation) (Paul and Clark, 1996). The nitrifying bacteria are aerobic, autotrophic and chemolithotrophic (strictly aerobic). They use the energy generated from oxidation of ammonia or nitrate for growth and carbon dioxide as carbon source (Davies *et al.*, 2001). The most commonly recognized genus of bacteria is that of *Nitrosomonas* for the ammonia oxidation process and *Nitrobacter* for the nitrite oxidation process (Lee *et al.*, 2009). These two oxidative stages can be summarized as follows:

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O \qquad [2\text{-}3]$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \qquad [2\text{-}4]$$

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \qquad [2\text{-}5]$$

A variety of environmental factors can affect the growth of nitrifying bacteria and further influence the efficiency of nitrification. These inhibiting factors include ammonia concentrations, temperature, pH value, dissolved oxygen concentration, inorganic carbon source, moisture and microbial population (Vymazal, 1995). For nitrification to occur in CWs the air temperature should be between 10–35 ℃. The optimum temperature for nitrification was between 20–30 ℃ (Nichols, 1983), and the optimum pH was 7.2–9.0 (Kadlec and Knight, 1996). The minimum temperature required for growth of *Nitrosomonas* and *Nitrobacter* were 5 ℃ and 4 ℃, respectively (Cooper *et al.*, 1996). The pH of a wetland system can change dramatically due to the nitrification process. If there is not a sufficient alkalinity concentration in wastewater, the pH will be depressed as the ammonia is oxidized and the nitrification rates might swiftly decline. Thus, appropriate chemicals such as lime should be replenished when the alkalinity in the process is reduced (Ahn, 2006).

The rate of nitrification is also significantly affected by the fraction of nitrifiers present in the wastewater. When the concentration of biodegradable organics, measured as $BOD_5$, is high, the heterotrophic bacteria, or bacteria that use organic carbon as a carbon source for metabolism, dominate the bacterial population. For this reason, significant nitrification does not happen before substantial BOD removal (Cottingham *et al.*, 1999).

#### 2.6.4.7 Denitrification

Denitrification is the stepwise reduction of nitrate to nitrite to nitrous oxide and nitrogen gas. This process is shown in the following:

$$2NO_3^- \rightarrow 2NO_2^- \rightarrow 2NO \rightarrow N_2O \rightarrow N_2 \quad [2\text{-}6]$$

Many researchers have reported that denitrification is the major mechanism for nitrogen removal from CWs. They found that approximate 60-95% of TN and 75-90% of $NO_3^-$ removal resulted from denitrification (Brix, 1994; Hammer and Knight, 1994; Lee *et al.*, 2009; Stengel *et al.*, 1987). Denitrification is an anaerobic process (dissolved oxygen should be less than 3mg in a CW) that is performed primarily by facultative heterotrophic bacteria. The most common and well-known genus of denitrifying bacteria are *Bacillus*, *Micrococcus*, *Pseudomonas*, *Aeromonas* and *Vibrio* (Grant and Long, 1981; Vymazal, 2007).

The primary factors to influence the rates of denitrification include the quantity of carbon source (Gersberg *et al.*, 1984; Van Oostrom and Russell, 1994), the absence of oxygen, redox potential, temperature, pH values, presence of denitrifier, soil moisture, soil type, hydroperiod, water level, presence of overlying water (Bastviken *et al.*, 2005; Focht and Verstraete, 1977; Sirivedhin and Gray, 2006; Vymazal, 1995), and the diffusion rate of $NO_3^-$ toward the denitrification sites (Nichols, 1983). Under acidic conditions the denitrification rate is slower compared to neutral or alkaline conditions. The optimum pH for denitrification ranges from 6 to 8. At a pH of less than 6 the conversion of nitrous oxide ($N_2O$) to nitrogen gas ($N_2$) is inhibited and below pH 4 the denitrification is negligible or absent (Nichols, 1983; Paul and Clark, 1996). Moreover, denitrification is temperature dependent and can occur in temperatures from 25 to 60 ℃ (Hammer and Knight, 1994). The denitrification rate doubles with each 10 ℃ increase between 11-35 ℃ and decrease rapidly below 5 ℃, although it is still detectable at 2 ℃ (Bremner and Shaw, 1958; Nichols, 1983). Numerous studies have indicated the importance of organic matter for denitrification (Gersberg *et al.*, 1984; Killingstad *et al.*, 2002). The nitrogen removals can be enhanced continually by supplementing sources of carbon. Gersberg *et al.* (1984) and Van Oostrom and Russell (1994) reported that carbon biomass produced by aquatic plants in CWs was sufficient to sustain optimal denitrification.

### 2.6.4.8 ANAMMOX

The recent discovered anaerobic ammonium oxidation (ANAMMOX) is an autotrophic process by which bacteria conversion of $NO_2^-$ and $NH_4^+$ to $N_2$. This process provides a potential alternate mechanism for the study of nitrogen removal in constructed wetland systems (Bialowiec *et al.*, 2011; Mulder *et al.*, 1995; Paredes *et al.*, 2007; Tao and Wang, 2009). ANAMMOX process is shown as follows:

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \qquad [2\text{-}7]$$

In this process, $NH_4^+$ is autotrophically oxidized to $N_2$ while $NO_2^-$ serves as electron acceptor under anaerobic conditions. Anammox saves up to 90% of operation cost as less energy for aeration and no organic carbon sources are required (Chamchoi and Nitisoravut, 2007). However, the long start-up time, the high sensitivity of the anammox bacteria to oxygen concentration, and nitrite accumulation limit the application of the process (Dong and Sun, 2007).

When the anammox bacteria co-function with autotrophic nitroso-bacteria via the following route in a single reactor, the removal mechanism is known as ‘completely autotrophic nitrogen removal over nitrite (CANON) (Third *et al.*, 2001).

$$NH_4^+ + 1.32NO_2^- + 0.13H^+ \rightarrow 1.02N_2 + 0.26NO_3^- + 2.03H_2O \qquad [2\text{-}8]$$

According to recent studies (Cui *et al.*, 2005; Mosquera-Corral *et al.*, 2005; Wang and Yang, 2004), the anammox and CANON processes in CWs might be influenced by some key variables including temperature, pH value, free ammonia, free nitrous acid, hydraulic retention time (HRT), dissolved oxygen concentration, salt, organic compounds, and hydroxylamine. Further research on the characteristics of anammox bacteria and their optimal growth conditions is needed to be better understand as to stimulate nitrogen removal routes in varied CWs (Lee *et al.*, 2009; Vymazal, 2007).

#### 2.6.4.9 Plant uptake

Plant uptake is one of the major mechanisms to removal nitrogen from CWs. The process, which is also known as plant assimilation, converts inorganic nitrogen into organic compounds as building blocks for plant cells and tissues (Vymazal, 1995).

Rooted macrophytes obtain nearly all nutrients from the sediment, whereas floating plants assimilate nutrients directly from the water column (Wetzel, 2001). Most wetland plants are capable of absorbing any form of soluble nitrogen (Atkin, 1996). However, their preferential uptake depends on the nitrogen forms available in the sediments and soils (Lambers *et al.*, 1998). For example, wetland plant species may favour $NH_4^+$ rather than $NO_3^-$ if the habitats with restricted nitrification, where $NH_4^+$ prevails (Garnett *et al.*, 2001; Kronzucker *et al.*, 1997). The capacity of aquatic macrophytes to assimilate and to store nitrogen is dependent on their net productivities (growth rates), the concentration of nutrients in plant issue, and the ultimate potential for biomass accumulation (i.e. maximum standing crop). Thus, desirable features of vegetation used to remove nutrient would include rapid growth, high concentration of nutrients in the plant issue, and the capability to attain a high standing crop (Reddy and DeBusk, 1987; Vymazal, 2007). However, at the end of growing season such as fall, aquatic plants may die back and the leaves and stalks eventually fall to wetland beds where they break down (Kadlec and Knight, 1996). If the bulk of nutrients have not been translocated to the roots or rhizomes as is the case with some macrophytes, nitrogen will eventually release back to the overlying water during the winter season (Vymazal, 2007). The values for nutrient uptake and content of wetland vegetations from literature study are summarized in Table 2-5.

Table 2-5 Nutrient uptake and content of wetland vegetations (Langergarber, 2005)

| Literature | Plant species | N uptake | N content | P uptake | P content |
|---|---|---|---|---|---|
| Kadlec and Knight (1996) | *Phragmites* spp. | | 2.47% of DW | | 0.18% of DW |
| Tanner (1996) | *Schoenoplectus validus*, *Phragmites australis*, *Glyceria maxima*, *Baumea articulata*, *Bolboschoenus fluviatilis*, *Cyperus involucratus*, *Juncus effusus* and *Zizania latifolia* | 744 mg N $m^{-2}$ $d^{-1}$ | - | 104 mg P $m^{-2}$ $d^{-1}$ | - |
| Tanner (2001) | *Schoenoplectus tabernaemontani* (C.C. Gmelin) Palla | 200-300 mg N $m^{-2}$ $d^{-1}$ | - | 50-100 mg P $m^{-2}$ $d^{-1}$ | - |
| Meuleman *et al.*, (2003) | *Phragmites* spp. | 6.2 mg N $m^{-2}$ $d^{-1}$ | - | 0.96 mg P $m^{-2}$ $d^{-1}$ | - |
| Meuleman *et al.*, (2003) | *Phragmites* spp. (harvested) | 6.0 mg N $m^{-2}$ $d^{-1}$ | - | 0.55 mg P $m^{-2}$ $d^{-1}$ | - |
| Mavrogianopoulos *et al.*, (2002) | *Arundo donax* | - | 2% of DW | | 0.9% of DW |
| Stottmeister *et al.*, (2003) | *Schoenoplectus lacustris* | - | | 0.22 mg P $m^{-2}$ $d^{-1}$ | 0.15-1.05% of DW |

DW, dry weight.

### 2.6.4.10 Ammonia adsorption

In CWs, ammonium ($NH_4^+$) can be absorbed from wastewater through cation exchange adsorption to soil minerals, detritus, sediments or organic matter (Kadlec and Knight, 1996; Vymazal, 2007). There are several factors that can influence the rate and extent of ammonia adsorption, such as the type and amount of clay, alternating submergence and drying patterns, characteristics and amount of soil organic matter, submergence period, and the presence of vegetation (Savant and DeDatta, 1982; Vymazal, 2007). The absorbed ammonia is bound loosely to the substrates and can be released easily when water chemistry conditions change (Lee *et* *al.*, 2009). When the ammonia concentration in the overlying water is reduced as a result of nitrification or increased rainfall, ammonia will be desorbed to regain the equilibrium. By contrast, when the ammonia concentration in water column increased, the ammonia adsorption can be significantly enhanced (Lee *et al.*, 2009; Vymazal, 2007). If substrates exposed to oxygen due to draining or dry climates, adsorbed ammonium may subsequently be oxidized to nitrate (Connolly *et al.*, 2004; Kadlec and Knight, 1996).

#### 2.6.4.11 Sedimentation

Most particulate organic nitrogen removal in CWs is mainly related to sedimentation to wetland bed or plant stems (Kadlec and Knight, 1996; Taylor *et al.*, 2005). Residence time plays a critical role in nitrogen sedimentation process (Brueske and Barrett, 1994; Kadlec and Bastiaens, 1992). Recently, an enhanced sedimentation technique that implements magnesium-ammonium-phosphate (MAP) as added precipitation reagent has been successfully developed for the removal of nitrogen and phosphorus in wastewater treatment processes. This technique has the potential to be considered and applied within CWs (Lee *et al.*, 2009).

## 2.6.5 Mechanisms for phosphorus removal in constructed wetlands

### 2.6.5.1 Introduction

The major removal processes for phosphorus in CWs include sedimentation, precipitation, soil adsorption, and plant uptake (Kadlec and Knight, 1996; Reddy *et al.*, 1999). Fig. 2-2 presents phosphorus dynamics in a CW system. However, some processes have only a limited capacity, and once the phosphorus assimilating/adsorbing capacity is reached or exceeded no further removal can be achieved. Kadlec and Knight (1996) reported that accumulative phosphorus removal processes essentially follow the first order reactions, which means that the removal of phosphorus to new soils is proportional to the concentration of phosphorus in the surface waters, and the surface area of wetland. Time should be allowed for a CW system to reach equilibrium and this will consequently result in stable wastewater treatment performance. In Kadlec's model the equilibrium was achieved after two years despite the plant species composition and other biotic components might continue to adapt over a longer period of time.

### 2.6.5.2 Forms of phosphorus within wetland systems

Phosphorus entering a wetland is typically present in inorganic and organic phosphate forms and can either be dissolved in the water or suspended (attached to particles in the water column as particulates). The particulate and dissolved organic fractions can be further classified as labile (reactive) and refractory (non-reactive) components (Reddy *et al*., 1999).

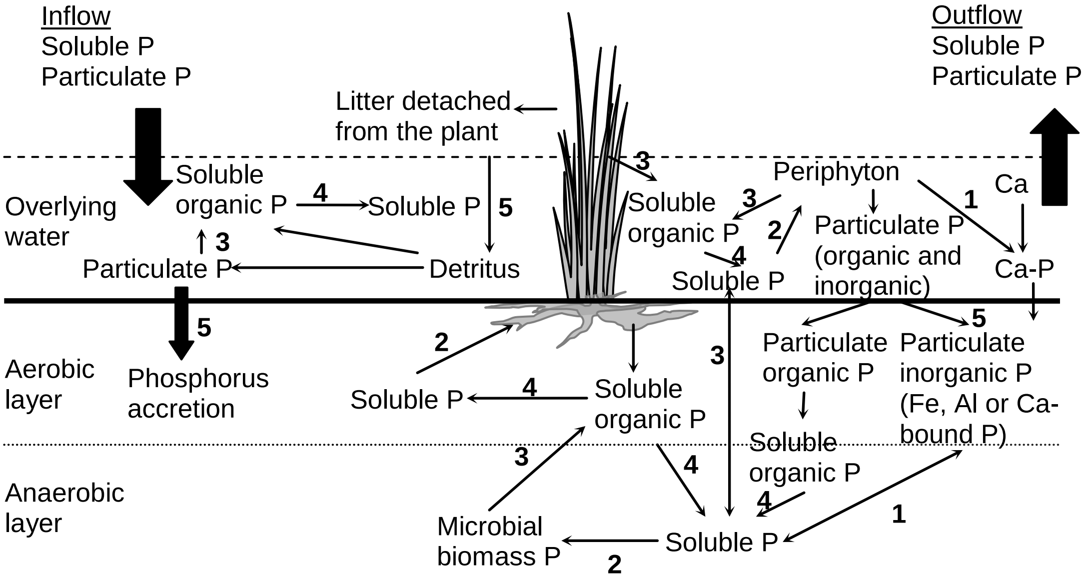



Figure 2-2 Phosphorus transformations in soil and water column of wetlands (modified from Mitsch and Grosselink, 2007). P, phosphorus; Ca, Calcium; Fe, Iron; Al, Aluminium. 1 = adsorption and desorption; 2 = precipitation and dissolution; 3 = fragmentation and leaching; 4 = mineralization; 5 = sedimentation and burial.

The phosphorus forms found within the substrate and sediment are often delineated into inorganic and organic pools of phosphorus. The major pools of inorganic phosphorus ($P_i$) are defined as loosely adsorbed phosphorus, iron and aluminium phosphorus, and calcium and magnesium bound phosphorus. Reddy *et al.* (1995) further stated that the loosely adsorbed phosphorus is essential for plant growth and controls the P concentration of the overlying water column by responding to external phosphorus loadings. These $P_i$ forms are not discrete entities because the transformations between the forms occur continuously to maintain equilibrium conditions (Sharpely, 1995). The organic phosphorus ($P_o$) primarily consists of the forms of phosphorus associated with phospholipids, inositols and fulvic acids, and forms of humic acids. $P_o$ should be hydrolysed to inorganic forms before being considered as bioavailable forms (Graham *et al.*, 2005).

### 2.6.5.3 Plant uptake

The capacity of aquatic macrophytes to take up phosphorus is dependent on their growth rates, the water depth, the sediment characteristics, the oxygen transfer capability of the plants into the rhizosphere zone, biochemical and physico-chemical processes functioning at the root-water-sediment interface, plant density per unit area, plant harvesting and climate (Reddy *et al.*, 1995). The values for phosphorus uptake and content of selected macrophytes from previous studies are summarized in Table 2-4. Similar to nitrogen uptake, the potential rate of phosphorous uptake is limited by the plants' net productivity and the concentration of phosphorous in plant tissue. Several studies have indicated that a significant liner relationship exists between plant biomass and nutrient removal from wastewater (Kadlec and Knight, 1996; Tanner, 1996). In addition, the storage capacity is also dependent on phosphorus concentration in plat tissues (Vymazal, 2007).

As aquatic plants grow, there is uptake of phosphorus by macrophytes which will continue until after the plant is fully grown. At the end of growing season, some types of aquatic plants die back. If the bulk of nutrients have not been stored at the roots and rhizomes, phosphorus will eventually return back to the wetland systems (Reddy *et al.*, 1999; Vymazal, 1995). New growth of these macrophytes will require phosphorus uptake during early spring the next year so that a cycle can be eventually developed where the uptake phosphorus in growing seasons will equal the phosphorus release due to dead plant decomposition. Thus, if the vegetation is not harvested, the macrophytes will bring about no net phosphorus removal (Verhoeven and Meuleman, 1999; Vymazal, 2007).

#### 2.6.5.4 Physical settlement and accretion

Physical settlement and accretion is considered as one of the most important phosphorus removal processes in CWs. Consequently, wetlands are assumed to act as a long-term phosphorus sink as most of the retained phosphorus ends up in the sediment-litter compartment (Richardson, 1985). If a CW is nutrient-enhanced, phosphorus accumulation in substrates can result in peat accretion rates that are proportional to the concentration of phosphorus within the overlying water column (Craft and Richardson, 1993). Kadlec (1994) supported this statement indicating that the wetland biogeochemical cycle can operate to accrete new soils and sediments which contain phosphorus and at the same time this soil-building processes offer a more permanent storage of phosphorus.

#### 2.6.5.5 Chemical precipitation

Chemical precipitation, which refers to the conversion of soluble phosphorus to insoluble particulate forms, has been commonly used for phosphorus removal. A variety of cations can precipitate phosphate under certain conditions and the most often used are calcium (Ca), iron (Fe), aluminium (Al), and Magnesium (Mg)

(Tchobanoglous *et al.*, 2003; Vymazal, 2007). Laboratory results showed that, the precipitation of phosphorus could be effective and economical when the chemical was added at a point where most of the initial TSS had already separated out. A major concern with the application of chemical precipitation is the additional sludge produced. The sediments and sludge might decrease the capacity of CWs to retain water and control flood.

#### 2.6.5.6 Soil adsorption

Phosphorus adsorption by substrates is considered as one of the dominant long-term mechanisms in CWs (Kadlec and Knight, 1996; Richardson, 1999). The adsorption capacity depends on the physico-chemical characteristics of soils and sediments such as the proportion of clay and mineral particles, the concentration of amorphous Al, Fe and Ca, and total organic carbon amount (McGechan and Lewis, 2002; Reddy *et al.*, 1995; Reddy *et al.*, 1999). However, the magnitude of phosphorus attenuation is finite, and once soil sorption sites become saturated due to prolonged nutrient loading, the substrates will become source of phosphorus rather than a sink (Kadlec and Knight, 1996; Richardson and Craft, 1993). Additionally, the amount of phosphorus absorbed was determined by the phosphorus concentration in soil porewater. In general, there is a net adsorption of phosphorus when soil porewater has significantly lower concentration of phosphorus than that of in the overlying water column, while a net desorption and release of phosphorus by substrates occurs at low influent phosphorus loadings (Reddy *et al.*, 1999). Patrick and Khalid (1974) observed that anaerobic soils released more phosphate to soil solutions with low phosphate concentrations and sorbed more phosphate from soil solutions with high soluble phosphate concentrations than did aerobic soils.

If wetland plant roots penetrate into the sediments and soils, it might reduce the void spaces available for water-substrate contact and hence reduce the amount of the substrate for phosphorus adsorption, but only to a limited degree as some of the phosphorus in the water will be transformed and assimilated by the plant root system (Faithful, 1996).

#### 2.6.5.7 Microbiota assimilation

In a CW system, the phosphorus requirement of all living microorganisms (bacteria, fungi, algae, micronivetebrates, *etc.*) makes the microbial uptake an important mechanism of phosphorus removal. The microbiota within CWs can consume phosphorus very rapidly due to their high growth and reproduction rates. Nearly all phosphorus used by microbial biomass is returned to the phosphorus cycle through bacterial decomposition (Kadlec and Wallace, 2009; Reddy *et al.*, 1995). However, the anaerobic condition in litter/detrital zone slows this decomposition and promotes organic matter accumulation. In addition, bacteria have also shown to produce refractory biomass compounds that contribute to the long-term sustainable phosphorus burial.

### 2.6.6 Heavy metal removal

Metal removal processes occurring in CWs primarily involve a series of mechanisms such as settling, sedimentation, plant uptake, adsorption, complexation, cation and anion exchange, chemical precipitation, photodegradation, phytoaccumulation, biodegradation, microbial activity, and plant uptake (Crites *et al.*, 1997; Reed *et al.*, 1995). Sedimentation has been considered as the dominant process in the removal of heavy metals from wastewaters in natural and constructed wetlands. However, sedimentation is not a simple straightforward physical process and can only occur after heavy metals have aggregated to large, denser-than-water particles through other mechanisms such as precipitation, co-precipitation, hydrolysis and oxidation of metals (Walker and Hurl, 2002). Through this complex processes, heavy metals are removed from wastewater and trapped in wetland sediments. In addition to physical removal mechanisms, a variety of chemical processes are also involved in the removal of heavy metals (Sheoran and Sheoran, 2006). In organic substrates, adsorption (the attachment of ions to soil particles) is one of the most important processes. Kadlec and Keoleian (1986) have reported that a wide range of metals including lead, copper, and uranium can strongly bind to organic matter. The adsorption of metals varies with the fluctuation of pH in the wastewater (Machemer and Wildeman, 1992). However, since organic matter can be biodegraded over time, thus adsorbed metals will eventually return back to wetland systems (ITRC, 2003). Biological removal, in particular plant uptake, is another significant pathway for heavy metal removal in the wetlands. The plant capacity for heavy metal uptake varies widely, depending on the nature of wetland plants and concentration of metals in plant tissue (Kadlec and Knight, 1996). The main route of heavy metal uptake by plants is through accumulation on the structure of roots. Emerged and submerged rooted plants have some potential for the extraction of metals from sediments and water, while rootless plants can extract metals only from water (Sriyaraj and Shutes, 2001). Microorganisms also provide noticeable amount of heavy metal reduction through uptake and storage. Various scientists have found that the metabolic processes play a significant role in the removal of heavy metals (Hallberg and Johnson, 2005; Russell *et al.*, 2003; Ye *et al.*, 2001).

## 2.7 International research related to contaminant removal by constructed wetlands

International research on CWs with respect to nutrient and other contaminants retention and/or removal has been carried out in Europe, North America, Asia, Australia and New Zealand. This section of the review will discuss aspects of this work. Table 2-6 presents a limited comparison of CW performances in representative countries.

Table 2-6 Average influent (in) and effluent (out) concentrations and loading rates of constructed wetlands in representative countries (Babatunde *et al.*, 2008; O'Hogain, 2003; Vymazal, 2001b).

| Water quality parameters | Concentration | | | Loading rate | | |
|---|---|---|---|---|---|---|
| | In (mg $l^{-1}$) | Out (mg $l^{-1}$) | TE (%) | In (kg $ha^{-1}$ $day^{-1}$) | Out (kg $ha^{-1}$ $day^{-1}$) | TE (%) |
| COD | | | | | | |
| Czech Republic | 211 | 53.0 | 75.0 | 86.4 | 22.5 | 74.0 |
| Denmark | 264 | 64.7 | 75.5 | 127.0 | 30.2 | 76.2 |
| Germany-L.Saxony | 430 | 133.0 | 69.1 | - | - | - |
| Germany-Bavaria | 234 | 69.4 | 70.3 | - | - | - |
| Ireland | 790 | 53.0 | 93.3 | - | - | - |
| Poland | 283 | 101.0 | 64.3 | 96.2 | 39.0 | 59.5 |
| Slovenia | 200 | 35.7 | 82.2 | 104.0 | 18.4 | 82.3 |
| Total P | | | | | | |
| Czech Republic | 6.6 | 3.2 | 51.5 | 3.1 | 1.8 | 41.9 |
| Denmark and UK | 8.6 | 6.3 | 26.7 | 3.3 | 2.6 | 21.2 |
| Germany-L.Saxony | 11.4 | 4.0 | 64.9 | - | - | - |
| Ireland | 13.0 | 1.5 | 88.5 | - | - | - |
| North America | 4.4 | 3.0 | 31.8 | 5.1 | 4.0 | 21.6 |
| Poland | 7.7 | 4.1 | 46.8 | 2.7 | 1.6 | 40.7 |
| Sweden | 5.0 | 2.1 | 58.0 | 4.0 | 1.6 | 60.0 |
| Total N | | | | | | |
| Czech Republic | 46.4 | 27.1 | 41.6 | 24.5 | 15.0 | 38.8 |
| Denmark | 36.6 | 20.9 | 42.9 | 11.5 | 7.8 | 32.2 |
| Germany-L. Saxony | 115.0 | 59.8 | 48.0 | - | - | |
| North America | 18.9 | 8.4 | 55.6 | 13.2 | 7.4 | 43.9 |
| Poland | 46.1 | 34.8 | 24.5 | 15.8 | 12.5 | 20.9 |
| Sweden | 25.3 | 15.1 | 40.3 | 15.8 | 8.7 | 44.9 |
| $NH_3$-N | | | | | | |
| Czech Republic | 28.1 | 16.1 | 42.7 | 13.1 | 8.2 | 37.4 |
| Denmark | 21.0 | 14.1 | 32.9 | 9.3 | 3.3 | 64.5 |
| Germany-L.Saxony | 80.5 | 4.5 | 94.4 | - | - | - |
| Ireland | 66.7 | 1.6 | 97.6 | - | - | - |
| North America | 6.0 | 4.5 | 23.4 | 7.0 | 6.4 | 8.6 |
| Slovenia | 28.7 | 7.7 | 73.2 | 15.1 | 3.9 | 74.2 |

In, influent; Out, effluent; TE, treatment efficiency; COD, chemical oxygen demand; N, nitrogen; P, phosphorus; $NH_3$-N, ammonia-nitrogen.

### 2.7.1 Europe

European countries have utilised CWs to a varied degree over the past 30 years. The most commonly used systems are soil or gravel based horizontal subsurface flow systems due to their low construction costs, less operation and maintenance demand. Stringent legal rules have led to the development of highly efficient vertical flow systems and combined systems (i.e. constructed wetlands in association with conventional biological processes) (Haberl *et al.*, 1995).

According to the Constructed Wetland Associate (CWA) UK database, there are now more than 1,000 CWs in the UK (Table 2-7). Most of these CWs are sub-surface flow and used for secondary and tertiary treatment, and nitrification of sewage/domestic wastewater for small villages (Cooper, 2007; Cooper and Green, 1995). In addition, the database presents more specific information on the performance of individual CW and reed bed. For instance, the Yorkshire CW systems have been in operation since the mid 1980s. They were mainly FWS, SSF (soil and gravel) and lagoon (floating algal mats or dense macrophytes) wetlands with hydraulic loading rate varying from 0.02 to 1.3 m $d^{-1}$. The phosphorus removal capacity was limited and the phosphorus concentrations, relative to the load, were highly variable and can not be correlated with the type of treatment wetland. The FWS-CWs achieved high effluent standards (in terms of contaminants’ concentration) but generally lower load removal than SSF-CW systems.

Table 2-7 Constructed Wetland Associate (CWA) UK database (Cooper, 2007).

| Breakdown of the bed type | | Breakdown of treatment applications | |
|---|---|---|---|
| Wetland type | No. | Wetland application | No. |
| Secondary sewage treatment beds | 107 | Sewage treatment | 874 |
| Tertiary treatment horizontal flow beds | 698 | Minewater treatment | 50 |
| Vertical flow (VF) bed | 70 | Landfill leachate treatment | 24 |
| VF beds | 49 | Industrial wastewater | 19 |
| Compact VF | 21 | Surface run-off treatment | 16 |
| Hybrid systems | 19 | Agricultural runoff treatment | 13 |
| Storm sewage overflow treatment | 46 | Road runoff treatment | 16 |
| Separate storm sewage overflow treatment beds | 6 | | |
| Combined storm sewage overflow and tertiary treatment beds | 40 | | |

Note: 1,012 wetland beds were recorded.

A FWS system in the Netherlands has reported a 26% reduction of nitrogen (126 g N $m^{-2}$ $yr^{-1}$) and less than 5% reduction of phosphorus (5 g P $m^{-2}$ $yr^{-1}$) after an operation period of 2 years. This system had a total water surface of 13,000 $m^2$ (serving a population up to 45,000) and a relatively short hydraulic retention time of 2.4 days (hydraulic loading rate 25 cm $d^{-1}$). The effluent from sewage treatment plants was pre-treated in a 3,483 $m^2$ pre-settling basin, and then divided over nine parallel surface-flow ditches, after which treated water was collected in a discharge ditch. Each wetland ditches were made up of two compartments of differing depth and vegetations (the first half that near the ditch inlet was 0.2 m deep and planted with emergent macrophytes; the second half was 0.4 m deep and planted with submerged aquatic macrophytes). The removal of nitrogen mostly occurred in the front sections of the ditches with emergent vegetation but little difference was noted between the sections of ditches for phosphorus removal. In general, the low concentrations of nitrogen and phosphorus in influent combined with high hydraulic loading rates were main reasons that the system performed less than expected (Toet *et al.*, 2005).

The removal of non-point source contaminants from farmyard runoff is rather difficult and often relies on the understanding of contaminant flux concentrations and the transfer mechanisms. Johannesson *et al.* (2010) investigated seven constructed wetlands with surface areas of 2,300-20,000 $m^2$ in southern Sweden. The study showed that phosphorus retention rates varied from 2.5 to 56 kg $ha^{-1}$ $yr^{-1}$ for studied systems, and the retention was correlated to the phosphorus load ($R^2$=0.025, $p$=0.004).The inflow total phosphorus (TP) fluxes were very variable and essentially transferred during stormflow resulted in a decrease in phosphorus loads. The outflow phosphorus concentrations were less variable than inflow phosphorus, which indicated that wetlands played an important role in the improvement of water quality from agricultural areas to receiving waters.

CWs have been used for wastewater treatment in the Czech Republic for more than two decades. They were mainly HF wetland systems with population equivalent (PE) varying from 101-500. In general, the removal capacity of 5-day biological oxygen demand ($BOD_5$) and TSS for Czech wetlands was very high; however, the removal of nutrients was much lower. The role of seasonal conditions on the removal of organics, TSS, and nutrients was very little (Vymazal, 2001b).

## 2.7.2 North America

There are a large number of wetland studies performed throughout the United States and Canada which vary from large open natural wetland treatment systems for farmyard and stormwater runoff to small compact vertical flow systems for sewage treatment.

A study by Knight *et al.* (2000) of treatment performance of 68 sites with a total of 135 pilot and full-scale wetland systems in US found that average concentration removal efficiencies were: $BOD_5$ 65%, TSS 53%, ammonia-nitrogen ($NH_3$-N) 48%, total nitrogen (TN) 42%, and TP 42%. This led to the conclusion that inlet concentrations and hydraulic loading rates played significant role in the overall efficiency of wetlands. These findings showed that adequate pre-treatment of wastewater and adequate wetland area must be considered in the overall design criteria as to meet water quality goals.

A practical design for a newly CW system which treats runoff from a non-point source prior to discharge into a tributary of the South Fork of the Great Miami River, Ohio, USA was shown in Fink and Mitsch (2004). The system was a 12,000 $m^2$ basin containing five individual permanent and seasonal small ponds linked by surface and subsurface flows. Annual average removal efficiencies for (nitrate+nitrite)-nitrogen (($NO_3$-N+$NO_2$)-N), orthophosphate (SRP) in 1999 were 30%, 62% and 37% respectively, although several major nutrient pulses were recorded due to large rain showers. It was concluded that, for newly constructed agricultural wetlands, the system needs one to three years to work effectively at the removal of ($NO_3$+$NO_2$)-N because of the development of the physical features and microbial community.

The efficiency of a series of small-scale wetland mesocosms to treat domestic wastewater was reported by Hench *et al.* (2003). The mesocosms were filled with pea gravel into two depths (45 or 60 cm) and planted with a mixture of *Typha*, *Scirpus* and *Juncus* species. The study was based on monitoring the inflow and outflow water quality on a monthly basis for a 2-year period, and found that, in general, the removal of contaminant was effective and the presence of vegetation further improved treatment efficiency. Reductions observed in the vegetated mesocosms showed removal rates of 83% for TSS, 42% for $BOD_5$, and 55% for TKN. It is also found that TSS reduction remained highly effective throughout the study period. However, the reductions in $BOD_5$ and TKN were noticeably decreased ($p<0.5$) at the second year of operation. Annual removal rates of approximately 74% for TKN and $BOD_5$ during the first year diminished to 31% and 13% respectively during the second year.

### 2.7.3 Asia

Since 1990s, Asian studies follow the trends of the North America and European regions as to the steady increase in utilising CWs for agricultural runoff and/or domestic sewage treatment.

Nakamura *et al.* (2002) presents a survey of the CWs in Japan which have a relatively high capacity for reducing TN and TP for a variety of treatment areas and design flow. The results showed that the HRTs for most CWs were shorter than 10 hours. However, as for those wetlands with a retention period longer than 10 hours, approximately 40% of TN and 60% of TP were removed. In addition, some wetland systems were found to be rather ineffective for the removal of TP, which probably because of limited absorption capacity of sediments, lack of oxygen, and relatively low phosphorus influent concentrations. It was suggested that the ceasing of CWs operating during winter period might regain the absorption capacity of sediments.

The application of CW systems to treat wastewater also rapidly developed in China due to its scarcity of water resources and freshwater shortages (Liu and Diamond, 2005). Since 1987, when the first CW system was built, there were more than 200 CWs (excluded pilot-scale constructed wetlands that were used mainly for research), ranging in area from 100 $m^2$ to 8,000 $m^2$, were in operation throughout China by 2006. In general, the average removal capacities of $NH_4$-N, TN, TP, COD and BOD for Chinese wetlands are 59.8%, 44.3%, 62.1%, 73.4%, and 81.8%, respectively (Liu *et al.*, 2009). An investigation of literature found that almost all authors concerned the availability of land required to implement CWs, and it might become one of the factors limited their broader use, in particular for southern China, where land resources are scarce and population density is high.

Lu *et al.* (2008) reported on a two year research programme analysing the nitrogen removal capacity, the nitrogen distribution pathways, and nitrogen species removal kinetics of a large CW (2,800 $m^2$) in the Danchi Valley, a subtropical region of China, receiving agricultural runoff. The CW was a free surface flow system planted with *Phragmites australis* and *Ziaznia caduciflora*. The results were expressed on a seasonal basis as the authors were concerned that microbial activity would decrease in the winter months thereby reducing the effectiveness of the wetland. The average removal rates of TN, nitrate, and $NH_4$-N were 445.8 mg N $m^{-2}$ $d^{-1}$, 82.6 mg N $m^{-2}$ $d^{-1}$ and 203.9 mg N $m^{-2}$ $d^{-1}$ respectively. There is no notable seasonal variation for the removal rate of N. It was also concluded that plant harvesting was more important in wetland treated agricultural runoff than in domestic wastewater.

In an experimental study of domestic wastewater treatment by CWs planted with rice in Thailand it was found that significant removal of COD, BOD, TKN, and TSS were achieved when the wastewater was inundated to a depth of 15 cm for 25 days. In addition, the study suggested wastewater was able to replace nature water to grow rice in dry season or throughout the year. The nutrients (N and P) in wastewater could ensure the rice gain production (Kantawanichkul and Duangjaisak, 2011).

### 2.7.4 Australia and New Zealand

The predominant wetlands research in Australia is with CWs and their application to improving water quality discharge for a number of industrial systems (i.e. sewerage treatment plants, processing plants). Much of this work commenced in 1970's (Mitchell *et al.*, 1995). The use of CW is, however, increasing throughout Queensland with Queensland Department of Natural Resources initiatives to integrate wetlands as a tertiary treatment process of sewerage treatment plants and other applications (Faithful, 1996).

A study by Greenway and Woolley (1999) of performances of nine pilot wetlands (eight surface flow and one subsurface flow) with different configurations in Queensland, Australia, indicated a 17-89% reduction in BOD to less than 12 mg $l^{-1}$, a 14-77% reduction in suspended solids to less than 22 mg $l^{-1}$, a 18-86% reduction in total nitrogen to 1.6-18 mg $l^{-1}$, and a 13% and 65% reduction in reactive phosphorus from the free water surface system and single household subsurface system respectively. This led to the conclusion that constructed free water surface wetland systems were a viable option for improving the quality of secondary sewage effluent by reducing BOD, SS, and with careful design, nitrogen. Low flow wetlands exhibited high capacity to polish effluent. However, effective long-term phosphorus removal was not observed. The paper also showed that a dual subsurface flow constructed wetlands combined with a settling pond are particularly effective to treat wastewater from a single household.

A 700 $m^2$ stormwater control wetland at Riverwood (in the south of Sydney) was designed with a preceding gross contaminant trap and emergent and littoral vegetations. Overall, the studied wetland showed 22% and 16% reductions in $(NO_3+NO_2)$-N and TN, with TKN and TP reduction at 9% and 12% respectively (Birch *et al.*, 2004). The gross contaminant trap was found to be an integral part of the wetland design, not only because of its role in removing coarse litter and sediment, but that it reduced inflow velocities thereby reducing the potential scouring and sedimentation in the initial stages of the wetland (Hunter and Claus, 1995).

CW studies have been conducted in New Zealand over the past two decades with an emphasis on treating rural runoff such as dairy farm wastewaters. Tanner *et al.* (2005) reported on the nitrogen and phosphorus budgets over two annual periods for an establishing surface-flow CW (260 $m^2$) dominated with *Typan orientalis* treating subsurface drainage from grazed, fertilised, dairy pastures in the North Island of New Zealand. The average TN mass removal efficiency of 79% (841 g $m^{-2}$ $yr^{-1}$) in the first year, declined to 21% (40 g $m^{-2}$ $yr^{-1}$) in the second year. The median TP inflow concentrations were between 0.1 to 0.2 g $m^{-3}$ of which the dissolved reactive forms comprised 92% of the influent. TP export rose by 101% (5.0 g $m^{-2}$ $yr^{-1}$) after the treatment in the first year, but decreased by 12% (0.2 g $m^{-2}$ $yr^{-1}$) in the second year. It is important to note that the performance of the treatment wetland might be affected by both establishment/maturation factors and year-to-year seasonal variations.

Sukias & Tanner (2004) reported on the performance of seven wetlands treating domestic wastewater in the Waikato region, New Zealand. The assessment of regular monitoring data from each wetland showed that removals of BOD and SS were effective, both on a loading per unit area and percentage reduction basis. Phosphorus removal was not significant and generally negligible in either wetland system. *Glyceria maxima*, which dominated in several of studied wetlands, typically has relatively poor oxygen release characteristics. This wetland species might result in the poor $NH_4$-N removal. The authors also suggested that the wetland managers and operators should focus on monitoring their systems for trend analysis or enhancing the treatment performance, rather than on caring about "whether wetlands achieved the consent requirements".

During the course of the review of these international studies it was occasionally difficult to interpret data presented in the journal articles and proceeding papers. In addition, there are often a large number of variables influencing the contaminants (particularly N and P) removal processes which makes it very difficult to produce a simple optimum design for wetlands that will effectively remove contaminants and does not waste resources by incorporating excessive land area. However, given the successful experience, available data and the increasing research into wetlands it should become easier for managers to implement designs and maintenances based on a knowledge of general biological, physical and chemical principles.

## *2.8 Long-term operational problems and maintenance*

### 2.8.1 Wetland ageing

The long-term contaminant removal capabilities of CWs appear to be somewhat unreliable and have not yet been fully taken into consideration (Brix *et al.*, 2007; Mustafa *et al.*, 2009). In recent years many of the research publications indicated that wetland ageing may contribute to a decrease in nutrient retention over time.

Braskerud (2002) examined on the nitrogen retention in four surface-flow CWs with surface areas of 350 to 900 $m^2$ which treated agricultural and stormwater runoff in Norway. The average nitrogen retention was only 3 to 15% of the N-input due to the relatively high hydraulic loading rate (0.7 to 1.8 m $d^{-1}$) and low temperatures (-8 to 18 ℃) and resulted in mean retention of 50 to 285 g nitrogen $m^{-2}$ per year. The retention performance for organic N, $NH_4$-N and $NO_3$-N was shown decrease as CWs age. The author suggested that mineralization (ammonification) could convert the organic N to $NH_4$. The amount of organic N accumulated in wetland sediment increased with the age of CWs which might stimulate the microbiological decomposition and mineralization. As a result, the organic N could make small CW systems to net exporters of inorganic nitrogen in a long-term perspective.

The efficiency of 32 CWs situated in two adjacent catchment areas of the rivers Kävlinge and Höje in southern Sweden was reported by Hasson *et al.* (2005). The analyses were based on the data from 2000, expect for the measures of nitrogen and phosphorus, which were sampled in July and November 2001, and found that, in general, retention of both phosphorus and nitrogen was highly variable and some wetlands leaked nutrients downstream. Six wetlands (19%) released phosphorus downstream in both sampling events (July and November), whereas 31% systems had negative retention in one of the events. A possible reason for summer leakages of phosphorus was the combined effect of wetland age, low oxygen concentrations and high temperatures which resulted in the release of phosphorus from sediments. With respect to nitrogen, 9% investigated wetlands always leaked nitrogen downstream, while 28% had negative retention in either July or November. Unlike phosphorus, the nitrogen retention, particularly denitrification process, was significantly enhanced by the temperature. However, there was no clear relationship between constructed wetland age and nitrogen retention.

In a comparative study of domestic raw wastewater treatment in Ireland between a new and a mature integrated constructed wetland (ICW) systems it was found that the old removal efficiencies for $NH_4$-N, $NO_3$-N, and MRP were 58%, -80.8% and 34.0%, respectively. The effluent $NO_3$-N and MRP concentrations gradually increased with operational times. The analyses results showed that the system produced an effluent $NH_4$-N, $NO_3$-N and MRP concentrations of three times higher for the fourth year of its operation than for the first 3 years due to overloading. $NH_4$-N and $NO_3$-N were both released from the ICW system. It was concluded that the denitrification rate started to decrease as the ICW aged (Kayranli *et al.*, 2010; Scholz, 2010).

The cover of vegetation within wetland beds may increase with the age of CWs. In fact, the vegetation itself functions as a temporary storage of nutrients. Rooted macrophytes take up large quantities of nutrients in growing seasons. If the vegetation is not harvested, most of trapped nutrient end up in the litter compartment. A large proportion of these nutrients will be released again through leaching and organic matter mineralization in autumn and winter, and only a very small part of the nutrients preserves in the plant as additional long-term storage in rhizome material. By contrast, if the vegetation is harvested, the amount of nutrients released in non-growing season is substantially lower (Brix, 1994; Kadlec and Knight, 1996; Verhoeven and Meuleman, 1998). This finding gives wetland age an additional effect.

Much of the research on long-term treatment performance of CWs has shown that nutrient retention decreased with constructed wetlands age, trapped nutrients might be exported from the wetlands. However, it is very difficult to draw conclusions about the conditions that could completely prevent nutrient release from constructed wetlands.

### 2.8.2 Wetland sediments

Sediments accumulation in wetland systems may take place over long period and is influenced by geomorphology, hydrology, nutrient load and macrophytes cover (Anderson and Mitsh, 2006). Wetland sediments comprise organic materials from influent, dead plant stem, roots and rhizomes, and also from indecomposable fractions of algae, fungi, invertebrates and bacteria (Kadlec, 2009; Mustafa and Scholz, 2011; Scholz, 2011).

In CWs, sediments play significant role in removing and/or retaining contaminants from wastewaters (Knox *et al.*, 2006). In general, contaminant removal and/or retention within wetland sediments may be achieved by abiotic (physical and chemical) processes or biotic (microbial and phytological) processes. The major abiotic processes include settling, sedimentation, sorption to organic matter or mineral phases, oxidation and hydrolysis, formation of carbonates, formation of insoluble mineral phases, and binding to iron and manganese oxides. In these processes, particulate matter and suspended solids are mainly removed by settling and sedimentation; sorption, which includes adsorption and absorption, can result in the retention of contaminants; metals are converted into an insoluble precipitate through chemical precipitation (DuLaing *et al.*, 2009; Knox *et al.*, 2010). Considering a rich microbial population in sediment, biotic processes such as biodegradation and plant rhizosphere uptake are also important in relation to the treatment performance of CWs. Some microbial and phytological processes taking place in wetland sediments include aerobic/anaerobic biodegradation (i.e. microbial metabolic processes), phytoaccumlation, phytostabilization, phytodegradation, rhizodegradation, and phytovolatilization/evapotranspiration (Halverson, 2004).

On the other hand, sediments may also remobilise contaminants when environmental conditions change. This potential release phenomenon has become a growing concern for wetland management.

### 2.8.3 Wetland maintenance

Maintenance of CWs falls into several different categories; however, aesthetic/nuisance maintenance and functional maintenance are two key areas to focus on (Hobart City Council, 2006).

#### 2.8.3.1 Aesthetic/nuisance maintenance

CWs can create wildlife habitats and can also become an attractive community feature. Aesthetic maintenance is important to enhance the visual appearance and appeal of a wetland system. The following activities should be included in an aesthetic maintenance plan and performed periodically (Hunt and Lord, 2006):

- Clean away floating trash and debris.
- Trim grass and plants around fences, outlet structures, hiking/cycling path, etc.
- Remove weeds and invasive plant species.
- Pay attention to tasks such as painting, tree pruning, leaf collection, and grass cutting to create an attractive appearance of a wetland.

#### 2.8.3.2 Functional maintenance

Functional maintenance includes routine (preventive) and corrective maintenance. These activities are able to maintain treatment efficiency of CWs and to prevent safety issues (Shih *et al.*, 2009).

Preventive maintenance should be done on a regular basis. Examples of preventive maintenance include:

- Inspect vegetative cover during both growing and non-growing period.
- Mow the grass considering site specifications and grass type.
- Maintain mechanical components in accordance with manufacturers' instructions.
- Control and eliminate mosquito breeding habitats.
- Remove accumulated wetland sediments

Attention could be paid on wetland sediments removal. Accumulated sediments should be removed before they impact wetland operation and performance or the pond storage volume has reached (Scholz, 2006). The desludging frequency may vary considerably between wetland systems and individual cells. If a large initial cell is applied to capture most of sediments and particulate contaminants, a relative frequent desludging for that pond should be necessary. While if a wetland system is designed into smaller ponds, it is likely to expect a greater spread of sediment within wetland ponds, therefore, a less desludging frequency is required but more cells should be involved (Scholz *et al.*, 2007).

When there is an emergency or a problem that should be corrected as soon as possible, the corrective maintenance is required to perform as to restore the intended operation and safe situations of wetlands. The delay of addressing a corrective maintenance issue may cause the adverse impacts on the treatment efficiency and integrity of the wetland. Corrective maintenance tasks include debris and sediment removal, structural damage inspections and remediation, erosion management, general facility maintenance including fence repair (Hobart City Council, 2006).

## 2.9 Summary

This chapter presents the significant mechanisms for contaminant removal in CWs. Special emphasis is given to nutrient (nitrogen and phosphorus) removal. The application of CWs for wastewater treatment has also been examined with primary attention given to raw effluent quality, nutrient removal efficiencies, and age of the wetland. The management of CWs with respect to long-term operational problems is also addressed.

# Chapter 3

# Integrated Constructed Wetlands

## 3.1 Introduction

This chapter presents an overview of integrated constructed wetland (ICW) by focusing on studies conducted during the past decade. The specific issues addressed in this chapter are:

- the integrated constructed wetland (ICW) concept;
- the advantages, disadvantages/limitations of ICWs;
- ICW design consideration, such as site selection, wetland sizing, aspect ratio, hydraulic retention time and flow velocity;
- the role of vegetation and recommendations for proper plant species;
- potential of groundwater contamination; and
- the success of ICW application in treating farmyard runoff and domestic wastewater.

## 3.2 Integrated constructed wetland concept

The ICW concept (Fig. 3-1) was developed in the early 1990s to address water pollution and provide ecological and other wetland ecosystem services (i.e.

biodiversity enhancement) by reanimating wetland infrastructure (Harrington *et al.*, 2005). Fig.3-2 shows the technology envelope of ICW. Compared to conventional constructed wetland systems, ICWs are the explicit integrations of (Harrington *et al.*, 2007):

- the containment and treatment of influents within emergent vegetated areas using wherever possible local soil material;
- the aesthetic placement of the containing wetland structure into the local landscape towards enhancing a site's ancillary values; and
- enhanced habitat diversity and nature management.

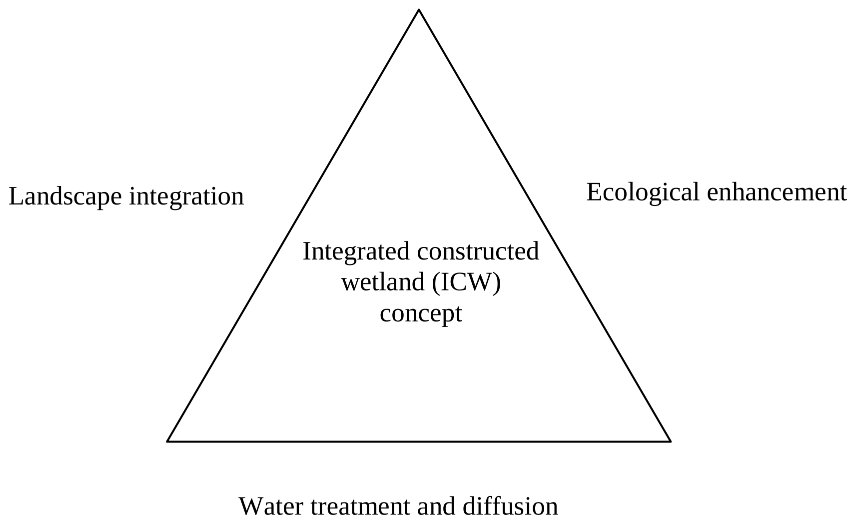



Figure 3-1 Integrated constructed wetland conceptual framework (Harrington *et al.*, 2005; Harrington *et al.*, 2007; Scholz *et al.*, 2007).

In 2000, thirteen pioneering ICW systems were designed and constructed to treat farmyard runoff and/or domestic wastewater within the Anne Valley in south County Waterford, Ireland. The main functional features of ICWs are shallow water depth, dense emergent vegetation, sequential flow through a series of wetland cells and the use of on-site materials and topography (Scholz *et al.*, 2007). The use of locally available soils is a key factor delivering adequate area at acceptable cost and thus there is a general absence of synthetic (i.e. concrete or plastic) liners. ICW utilizes the same structures and biogeochemical processes that exist in natural and artificial wetlands to effectively treat wastewater (Scholz *et al.*, 2007) and diffuse contaminant (Harrington *et al.*, 2011).

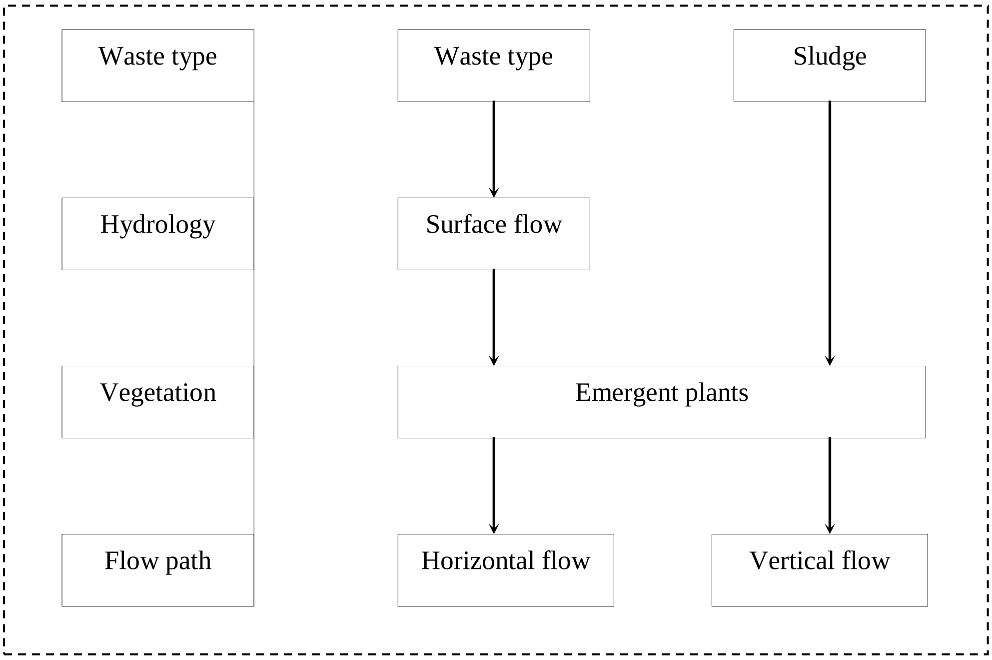



Figure 3-2 Integrated constructed wetland technology envelope (Mustafa, 2009).

## 3.3 Advantages and limitations

ICWs have multi-cellular configurations that provide effective, reliable and ecologically sound wastewater treatment results. ICWs are economical and simple to construct, operate and maintain, in particular when compared with conventional wastewater treatment facilities. If constructed on suitable terrain (gently sloping land), there is little or no energy input required. In addition, ICWs are able to fit the landscape and to enhance biodiversity and habitats. Due to shallow surface flow and dense plant cover, the odour problems can be greatly minimized. Accumulated sediments and particulate matter can be disposed of by spreading over agricultural land.

Since the application of ICWs is relatively new, however, many problems and limitations may exist. ICWs require relatively a large amount of land area to be effective. The inconsistencies of treatment performance can occur under adverse weather conditions such as cold temperature, droughts, heavy rainfalls and snow melts. The design criteria for ICW have not been fully developed considering a wide range of site specifications, climates, landscape planning, and discharge standards. Although numerous research has been completed over the past decade, there is a lack of long-term (>10 years) recorded data concerning the performance and efficiency of full-scale ICW systems. The potential of nutrient releases from wetland sediments back to system may impact local streams. ICWs also potentially contribute to the emission of greenhouse gases (Mitsh *et al.*, 2001; Thiere *et al.*, 2011). Due to the absence of artificial liners, infiltration of wastewater can occur and cause contamination to groundwater.

## 3.4 Vegetation

Harrington and Ryder (2002) reported that vegetation planted in an ICW system performed numerous valuable environmental functions. They can purify water through microbial biofilm around root zone, facilitate to retain nutrient, filter out suspended solids, and control odours and pathogens. Moreover, through research carried out by Holcová *et al.* (2009) it was found that the vegetation stands could covert a significant amount of water from liquid to gas via evapotranspiration and thus prolong water retention time in the system. The appropriate choice of vegetation type therefore plays significant roles in the overall functioning of ICWs.

The primary vegetation types used in ICW systems are emergent plant species (helophytes) (Carty *et al.*, 2008). Helophytes are able to release organic substances into the rhizosphere to supply microorganisms within sediments and substrates (Barber and Martin, 1976). In addition, the atmospheric oxygen is transported from the parts of the plants above the surface by diffusive and/or convective mechanism via gas channel tissues inside the plants down to the roots (Armstrong *et al.*, 1994; Wieβner *et al.*, 2002). The soil and wastewater characteristics influence the dominant species of helophyte and their treatment capacity (Scholz *et al.*, 2007).

It should be mentioned that, unlike to many other CW systems, the common reeds (*Phragmites australis*) was not widely applied to ICW systems as it may gradually colonize wetland cell and thus exhibiting substantially less ecosystem services and decrease of biodiversity (Carty *et al.*, 2008; Peter and Burdick, 2010). Table 3.1 lists suitable plants that have been used commonly in international CWs for wastewater treatment.

Table 3-1 List of suitable emergent wetland plants used in constructed wetlands (Preston and Croft, 1997).

| Plant species | Common names | Comments |
|---|---|---|
| *Phragmites australis* | Common reed | Tall bamboo-like reed with feathery flowers. Widely used in constructed wetlands in many parts of the world where it occurs naturally. |
| *Iris pseudacorus* | Yellow flag iris | Tall yellow-flowered iris. Grow rapidly and spread quickly. Can displace other tall emergent vegetation. |
| *Glyceria maxima* | Reed sweet grass | Quick to establish. Tends to overgrow and dominate other species and have lower wildlife habitat values. |
| *Typha latifolia* | Reedmace or Cattail | Widely used in constructed wetlands. It tends to produce large accumulations of standing and decomposing litter, and can be invasive in nutrient-rich situation, excluding other more desirable species. |
| *Carex riparia* | Greater pond sedge | Evergreen and fast grow. Commonly found across Europe and Asia. Can form large stands if the water flow is slow. |
| *Scirpus lacustris* | Bulrush | Good establishment and growth. Mostly used in North America, Australia and New Zealand. Roots penetrate up to 79-80 cm resulting in greater root-zone aeration and microbial nitrification. |
| *Typha angustifolia* | Lesser bulrush | Tall, robust with slender, lance-shaped, grey-green deciduous leaves. It is of value for protecting banks. |
| *Sparganium erectum* | Branched bur reed | Up to a height of about 1.5m. Grows by still or slowly flowing water. Widespread throughout Britain and Ireland. It is very tolerant of eutrophic conditions. |

## 3.5 Wildlife habitats

Wetlands can yield beneficial results in wildlife habitat enhancement or creation. This might be particularly effective where there is a large site size, emergent vegetative cover, exceptional water quality requirements and/or the presence of impermeable clay subsoil (Pankratz *et al.*, 2007).

The wetland habitats can be identified by several unique characteristics including the presence of water, the flow regime, the wetland shape and size, and the type and nature of vegetation (van der Valk, 2006). Water levels in a wetland may range from at the ground level to greater than 1 m. Water condition is the greatest contributing factor to influence the colonization of wetlands by wildlife. The flow of water is slow to stagnant in many wetlands and it may result in a low level of dissolved oxygen in the water as there is little interaction between the water body and the atmosphere above. This is a major limiting factor for many aquatic organisms so that only those that are specially adapted can survive. In addition, wetlands vary widely in shape and size. If the wetland is designed to be broad and shallow, the surface water can be close to ambient temperature with little buffering capacity. When there is an increase in temperature, the water might reduce the capacity to dissolve oxygen and impose potential risk on aquatic organisms. Another significant factor determining the biodiversity in a wetland is the height, arrangement, and density of wetland plants. Different species of plants can influence light level, water temperatures, oxygen concentrations and water chemistry and consequently increases the diversity of microhabitats. Wildlife will therefore select the most suitable vegetative zone for their needs, such as food and nesting (Openfield Ecological Service, 2008).

The construction of ICWs has been a success on habitat restoration and biodiversity enhancement. These systems have the capacity to fit into the landscape and provide suitable habitat for a wide range of biota, including nesting birds, fish, amphibians and invertebrates (Jurado *et al.*, 2010). It should be noticed that enhanced biodiversity is not the side benefit of establishing and developing the ICW, it is the primary reason the ICW works in the first place (Harrington *et al.*, 2005; Scholz *et al.*, 2007).

### 3.6 Design considerations

The guidelines regarding design, operation and maintenance of farm constructed wetlands (including ICW) have been proposed by Carty *et al.* (2008). Factors that determine the selection of most appropriate site include: local climate, topography, geology, hydrology, soils and subsoils, size/extent and type of receiving water body, flora and fauna, archaeological and architectural features, land availability, and environmental enhancement value. These site characteristics should be carefully investigated through a comprehensive site-specific assessment combining site survey and desk study. When conducting site assessment, the information on wells, springs, water table elevation, aquifers, nearby surface and groundwater supplies should also be studied.

Wetland sizing is crucial in controlling both the hydraulic loading rate and water retention time required to provide maximum contact and reaction opportunities (Ellis *et al.*, 2003). Scholz *et al.* (2010) suggested that much greater farmyard runoff treatment performance, in particular for phosphorus (as molybdate reactive phosphorus, MRP) removal, can be expected if the wetland area was at least 1.3 times that of farmyard area, and the minimum number of cells for a ICW system should be four, however, more cells might enhance treatment efficiency and aesthetical appeal. As a general rule of thumb, the ICW area should typically be approximately 1-2% of any individual farm area. However, this approximate figure should only be used for preliminary sizing.

An aspect ratio (length:width) of 1:1 (in square or round shape) for the ICW pond has been recommended by Scholz *et al.* (2007) as to achieve a less than 1 mg $l^{-1}$ outlet MRP concentration. However, pond shape is often adjusted so a given number of ponds can fit within a given distance, e.g. three small ponds along one large pond so that dikes line up.

In order to achieve a satisfactory treatment result, the optimal hydraulic retention times are required. The hydraulic effectiveness of the free water surface flow CWs can be maximized by the following measures: segmentation of the system into a number of wetland cells of appropriate configuration; avoidance of preferential flow; dense vegetation stand; and management of the water depth to ensure optimal functioning (Carty *et al.*, 2008; Scholz, 2007; Scholz *et al.*, 2007). High flow velocity may damage the plants physically and cause a decline in treatment efficiency. On the other hand, reducing flow velocity may prolong the contact time and promote the sedimentation, adsorption, biotic processes and retention of nutrients (Reuter *et al.*, 1992).

## 3.7 Groundwater infiltration

Due to the use and reworking of in situ soils as wetland cell liner, the potential degradation of groundwater quality through contaminated water infiltration cannot be ignored. In general, ICW are underlain by at least 1.0 m of subsoil, with a hydraulic conductivity of $10^{-8}$ m $s^{-1}$ (Carty *et al.*, 2008). As the contaminated influent passes through the system, the suspended organic matter accumulates on the soil surface and subsequently slows the infiltration through sealing substrates (Mustafa *et al.*, 2009; Scholz, 2006). Furthermore, biogeochemical processes can occur within wetland sediments. Some of these play an important role in, for instance, the clogging of the soil matrix, biomass accumulation, and/or biogas (i.e. methane) formation through soil microbes (Tokida *et al.*, 2005; Zhao *et al.*, 2009).

## 3.8 Applications

### 3.8.1 Farmyard runoff treatment

Farmyard runoff could adversely impact surface and groundwater quality if it is allowed to enter a watercourse. Excessive amounts of nutrients, such as nitrogen and phosphorus, can increase aquatic plant growth and subsequently cause eutrophication. Nitrogen, in the form of $NH_3$, is toxic to aquatic life. Although the organic matter acts as a "fuel" for microscopic aquatic organisms, the breakdown of this organic material can result in a reduction of the amount of dissolved oxygen. Suspended solids carried in the runoff may contribute to silting, decreasing cell volume, and interfering with wildlife habitat. Runoff may also contain pathogenic (disease-causing) organisms, which if present in sufficient numbers, create a health hazard. For these reasons, farmyard runoff must be properly treated before entering a recipient water body (Edwards *et al.*, 2008).

ICWs have been recognized as a suitable option for treating farmyard runoff (Carty *et al.*, 2008). In recent years there has been a number of research published which have essentially reported the findings of the ICW application. Dunne *et al.* (2005a) evaluated the seasonal effectiveness of ICW site 9 (4,800 $m^2$) to treat runoff from 42-cow organic dairy unit with an open yard area of 2,031 $m^2$. The water balance analysis showed that 27% of hydrological input to the wetland was farmyard dirty water, whereas rainfall on wetland, along with wetland bank inflows accounted for 45% and 28% respectively. The authors found that phosphorus retention by the wetland varied with season (5-84%) with least amounts being retained during winter. In general, ICWs can be considered as a suitable alternative to manage farmyard dirty water which contains considerable amounts for nutrients and contaminants.

Scholz *et al.* (2010) have investigated the nutrient removal performance of twelve full-scale ICW systems with different size, number of cell, ICW to yard area ratio, and influent nutrient concentration. The monitoring data between August 2001 and August 2007 showed greater than 90% reduction in molybdate reactive phosphorus and no significant seasonal variations was observed. In addition, the concentration reductions in ammonia-nitrogen ($NH_3$-N), organic matter such as biological oxygen demand (BOD) and chemical oxygen demand (COD), and total suspended solids (TSS) were effective (Table 3-2).

In another ICW based study, Mustafa *et al.* (2009) evaluated the long-term performance of ICW site 11 that has been operating for 7 years and likely annual and seasonal variations in nutrient removal. It was reported that nutrient including ammonia-nitrogen and molybdate reactive phosphorus were effectively removed after long-term operation, and that the removal of BOD, COD, TSS, total coliforms and *Escherichia coli* values has also been achieved. Some seasonal differences were noted over seven-year's monitoring whereby increases in outflow $NH_3$-N and MRP concentrations during autumn than summer due to reduced outflow and longer retention time in the period of summer.

Table 3-2 Site characteristics and nutrient treatment efficiencies of 12 integrated constructed wetlands in the Anne Valley (near Waterford, Ireland) treating farmyard runoff (Mustafa *et al.*, 2009; Scholz *et al.*, 2007).

| ICW site No. | Farmyard Area ($m^2$) | ICW Area ($m^2$) | Total Cell No. | ICW to Yard Area Ratio | $NH_3$-N TE (%) | MRP TE (%) |
|---|---|---|---|---|---|---|
| 1 | 4,500 | 3,906 | 9 | 0.9 | 99.8 | 99.7 |
| 2 | 14,750 | 22,966 | 4 | 1.6 | 99.7 | 98.2 |
| 3 | 5,400 | 10,288 | 6 | 1.9 | 97.9 | 81.4 |
| 4 | 9,200 | 10,327 | 6 | 1.1 | 97.7 | 92.9 |
| 5 | 4,000 | 3,940 | 4 | 1.0 | 99.3 | 98.3 |
| 6 | 9,800 | 12,691 | 6 | 1.3 | 99.3 | 98.8 |
| 8 | 2,300 | 3,940 | 5 | 2.0 | 99.0 | 97.2 |
| 9 | 4,800 | 7,964 | 5 | 1.7 | 98.5 | 96.2 |
| 10 | 2,100 | 4,375 | 5 | 2.1 | 99.2 | 99.6 |
| 11 | 5,000 | 7,676 | 4 | 1.5 | 99.1 | 92.0 |
| 12 | 13,600 | 10,748 | 7 | 0.8 | 99.2 | 99.0 |
| 13 | 5,000 | 5,610 | 6 | 1.1 | 99.0 | 93.3 |

No., number; TE, treatment efficiency; $NH_3$-N, ammonia-nitrogen; MRP, molybdate reactive phosphorus.

### 3.8.2 Domestic wastewater treatment

ICW systems have also been used to treat and control the quality of domestic wastewater in Ireland for the past decade. In a comparative study of domestic wastewater treatment between two ICW systems with different operational period it was found that both young and mature ICW systems successfully removed the contaminant parameters that commonly present in domestic wastewater (Table 3-3).

Concerning the young ICW system with only one year operation period, the nutrient removal efficiencies were significantly high (99.0% for $NH_3$-N; 99.2% for MRP). The mature ICW with approximately seven years' operation period, by contrast, has achieved relatively high effluent standards but generally lower contaminant removal efficiencies. Nevertheless, ICW is seen as a valuable and appropriate technology to treat domestic wastewater, in particular for small communities (Kayranli *et al.*, 2010).

Table 3-3 Comparison of contaminant treatment efficiencies of two studied integrated constructed wetland sites treating domestic wastewater (Kayranli *et al.*, 2010).

| Parameters | Glaslough ICW (February 2008 – March2009) | | Dunhill ICW site 7 (August 2001 – January 2006) | |
|---|---|---|---|---|
| | n | TE (%) | n | TE (%) |
| BOD | 45 | 99.4 | 23 | 95.2 |
| COD | 65 | 97.0 | 25 | 89.1 |
| TSS | 62 | 99.5 | 24 | 97.2 |
| $NH_3$-N | 67 | 99.0 | 24 | 58.2 |
| $NO_3$-N | 67 | 93.5 | 9 | -12.0 |
| MRP | 66 | 99.2 | 25 | 34.0 |

n, sample number; TE, treatment efficiency; BOD, biochemical oxygen demand; COD, chemical oxygen demand; TSS, total suspended solids; $NH_3$-N, ammonia-nitrogen; $NO_3$-N, nitrate-nitrogen; MRP, molybdate reactive phosphorus.

## 3.9 Summary

This chapter describes the concept of integrated constructed wetland. Special emphasis is given to ICW design considerations and potential infiltration of polluted water to groundwater. The ICW treatment efficiency in nutrients and other contaminants removal from farmyard runoff and domestic wastewater is further confounded by the interpretations of data presented in published journal articles.

# Chapter 4

# Materials and Methods

## *4.1 Introduction*

In general, this chapter describes the methodological aspects of data collection and analysis to achieve the research objectives. The first section describes the experimental design and approach used in this study. The second section provides detailed information on eight constructed wetland (CW) or integrated constructed wetland (ICW) sites that have been involved. Furthermore, the third section describes monitoring and analysis procedures for water quality and wetland hydrology. Finally, the statistical techniques employed for data analysis are also presented.

## *4.2 Experimental set-up*

As to simulate contaminant retention and/or release processes by saturated wetland sediments, five experimental mesocosms were set up at the Institute for Infrastructure and Environment, The University of Edinburgh, United Kingdom. Details of mesocosm design are illustrated in Figs. 4-1 and 4-2. The laboratory room temperature was maintained at 15 ℃. Artificial light was provided by programmable controlled UV lights (model: F36W/GRO) on a 12:12 h light/dark cycle. The mesocosms were constructed using polyvinyl chloride drainage pipes with identical dimensions (height: 83 cm; diameter: 10 cm). Seven plastic taps were evenly placed around the circumference of the pipe. The outlet vinyl tubings (1.2 cm internal diameter) were located at the centre of the bottom plate to collect leachate from each mesocosm.

Experiments were carried out in two periods. Substantial, unexpected release of contaminants from sediments into overlying water column has been found in tested mesocosms during the experimental period 1. In response, further study was performed to investigate the migration of contaminants by the rest of soil profiles (without sediments) in the second period. Alternations to experimental set-up were made correspondingly.

In the first period of experiment, mesocosms 1 and 2 were fed with lightly contaminated farmyard runoff between February 19, 2009 and February 25, 2011. The runoff samples, which collected from an outdoor drain at the Gorgie City Farm (Gorgie Road, Edinburgh), were diluted 2 times with tap water due to its high levels of ammonia and nitrogen. The three other mesocosms (mesocosms 3, 4 and 5) were fed with domestic wastewater between May 14, 2009 and February 25, 2011. The wastewater samples were taken from the inflow (after coarse screen) of the Seafield Wastewater Treatment Plant (Marine Esplanade, Seafield Road, Edinburgh). These mesocosms were consistently flooded with wastewater up to the top (at a depth of 10 cm). The hydraulic loading rate was approximately $9.14\times10^{-3}$ m $d^{-1}$.

Mesocosms 2, 3 and 4 were packed with four successive layers of aggregates (from bottom to top): 5 cm of small gravel (1.2-5.0 mm), 5 cm of sand (0.6-1.2 mm), 25 cm of sodium bentonite clay (permeability of $10^{-9}$ m $s^{-1}$) and 35 cm of core sediment (incorporating plants if applicable). The arrangement of soil liner, type, depth and permeability was according to the full-scale ICW systems. Core sediment samples were taken directly from the surface of ICW site 7 (cell 1) and site 11 (cell 1), respectively. Samples (Fig. 4-3) were packed into three main sections: litter, sediment and clay. Sediment can be further divided into top, middle and bottom layers. According to the study performed by Mustafa (2009), the levels of nitrogen and phosphorus in wetland sediments were found to be 21.9 ± 5.01 g/kg and 3.41 ± 0.85 g/kg respectively. Further details of these two ICW sites can be found in sections 4.3.1 and 4.3.2.

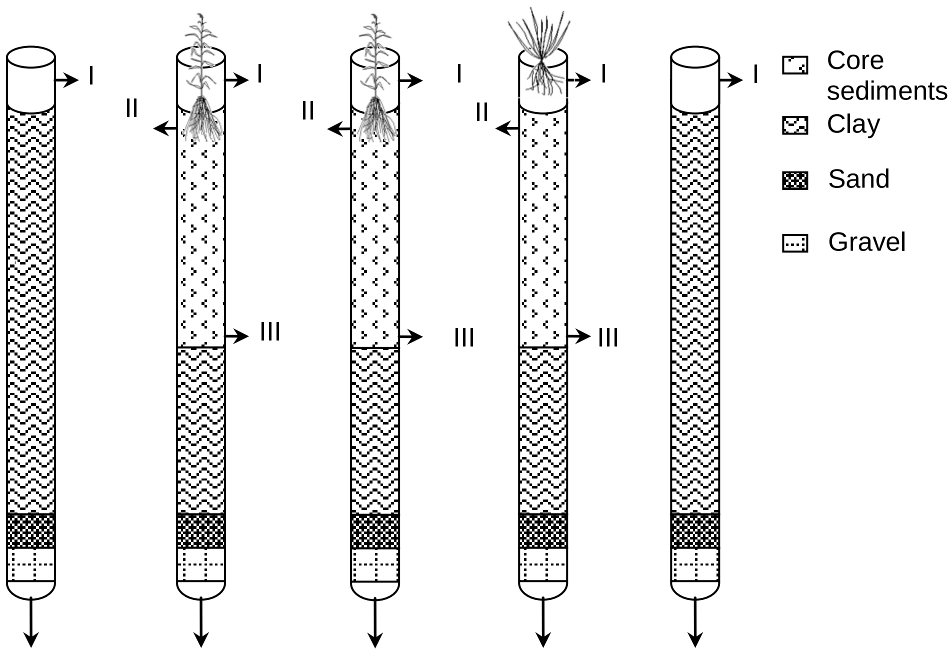



Figure 4-1 Schematic diagram of integrated constructed wetland mesocosms.

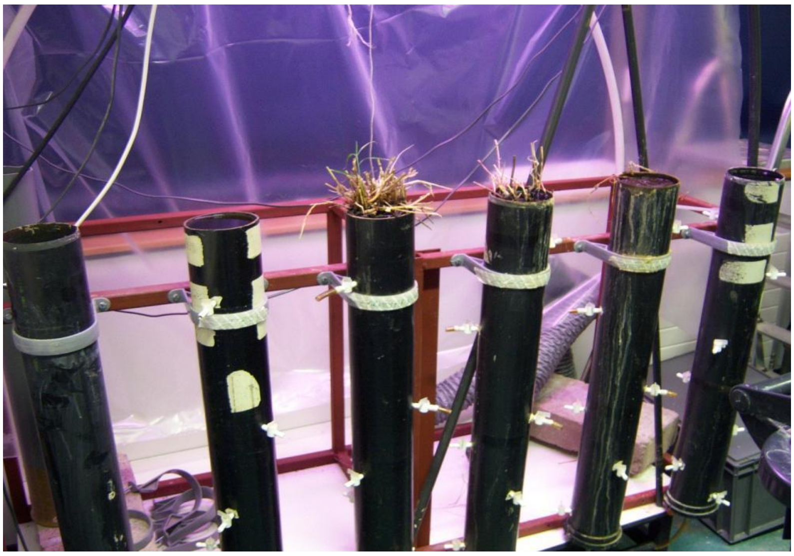


Figure 4-2 Photograph of integrated constructed wetland mesocosms.

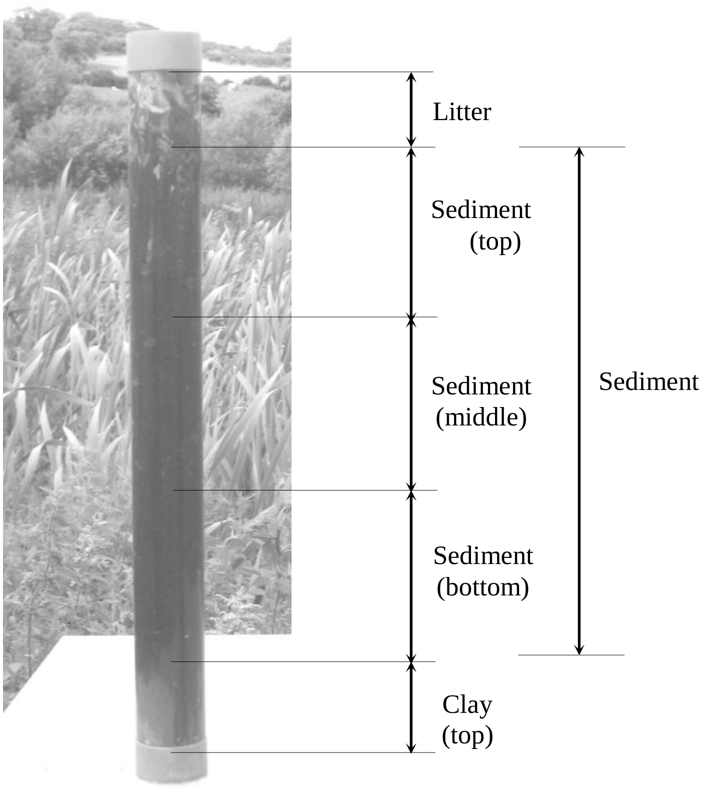



Figure 4-3 Core sediment sample collected from cell 1 of ICW 11.

(Photo from Dr Asif Mustafa)

Two control mesocosms (mesocosms 1 and 5) were set up as benchmarks to ensure the same flow conditions and saturation ratios. The soils and aggregates (from bottom to top) contained 5 cm of small gavel (1.2-5.0 mm), 5 cm of sand (0.6-1.2 mm), and 60 cm of sodium bentonite clay (permeability of $10^{-9}$ m $s^{-1}$).

Mesocosms 2 and 3 were planted with *Phragmites australis* (Cav) Trin. ex Steud; whereas mesocosm 4 was planted with *Agrostis stolonifera* L. rhizomes. The control mesocosms were left unplanted. The *Phragmites australis* were obtained from the outdoor wetland rig constructed for previous research studies at The King's Buildings, Edinburgh; *Agrostis stolonifera* were obtained from ICW site 7 in Waterford. The site description of ICW site 7 is present in the section 4.3.1.

After the completion of the first period of experiment, the core sediment samples and plants were taken out from mesocosms 2, 3 and 4. These mesocosms were subsequently replanted with *Phragmites australis* (mesocosms 2 and 3) and *Agrostis stolonifera* (mesocosm 4) to conduct comparative experiments. After planting the water level in individual mesocosm was raised by 2 cm per week until the target depth of 10 cm was reached. The same operational conditions were applied. The second period of experiment was carried out between May 13, 2011 and May 28, 2012.

## *4.3 Site description*

### 4.3.1 Integrated constructed wetland site 7

The ICW site 7 in Dunhill (County Waterford, south-eastern part of Ireland) is situated at a longitude of 07°02’40” W and a latitude of 52°11’28” N (Fig. 4-4). The system covers a total area of 0.3 ha and has been used to treat local sewage since February 2001. Domestic wastewater from nearby households is collected via the sewage system and then piped to the single influent entry point located at the first cell. From there, the wastewater flows through four wetland cells sequentially before entering the Annestown stream. The average wastewater inflow and outflow is approximately 40 $m^3$ $d^{-1}$ and 24 $m^3$ $d^{-1}$, respectively. Assume that the depth of water in wetland cells is approximately 0.4 m, the hydraulic loading rate (HLR) and hydraulic retention time (HRT) are 1.1 cm $d^{-1}$ and 36.4 days. According to the soil classification by Irish Forest Services (IFS), the local soils of ICW site 7 are mainly mineral alluvium. The subsoils are a combination of undifferentiated alluvium and acid volcanic till. The primary vegetation types used in the system are emergent plant species (helophytes).

Figure 4-4 The integrated constructed wetland site 7 in Dunhill (Photo from Dr Rory Harrington).

### 4.3.2 Integrated constructed wetland site 11

The ICW site 11 is located at a longitude 10°51’50” W and a latitude of 51°13’06” N. It was commissioned in February 2001 to treat farmyard and roof runoff. The system has a total area of 0.76 ha. The influent which comes from a dairy farm of 0.5 ha with 77 cows is conveyed by gravity to the system. Fig. 4-5 presents the ICW system’s layout. Of four consecutive unlined ICW cells, the first three cells are densely vegetated while the last cell had only sparse vegetation (Mustafa *et al.*, 2009). According to the soil classification by Irish Forest Services (IFS), the ICW 11 site has soils derived from a mainly mineral alluvium. The subsoil has a texture of alluvium undifferentiated soils (Mustafa, 2009). Due to lack of hydraulic data, the HLR and HRT of ICW site 11 can not be calculated. Details of the wetland vegetation species within each wetland cell are summarized in Table 4-1.

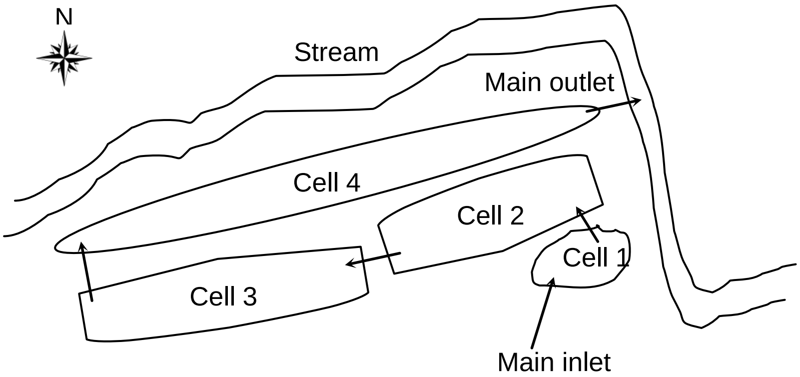



Figure 4-5 Schematic of the integrated constructed wetland site 11.

Table 4-1 The details of wetland cells and vegetation species for the integrated constructed wetland site 11 (Mustafa *et al.*, 2009).

| Wetland cell | Area ($m^2$) | Vegetation density (%) | Number of vegetation species | Vegetation cover by species |
|---|---|---|---|---|
| 1 | 1,208 | 100 | 2 | *Typha latifolia* (80%) and *Carex riparia* (20%) |
| 2 | 1,906 | 100 | 3 | *Glyceria maxima* (50%), *Carex riparia* (35%) and *Typha latifolia* (15%) |
| 3 | 2,126 | 100 | 5 | *Glyceria maxima* (40%), *Philarius arundiraecae* (25%), *Carex riparia* (20%), *Juncus effusus* (10%) and *Typha latifolia* (5%) |
| 4 | 2,435 | 1 | 1 | Open water (99%) and *Juncus effusus* (0.8%) and others (0.2%) |

### 4.3.3 Glaslough integrated constructed wetland site

Glaslough ICW system is located within the Castle Leslie Estate walls in the County Monaghan, Ireland at a longitude of 06°53’37.94” W and a latitude of 54°19’6.01” N. The system was commissioned in October 2007 to treat combined sewage from the village of Glaslough and to improve the water quality of the Mountain Water River, which flows through the site. The design capacity of the system is 1,750 population equivalents and covers a total area of 6.74 ha in total. The surface area of the constructed cells is 3.25 ha.

Figure 4-6 An aerial photograph of the Glaslough integrated constructed wetland system (Photo from Mawuli Dzakpasu).

The untreated influent wastewater is pumped directly into one of the receiving sludge ponds. The wastewater subsequently flows by gravity through five sequential unlined cells, and the effluent of the last pond discharges to the adjacent Mountain Water River. The wetland cells were densely vegetated with *Carex riparia* Curtis, *Phragmites australis* (Cav.) Trin. ex Steud., *Typha latifolia* L., *Iris pseudacorus* L., *Glyceria maxima* (Hartm.) Holmb., *Glyceria fluitans* (L.) R. Br., *Juncus effusus* L., *Sparganium erectum* L. ememd Rchb, *Elisma natans* (L.) Raf., and *Scirpus pendulus* Muhl (Fig. 4-6).

### 4.3.4 Wildfowl & Wetland Trust constructed wetland sites

The Wildfowl & Wetlands Trust (WWT) is a UK conservation organisation saving wetlands for wildlife and people. Sixteen wetland treatment systems have been constructed at nine wetland centres across the UK, and are currently used to treat water coming into or leaving the reserves and wastewater generated from these centres (WWT, 2008).

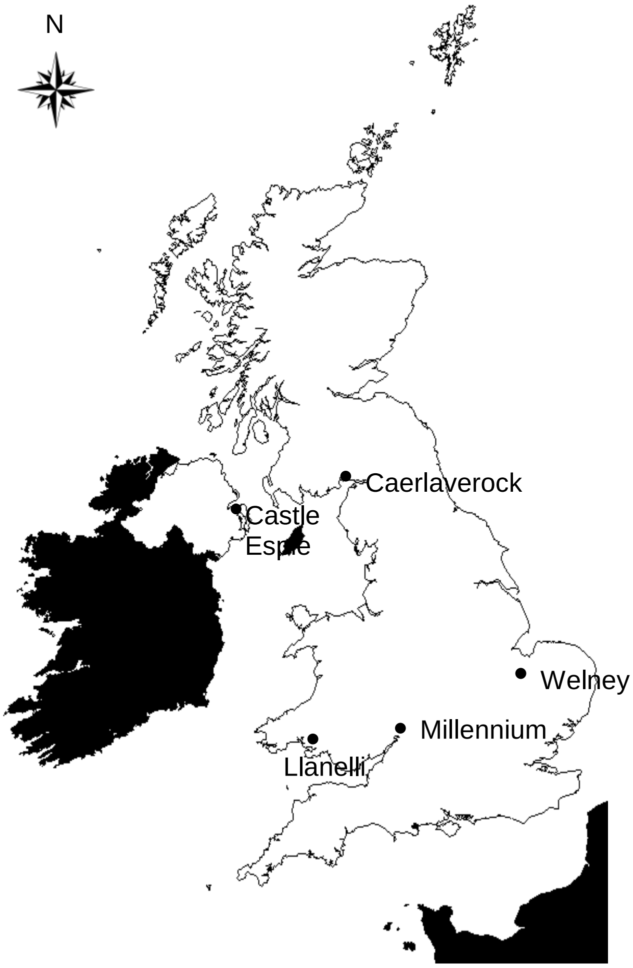



Figure 4-7 The Wildfowl & Wetlands Trust constructed wetland site locations.

Table 4-2 Summary information for Wildflow & Wetlands Trust representative constructed wetlands.

| Site | Influent | Plant Species | System Description |
|---|---|---|---|
| Caerlaverock | Raw sewage | *Phragmites australis* | Stage 1: Septic tank<br>Stage 2: HF-CW cell (125 $m^2$)<br>Stage 3: FWS-CW cell (125 $m^2$) |
| Castle Espie | Raw sewage | *Phragmites australis* | Stage 1: Septic tank<br>Stage 2: Two parallel wetland cells<br>- HF-CW cell (150 $m^2$)<br>- FWS-CW cell (150 $m^2$) |
| Llanelli | Tertiary treated sewage | *Phragmites australis* and *Iris pseudacorus* | Stage 1: Settling pond (3,000 $m^2$)<br>Stage 2: Two parallel FWS-CW cells (2,800 $m^2$ each)<br>Stage 3: Two parallel FWS-CW cells (5,625 $m^2$ each) |
| Millennium | Raw sewage | *Phragmites australis*, *Iris pseudacorus*, *Carex riparia* and others | Stage 1: Settlement tank<br>Stage 2: VF-CW cell (400 $m^2$)<br>Stage 3: Settlement pond<br>Stage 4: HF-CW cell (50 $m^2$)<br>Stage 5: Two parallel FWS-CW cells (75 $m^2$ each)<br>Stage 6: VF-CW phosphate removal cell (100 $m^2$) |
| Welney | Raw sewage | *Phragmites australis*, *Typha latifolia*, *Sparganium etectum*, *Epilobium hirsutum*, *Glyceria maxima*, *Alisma plantago-aquatica*, *Lemna minor* and others | Stage 1: Septic tank<br>Stage 2: Four HF-CW cells (105 $m^2$ each)<br>Stage 3: FSW-CW ditch (100 $m^2$)<br>Stage 4: Tertiary FSW-CW cell (100 $m^2$) |

HF, horizontal subsurface flow; FWS, free water surface flow; VF, vertical flow; CW, constructed wetland.

The locations of five representative CW systems are shown in Fig. 4-7. Each wetland system has a unique design configuration and operation period. In addition, hydraulic loading rates and retention times vary considerably. A wide range of vegetation species were planted in wetland cells and channels. More detailed information is provided in Table 4-2. The following paragraphs will briefly describe the configurations of five wetland systems investigated in this study.

#### 4.3.4.1 Caerlaverock

The Caerlaverock CW system is situated in the north Solway Coast, Dumfriesshire, Scotland, and consists of two consecutive wetland cells as shown in Fig. 4-8. Following a septic tank for settling and pre-treatment, the sewage is piped to the first inspection chamber and subsequently to a gravel-filled horizontal subsurface flow (HF) wetland planted with *Phragmites australis*. After that, the water flows into an intermediate inspection chamber and from there into a free water surface flow (FWS) CW cell (Fig. 4-9). The treated water then flows through a third chamber and is finally piped into a wildlife pond. Wastewater can also be piped directly to the intermediate inspection chamber between the primary and secondary beds. From the intermediate inspection chamber, effluent can be piped directly to the wildlife pond. Thus either or both wetland cells can be bypassed.

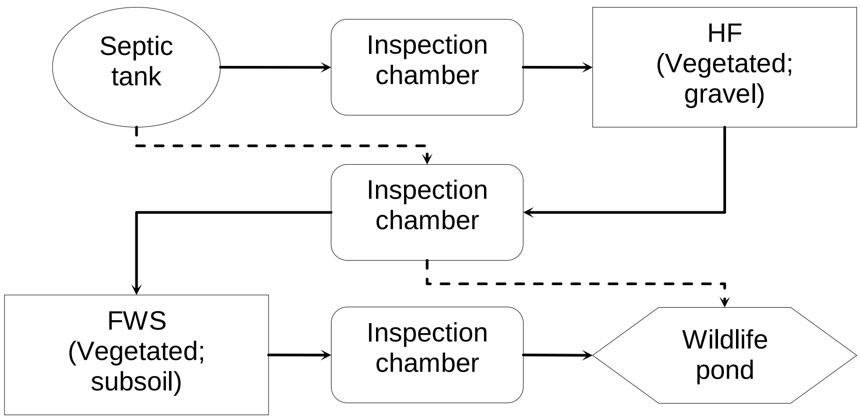



Figure 4-8 Schematic of the Caerlaverock constructed wetland system.

Figure 4-9 The free surface flow wetland cell in the Caerlaverock constructed wetland system (Photo from Dr Sally Mackenzie).

#### 4.3.4.2 Castle Espie

Castle Espie CW system, which comprised of two parallel cells, is situated in the County Down, Northern Ireland. Before entering the wetlands, sewage from various locations around the county centre is collected in a septic tank. The wastewater then passes through a splitter chamber and distributes the sewage into two CW systems (Fig. 4-10). Of two planted (*Phragmites australis*) cells, one is a HF-CW with a gravel substrate (Fig. 4-11) and the other is a FWS-CW that has a soil filled substrate. The treated sewage is discharged into a brook and eventually enters Strangford Lough.

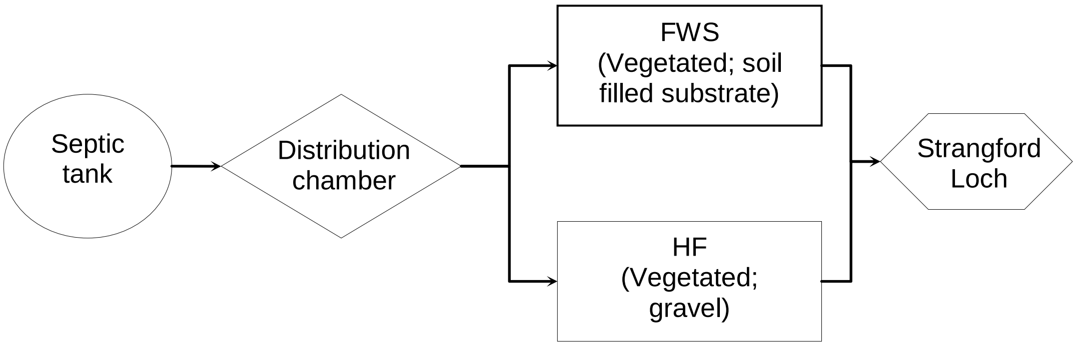



Figure 4-10 Schematic of the Castle Espie constructed wetland system.

Figure 4-11 The horizontal subsurface flow wetland cell in the Castle Espie constructed wetland system (Photo from Dr Sally Mackenzie).

### 4.3.4.3 Llanelli

Llanelli treatment wetland is located on the Burry Inlet (Fig. 4-12). Tertiary treated sewage enters the settling pond (Fig. 4-13) first and is then distributed into two parallel primary FWS-CW cells (Fig. 4-14). After the primary stage of treatment, the effluent then flows into another two parallel secondary FWS-CW cells (Fig. 4-15) for further polish. All four cells have sub-soil substrate. Treated wastewater is collected at the end of the secondary cells and discharged into a balancing pond, from where the water is distributed to the rest of the reserve and finally discharged into the Burry Inlet Ramsar site and SPA. Vegetation cover at the primary and secondary treatment CW cells mainly consists of *Iris pseudacorus* L. (Yellow Iris or Yellow Flag) and *Phragmites australis*, respectively.

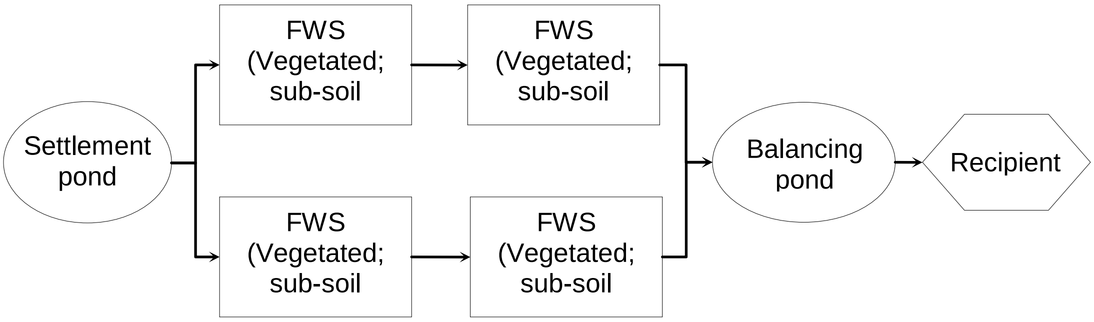



Figure 4-12 Schematic of the Llanelli constructed wetland system.

Figure 4-13 Settlement pond in the Llanelli constructed wetland system (Photo from Dr Sally Mackenzie).

Figure 4-14 The left hand primary free surface flow wetland cell in the Llanelli constructed wetland system (Photo from Dr Sally Mackenzie).

Figure 4-15 The right hand secondary free surface flow wetland cell in the Llanelli constructed wetland system (Photo from Dr Sally Mackenzie).

#### 4.3.4.4 Millennium

The Millennium system was constructed at Slimbridge (England) in 1999 (Fig. 4-16). Treated sewage from the primary settlement tank is fed intermittently into a single gravel-filled vertical flow (VF) wetland cell planted with *Phragmites australis* (Fig. 4-17). The effluent is further treated in a settlement pond, and then it is introduced into a HF-CW cell which is filled with gravel and planted with *Iris pseudacorus* and *Carex riparia* Curtis. From here, the water subsequently flows into two parallel FWS-CW cells. After that, the wastewater enters a vertical flow phosphate stripping CW cell, and ultimately flows into a wildlife lake.

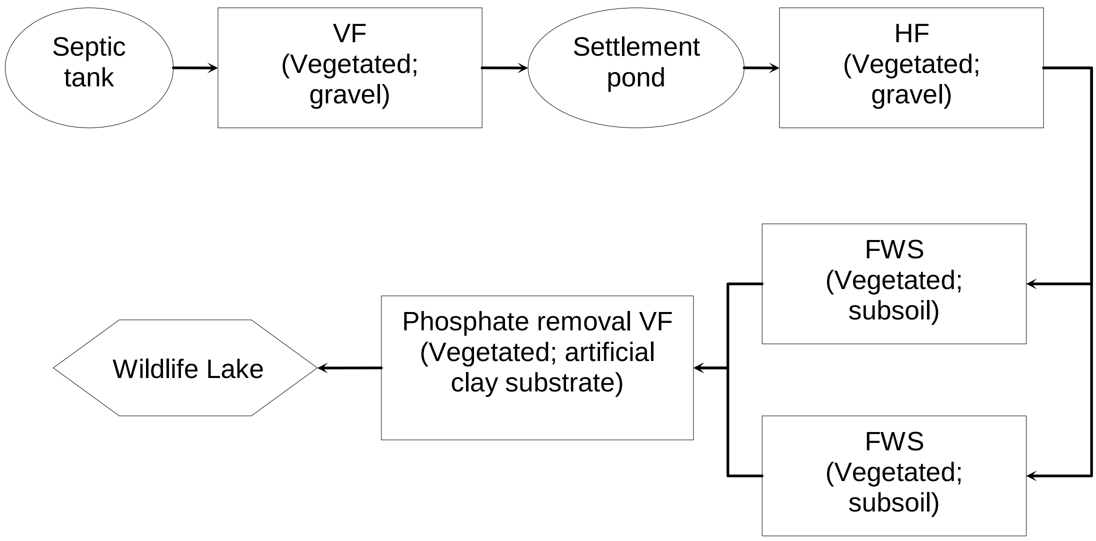



Figure 4-16 Schematic of the Millennium constructed wetland system.

Figure 4-17 The first vertical flow wetland cell in the Millennium constructed wetland system (Photo from Dr Sally Mackenzie).

#### 4.3.4.5 Welney

Welney wetland is located 26 miles north of Cambridge, England (Fig. 4-18). Sewage from visitor centre passes through a septic tank, followed by four parallel HF-CW cells planted with *Phragmites australis* (Fig. 4-19) before discharging into an overland flow ditch (Fig. 4-20). Four cells are all filed with flint and gravel. From the ditch, effluent continuously enters a tertiary gravel-filled FWS-CW (Fig. 4-21). After this, treated sewage is finally discharged into another ditch, which is monitored by the Environment Agency on a quarterly basis.

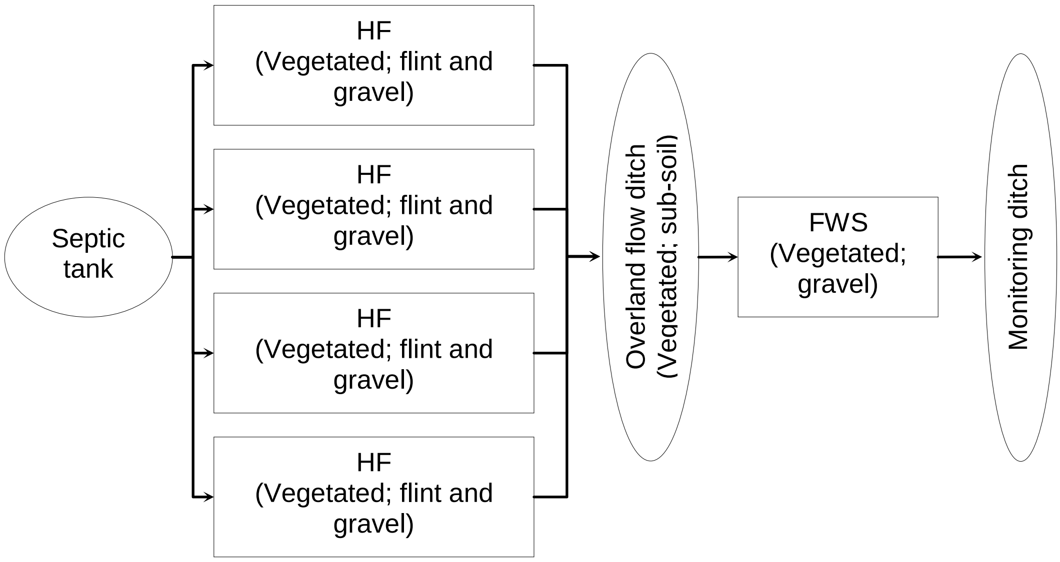



Figure 4-18 Schematic of the Welney constructed wetland system.

Figure 4-19 The horizontal subsurface wetland cell in the Welney constructed wetland system (Photo from Dr Sally Mackenzie).

Figure 4-20 The overland flow ditch in the Welney constructed wetland system (Photo from Dr Sally Mackenzie).

Figure 4-21 Tertiary free surface flow wetland cell in the Welney constructed wetland system (Photo from Dr Sally Mackenzie).

## 4.4 Water quality monitoring and analysis

### 4.4.1 Mesocosms water quality monitoring and analysis

In the first period of experiment, water samples (up to 75 ml each) were collected weekly from top to bottom taps (tap I to tap III) for mesocosms 2, 3 and 4. Virtually no water infiltrated into deeper layers due to the presence of bentonite clay and biomass. Therefore, water could not be collected from the remaining sampling points (below tap III). The first eight weeks for mesocosms 1 and 2 and the first four weeks for mesocosms 3 to 5 were seen as the start-up periods, which characterized by typical system instability; therefore, the data have not been included in this thesis.

In the second period, water samples were taken from the overlying water column and the surface of substrates for mesocosms 2, 3 and 4 each week. Similar to period 1, due to the start-up phenomena, the data used for further analysis is between July 8, 2011 and May 28, 2012.

Collected samples were analysed for pH, electrical conductivity (EC), total dissolved solids (TDS) and temperature (T) by using the EC/TDS/pH/Temperature Meter (model: HI99300; HANNA Instruments, Bedfordshire, UK). The redox potential (RP) value was measured using the ORP measurement device (model: HI98201; HANNA Instruments, Bedfordshire, UK). Dissolved oxygen (DO) was determined by the handheld Oxygen Meter (model: Oxi 315i; WTW Laboratory Products, Weilheim, Germany). Samples of 50 ml were filtered by using glass fibre filter paper (model: FB59441; Fisherbrand Microbiology Products, Leicestershire, UK) to determine total suspended solids (TSS). The chemical oxygen demand (COD) was determined by the Palintest COD standard measuring method (model: PL 450;

Palintest Limited, Tyne & Wear, UK) and Hach Lange cuvette tests (model: LCK614 COD cuvette test 50-300 mg $l^{-1}$; Hach LANGE, UK). Above analysis were conducted at University of Edinburgh (AGB building), and all instruments were calibrated before testing. Meanwhile, frozen samples were shipped by overnight courier on dry ice (around -20 ℃) to Waterford County Council water laboratory where concentrations of ammonia-nitrogen ($NH_3$-N), nitrate-nitrogen ($NO_3$-N), nitrite-nitrogen ($NO_2$-N), molybdate reactive phosphorus (MRP) and chloride (Cl) were analyzed using APHA (2005) unless mentioned otherwise.

### 4.4.2 Integrated constructed wetlands water quality monitoring and analysis

A suite of automated sampling and monitoring instrumentation, such as the ISCO 4700 Refrigerated Automatic Wastewater Sampler (Teledyne Isco, Inc., NE, USA), was used for weekly wetland surface water sampling. Furthermore, the water quality of Mountain Water River and Glaslough Stream are also monitored.

The collected water samples were analysed weekly for several parameters including COD, $NH_3$-N, $NO_3$-N, and MRP at the Monaghan County Council wastewater laboratory, by following Standard Methods for the Examination of Water and Wastewater (APHA, 2005), using kits supplied by HACH Lange (HACH Company, Loveland, CO, USA). The reactor digestion method, followed by colorimetric analysis (Method 8000), was used to measure COD, whereas $NH_3$-N and $NO_3$-N were determined by the Nessler method (Method 8038) and the cadmium reduction method (Method 8171), respectively. MRP was determined by the ascorbic acid method (Method 8048). All analysis was done by using the HACH DR/2010 portable datalogging spectrophotometer (HACH Company, Loveland, CO, USA).

### 4.4.3 Wildfowl & Wetland Trust constructed wetlands water quality monitoring and analysis

The WWT initiated a chemical water quality monitoring programme in 2005 to evaluate the treatment performance of CWs and to optimise their functioning. Water samples were taken from the inflow and outflow of representative wetland systems. Collected samples were analyzed for a range of water quality parameters including $NH_3$-N, $NO_3$-N, $NO_2$-N, and ortho-phosphate-phosphorus ($PO_4$-P) by using the Chemet system (CHEMetrics, Inc., Midland, VA, USA). EC and pH values were also measured. Total phosphorus (TP), TSS, and biochemical oxygen demand (BOD) were examined by the Phosyn Laboratories based in York, England. The frequency of sampling was once per month between 2005 and 2008. However, samples were only taken every second month due to financial constraints from 2009 onwards. Except for Castle Espie, samples were sent to the Phosyn laboratories for accuracy check once per season.

## *4.5 Wetland hydrological monitoring*

In general, most studied CW or ICW systems in this research are not fully engineered treatment wetlands and the inflow and outflow rates are probably unknown (Mustafa *et al.,* 2009), however, extensive instrumentation has been installed at Glaslough

ICW site to monitor wetland hydrology. In the Glaslough ICW system, all water-flows into and out of each cell were measured and recorded with the Siemens Electromagnetic Flow Meters FM MAGFLO and MAG5000 (Siemens Flow Instruments A/S, Nordborgrej, Nordborg, Demark) and their allied computer-linked data loggers. Mean flows were recorded at 1-min interval frequency. A weather station is located beside the inlet pump sump to measure local temperature, precipitation and evapotranspiration. Precipitation and evapotranspiration were measured as the amount of water falling on, or evaporating from, the wetland cell surface, respectively.

## *4.6 Statistical analysis*

### 4.6.1 Multiple regression analysis

Multiple regression is the instrument used to develop an optimal equation for predicting the value of a dependent or criterion variable from several independent or predictor variables. The model includes a set of regression coefficients $b_i$, indicating the degree to which each independent variable contributed to the prediction. The general multiple regression equation for $k$ independent variables is shown in Eq. 4-1 (Tabachnick and Fidell, 2001):

$$Y = a + b_1 X_1 + b_2 X_2 + \cdots + b_k X_k \qquad [4\text{-}1]$$

*R-Square* ($R^2$), also known as the coefficient of determination, is a commonly used statistic to examine model fit. In essence, this is a measure of how good a prediction of dependent variable that we can make by knowing the independent variables. $R^2$ is 1 minus the ratio of residual variability. When the variability of the residual values around the regression line relative to the overall variability is small, the predictions from the regression equation are good. In most cases, $R^2$ will fall somewhere between 0.0 and 1.0. The $R^2$ value is an indicator of how well the model fits the data (i.e., an $R^2$ close to 1.0 indicates that we have accounted for almost all of the variability with the variables specified in the model) (Wilkinson, 1979).

Multiple regression analysis is normally implemented using forward or backward stepwise regression to determine which variables should be included in the final subset to explain the maximum amount of variance. The model first identifies a single best predictor and continues to add variables, one at a time, until the increment in explained variance is no longer significant at the 0.05 level (Keppel and Zedeck, 1989).

The multiple regression models have been successfully used for comprehensive assessment of wetland systems. Babatunde *et al.* (2011) applied multiple regression models to predict the final effluent concentration of contaminants (i.e. $BOD_5$, COD, $NH_3$-N, and TP). The authors found that the predicted results were acceptable; however, some errors also existed. In addition, Gikas *et al.* (2011) reported on the great appropriateness for the prediction of CW performance by multiple regression models. Tunçsiper *et al.* (2006) indicated that multiple regression models were found to provide better predictions of effluent concentration than first-order plug flow models. However, they further concluded that the performance of

CWs could hardly be accurately predicted by using simple models because the transformation of contaminants in CWs was complicated and many other factors may directly or indirectly affect the process.

### 4.6.2 Principal component analysis

Principal component analysis (PCA) is a mathematical dimension-reduction procedure that attempts to explain the maximum amount of variables in a data matrix in terms of a small number of dimensions, or components. The trends and similarities existing in multivariate data obtained from this statistical technique can be illustrated in a bi-plot display which shows both the loadings and the scores for two selected components in parallel (Davis, 1986).

From the mathematical perspective, a PCA is concerned with explaining the variance covariance structure of a high dimensional random vector through a few linear combinations of the original component variables. Consider a $p$ dimensional random vector $X = (X_1, X_2, ..., X_p)$, $k$ principal components ($k < p$) of $X$ are random variables $Y_1, Y_2, ..., Y_k$ which are defined by the following formulae:

$$
\begin{aligned}
Y_1 &= l_1^{'}X = l_{11}X_1 + l_{12}X_2 + \ldots + l_{1p}X_p \\
Y_2 &= l_2^{'}X = l_{21}X_1 + l_{22}X_2 + \ldots + l_{2p}X_p \\
&\vdots \\
Y_k &= l_k^{'}X = l_{k1}X_1 + l_{k2}X_2 + \ldots + l_{kp}X_p
\end{aligned}
\qquad [4\text{-}2]
$$

Where the coefficient vectors $l_1, l_2, \ldots l_k$ are chosen according to following conditions: first principal component = linear combination that maximizes variation of ($l_1'X$) and $\|l_1\|$=1; second principal component = linear combination that maximizes variation of ($l_2'X$), $\|l_2\|$=1, and covariation of ($l_1'X$, $l_2'X$)=0; … $j$th principal component = linear combination that maximizes Var($l_j'X$) and $\|l_j\|$ =1, and covariation of ($l_k'X$ , $l_j'X$) =0 for all $k< j$.

This computing procedure indicates that the principal components are those linear combinations of the original variables which maximize the variance of the linear combination and which have zero covariance (and hence zero correlation) with the previous principal components. It can be proved that exactly *p* linear combinations existed. However, only the first few of them (typically first two or three principal components) explain most of the variance in the original data (Jolliffe, 2002; Timm, 2002).

PCA has increasingly been used to study the treatment performance of CWs. Scholz *et al.* (2007) employed PCA to detect the relationships between the water quality variables for the inflow and outflow from full-scale ICW systems. PCA was also applied to verify the link between the microbiological activities and contaminant removal efficiencies of five vertical flow CWs by Chazarenc *et al.* (2010).

### 4.6.3 Redundancy analysis

The redundancy index, which was introduced by Stewart and Love (1968), measures the proportion of total variance of the variables in one set accounted for by regression on those of the other. Based upon the index, redundancy analysis (RDA) was developed by van den Wollenberg (1977) as an extension of multiple linear regression and principal component analysis to include external explanatory variables.

RDA is a straightforward analysis tool and provides a low dimensional representation of the linear relationships between dependent and independent variables. As for the explanatory variables, they can be qualitative or quantitative. Graphically, the results of RDA are presented in the form of biplots. Typically, the canonical axes ($X$ and $Y$) of RDA biplots represent linear combinations of the explanatory variables. The length and position of an explanatory variable's arrow illustrate its significance on the canonical axes. The longer the arrow, the more important is the trait. The relationship between an explanatory variable and the axis is estimated by dropping a perpendicular between the tip of the arrow and the canonical axes. Large numerical value of an explanatory variable will be found on the right of the $X$-axis or on the top of the $Y$-axis. The dependent variables are then understood as a function of the main canonical axes. The projection at right angle of a dependent variable arrow onto the canonical axis approximates the value of that dependent variable on the axis (Legendre and Legendre, 2012).

RDA has been applied recently to CW research. For instance, Maltais-Landry *et al.* (2009) used RDA to test the effects of artificial aeration, species of macrophytes and temperature on global treatment efficiency of CWs. Zhang *et al.* (2010) also used RDA to identify the relationship between microbial communities and wetland plants.

### 4.6.4 Self-organizing map

The self-organizing map (SOM) is an artificial neural network algorithm that has been widely used for engineering problems and data mining. The SOM is a unique tool that can run unsupervised to reduce the amount of data by clustering, and to project the nonlinear data onto a lower-dimensional regular lattice of neurons at the same time (Kohonen *et al.*, 1996). The SOM can be visualized through U-matrix and the component planes. The U-matrix visualizes distances between neighbouring map units, and thus shows the cluster structure of the map: high values of the U-matrix indicate a cluster border, uniform area of low values indicate cluster themselves. Each component plane indicates the values of one variable in each map unit (Vesanto *et al.*, 1999).

The self-organizing maps generally can be formed by three steps including completion, cooperation and synaptic adaptation (Gounane *et al.*, 2011). If there are $N$ input units, the input patter can be written as $X$={$x_1$, $x_2$, ... $x_n$} and the connection weights between the input units $i$ and the neurons $j$ in the computation layer can be written as $W_j$={$w_{j1}$, $w_{j2}$,...$w_{jn}$}. The Euclidean distance ($d_i$) between the input vector $x$ and the weight vector $w$ for each neuron $j$ can be computed as:

$$d_i = \sqrt{\sum_{j=1}^{n}\left(x_i - w_{ji}\right)^2}\;; \qquad i = 1,2,...,N \qquad [4\text{-}3]$$

The neuron whose weight vector comes closest to the input vector (i.e. is most similar to it) is declared the winner – best match unit (BMU). In this way the continuous input space can be mapped to the discrete output space of neurons by a simple process of competition between the neurons.

When the winner neuron *c* is determined, the closed neighbour neurons tend to get excited. There is a topological neighbourhood that decays with distance. An exponential decay function is therefore used to determine the size of the neighbourhood. This function is normally chosen to be Gaussian centred in the winner unit *c*, such as

$$h_{ji}(t) = \exp\left\{-\|r_c - r_i\|^2 \Big/ \left[2\sigma^2(t)\right]\right\} \qquad [4\text{-}4]$$

Where *t*, time; $h_{ji}(t)$, topological neighbourhood function centred in the winner unit *c* at time *t*; $r_c$ and $r_i$, positions of nodes *j* and *i* on the SOM grid; $\sigma(t)$, neighbourhood radius.

A special feature of the SOM is that the size $\sigma$ of the neighbourhood needs to decrease with time. A popular time dependence is an exponential decay:

$$\sigma(t) = \sigma \exp(-t/\tau_\sigma) \qquad [4\text{-}5]$$

Where $\tau_\sigma$ is the time constant of the algorithm.

The weight vectors of the winning node and those of its adjacent neurons are then adjusted to match the input data using the following equation, thus brining the weight vectors further into agreement with the input vector (Vesanto *et al.*, 1999). At each step *t* of the random sequence of the given $x(t)$ values, the values of $w_i$ are gradually and adaptively changed in the self-organizing process.

$$w_i(t+1) = w_i(t) + \alpha(t)h_{ji}(t)[x(t) - w_i(t)] \qquad [4\text{-}6]$$

Where *t*, time; $\alpha(t)$, learning rate at *t*; and all the other variables are as defined above.

The quality of the trained SOM is measured by total average quantization error and total topographic error. The quantization error is

$$q_e = \frac{1}{N}\sum_{i=1}^{N}\|x_i - w_c\| \qquad [4\text{-}7]$$

Where $q_e$, quantization error; $x_i$, *i*th data sample or vector; $w_c$, prototype vector of the best matching unit of $x_i$. The topographic error is

$$t_e = \frac{1}{N}\sum_{i=1}^{N}u_i(x_i) \qquad [4\text{-}8]$$

Where $u_i$, binary integer such that it is equal to 1 if the first and second best matching units for $x_i$ are not adjacent units; otherwise it is zero (Rustum and Adeloye, 2007).

SOM application to CW study is rare and is normally related to assessing the water quality of ICW system effluent and identifying the corresponding correlations and similarities between variables (Scholz *et al.*, 2007). On the other hand, the SOM model has been successfully used as an effective prediction tool for CWs monitoring and management. Lee and Scholz (2006) employed SOM to elucidate heavy metal removal mechanisms and to predict effluent heavy metal concentrations for experimental constructed wetlands treating urban runoff. SOM was also applied to predict the nitrogen and phosphorus removal efficiencies within ICW systems by using water quality variables which can be measured time-efficiently and cost-effectively (Zhang *et al.*, 2008).

### 4.6.5 Statistical packages

In this study, forward stepwise regression analysis was carried out with Minitab 12. Principal component analysis was conducted by Matlab 9.0. Redundancy analyses were employed by the programme Canoco for Windows 4.5 (Ter Braak, 2003), and the corresponding graphics were created with CanoDraw for Windows 4.1 (Šmilauer, 2003). The SOM toolbox (version 2) for Matlab 5.0 developed by the Laboratory of Information and Computer Science at the Helsinki University of Technology was applied for data analysis and predication of wastewater treatment performance. The toolbox can be downloaded for free from http://www.cis.hut.fi/projects/somtoolbox/ (Vesanto *et al.*, 1999).

## *4.7 Summary*

This chapter describes the set-up of experimental ICW mesocosms and their operational conditions. The detailed information of eight full-scale ICW or CW systems has also been present. In addition, this chapter covers specific methods for water quality and wetland hydrology monitoring and analysis. Last but not the least, the tools used for statistical analysis and treatment performance prediction have been described.

It should be mentioned that many people has contributed to different methods and tasks involved in this study as shown in Table 4-3.

Table 4-3 Methods and tasks related to this study and the contribution of various people.

| Project facet | Tasks | Contributors | | | | |
|---|---|---|---|---|---|---|
| | | A | B | C | D | E |
| Integrated constructed wetland mesocosm experiment | Experimental setup (1st period) | | √ | √ | | |
| | Experimental setup (2nd period) | √ | | | | |
| | Sampling | √ | √ | | | |
| | Water quality analysis | √ | √ | √ | | |
| | Data treatment | √ | √ | | | |
| | Data analysis | √ | √ | | | |
| | Application of statistical tools | √ | | | | |
| Glaslough ICW hydrological and contaminant removal performance assessment | Hydrological data collection | √ | | | √ | |
| | Hydrological data analysis | √ | | | √ | |
| | Sampling | | | | √ | |
| | Water quality analysis | | | √ | √ | |
| | Data treatment | √ | | | √ | |
| | Data analysis | √ | | | √ | |
| Wildfowl & Wetland Trust constructed wetlands performance evaluation | Sampling and water quality analysis | | | | | √ |
| | Data treatment | √ | | | | |
| | Data analysis | √ | | | | |

A, Yu Dong; B, Birol Kayranli; C, Waterford County Council staff; D, Mawuli Dzakpasu; E, Wildfowl & Wetland Trust staff.

# Chapter 5

# Nutrient and Other Contaminants Release from Mature Integrated Constructed Wetland Sediments

## *5.1 Introduction*

This chapter investigates the release of nutrient and other contaminants from mature integrated constructed wetland (ICW) sediments based on mesocosm studies. The results obtained from two experimental periods are presented and performances of ICW mesocosms are compared with corresponding full-scale systems. Furthermore, the experimental results were analyzed by using four statistical models (multiple regression models, principal component analysis, redundancy analysis, and the self-organizing map model) to find out the impacts of physico-chemical parameters on treatment efficiencies of selected contaminants. Parts of the chapter have been published as articles in Journal of Environmental Engineering and Water and Environment Journal.

## 5.2 Influent characteristics

As can be seen from Table 5-1, the influent wastewater quality varied considerably during the course of two experimental periods. These variations were consistent with other studies that have indicated the characterisation of farmyard runoff and domestic wastewater to be a particularly difficult exercise (Edwards *et al.*, 2008; Jefferson *et al.*, 2001). The variations in domestic wastewater were found to be the most prominent in terms of the $NH_3$-N and Cl whose concentrations varied from 9.5±4.0 to 3.4±3.1 mg $l^{-1}$ and from 106.3±43.3 to 47.4±24.6 mg $l^{-1}$ for period 1 and 2 respectively.

Table 5-1 Variability in influent farmyard runoff and domestic wastewater quality.

| Parameter | Farmyard runoff | | Domestic wastewater | |
|---|---|---|---|---|
| | Period I | Period II | Period I | Period II |
| | Mean ± SD (n) | Mean ± SD (n) | Mean ± SD (n) | Mean ± SD (n) |
| COD | 89.4 ± 29.3 (77) | 90.4 ± 43.5 (44) | 68.4 ± 41.4 (75) | 54.7 ± 17.3 (44) |
| $NH_3$-N | 1.3 ± 1.3 (71) | 0.8 ± 0.7 (44) | 9.5 ± 4.0 (65) | 3.4 ± 3.1 (44) |
| $NO_3$-N | 1.1 ± 1.7 (68) | 1.1 ± 1.9 (44) | 0.3 ± 0.2 (49) | 1.5 ± 2.2 (44) |
| MRP | 0.9 ± 0.7 (72) | 0.7 ± 0.6 (44) | 1.2 ± 0.6 (68) | 1.6 ± 0.8 (44) |
| Cl | 25.7 ± 16.6 (73) | 38.3 ± 15.8 (44) | 106.3 ± 43.3 (69) | 47.4 ± 24.6 (44) |
| TSS | 32.5 ± 14.5 (79) | 32.3 ± 46.1 (44) | 32.2 ± 15.5 (73) | 32.7 ± 50.0 (44) |
| DO | 3.9 ± 1.2 (81) | 3.9 ± 1.4 (44) | 3.3 ± 1.1 (75) | 3.3 ± 1.3 (44) |
| EC | 0.3 ± 0.2 (80) | 0.4 ± 0.1 (44) | 0.6 ± 0.1 (73) | 0.4 ± 0.2 (44) |
| RP | -68.3 ± 84.2 (67) | -73.9 ± 52.7 (44) | -77.6 ± 80.6 (71) | -67.3 ± 53.6 (44) |
| T | 17.9 ± 2.6 (81) | 16.7 ± 1.1 (44) | 16.8 ± 2.4 (74) | 17.0 ± 1.0 (44) |
| pH | 6.8 ± 0.4 (81) | 7.6 ± 0.4 (44) | 6.7 ± 0.3 (74) | 7.0 ± 0.4 (44) |

n, sample number; SD, standard deviation; COD, chemical oxygen demand (mg $l^{-1}$); $NH_3$-N, ammonia-nitrogen (mg $l^{-1}$); $NO_3$-N, nitrate-nitrogen (mg $l^{-1}$); MRP, molybdate reactive phosphorus (mg $l^{-1}$); TSS, total suspended solid (mg $l^{-1}$); Cl, chloride (mg $l^{-1}$); DO, dissolved oxygen (mg $l^{-1}$); EC, electrical conductivity (mS $cm^{-1}$); RP, redox potential (mV); T, water temperature (℃).

## *5.3 Physico-chemical parameters*

### 5.3.1 Experiment period I

In general, similar vertical trend of physico-chemical parameters can be found in mesocosms 2, 3 and 4 (Tables 5-2, 5-3, 5-4). For instance, mean pH value was highest near the bottom of sediment layer and slightly decreased near the superficial layer of sediment. A significant increase of pH value in two control mesocosms was recorded. In addition, a general increase in mean electrical conductivity (EC) value and dissolved oxygen (DO) concentration with column depth were observed. Vertical mean redox potential (RP) profile of mesocosm 2 was similar to that of mesocosm 3, with the lowest value near the superficial sediment layer (sampling point II). However, the lowest mean RP value was recorded at overlying water in mesocosm 4. It can be assumed that due to temperature-controlled conditions, there is no obvious difference in water temperature between individual sampling points throughout the study period.

### 5.3.2 Experiment period II

Tables 5-5, 5-6 and 5-7 show the water quality variables and contaminant treatment efficiency for modified mesocosms. Mean pH value and DO concentration decreased with the depth of column in mesocosm 2, yet they experienced a slight increase in control mesocosm. For domestic wastewater mesocosms, averaged pH values at overlying water were lower than that at the superficial substrate layer. Mean DO concentrations decreased at sampling point I and then increased at sampling point II.

In general, a increase in EC value and a decrease in RP value with depth of column were evident for three planted mesocosms. Similar to experimental period I, no significant temperature variation can be observed.

## 5.4 Chemical oxygen demand

In both periods, COD concentrations at individual sampling point were significant higher than those of influent (one-way ANOVA) and consistently increased with the depth of column with exception of mesocosm 2 in the second experimental period. These results indicated that the ICW mesocosms acted as sources of COD rather than as sinks. The sediment layers and substrates released substantially accumulated organic matter in comparison to the amount of incoming organic matter that could be degraded. On the other hand, the COD concentrations in control mesocosms roughly proportionally responded to the influent COD concentrations.

This finding is in agreement with other studies carried out in recent years. Hunt & Poach (2001) explained that CW systems cannot completely remove carbon and solid compounds because of the microbial and vegetative decay which continuously releases organic matter to the system. In addition, the reduction of organic matter in CWs can be the result of aerobic heterotrophic bacteria (Vymazal, 2007) and a considerable amount of oxygen is therefore required to decompose the organic pollutants. However, due to relatively high concentrations of ammonia in mesocosms, more than 90% of the above-ground plants were dead after operation of approximately three months in both experimental periods.

Table 5-2 Water quality variables and treatment efficiencies for farmyard runoff mesocosms 1 and 2 (April 2009–February 2011).

| Variable | Unit | n | Influent | | Control (Mesocosm 1) | | | Mesocosm 2 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Tap I | | | Tap II | | | Tap III | | |
| | | | Mean | SD | Mean | SD | TE % | Mean | SD | TE % | Mean | SD | TE % | Mean | SD | TE % |
| COD | mg $l^{-1}$ | 77 | 89.4 | 29.3 | 121.1 | 22.0 | -35.5 | 100.3 | 26.7 | -12.2 | 103.7 | 22.6 | -16.0 | 135.1 | 38.8 | -51.1 |
| $NH_3$-N | mg $l^{-1}$ | 71 | 1.2 | 1.3 | 0.1 | 0.1 | 91.7 | 2.9 | 2.2 | -141.7 | 16.2 | 4.5 | -1250.0 | 75.3 | 15.0 | -6175.0 |
| $NO_3$-N | mg $l^{-1}$ | 68 | 1.1 | 1.7 | 21.2 | 4.4 | -1827.3 | 0.3 | 0.4 | 72.7 | 0.6 | 0.7 | 45.5 | 1.0 | 0.9 | 9.1 |
| MRP | mg $l^{-1}$ | 72 | 0.9 | 0.7 | 3.5 | 1.2 | -288.9 | 2.7 | 1.0 | -200.0 | 3.4 | 1.2 | -277.8 | 10.9 | 2.2 | -1111.1 |
| Cl | mg $l^{-1}$ | 73 | 25.7 | 16.6 | 216.1 | 39.1 | -740.9 | 61.2 | 19.1 | -138.1 | 55.3 | 18.9 | -115.2 | 178.9 | 91.8 | -596.1 |
| TSS | mg $l^{-1}$ | 79 | 32.5 | 14.5 | 36.4 | 23.1 | -12.0 | 57.6 | 42.9 | -77.2 | 112.2 | 75.6 | -245.2 | 49.4 | 44.5 | -52.0 |
| DO | mg $l^{-1}$ | 81 | 3.9 | 1.2 | 4.3 | 0.9 | - | 2.1 | 0.6 | - | 2.9 | 0.8 | - | 3.6 | 0.8 | - |
| EC | mS $cm^{-1}$ | 80 | 0.3 | 0.2 | 1.3 | 0.2 | - | 0.5 | 0.1 | - | 0.7 | 0.1 | - | 2.1 | 0.3 | - |
| RP | mV | 67 | -68.3 | 84.2 | -93.0 | 88.9 | - | -132.5 | 76.0 | - | -180.0 | 113.9 | - | -93.4 | 95.4 | - |
| T | °C | 81 | 17.9 | 2.6 | 16.6 | 1.7 | - | 17.0 | 1.7 | - | 17.3 | 2.1 | - | 16.7 | 1.4 | - |
| pH | - | 81 | 6.8 | 0.4 | 7.6 | 0.3 | - | 6.4 | 0.2 | - | 6.0 | 0.2 | - | 6.9 | 0.4 | - |

n, sample number; COD, chemical oxygen demand; $NH_3$-N, ammonia-nitrogen; $NO_3$-N, nitrate-nitrogen; MRP, molybdate reactive phosphorus; Cl, chloride; TSS, total suspended solids; DO, dissolved oxygen; EC, electrical conductivity; RP, redox potential; T, water temperature; SD, standard deviation; TE, treatment efficiency; Tap I: overlying water (effluent); Tap II: values measured near the superficial sediment layer; Tap III: value measured near the bottom of sediment layer.

Table 5-3 Water quality variables and treatment efficiencies for domestic wastewater mesocosms 3 and 5 (June 2009–February 2011).

| Variable | Unit | n | Influent | | Control (Mesocosm 5) | | | Mesocosm 3 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Tap I | | | Tap II | | | Tap III | | |
| | | | Mean | SD | Mean | SD | TE % | Mean | SD | TE % | Mean | SD | TE % | Mean | SD | TE % |
| COD | mg $l^{-1}$ | 75 | 68.4 | 41.4 | 79.8 | 37.4 | -16.7 | 77.9 | 36.0 | -13.9 | 116.4 | 45.0 | -70.2 | 142.2 | 51.6 | -107.9 |
| $NH_3$-N | mg $l^{-1}$ | 65 | 9.5 | 4.0 | 0.2 | 0.3 | 97.9 | 6.9 | 7.4 | 27.4 | 39.1 | 21.2 | -311.6 | 37.8 | 29.4 | -297.9 |
| $NO_3$-N | mg $l^{-1}$ | 49 | 0.3 | 0.2 | 8.1 | 5.7 | -2600.0 | 0.5 | 0.3 | -66.7 | 0.5 | 0.5 | -66.7 | 0.8 | 0.7 | -166.7 |
| MRP | mg $l^{-1}$ | 68 | 1.2 | 0.6 | 3.3 | 1.1 | -175.0 | 3.0 | 1.9 | -150.0 | 3.5 | 1.8 | -191.7 | 2.8 | 1.1 | -133.3 |
| Cl | mg $l^{-1}$ | 69 | 106.3 | 43.3 | 473.3 | 86.2 | -345.2 | 223.3 | 47.7 | -110.1 | 217.6 | 45.1 | -104.7 | 359.8 | 188.8 | -238.5 |
| TSS | mg $l^{-1}$ | 73 | 32.2 | 15.5 | 18.0 | 15.5 | 44.1 | 11.9 | 10.3 | 63.0 | 12.2 | 15.0 | 62.1 | 23.9 | 20.0 | 25.8 |
| DO | mg $l^{-1}$ | 75 | 3.3 | 1.1 | 3.6 | 0.9 | - | 2.2 | 0.7 | - | 2.6 | 0.5 | - | 3.5 | 1.0 | - |
| EC | mS $cm^{-1}$ | 73 | 0.6 | 0.1 | 2.2 | 0.2 | - | 1.0 | 0.2 | - | 1.3 | 0.2 | - | 2.3 | 0.6 | - |
| RP | mV | 71 | -77.6 | 80.6 | -93.0 | 83.9 | - | -171.2 | 66.4 | - | -204.9 | 102.2 | - | -162.2 | 97.6 | - |
| T | $^{\circ}C$ | 74 | 16.8 | 2.4 | 16.6 | 1.8 | - | 16.9 | 1.9 | - | 16.6 | 1.4 | - | 17.0 | 1.6 | - |
| pH | - | 74 | 6.7 | 0.3 | 7.5 | 0.2 | - | 6.6 | 0.2 | - | 6.6 | 0.2 | - | 7.6 | 0.7 | - |

n, sample number; COD, chemical oxygen demand; $NH_3$-N, ammonia-nitrogen; $NO_3$-N, nitrate-nitrogen; MRP, molybdate reactive phosphorus; Cl, chloride; TSS, total suspended solids; DO, dissolved oxygen; EC, electrical conductivity; RP, redox potential; T, water temperature; SD, standard deviation; TE, treatment efficiency; Tap I: overlying water (effluent); Tap II: values measured near the superficial sediment layer; Tap III: value measure near the bottom of sediment layer.

Table 5-4 Water quality variables and treatment efficiencies for domestic wastewater mesocosms 4 and 5 (June 2009–February 2011).

| Variable | Unit | n | Influent | | Control (Mesocosm 5) | | | Mesocosm 4 Tap I | | | Mesocosm 4 Tap II | | | Mesocosm 4 Tap III | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Mean | SD | Mean | SD | TE % | Mean | SD | TE % | Mean | SD | TE % | Mean | SD | TE % |
| COD | mg $l^{-1}$ | 75 | 68.4 | 41.4 | 79.8 | 37.4 | -16.7 | 79.4 | 30.7 | -16.1 | 102.5 | 44.0 | -49.9 | 114.8 | 42.1 | -67.8 |
| $NH_3$-N | mg $l^{-1}$ | 65 | 9.5 | 4.0 | 0.2 | 0.3 | 97.9 | 11.1 | 9.9 | -16.8 | 31.1 | 19.1 | -227.4 | 40.1 | 14.4 | -322.1 |
| $NO_3$-N | mg $l^{-1}$ | 49 | 0.3 | 0.2 | 8.1 | 5.7 | -2600.0 | 0.4 | 0.3 | -33.3 | 0.7 | 0.6 | -133.3 | 0.9 | 0.8 | -200.0 |
| MRP | mg $l^{-1}$ | 68 | 1.2 | 0.6 | 3.3 | 1.1 | -175.0 | 3.2 | 1.7 | -166.7 | 4.1 | 2.3 | -241.7 | 4.2 | 2.0 | -250.0 |
| Cl | mg $l^{-1}$ | 69 | 106.3 | 43.3 | 473.3 | 86.2 | -345.2 | 154.3 | 28.8 | -45.2 | 160.8 | 31.6 | -51.3 | 221.0 | 65.3 | -107.9 |
| TSS | mg $l^{-1}$ | 73 | 32.2 | 15.5 | 18.0 | 15.5 | 44.1 | 23.0 | 18.4 | 28.6 | 8.0 | 10.2 | 75.2 | 19.7 | 19.2 | 38.8 |
| DO | mg $l^{-1}$ | 75 | 3.3 | 1.1 | 3.6 | 0.9 | - | 1.9 | 0.5 | - | 2.4 | 0.4 | - | 3.0 | 0.8 | - |
| EC | mS $cm^{-1}$ | 73 | 0.6 | 0.1 | 2.2 | 0.2 | - | 0.8 | 0.1 | - | 1.0 | 0.1 | - | 1.4 | 0.2 | - |
| RP | mV | 71 | -77.6 | 80.6 | -93.0 | 83.9 | - | -218.1 | 118.1 | - | -207.8 | 110.1 | - | -212.9 | 105.1 | - |
| T | °C | 74 | 16.8 | 2.4 | 16.6 | 1.8 | - | 17.0 | 1.7 | - | 17.2 | 2.1 | - | 16.6 | 1.3 | - |
| pH | - | 74 | 6.7 | 0.3 | 7.5 | 0.2 | - | 6.3 | 0.3 | - | 6.2 | 0.2 | - | 6.8 | 0.3 | - |

n, sample number; COD, chemical oxygen demand; $NH_3$-N, ammonia-nitrogen; $NO_3$-N, nitrate-nitrogen; MRP, molybdate reactive phosphorus; Cl, chloride; TSS, total suspended solids; DO, dissolved oxygen; EC, electrical conductivity; RP, redox potential; T, water temperature; SD, standard deviation; TE, treatment efficiency; Tap I, overlying water (effluent); Tap II: values measured near the superficial sediment layer; Tap III: value measure near the bottom of sediment layer.

Table 5-5 Water quality variables and treatment efficiencies for farmyard runoff mesocosms 1 and 2 (July 2011–May 2012).

| Variable | Unit | n | Influent | | Control (Mesocosm 1) | | | Mesocosm 2 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Tap I | | | Tap II | | |
| | | | Mean | SD | Mean | SD | TE % | Mean | SD | TE % | Mean | SD | TE % |
| COD | mg $l^{-1}$ | 44 | 90.4 | 43.5 | 138.6 | 14.6 | -53.3 | 139.4 | 38.8 | -54.2 | 130.9 | 27.8 | -44.8 |
| $NH_3$-N | mg $l^{-1}$ | 44 | 0.8 | 0.7 | 0.1 | 0.1 | 87.5 | 3.6 | 2.2 | -350.0 | 41.6 | 22.0 | -5100.0 |
| $NO_3$-N | mg $l^{-1}$ | 44 | 1.1 | 1.9 | 21.6 | 3.6 | -1863.6 | 0.1 | 0.3 | 90.9 | 0.1 | 0.1 | 90.9 |
| MRP | mg $l^{-1}$ | 44 | 0.7 | 0.6 | 4.2 | 0.9 | -500.0 | 1.9 | 1.2 | -171.4 | 0.1 | 0.3 | 85.7 |
| Cl | mg $l^{-1}$ | 44 | 38.3 | 15.8 | 357.1 | 96.7 | -832.4 | 107.2 | 27.9 | -179.9 | 179.5 | 48.6 | -368.7 |
| TSS | mg $l^{-1}$ | 44 | 32.3 | 46.1 | 171.4 | 112.1 | -430.7 | 42.3 | 60.0 | -31.0 | 277.7 | 123.8 | -759.8 |
| DO | mg $l^{-1}$ | 44 | 3.8 | 1.4 | 3.8 | 1.2 | - | 2.1 | 0.9 | - | 1.4 | 0.8 | - |
| EC | mS $cm^{-1}$ | 44 | 0.3 | 0.1 | 2.1 | 0.5 | - | 1.0 | 0.2 | - | 2.5 | 1.0 | - |
| RP | mV | 44 | -73.9 | 52.7 | -97.5 | 49.7 | - | -78.6 | 46.0 | - | -247.8 | 18.8 | - |
| T | $^{\circ}C$ | 44 | 16.7 | 1.1 | 16.9 | 0.9 | - | 17.1 | 1.0 | - | 17.1 | 0.7 | - |
| pH | - | 44 | 7.6 | 0.4 | 8.1 | 0.1 | - | 7.2 | 0.3 | - | 6.5 | 0.2 | - |

n, sample number; COD, chemical oxygen demand; $NH_3$-N, ammonia-nitrogen; $NO_3$-N, nitrate-nitrogen; MRP, molybdate reactive phosphorus; Cl, chloride; TSS, total suspended solids; DO, dissolved oxygen; EC, electrical conductivity; RP, redox potential; T, water temperature; SD, standard deviation; TE, treatment efficiency; Tap I: overlying water (effluent); Tap II: values measured near the superficial substrate layer.

Table 5-6 Water quality variables and treatment efficiencies for domestic wastewater mesocosms 3 and 5 (July 2011–May 2012).

| Variable | Unit | n | Influent | | Control (Mesocosm 5) | | | Mesocosm 3 Tap I | | | Mesocosm 3 Tap II | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Mean | SD | Mean | SD | TE % | Mean | SD | TE % | Mean | SD | TE % |
| COD | mg $l^{-1}$ | 44 | 54.7 | 17.3 | 65.9 | 7.4 | -20.5 | 100.9 | 12.4 | -84.5 | 145.7 | 28.6 | -166.4 |
| $NH_3$-N | mg $l^{-1}$ | 44 | 3.4 | 3.1 | 0.2 | 0.2 | 94.1 | 3.3 | 1.5 | 2.9 | 3.5 | 1.7 | -2.9 |
| $NO_3$-N | mg $l^{-1}$ | 44 | 1.5 | 2.2 | 11.1 | 8.2 | -640.0 | 0.2 | 0.3 | 86.7 | 0.1 | 0.1 | 93.3 |
| MRP | mg $l^{-1}$ | 44 | 1.6 | 0.8 | 4.7 | 1.4 | -193.8 | 2.3 | 1.2 | -43.8 | 2.6 | 1.3 | -62.5 |
| Cl | mg $l^{-1}$ | 44 | 47.4 | 24.6 | 373.3 | 121.0 | -687.6 | 143.7 | 37.2 | -203.2 | 275.7 | 130.7 | -481.6 |
| TSS | mg $l^{-1}$ | 44 | 32.7 | 49.9 | 25.0 | 29.3 | 23.5 | 14.5 | 37.9 | 55.7 | 25.9 | 39.0 | 20.8 |
| DO | mg $l^{-1}$ | 44 | 3.3 | 1.3 | 3.9 | 0.9 | - | 2.1 | 0.6 | - | 3.2 | 0.8 | - |
| EC | mS $cm^{-1}$ | 44 | 0.4 | 0.2 | 2.1 | 0.4 | - | 0.9 | 0.1 | - | 1.6 | 0.7 | - |
| RP | mV | 44 | -67.3 | 53.6 | -85.0 | 37.0 | - | -70.7 | 46.9 | - | -72.5 | 49.7 | - |
| T | °C | 44 | 17.0 | 1.0 | 16.6 | 1.0 | - | 17.1 | 1.3 | - | 16.9 | 1.0 | - |
| pH | - | 44 | 6.9 | 0.4 | 8.0 | 0.2 | - | 7.1 | 0.2 | - | 8.1 | 0.4 | - |

n, sample number; COD, chemical oxygen demand; $NH_3$-N, ammonia-nitrogen; $NO_3$-N, nitrate-nitrogen; MRP, molybdate reactive phosphorus; Cl, chloride; TSS, total suspended solids; DO, dissolved oxygen; EC, electrical conductivity; RP, redox potential; T, water temperature; SD, standard deviation; TE, treatment efficiency; Tap I: overlying water (effluent); Tap II: values measured near the superficial substrate layer.

Table 5-7 Water quality variables and treatment efficiencies for domestic wastewater mesocosms 4 and 5 (July 2011–May 2012).

| Variable | Unit | n | Influent | | Control (Mesocosm 5) | | | Mesocosm 4 Tap I | | | Mesocosm 4 Tap II | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Mean | SD | Mean | SD | TE % | Mean | SD | TE % | Mean | SD | TE % |
| COD | mg $l^{-1}$ | 44 | 54.7 | 17.3 | 65.9 | 7.4 | -20.5 | 101.3 | 10.6 | -85.2 | 174.1 | 39.2 | -218.3 |
| $NH_3$-N | mg $l^{-1}$ | 44 | 3.4 | 3.1 | 0.2 | 0.2 | 94.1 | 3.8 | 1.3 | -11.8 | 12.6 | 9.5 | -270.6 |
| $NO_3$-N | mg $l^{-1}$ | 44 | 1.5 | 2.2 | 11.1 | 8.2 | -640.0 | 0.3 | 0.7 | 80.0 | 0.4 | 0.8 | 73.3 |
| MRP | mg $l^{-1}$ | 44 | 1.6 | 0.8 | 4.7 | 1.4 | -193.8 | 2.6 | 1.6 | -62.5 | 2.5 | 2.0 | -56.3 |
| Cl | mg $l^{-1}$ | 44 | 47.4 | 24.6 | 373.3 | 121.0 | -687.6 | 132.7 | 39.7 | -180.0 | 275.1 | 129.2 | -480.4 |
| TSS | mg $l^{-1}$ | 44 | 32.7 | 49.9 | 25.0 | 29.3 | 23.5 | 23.6 | 42.8 | 27.8 | 27.3 | 34.0 | 16.5 |
| DO | mg $l^{-1}$ | 44 | 3.3 | 1.3 | 3.9 | 0.9 | - | 1.8 | 0.7 | - | 2.9 | 1.2 | - |
| EC | mS $cm^{-1}$ | 44 | 0.4 | 0.2 | 2.1 | 0.4 | - | 0.9 | 0.1 | - | 1.7 | 0.7 | - |
| RP | mV | 44 | -67.3 | 53.6 | -85.0 | 37.0 | - | -78.1 | 52.0 | - | -83.3 | 50.8 | - |
| T | ℃ | 44 | 17.0 | 1.0 | 16.6 | 1.0 | - | 17.1 | 0.9 | - | 16.9 | 0.7 | - |
| pH | - | 44 | 6.9 | 0.4 | 8.0 | 0.2 | - | 7.1 | 0.2 | - | 7.4 | 0.5 | - |

n, sample number; COD, chemical oxygen demand; $NH_3$-N, ammonia-nitrogen; $NO_3$-N, nitrate-nitrogen; MRP, molybdate reactive phosphorus; Cl, chloride; TSS, total suspended solids; DO, dissolved oxygen; EC, electrical conductivity; RP, redox potential; T, water temperature; SD, standard deviation; TE, treatment efficiency; Tap I: overlying water (effluent); Tap II: values measured near the superficial substrate layer.

This change in plant presence may considerably affect the oxygen transfer to the sediment and substrate layers and aerobic decomposition processes were thus reduced. It is also believed that the organic matter content and corresponding decomposition were influenced by parameters such as temperature (Barber *et al.*, 2001), organic matter quality (Turcq *et al.*, 2002), residence time (Yu *et al.*, 2002), vegetation pattern, wetland maturity, structure of rooting media, sedimentation rate, sediment texture, and sediment reworking (Shepherd *et al.*, 2007).

Although results showed organic matter release in all tested mesocosms through the course of two experimental periods, the COD release magnitude was higher in the second experimental period. For instance, the COD concentration was increased from 89.4 mg $l^{-1}$ at the inlet to 100.3 mg $l^{-1}$ at the outlet (-12.2%) in mesocosm 2 in the first experimental period, however, it varied significantly from 90.4 mg $l^{-1}$ at the inlet to 139.4 mg $l^{-1}$ (-50.4%) at outlet in the second experimental period. The result indicated that wetland sediments functioned as an organic matter buffer by either retaining or releasing COD into overlying water column, depending on the physic-chemical parameters of the CW system.

## 5.5 Nitrogen

In general, the $NH_3$-N concentrations in overlying water column were relatively higher than those for the influent except for mesocosm 3 in the second experimental periods. This showed that the $NH_3$-N accumulated at the sediment or substrate layers was subsequently released into overlying water. In a CW system, the removal of $NH_3$-N is considered to occur mainly via pathway of nitrification followed by denitrification. In addition, $NH_3$-N may also subject to sorption of both organic and inorganic substrates through ion exchange. The ionized and adsorbed $NH_3$-N is bound loosely to the substrate such as sediment and can be easily released when water chemistry and other environmental factors change (Kadlec, 2009). On the other hand, kinetic ammonification (mineralization) of organic nitrogen proceeds more rapidly than nitrification, thus creating the potential increase in $NH_3$-N concentration in the effluent. Previous studies have confirmed these findings. For instance, Hammer & Knight (1994) reported that the nutrient removal efficiency, especially for $NH_3$-N, was relatively low within most wetland systems. In addition, Reinhardt *et al.* (2006) assessed the nitrogen removal efficiencies in a small constructed wetland located in Switzerland and revealed that the TN reduction was 27%. In comparison, $NH_3$-N removal rate was only -1% which also indicated the release of $NH_3$-N from CW systems.

The low nitrification rates in tested mesocosms could be caused by a number of factors including oxygen shortage, low pH values and low temperature. The nitrification process is very oxygen demanding. As mentioned above, plants did not grow well and resulted in a low rate of oxygen transformation to sediment and substrate layers (DO<4 mg $l^{-1}$). In addition, pH value is also a key influencing factor. When pH value drops to below 7, nitrification rates swiftly decline (Ahn, 2006). The pH values in superficial sediment layers were mainly ranging between 6 and 7. The relatively low pH values could adversely affect the nitrification process. In contrast, pH values of overlying water samples in control systems were above 7. This difference in pH resulted in an obvious enhancement of the nitrification processes (more than 85% $NH_3$-N removal) in control systems.

Moreover, temperature also plays an important role in the nitrification and denitrification processes (Langergraber, 2008). Varying temperatures affect both microbial activity and oxygen diffusion rates in wetland systems. Vymazal (2007) reported that the optimum temperature range for nitrification was between 30 and 40 ℃ in soils. At low temperature, nitrification can be insufficient to prevent a net increase in ammonia concentration. The experimental temperature was maintained at 15 $^{o}$C which might be another reason to cause low $NH_3$-N removal efficiencies.

There is also strong evidence to suggest that nitrification rate can be prohibited by high organic loading (Hamersley and Howes, 2002; Kouki *et al.*, 2009; Zhao *et al.*, 2009). The relatively high COD concentrations in the mesocosms probably lessened nitrification as well.

In experimental period 1, the release of $NO_3$-N from mature sediment can be observed in mesocosms 3 and 4. However, generally higher average $NO_3$-N reduction occurred within three tested mesocosms in period 2. Compared to planted mesocosms, significantly higher $NH_3$-N and lower $NO_3$-N concentrations were recorded in effluent of control systems. This effective oxidation of ammonia (nitrification) was due to increased DO concentrations. On the other hand, the high DO levels in the overlying water could limit denitrification process.

## *5.6 Phosphorus*

The results from both experimental periods indicated that sediments and substrates were saturated with MRP and acting as a source for MRP. Similar to planted mesocosms, a general trend of MRP release was also observed in both control mesocosms. These findings were supported by Moortel *et al.* (2009), who suggested that surface flow and subsurface flow CWs initially remove phosphorus and later on release it again from the substrate once sorption sites become saturated. A study by Mann & Bavor (1993) monitored the performance of a full-scale subsurface flow gravel wetland over 2 years and demonstrated that non-reactive substrates could remove significant amount of phosphorus, but that sites quickly became saturated. Kayranli *et al.* (2010) reported that the MRP removal efficiency decreased in the course of the research period due to blockage of the adsorption sites within wetland soils and sediments.

In addition, this finding also agreed with Reddy *et al.* (1999), who indicated that there was generally a net absorption of phosphorus when sediment and soil porewater had significantly lower concentration of phosphorus than that of in the overlying water, while a net desorption and release of phosphorus by substrates occurred at low influent phosphorus concentrations.

It is also believed that the carbon concentration may also influence the phosphorus removal efficiency either by blocking the adsorption sites or by competing for them with phosphates (Vohla *et al.*, 2007).

The phosphate-accumulating microorganisms are sensitive to high salinity (Scholz, 2006). Zhang *et al.* (2008) evaluated the nutrient removal performance of CWs using self-organisation map models and reported that chloride concentration and EC value correlated well with MRP treatment performance, indicating that increased salt concentrations had negative effects on MRP removal. As for tested mesocosms, the mean chloride concentrations at all sampling points were relatively higher than those of the corresponding influent concentrations which probably accelerated the release of phosphorus from the mature sediment and substrate.

Table 5-8 Influent and effluent water quality and treatment efficiencies of the first cell in integrated constructed wetland site 7 and 11 near Waterford (2001–2009).

| | | ICW site 7 cell 1 | | | | ICW site 11 cell 1 | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | n | Influent | Effluent | TE | n | Influent | Effluent | TE |
| COD | Mean | 4 | 417.5 | 187.5 | 55.1 | 15 | 1470.9 | 2751.3 | -87.1 |
| | SD | | 196.0 | 79.3 | | | 1444.3 | 4295.8 | |
| $NH_3$-N | Mean | 6 | 55.6 | 49.4 | 11.1 | 127 | 41.8 | 26.5 | 36.5 |
| | SD | | 19.6 | 16.7 | | | 39.2 | 16.7 | |
| $NO_3$-N | Mean | 6 | 1.9 | 1.6 | 14.5 | 59 | 3.9 | 0.9 | 78.2 |
| | SD | | 1.8 | 1.8 | | | 10.8 | 1.8 | |
| MRP | Mean | 6 | 7.6 | 7.4 | 2.4 | 126 | 12.1 | 6.8 | 44.0 |
| | SD | | 2.4 | 2.0 | | | 9.7 | 4.7 | |

n, sample number; TE, treatment efficiency (%); COD, chemical oxygen demand (mg $l^{-1}$); $NH_3$-N, ammonia-nitrogen (mg $l^{-1}$); $NO_3$-N, nitrate-nitrogen (mg $l^{-1}$); MRP, molybdate reactive phosphorus (mg $l^{-1}$); SD, standard deviation.

Note: the extremely high COD influent concentrations were attributed to the accumulation of organic matter at the inlet area.

Table 5-9 Comparison of selected contaminant treatment efficiencies between integrated constructed wetland mesocosms and full-scale systems.

| TE (%) | Site 11 cell 1 | Mesocosm 2 Effluent | Site 7 cell 1 | Mesocosm 3 Effluent | Mesocosm 4 Effluent |
|---|---|---|---|---|---|
| COD | -87.1 | -12.2 | 55.1 | -13.9 | -16.0 |
| $NH_3$-N | 36.5 | -131.2 | 11.1 | 27.1 | -17.0 |
| $NO_3$-N | 78.2 | 68.5 | 14.5 | -70.4 | -51.9 |
| MRP | 44.0 | -193.6 | 2.4 | -156.9 | -180.2 |

TE, treatment efficiency; COD, chemical oxygen demand; $NH_3$-N, ammonia-nitrogen; $NO_3$-N, nitrate-nitrogen; MRP, molybdate reactive phosphorus.

## 5.7 Comparison to full-scale integrated constructed wetland systems

Since the utilization of multi-cellular configuration for full-scale ICW systems, no diminution of overall treatment performance has been observed over 15-year period of operation (Harrington *et al.*, 2011). However, the long-term effectiveness of individual cells, in particular the first cell which receives the heaviest contaminant loading, is less known. Once the first cell starts to release contaminants, there is a potential risk of cascading transfer of intercepted contaminants to following cells and consequently cause the adverse impact on removal performance of the overall ICW system.

As shown in Table 5-8, the cell 1 of site 7 has not proved to be effective for contaminant removal, in particular for MRP (2.4%). In fact, the initial years after construction, the removal efficiency of MRP in ICW site 7 was very high (>90%). However, it significantly decreased over operation time. This decline in MRP reduction was more evident for cell 1.

The COD treatment efficiency was drastically reduced in the first cell of site 11. The results indicated that the high influent COD concentration and lack of harvest probably could accelerate the occasional release of organic matter to overlying surface water. The effective $NO_3$-N reduction (78.2%) was observed in this cell as well. The enhanced denitrification process might be attributed to the increased COD concentrations. This finding is agreement with Kadlec (2002) and Lin *et al.* (2007) suggesting that organic carbon is probably the most important factor in stimulating nitrate removal when nitrate level is not limited.

Relative to full-scale systems, the ICW mesocosms were generally under performed, though some results were similar to those recorded in the first cell of full-scale ICWs (Table 5-9). This observation pointed out potential release of nutrients and other contaminants from ICW systems over long-term operation. However, mesocosms might have lacked the heterogeneity and exposure to fluctuating meteorological that likely enhance removal processes such as nitrification in full-scale systems. In addition, these small-scale mesocosms may also possibly exaggerate the release effects, resulting in elevated rates of decline in removal performance that could be representative of a full-scale ICW system.

## 5.8 Factors affecting nutrient and other contaminants release from sediments

The previously discussed factors affecting the release of nutrients and other contaminants by sediment mainly based on findings from other studies. The aim of this section is to investigate the statistical relationships between physico-chemical parameters and contaminant treatment efficiency in ICW mesocosms. These performed analyses enable the further interpretation of contaminant retention and/or release processes inside ICW treatment systems.

### 5.8.1 Description of the experimental database

Only data collected from the first experimental period was included. The database contained 81 entries for mesocosm 2, and 76 entries for mesocosms 3 and 4 respectively. Each entry includes physico-chemical parameters (T, pH, EC, DO, RP, and Cl) recorded at influent and sampling point I (effluent), II (near superficial sediment layer) and III (near the bottom of sediment layer), and treatment efficiencies (%, negative values denote release rate) of COD, $NH_3$-N, $NO_3$-N, and MRP at corresponding sampling points.

### 5.8.2 Multiple regression analysis

In this study, the forward stepwise regression method was applied to find out linear relationships between physico-chemical variables and the treatment efficiency of contaminant and to develop the regression models. The physic-chemical variables include influent and collected water sample values of T (℃), pH, EC (mS $cm^{-1}$), RP (mV), DO (mg $l^{-1}$) and Cl concentration (mg $l^{-1}$). The instructions of the program were set up at $p$ = 0.05, maximum steps = 100, sweep delta =$10^{-7}$, and inverse delta = $10^{-12}$. Where, $p$ is to guide the forward stepwise entry of effects into the model by the significant levels ($p$-values); sweep delta is used to detect redundant columns in the design matrix, and to evaluate the estimability of hypotheses; and inverse delta is applied to check for matrix singularity in matrix inversion calculations (StatSoft, 2012).

Table 5-10 shows the relationship equations and their respective regression coefficient ($R^2$) values in each mesocosm. The signs (plus or minus) represent the particular relationship (positive or negative) of this parameter with the contaminant treatment efficiency. $R^2$ values above 0.5 indicate the existence of significant linear relations (Hijosa-Valsero *et al.*, 2011). Thus, only a few models are to be considered valid. However, this does not necessarily specify that the treatment of contaminant is not correlated to physico-chemical parameters. This can only demonstrate that the relationship between them is not significantly linear.

For those valid models, the influent RP values showed positive impacts on COD removal (negative impacts on COD release). This finding is supported by the experimental results showing that redox properties of influent and vegetation bed played the most significant role in the degradation of organic compounds (Šíma *et al.*, 2009). In addition, Garcí a *et al.* (2004) conducted a comparative study between two similar HF reed beds and found that the CW with highest RP value (the most aerobic system) was most efficient in removal of COD, $BOD_5$, ammonia, and dissolved reactive phosphorus.

In general, in the models where $R^2 > 0.5$, physico-chemical parameters such as pH, T and EC value also affect contaminants treatment efficiencies, but there is no specific parameter can be defined to impact treatment efficiency of a particular contaminant. Thus, other statistical tests must be performed to explore the subtle existing relationships.

Table 5-10 Multiple regression equation models and regression coefficient (*R*-square) values for contaminants treatment efficiencies.

| | y (TE, %) | Equation | *R*-square |
|---|---|---|---|
| Mesocosm 2 | COD | $y = 0.49 \times RP_{IN} - 26.92 \times DO_{IN} + 112.71$ | **0.503** |
| | $NH_3$-N | $y = -12.86 \times Cl_{II} + 252.22$ | 0.162 |
| | $NO_3$-N | $y = -185.36 \times T_{III} + 53.50 \times T_{IN} + 2098.12$ | 0.219 |
| | MRP | $y = -52.21 \times T_{IN} - 244.16 \times pH_{IN} + 2282.14$ | 0.352 |
| Mesocosm 3 | COD | $y = 0.47 \times RP_{IN} - 17.74 \times DO_{IN} + 65.49$ | **0.501** |
| | $NH_3$-N | $y = 42.40 \times pH_{III} - 12.91 \times T_{IN} - 32.29 \times DO_{IN} + 31.51$ | **0.617** |
| | $NO_3$-N | $y = -21.95 \times T_{III} + 314.45$ | 0.148 |
| | MRP | $y = 0.32 \times Cl_{III} - 294.50$ | 0.222 |
| Mesocosm 4 | COD | $y = 0.49 \times RP_{IN} + 76.42 \times pH_{II} - 464.51$ | **0.514** |
| | $NH_3$-N | $y = -0.27 \times EC_{II} - 11.03 \times T_{IN} + 103.96 \times pH_{III} + 0.23 \times EC_{IN} + 26.32 \times DO_{III} - 464.23$ | **0.673** |
| | $NO_3$-N | $y = -39.82 \times T_{III} - 1.04 \times Cl_{IN} + 728.39$ | 0.471 |
| | MRP | $y = 0.47 \times EC_{IN} - 491.00$ | 0.155 |

TE, treatment efficiency; T, water temperature (℃); EC, electrical conductivity (mS $cm^{-1}$); DO, dissolved oxygen (mg $l^{-1}$); RP, redox potential (mV); Cl, chloride (mg $l^{-1}$); COD, chemical oxygen demand; $NH_3$-N, ammonia-nitrogen; $NO_3$-N, nitrate-nitrogen; MRP, molybdate reactive phosphorus; IN, influent; II, sample point II (values measured near superficial sediment layer); III, sample point III (values measured near the bottom of sediment layer).

### 5.8.3 Principal component analysis

In this particular study, four sub datasets (COD, $NH_3$-N, $NO_3$-N and MRP) for each mesocosm (12 sub datasets in total) have been applied to identify relationships among contaminant treatment efficiencies with measured water quality variables and to visualize them on the graphical output. The data entries were selected due to the absence of missing values. Table 5-11 shows the number of data entry for each sub dataset.

Table 5-11 Number of data entry for the principal component analysis.

| | Mesocosm 2 | Mesocosm 3 | Mesocosm 4 |
|---|---|---|---|
| Chemical oxygen demand | 66 | 61 | 62 |
| Ammonia-nitrogen | 63 | 56 | 58 |
| Nitrate-nitrogen | 58 | 44 | 45 |
| Molybdate reactive phosphorus | 63 | 57 | 58 |

Interpreting the PCA ordination, three distinct groupings (highlighted by circles) can be clearly in Fig. 5-1a. The result shows that COD treatment rates grouped well with pH and RP values in mesocosm 2. This result agrees with the finding from multiple regression analysis. In addition, pH values were also determined to correlate with the degradation (or release) of organic matter. In three tested mesocosms, the pH values slightly decreased at effluent and the superficial sediment layer, whereas increased at the bottom of sediment. The decline of pH values might be due to the breakdown of organic matter. Kimani *et al.* (2012) presented the preliminary results of a project in Kenya using CWs as a technique to treat wastewater generated by flower farms. The authors pointed out that a notable decrease in pH occurred in the gravel bed hydroponic section and retention cell which caused by the decomposition of organic matter. However, there are not many conducted studies to explore the pH changes inside a narrow neutral pH range and their influence on removal of organic matter in complex CWs.

The similar aggregation can be observed from Figs. 5-1b and 5-1c which indicated that EC value and Cl concentration may also relate with COD treatment efficiency. In mesocosms 3 and 4, a significant increase in electrical conductivity was recorded along with the depth of column. This finding suggested that ICW sediment acted as the main depositors of soluble ions. Since the degree of soil salinity is determined by measuring the EC of a soil-water mixture, the sediments and substrates of mesocosms can be categorised as non-saline (0-2.0 mS $cm^{-1}$) to slightly saline (2.1-4.0 mS $cm^{-1}$). The salinity of wetland is a significant factor because changes in soluble salts of sediment or soil can shift wetland environments (Yu *et al.*, 2012). The increased level of salinity with soil depth might be attributed to microbial activity and mineralization of organic matter or release of nutrients back into the overlying water, thus increasing dissolved ions content (Kimani *et al.*, 2012; Vymazal and Kröpfelová, 2009).

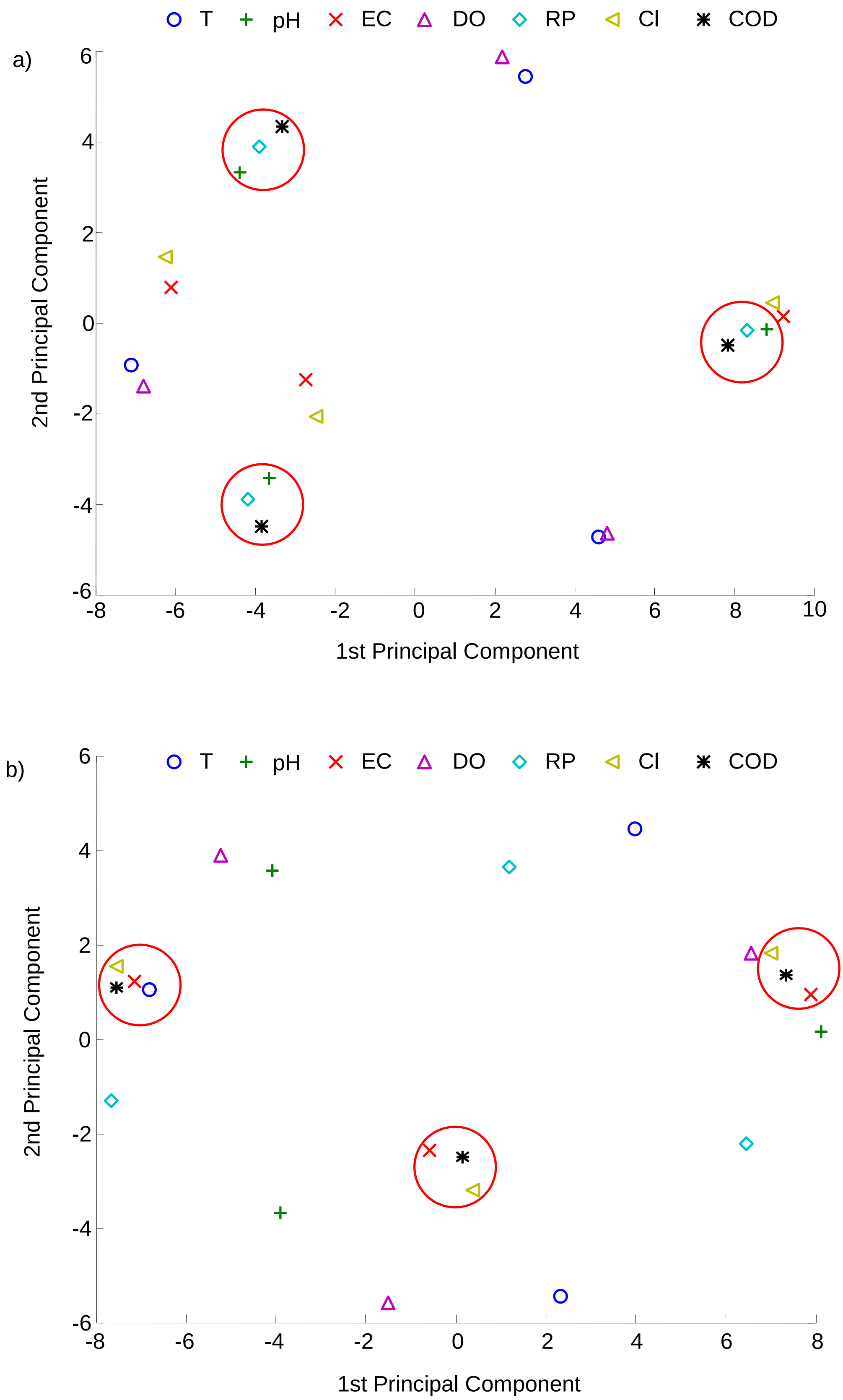
Fig. 5-2 shows the PCA ordinations for $NH_3$-N treatment efficiencies and physico-chemical parameters in mesocosms 2 to 4. The highlighted groupings suggest that Cl concentration, EC and RP values were likely to have influence on $NH_3$-N treatment performance in ICW mesocosms. This finding was in agreement with previous research. Wu *et al.* (2008) indicated that nitrogen removal in constructed mangrove wetlands was reduced by high artificial wastewater salinity. The reduction of $NH_3$-N and inorganic N dropped from 98% to 83% and from 78% to 56%, respectively, with influent salinity increasing from 0 to 60 mS $cm^{-1}$. Chapanova *et al.* (2007) reported that $NH_3$-N transformation is sensitive to the wastewater salinity. Ammonia conversion was significantly reduced after increasing the salinity of the influent. In addition, Dinçer and Kargi (1999) demonstrated that nitrification and denitrification rates would decrease if the salt content is above 2% and 1%, respectively.

The monitoring data showed that redox conditions in mesocosms were significantly reduced. According to Hunt *et al.* (1994) and a subsequent follow-up research conducted by Szögi *et al.* (2004), the highly reducing conditions which reflected persistent low oxygen in wetland sediment and soil may inhibit nitrification process and also decrease the long-term phosphorus removal efficiency. Moreover, Mitsch and Lohan (2005) investigated the effect of redox potential change on nutrient removal for a 3-ha CW. The authors suggested that the net export of $NH_3$-N, TP and soluble reactive phosphorus were largely affected by the differences of RP values between inflow and outflow. Wieβner *et al.* (2005) also reported that the $NH_3$-N removal processes could be firmly established at moderately reduced redox conditions (RP > -50 mV) in a laboratory-scale CW.

Fig. 5-3 shows the PCA ordinations for $NO_3$-N treatment efficiencies and physico-chemical parameters in three tested mesocosms. With the exception of mesocosm 2, no defined group can be observed in corresponding ordinations, thus there are limitations on the interpretation. As shown in Fig. 5-3a, the ordination suggested that the degradation of $NO_3$-N could depend on RP and pH values. Many previous studies have confirmed this result. Hunting and van der Geest (2011) indicated that measurements of RP values have predictive capability in approximating rates of denitrification in CWs. Similarly, Mansfeldt (2004) investigated the relationship between RP values in bulk soil and concentration of nitrate in the soil solution of two Gleysols and found out that the reduction of nitrate, which was involved in redox reaction, could be discerned by RP values.

Moreover, pH value in CWs may hamper the microbial processes and further effect nitrification and denitrification processes. Song *et al.* (2011) suggested that denitrification rates were positively correlated with pH values based on the results from a six-month study on two mesocosm-scale wetlands. Gale *et al.* (1993) conducted an experimental study to evaluate the $NO_3^-$ removal potential of wetland soils under anaerobic, denitrifying conditions. The finding indicated that $NO_3^-$ reduction was strongly inhibited at low pH.

With the exception of mesocosm 3 (Fig. 5-4b), the presented aggregations seen in Figs. 5-4a and 5-4c showed that there existed a relationship between EC value, Cl concentration and MRP treatment rates. Rejmánková and Sirová (2007) demonstrated that the activities of phosphatase (an extracellular enzyme) exhibited a significant response to salinity. The phosphorus removal rates of ICW systems decreased with increasing salt concentration, which was probably because the phosphate-accumulating microorganism cells had reached a certain threshold and subsequently resulted in reduced phosphate accumulation capabilities (Scholz, 2006; Zhang *et al*., 2008). Moreover, Tam and Wong (1996) suggested that phosphorus adsorption depended on the salinity and redox conditions in mangrove soils.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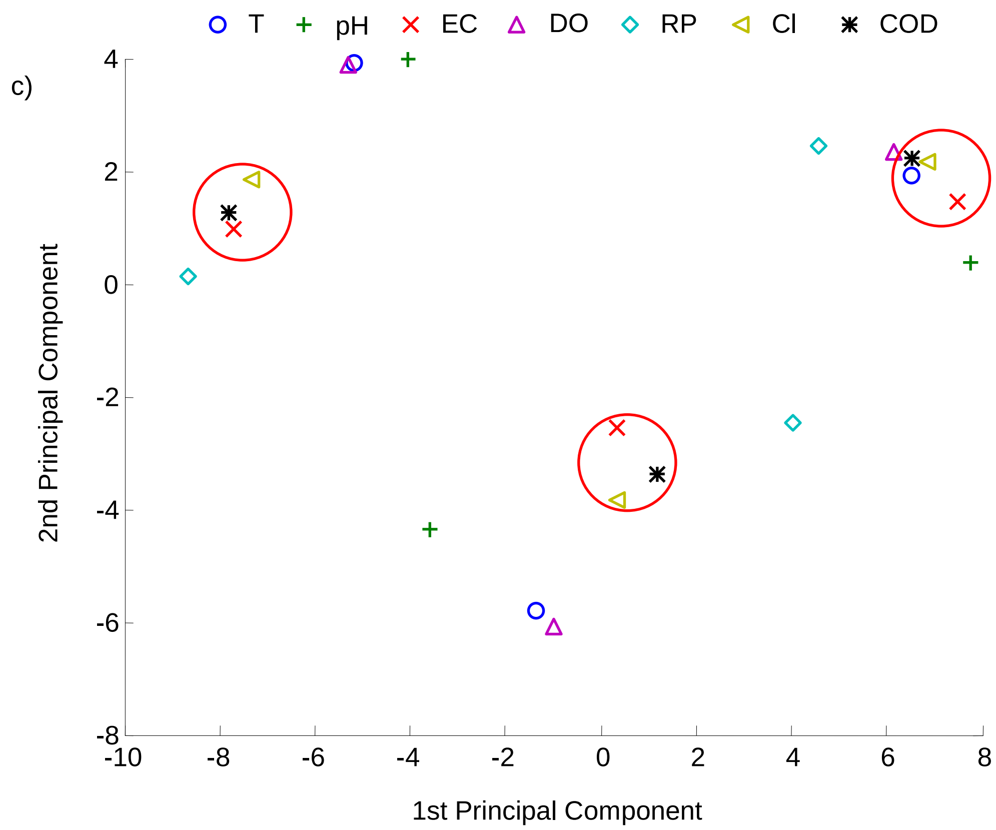
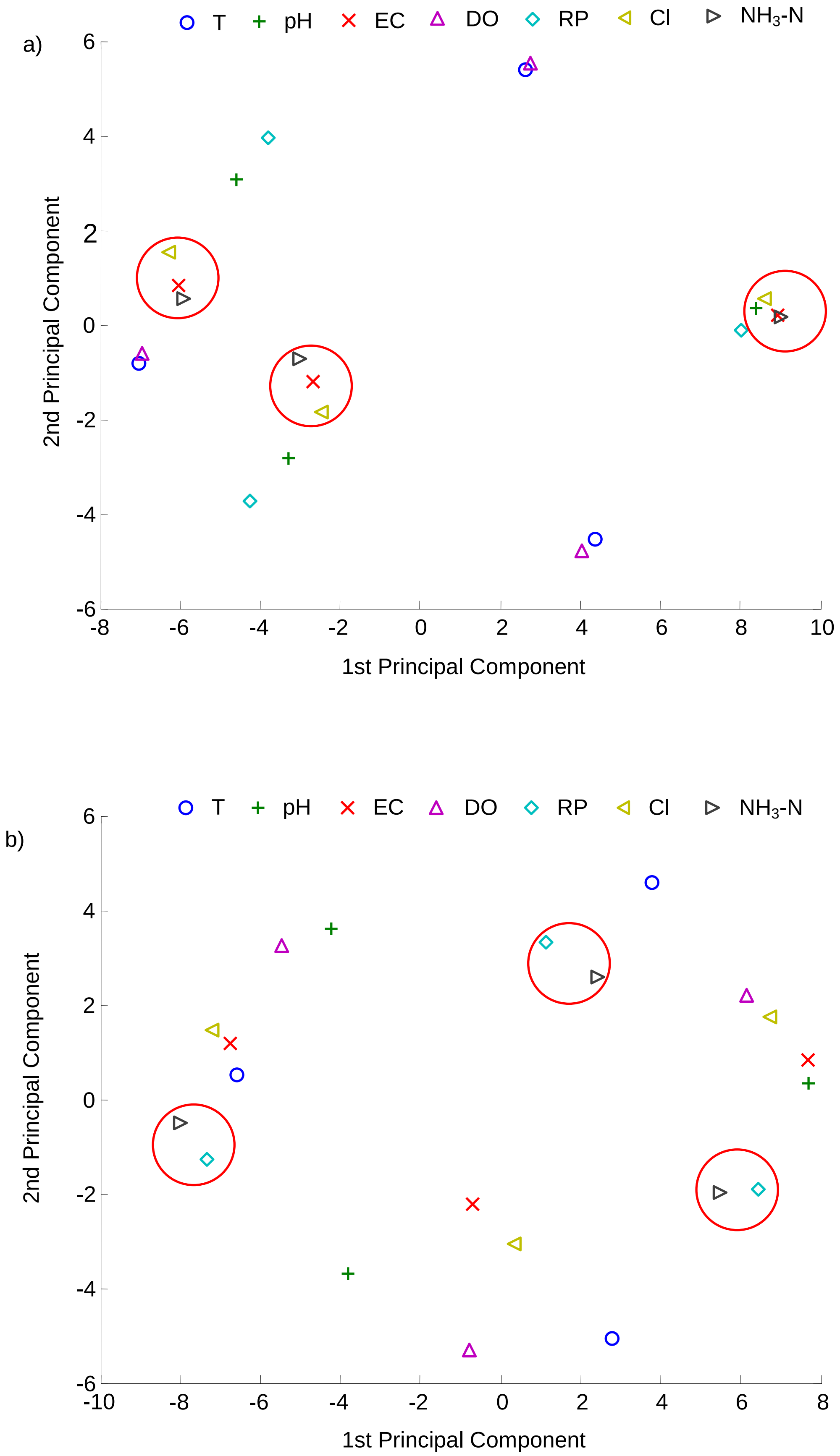



Figure 5-0-1 The principal component analysis ordinations of physico-chemical parameters and chemical oxygen demand treatment efficiency: a) mesocosm 2; b) mesocosm 3; c) mesocosm 4. T, water temperature (℃); EC, electrical conductivity (mS $cm^{-1}$); DO, dissolved oxygen concentration (mg $l^{-1}$); RP, redox potential (mV); Cl, chloride concentration (mg $l^{-1}$); COD, chemical oxygen demand treatment efficiency (%).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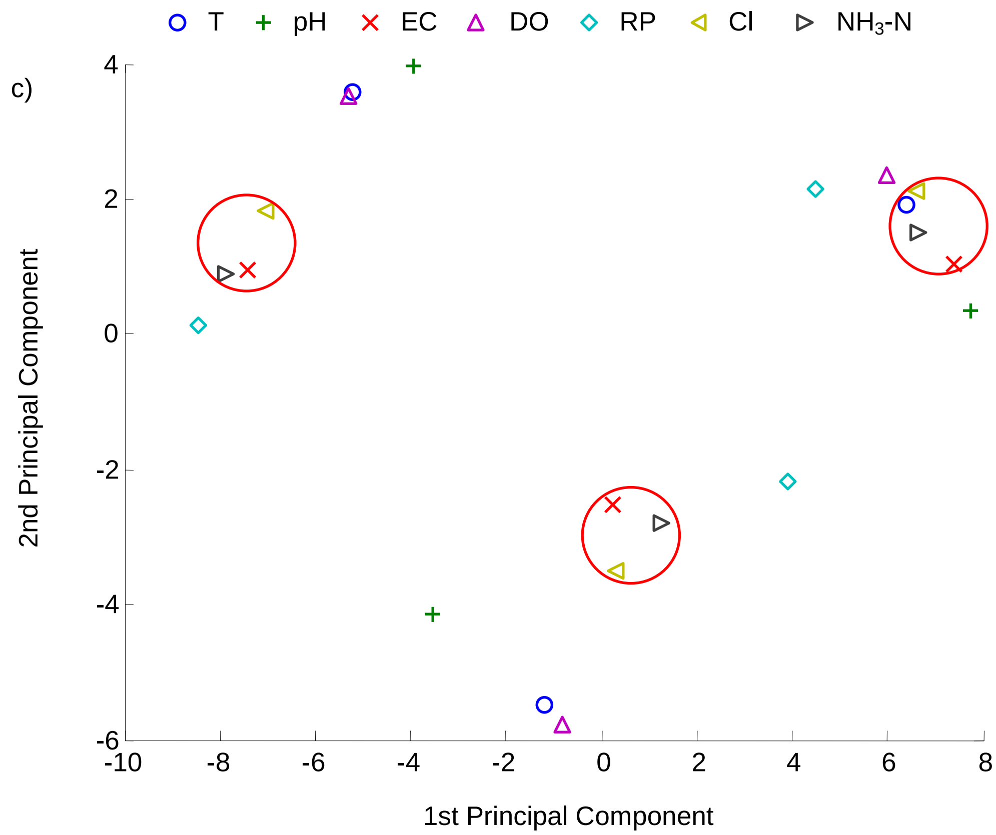
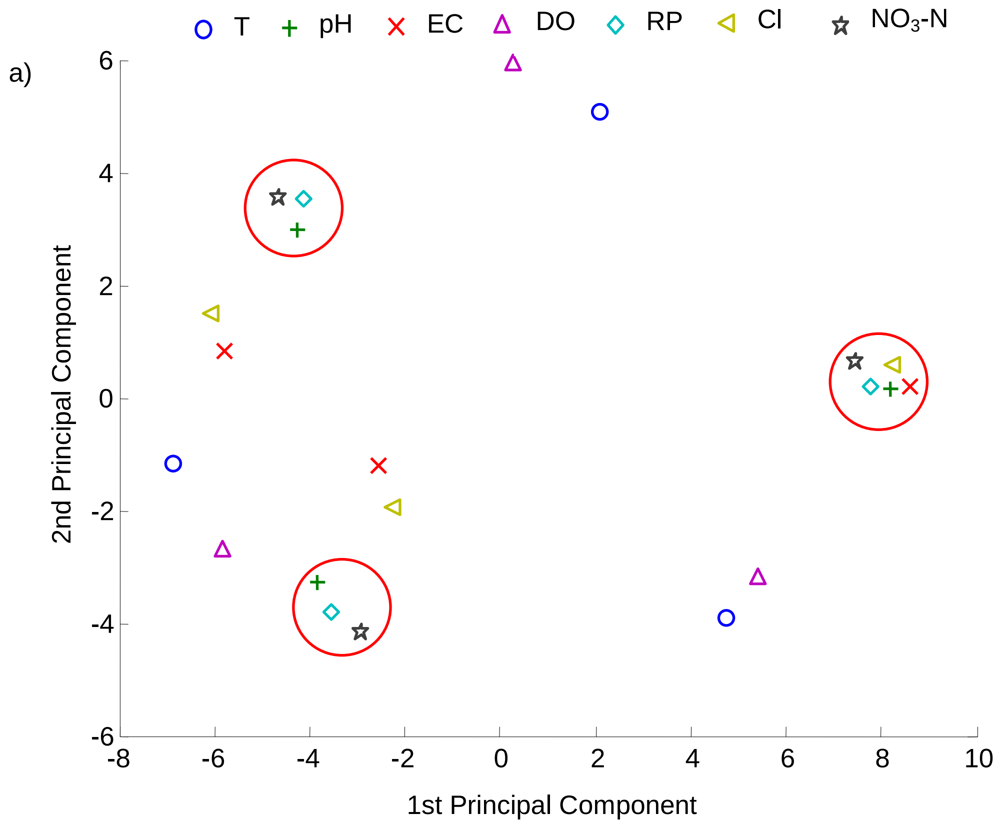



Figure 5-0-2 The principal component analysis ordinations of physico-chemical parameters and ammonia-nitrogen treatment efficiency: a) mesocosm 2; b) mesocosm 3; c) mesocosm 4. T, water temperature (°C); EC, electrical conductivity (mS $cm^{-1}$); DO, dissolved oxygen concentration (mg $l^{-1}$); RP, redox potential (mV); Cl, chloride concentration (mg $l^{-1}$); $NH_3$-N, ammonia-nitrogen treatment efficiency (%).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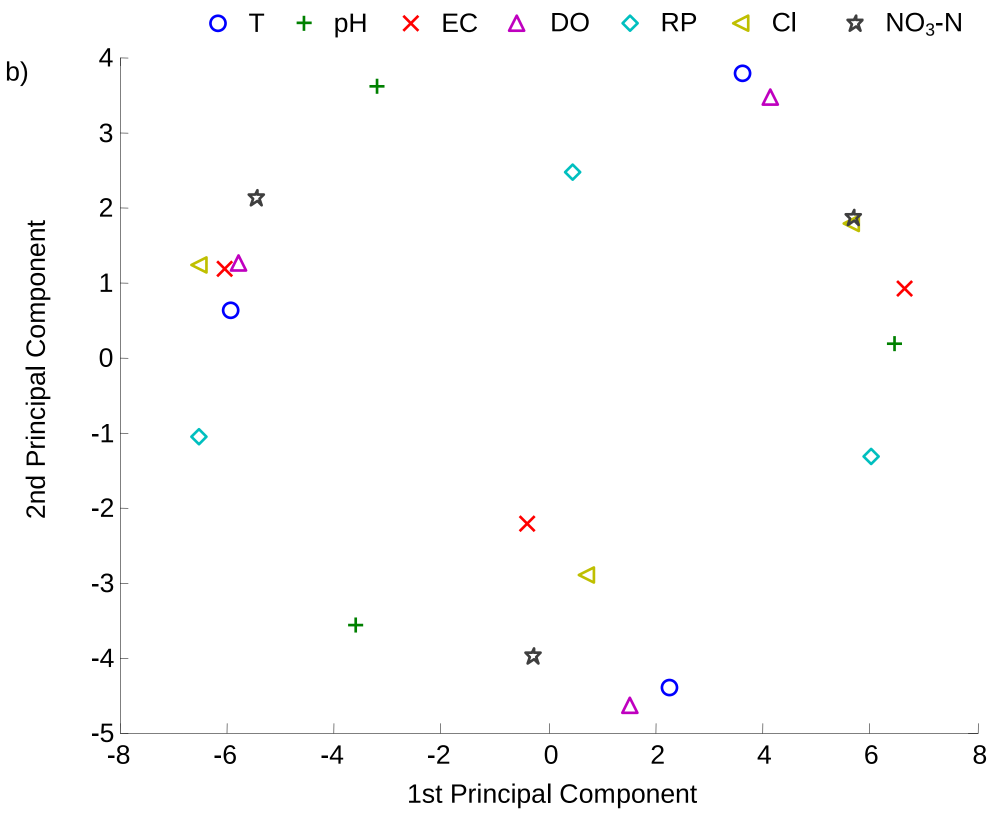
pH
EC
DO
RP
Cl
NO3-N
a)
2nd Principal Component
1st Principal Component


T
pH
EC
DO
RP
Cl
NO3-N
b)
2nd Principal Component
1st Principal Component

c)

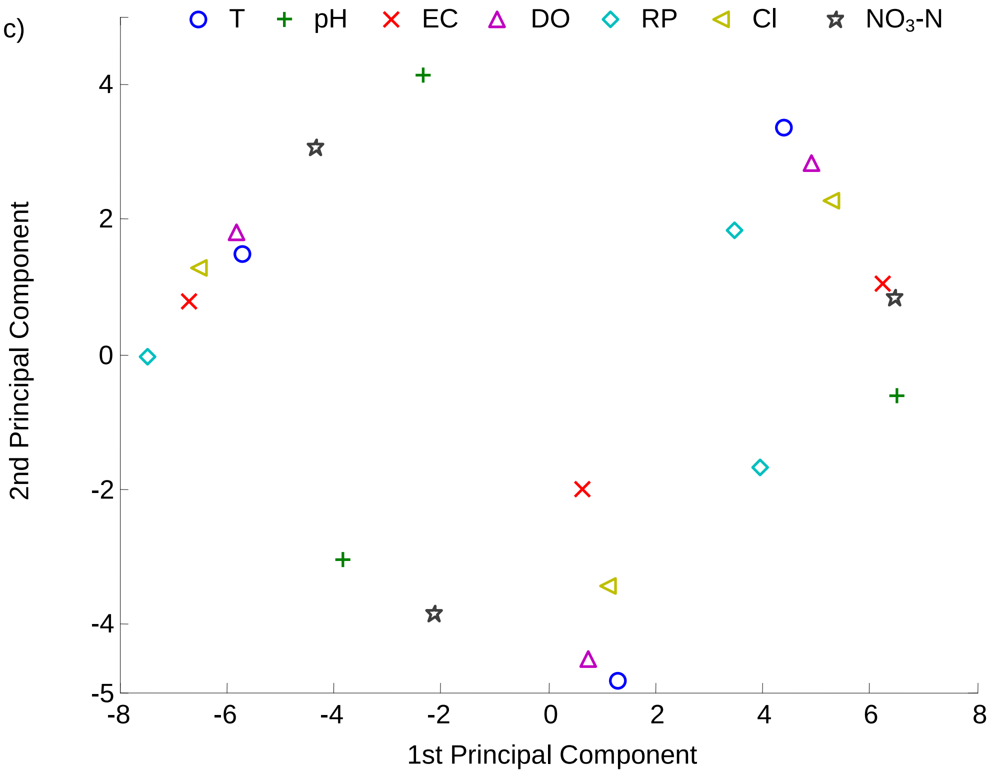
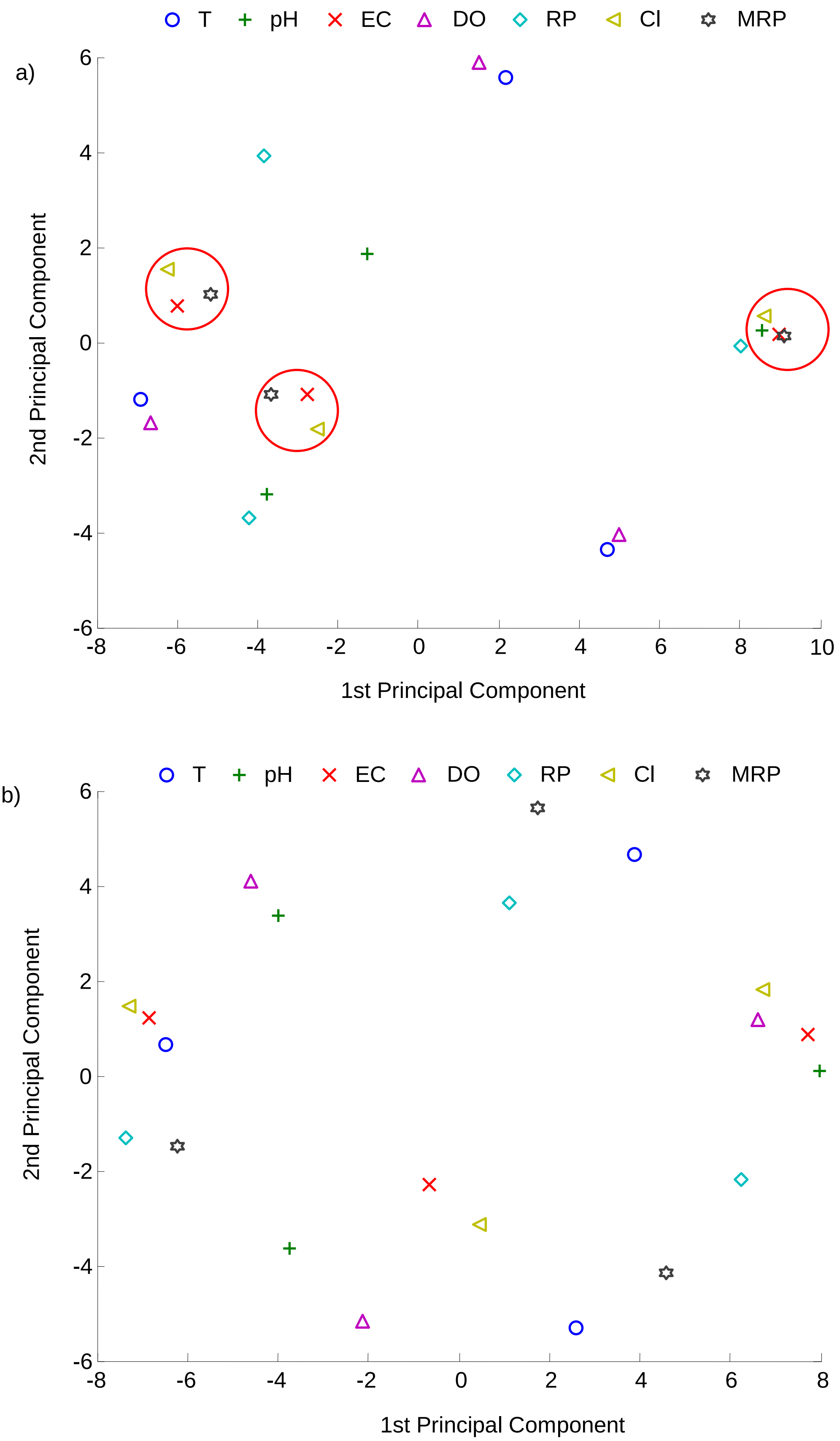



Figure 5-3 The principal component analysis ordinations of physico-chemical parameters and nitrate-nitrogen treatment efficiency: a) mesocosm 2; b) mesocosm 3; c) mesocosm 4. T, water temperature (℃); EC, electrical conductivity (mS $cm^{-1}$); DO, dissolved oxygen concentration (mg $l^{-1}$); RP, redox potential (mV); Cl, chloride concentration (mg $l^{-1}$); $NO_3$-N, nitrate-nitrogen treatment efficiency (%).



a)
T
pH
EC
DO
RP
Cl
MRP
2nd Principal Component
1st Principal Component
b)
T
pH
EC
DO
RP
Cl
MRP
2nd Principal Component
1st Principal Component

c)

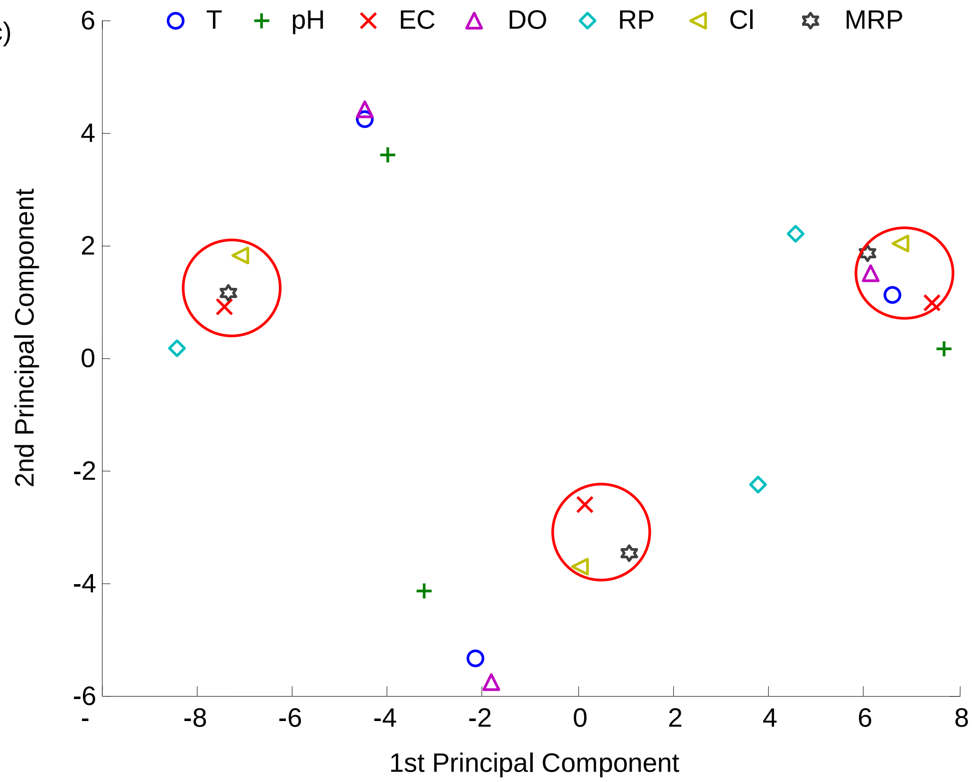



Figure 5-4 The principal component analysis ordinations of physico-chemical parameters and molybdate reactive phosphorus treatment efficiency: a) mesocosm 2; b) mesocosm 3; c) mesocosm 4. T, water temperature (℃); EC, electrical conductivity (mS $cm^{-1}$); DO, dissolved oxygen concentration (mg $l^{-1}$); RP, redox potential (mV); Cl, chloride concentration (mg $l^{-1}$); MRP, molybdate reactive phosphorus treatment efficiency (%).

### 5.8.4 Redundancy analysis

In this study, the similar datasets as those in MRA and PCA were employed. The dependent variables (species data) were treatment efficiencies (%) of four contaminants (COD, $NH_3$-N, $NO_3$-N and MRP). The independent variables (environment data) include the values of T (℃), pH, EC (mS $cm^{-1}$), DO (mg $l^{-1}$), RP (mV), and Cl concentration (mg $l^{-1}$) in influent, the superficial and bottom sediment layers. There is no co-linearity between independent variables can be detected considering all the tested inflation factor values were less than 20. RDA with the option of ‘centre and standardized by species’ was applied. The Monte Carlo permutation test was subsequently performed to overcome problems with distributional characteristics and to assess the significance of the first axis. The tests were based on 499 random permutations. The detailed information on interpretation for RDA has been introduced in Material and Methods chapter. In general, when the arrows of a independent (explanatory) variable and a dependent (response) variable point in the same direction, a positive correlation is expected; if they point in opposite directions, the correlation is expected to be negative. If the angle between a response and an explanatory variable is 90º, there is no correlation between variables could be expected.

Fig. 5-5 shows the RDA ordination diagram created using the data from mesocosm 2. In this figure, the treatment efficiency of COD was positively related to RP values and Cl concentrations and negatively correlated with DO concentrations. Due to the exactly opposite arrow directions of MRP and COD treatment efficiency, those explanatory variables, which were positively correlated to COD, were negatively related to MRP treatment efficiency, and vice versa. A negative correlation also existed between $NO_3$-N treatment efficiency and temperature. In addition, Cl concentrations and RP values were negatively correlated with $NH_3$-N elimination.

The RDA ordination diagram for mesocosm 3 (Fig. 5-6) indicates that the treatment efficiencies of COD and $NH_3$-N were positively correlated with temperature and negatively related to DO concentrations. A positive correlation can be observed between $NO_3$-N treatment efficiency and DO concentrations. Moreover, temperature could be negatively correlated to $NO_3$-N and MRP treatment efficiencies.

The RDA ordination diagram for mesocosm 4 (Fig. 5-7) shows that outstanding positive relationships could be found between the treatment efficiency of COD and Cl concentrations and RP values. However, due to the right opposite arrow direction, $NH_3$-N treatment efficiency could be negatively correlated with those two variables. $NO_3$-N treatment efficiency was positively correlated to DO concentrations. No distinct relationship could be found between MRP treatment rates with the explanatory variables.

The correlations between physico-chemical variables and contaminant treatment efficiency obtained by the RDA model were generally coincident with the respective MRA and PCA models. Moreover, DO concentrations were found to be correlated with most contaminants treatment performance as well. In three tested ICW mesocosms, the average DO levels in influent and effluent decreased from 3.9 to 2.1 mg $l^{-1}$, 3.3 to 2.2 mg $l^{-1}$ and 3.3 to 1.9 mg $l^{-1}$ respectively. However, a gradual increase in DO concentrations can be observed with increasing soil depth. The relatively low DO concentrations in water column and soil were not able to provide necessary oxygen for the reduction of COD and to the conversion of ammonium to nitrite and to nitrate. Similarly, other studies also have showed a low rate of COD removal and $NH_3$-N conversion in CW systems due to oxygen shortage (Brix and Schierup, 1990; Cottinham *et al.*, 1999; Maltais-Landry *et al.*, 2007).

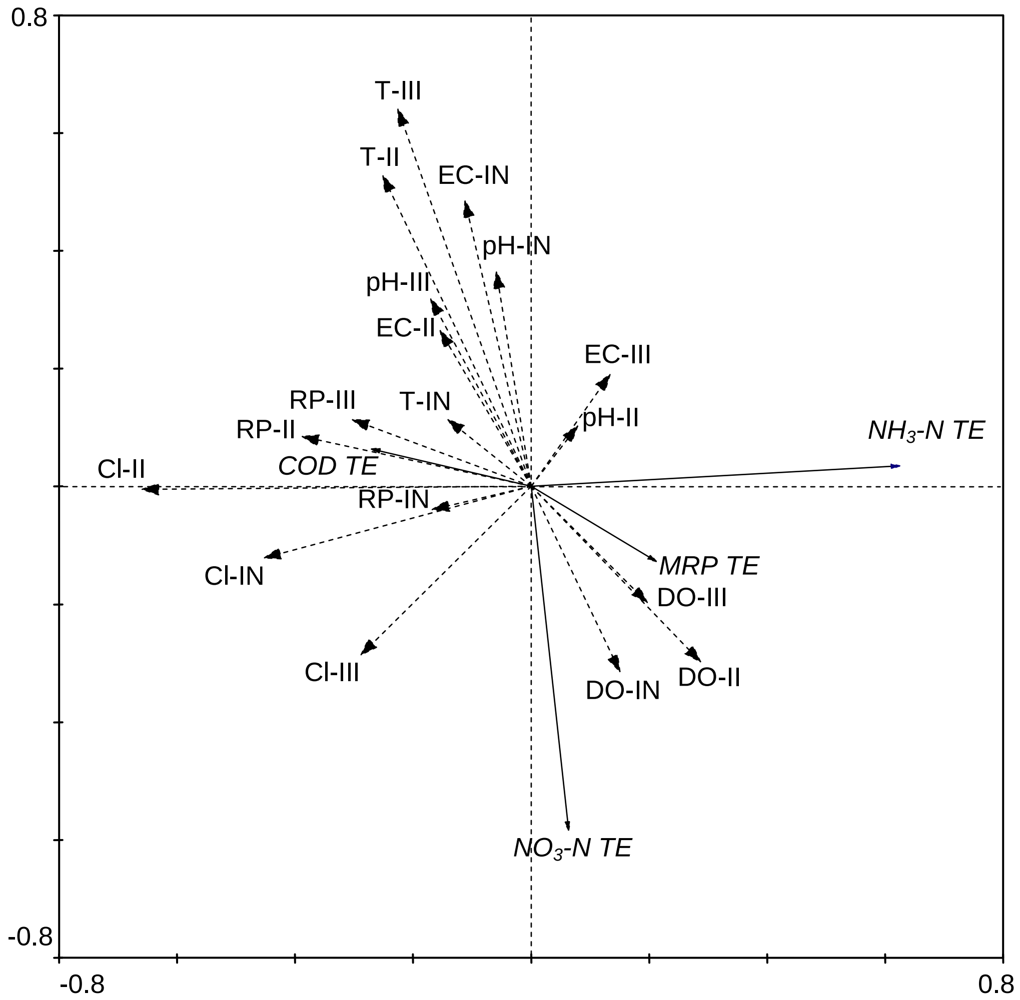



Figure 5-5 Ordination diagram for the redundancy analysis of mesocosm 2. The horizontal and vertical axes are the first and second RDA axes respectively. Physico-chemical variables (dotted lines): T, temperature (℃); EC, electrical conductivity (mS $cm^{-1}$); RP, redox potential (mV); DO, dissolved oxygen concentration (mg $l^{-1}$); Cl, chloride concentration (mg $l^{-1}$); Contaminant treatment efficiency (full lines): COD TE, chemical oxygen demand treatment efficiency (%); $NH_3$-N TE, ammonia-nitrogen treatment efficiency (%); $NO_3$-N TE, nitrate-nitrogen treatment efficiency (%); MRP TE, molybdate reactive phosphorus treatment efficiency (%); IN, influent; II, sampling point II; III, sampling point III.

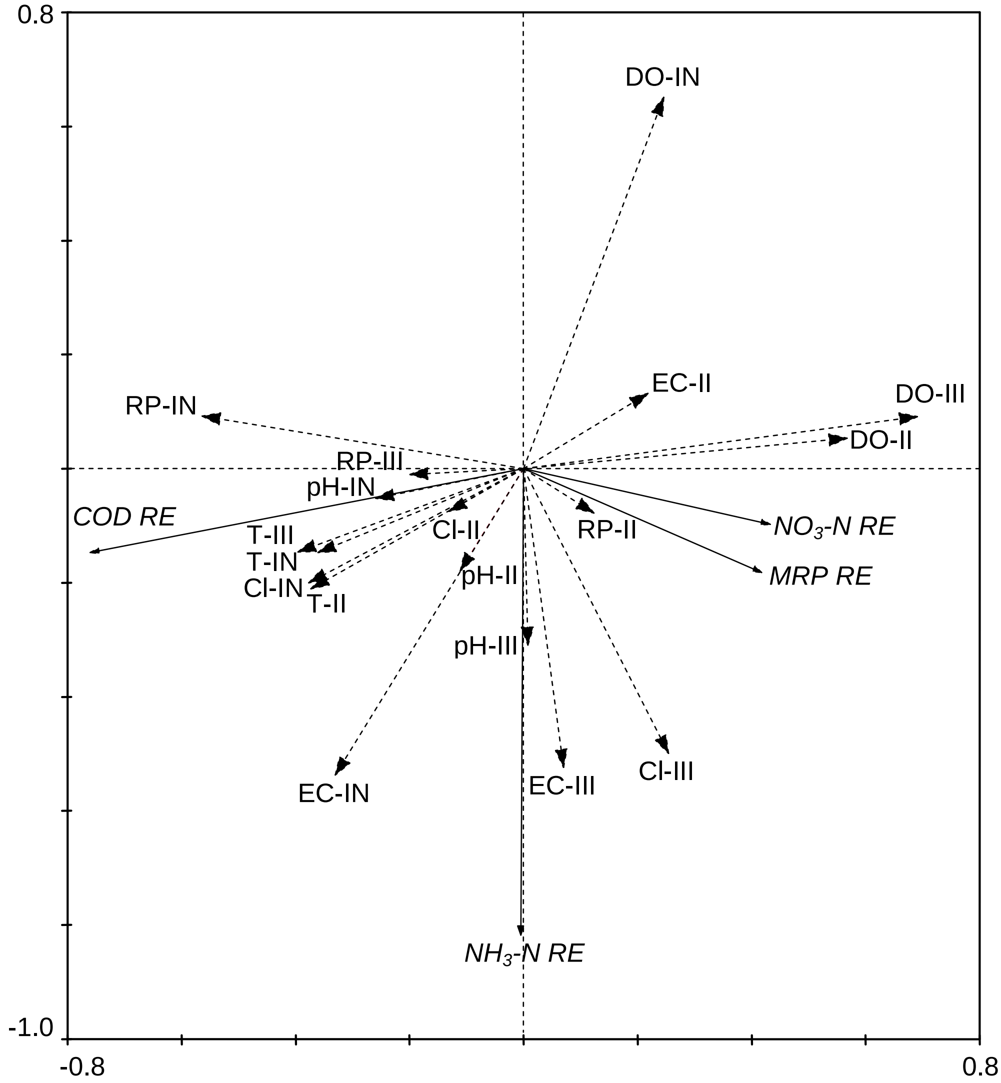



Figure 5-6 Ordination diagram for the redundancy analysis of mesocosm 3. The horizontal and vertical axes are the first and second RDA axes respectively. Physico-chemical variables (dotted lines): T, temperature (℃); EC, electrical conductivity (mS $cm^{-1}$); RP, redox potential (mV); DO, dissolved oxygen concentration (mg $l^{-1}$); Cl, chloride concentration (mg $l^{-1}$); Contaminant treatment efficiency (full lines): COD TE, chemical oxygen demand treatment efficiency (%); $NH_3$-N TE, ammonia-nitrogen treatment efficiency (%); $NO_3$-N TE, nitrate-nitrogen treatment efficiency (%); MRP TE, molybdate reactive phosphorus treatment efficiency (%); IN, influent; II, sampling point II; III, sampling point III.

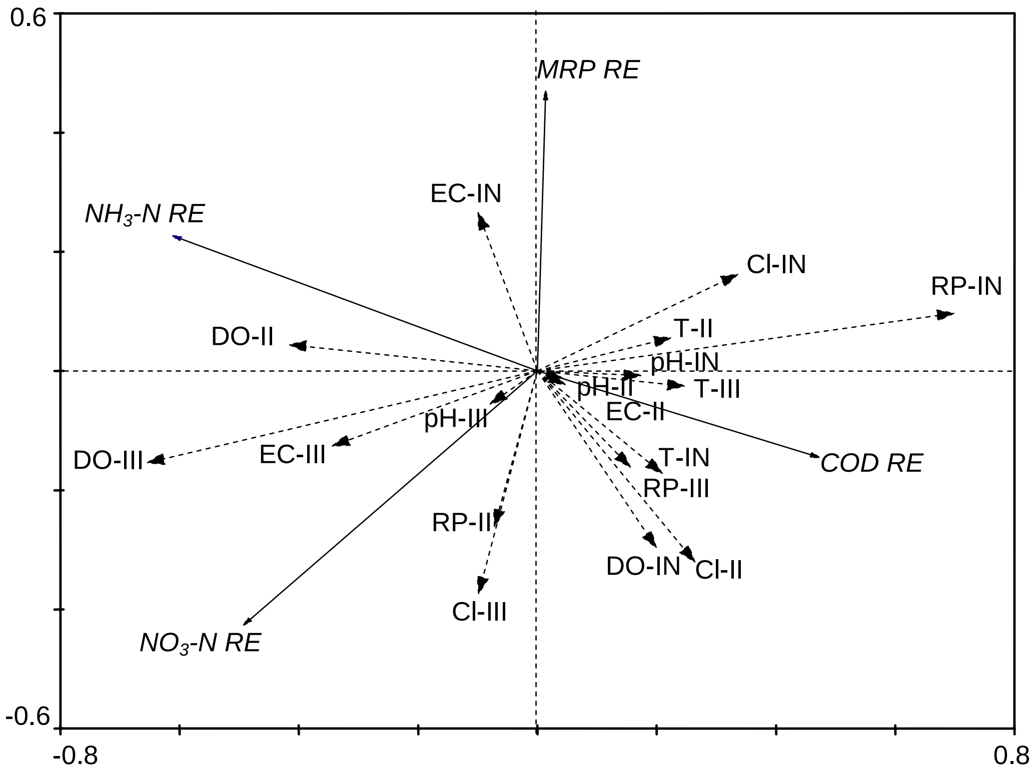


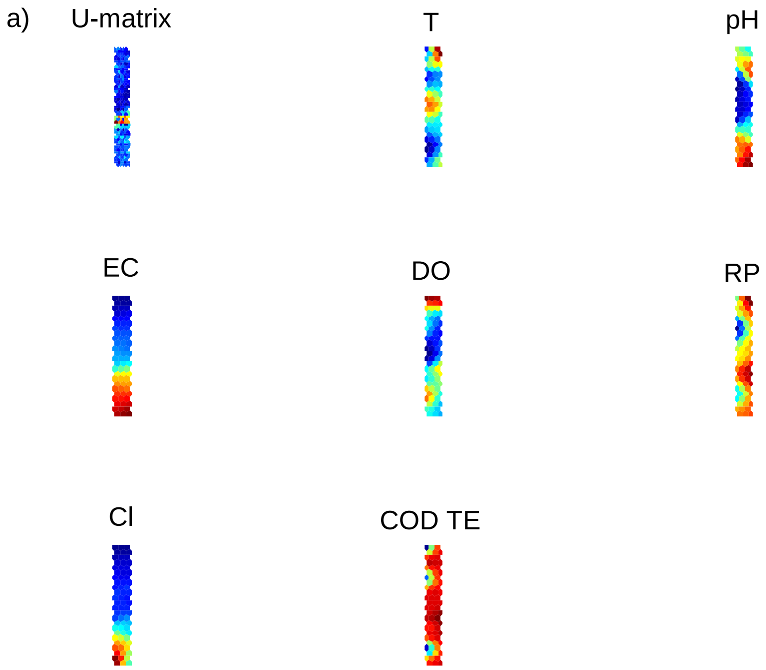

Figure 5-7 Ordination diagram for the redundancy analysis of mesocosm 4. The horizontal and vertical axes are the first and second RDA axes respectively. Physico-chemical variables (dotted lines): T, temperature (℃); EC, electrical conductivity (mS $cm^{-1}$); RP, redox potential (mV); DO, dissolved oxygen concentration (mg $l^{-1}$); Cl, chloride concentration (mg $l^{-1}$); Contaminant treatment efficiency (full lines): COD TE, chemical oxygen demand treatment efficiency (%); $NH_3$-N TE, ammonia-nitrogen treatment efficiency (%); $NO_3$-N TE, nitrate-nitrogen treatment efficiency (%); MRP TE, molybdate reactive phosphorus treatment efficiency (%); IN, influent; II, sampling point II; III, sampling point III.

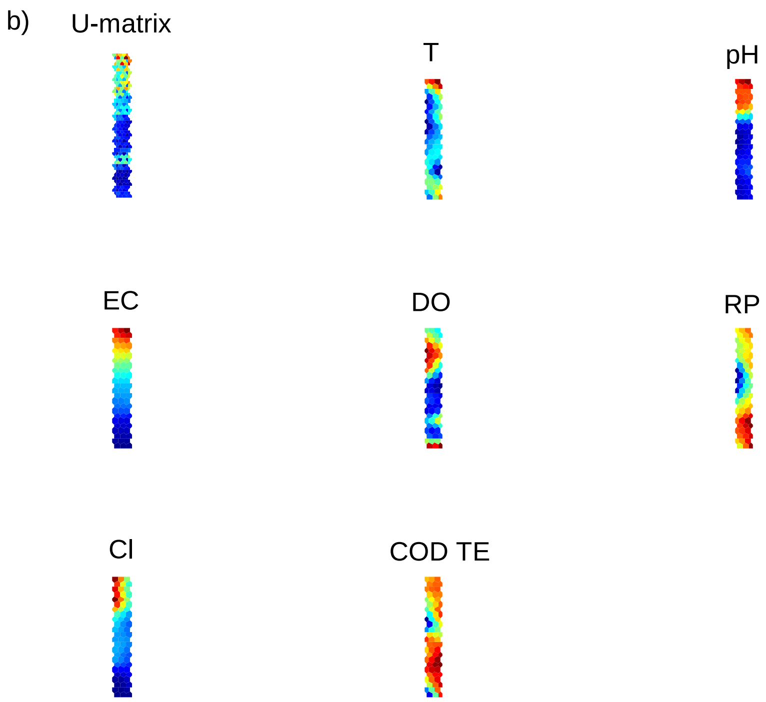
Tao *et al.* (2010) reported that the nitrification and organic matter decomposition were enhanced within an integrated vertical-flow constructed wetland by providing artificial aeration. Sonsa *et al.* (2011) also highlighted the role of oxygen as a main factor regulating contaminant removal efficiency in pilot-scale vertical constructed wetlands. In addition, oxygen availability might also enhance

MRP treatment efficiency. It is often believed that higher DO levels could prevent P release from the substrate (Faithful, 1996; Kim *et al.*, 2010).

### 5.8.5 Self organizing map

The relationships between COD, $NH_3$-N, $NO_3$-N and MRP treatment efficiencies with environmental parameters for mesocosm 2 can be visualized from component planes. As illustrated in Fig. 5-8a, the COD treatment efficiency is linked to RP values based on the visual comparison of the maps for parameters. This finding was consistent with the results obtained by previous models. However, there wasn't any obvious cluster that would visibly link the physico-chemical parameters to $NH_3$-N, $NO_3$-N and MRP treatment performances. In the case of mesocosms 3 and 4, the component planes in Figs. 5-8b and 5-8c also demonstrate a resemblance of the colouring patterns between COD treatment efficiency and RP value. Furthermore, as shown in Figs. 5-10b and 5-10c, the high-value and low-value areas in the component planes were almost opposite for $NO_3$-N treatment efficiencies and temperature values, which might indicate the existence of negative correlation between them. However, no strong correlation has been identified between particular environmental parameters and the treatment efficiencies of $NH_3$-N and MRP.


a)
U-matrix
T
pH
EC
DO
RP
Cl
COD TE


b)
U-matrix
T
pH
EC
DO
RP
Cl
COD TE

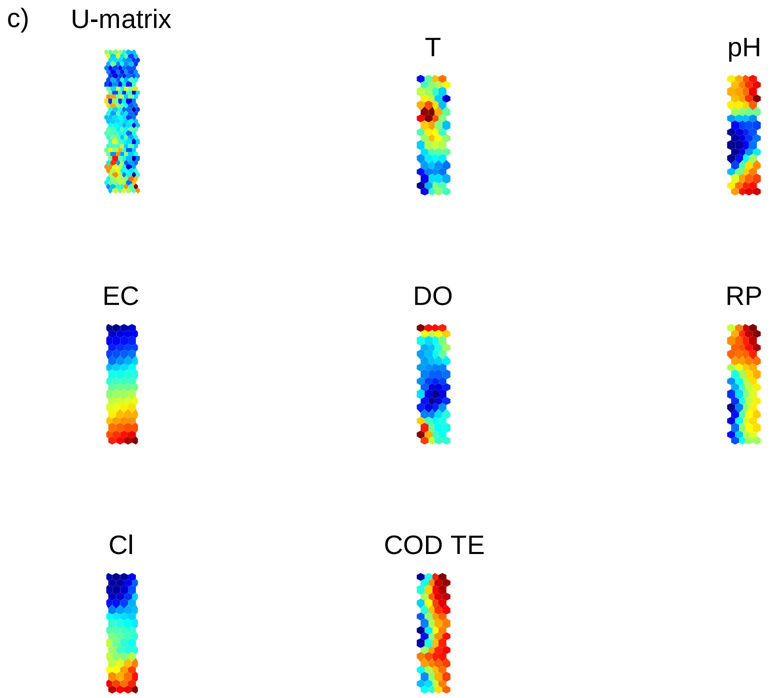
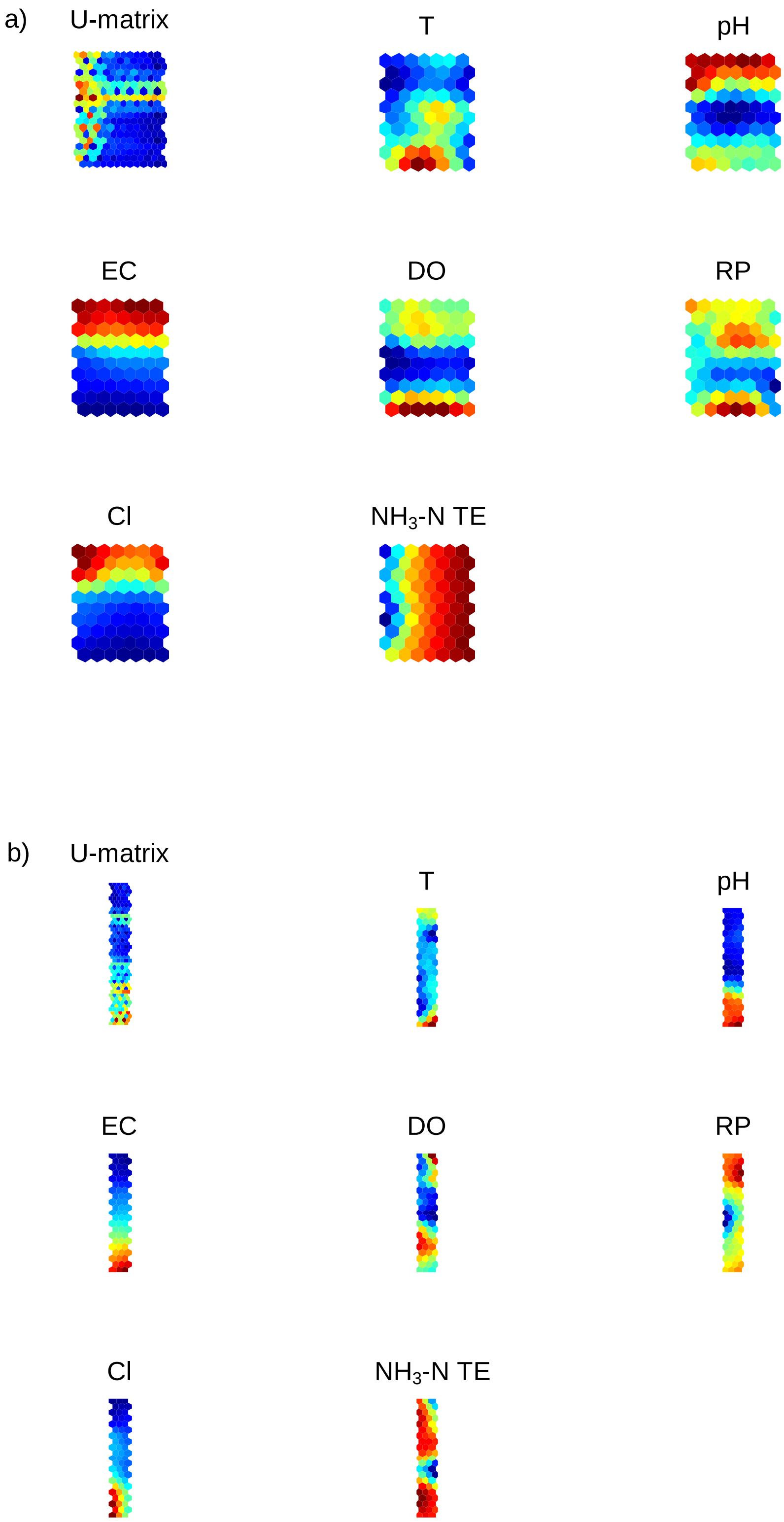



Figure 5-8 Component planes of the self-organizing map for chemical oxygen demand – visualization of the relationship between physico-chemical parameters and chemical oxygen demand treatment efficiency: a) mesocosm 2; b) mesocosm 3; c) mesocosm 4. T, temperature (℃); EC, electrical conductivity (mS $cm^{-1}$); DO, dissolved oxygen concentration (mg $l^{-1}$); RP, redox potential (mV); Cl, chloride concentration (mg $l^{-1}$); COD TE, chemical oxygen demand treatment efficiency (%).


a)
U-matrix
T
pH
EC
DO
RP
Cl
NH3-N TE
b)
U-matrix
T
pH
EC
DO
RP
Cl
NH3-N TE

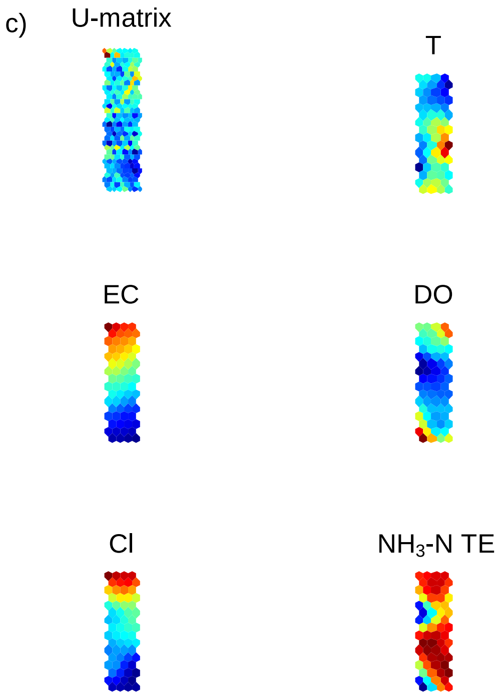
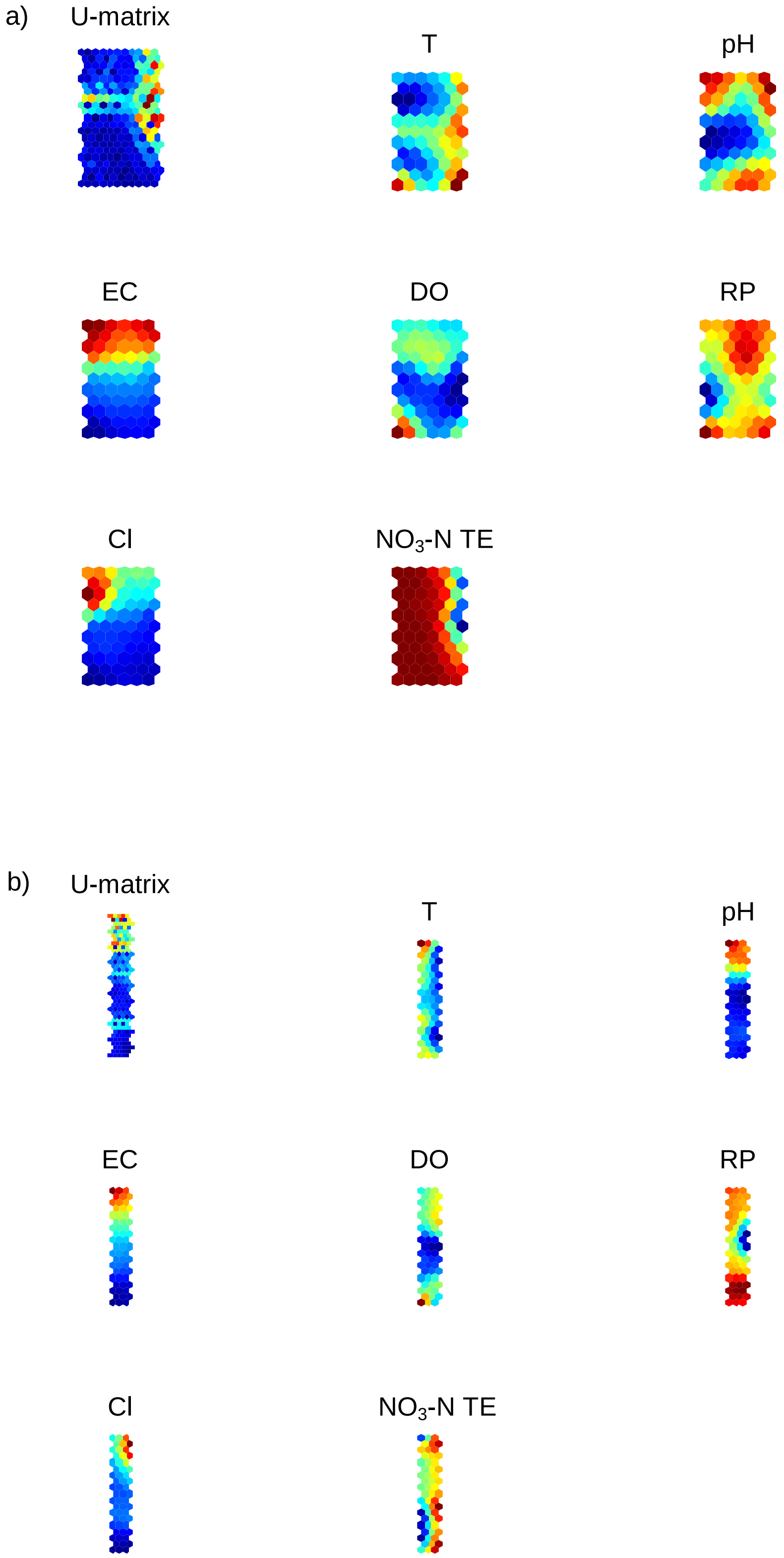



Figure 5-9 Component planes of the self-organizing map for ammonia-nitrogen – visualization of the relationship between physical-chemical parameters and ammonia-nitrogen treatment efficiency: a) mesocosm 2; b) mesocosm 3; c) mesocosm 4. T, temperature (℃); EC, electrical conductivity (mS $cm^{-1}$); DO, dissolved oxygen concentration (mg $l^{-1}$); RP, redox potential (mV); Cl, chloride concentration (mg $l^{-1}$); $NH_3$-N TE, chemical oxygen demand treatment efficiency (%).


a)
U-matrix
T
pH
EC
DO
RP
Cl
NO3-N TE
b)
U-matrix
T
pH
EC
DO
RP
Cl
NO3-N TE

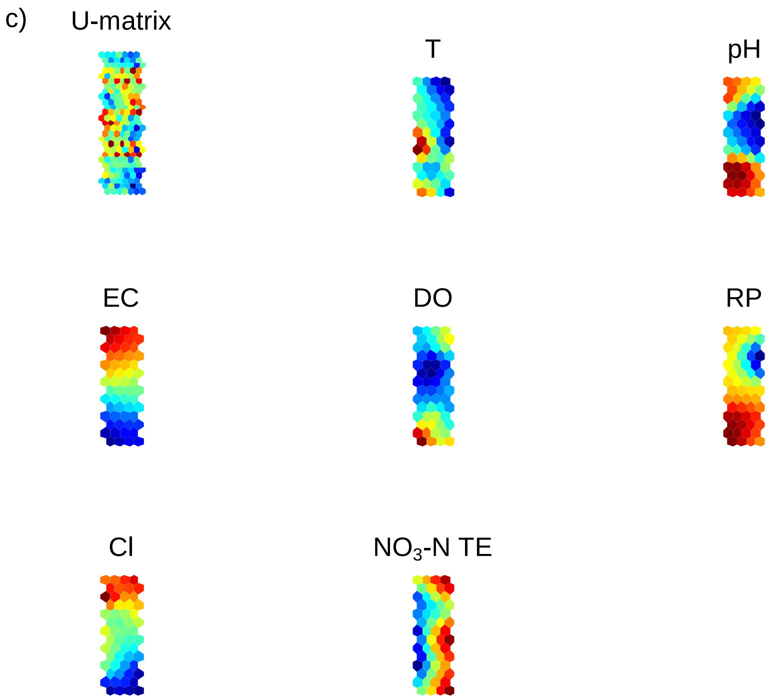
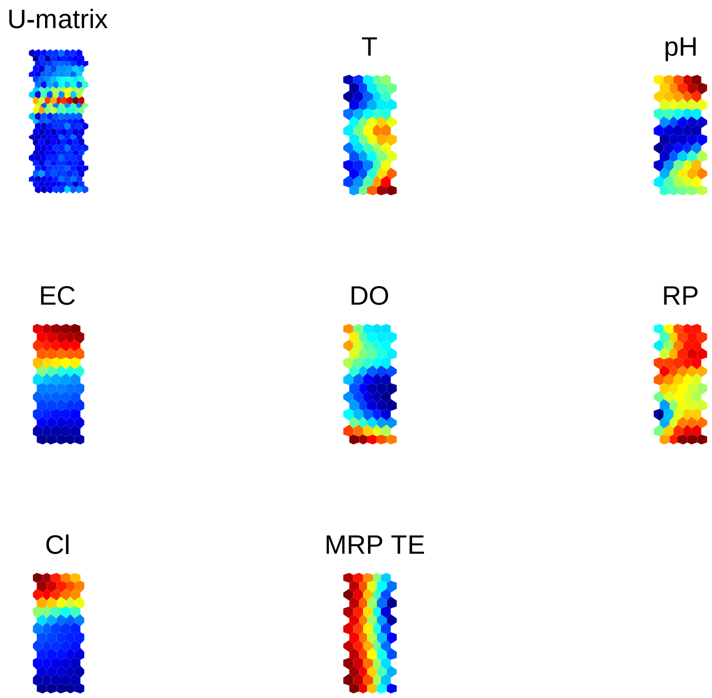
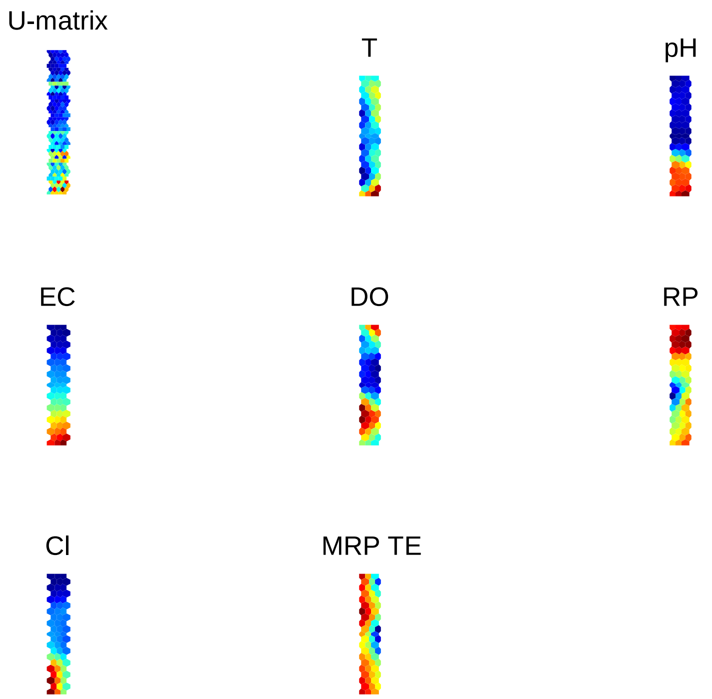



Figure 5-10 Component planes of the self-organizing map for nitrate-nitrogen – visualization of the relationship between physico-chemical parameters and nitrate-nitrogen treatment efficiency: a) mesocosm 2; b) mesocosm 3; c) mesocosm 4. T, temperature (°C); EC, electrical conductivity (mS $cm^{-1}$); DO, dissolved oxygen concentration (mg $l^{-1}$); RP, redox potential (mV); Cl, chloride concentration (mg $l^{-1}$); $NO_3$-N TE, nitrate-nitrogen treatment efficiency (%).

a)




b)



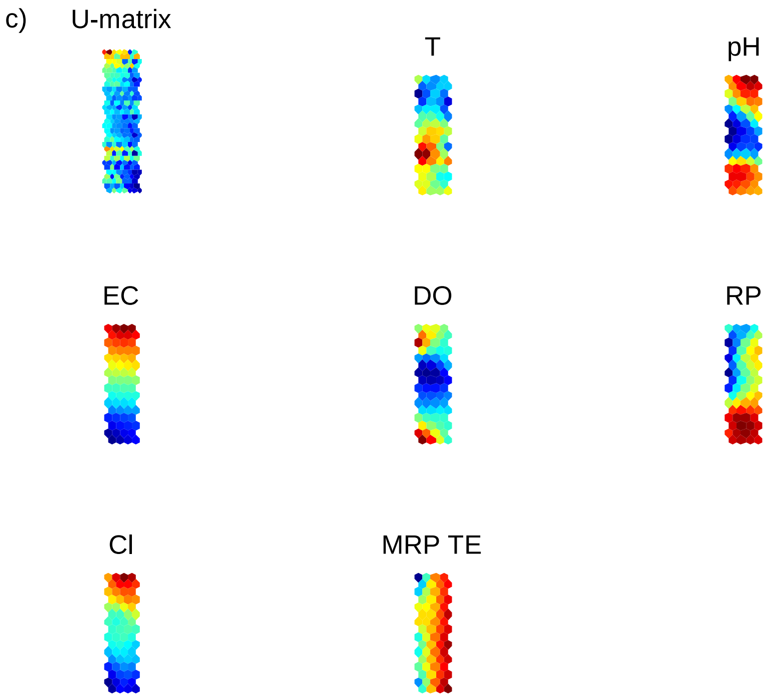



Figure 5-11 Component planes of the self-organizing map for molybdate reactive phosphorus – visualization of the relationship between physico-chemical parameters and molybdate reactive phosphorus treatment efficiency: a) mesocosm 2; b) mesocosm 3; c) mesocosm 4. T, temperature (°C); EC, electrical conductivity (mS $cm^{-1}$); DO, dissolved oxygen concentration (mg $l^{-1}$); RP, redox potential (mV); Cl, chloride concentration (mg $l^{-1}$); $NO_3$-N TE, nitrate-nitrogen treatment efficiency (%).

### 5.8.6 Influence of parameters on treatment performance in integrated constructed wetlands

In spite of the inconsistent results obtained from four selected statistical models, they were not significantly contradictory and the same variables have been highlighted considering the treatment efficiency of a certain contaminant. This statistical coincidence indicates the reliability of experimental data and analysis results. Based on previous research, it has been proved that physico-chemical parameters play important roles in the treatment of nutrients and organic matter in CWs, such as aerobic BOD degradation, microbial nitrification and denitrification. The above results are valuable for better understanding of factors that influence the key wetland processes.

The multiple regression models showed that there was significant linear relationship between RP values with COD treatment efficiency in three tested ICW mesocosms. Three advanced statistical tools (PCA, RDA, and SOM) were subsequently employed to carry out further investigations of subtle correlations. Findings show that Cl concentration and EC value can be linked to the treatment efficiencies of COD, $NH_3$-N, and MRP. Furthermore, RP value was found to connect to $NH_3$-N treatment performance as well. DO concentration contributed to the performance of COD, $NH_3$-N and MRP. Moreover, the temperature was attributed to the treatment of COD, $NO_3$-N and MRP even though only a narrow range has been recorded due to controlled conditions. The key findings associated with four performed analysis were similar. However, this is likely to be a coincidence related to this particular mesocosm based study.

## 5.9 Validation of estimation model

As PCA and RDA were not able to provide numerical outputs, and only few equations were reliable ($R^2 > 0.5$) according to multiple regression analysis, SOM was thus chosen as the predicting model to estimate contaminant removal performance of ICWs. The validation of SOM model was performed by using physico-chemical parameters and treatment efficiencies (COD, $NH_3$-N, $NO_3$-N and MRP) from mesocosms 3 and 4. MRA has not been selected because only the equations with $R^2$ value above 0.5 are acceptable. Considering the results obtained this study, it narrows down the application MRA. On the other hand, PCA and RDA are not included because they were not able to provide numerical estimations as an output.

As to estimate the treatment performance of an ICW system efficiently and cost-effectively, the measurement of selected predictor variable is supposed to be quick and convenient. Based on above statistical analysis results, EC and RP values were selected as input variables to estimate COD treatment efficiencies. Cl concentration and RP value were used to estimate $NH_3$-N treatment performance. DO concentration and RP value were identified to predict $NO_3$-N removal. Last but not the least, MRP treatment efficiency was predicted by DO concentration and EC value.

In order to validate SOM model, the dataset from mesocosms 3 and 4 were mixed in a random order, and then the new dataset was split into training and test sets. The input data with an odd row number was selected as training set, and the data with an even row number was combined as test set. This data arrangement would prevent the bias caused by experimental time. The SOM model was first trained with corresponding training datasets. Then the depleted data subset (test subset) was presented to the SOM to identify its best matching unit (BMU). The prediction values were obtained through checking their values in the BMU and then targeting the respective values in training set. After this matching process, the model was subsequently verified with the testing data subset (Fig. 5-12). For example, when predicting COD treatment performance, the COD efficiencies in test dataset were deleted and seen as missing values. After running the simulation, the predicted values obtained were compared with the actual COD treatment efficiency.

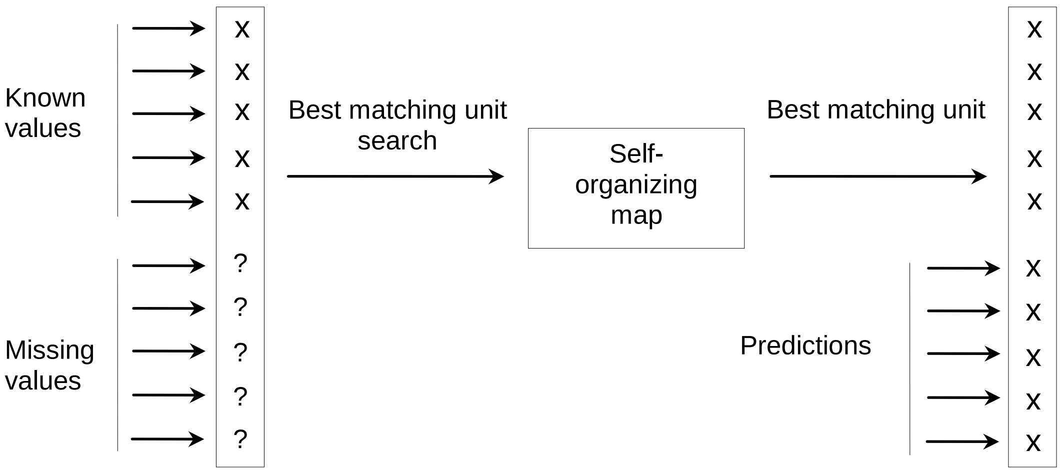



Figure 5-12 Predicting missing values of the dataset using the self organizing map.

The SOM modelling performance in predicting COD, $NH_3$-N, $NO_3$-N and MRP treatment efficiencies are shown in Fig. 5-13. Table 5-12 shows both the correlation coefficient between the measured and predicted values as well as the mean absolute scaled error (MASE) of prediction. In general, the SOM outputs tended to correctly reproduce the peaks and troughs in the actual data. In addition, the MASE values were relatively low (less than 0.5) indicating a relatively high accuracy in predication. However, compared to previous similar SOM applications performed by Lee and Scholz (2006), Rustum and Adeloye (2007), and Zhang *et al.* (2008), the correlation coefficients were relatively low. This suggests that the type of vegetation may potentially impact the contaminant treatment performance of mesocosms 3 and 4. This influence will be discussed in next section.

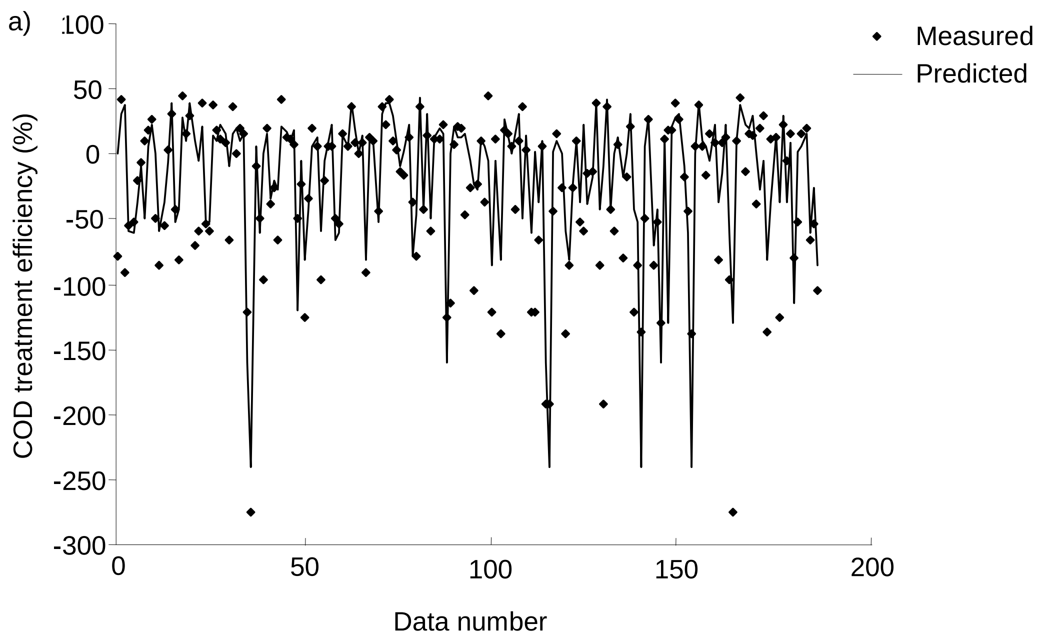
Table 5-12 The performance of the self-organizing map (SOM) to predict treatment efficiencies of chemical oxygen demand, ammonia-nitrogen, nitrate-nitrogen and molybdate reactive phosphorous.

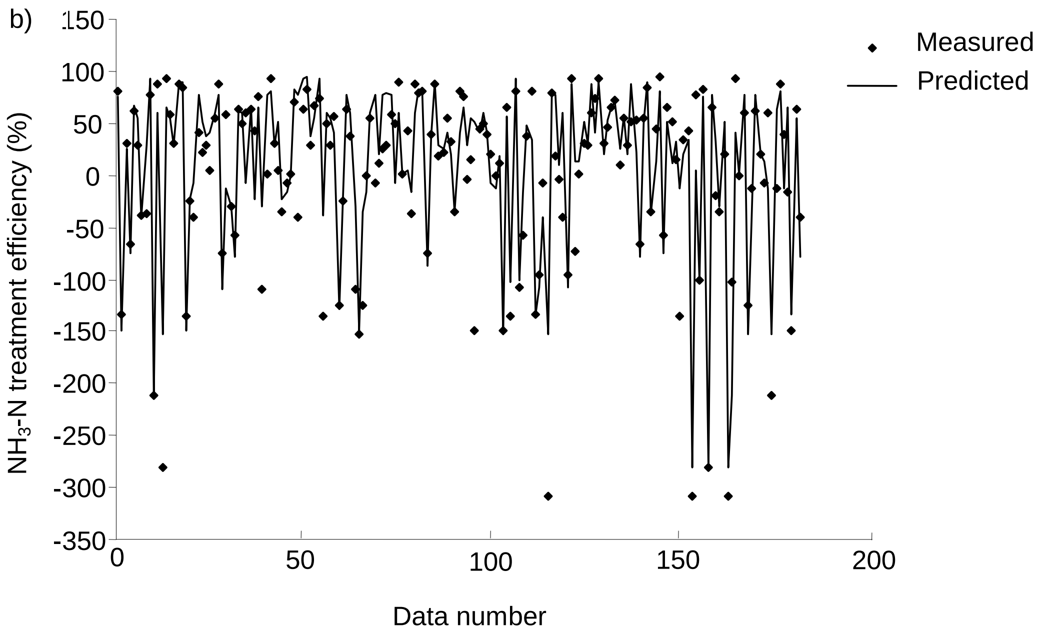
| TE (%) | n | MASE[a] | Correlation coefficient $R$ |
|---|---|---|---|
| Chemical oxygen demand | 184 | 0.44 | 0.756 |
| Ammonia-nitrogen | 171 | 0.30 | 0.883 |
| Nitrate-nitrogen | 133 | 0.38 | 0.746 |
| Molybdate reactive phosphorus | 172 | 0.35 | 0.792 |

n, number of data entry, TE, treatment efficiency

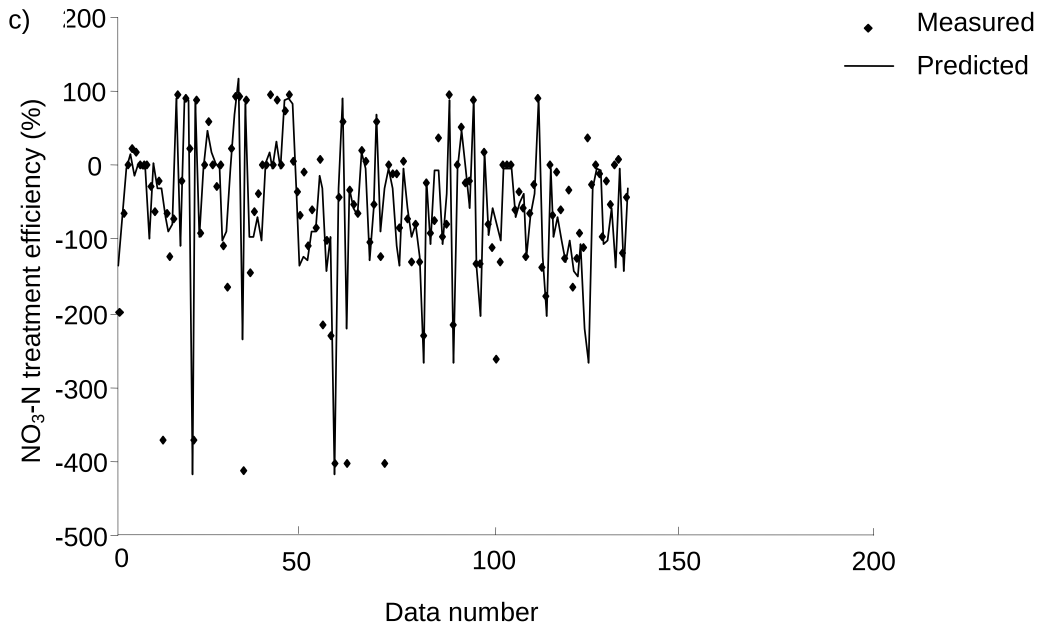
Note: [a] Mean absolute scaled error (MASE) = $\frac{1}{n}\sum_{i=1}^{n}|m_i - p_i| / (\frac{1}{n-1}\sum_{i=1}^{n}|m_i - m_{i-1}|)$

$m_i$ = measured values; $p_i$ = predicted values; and $n$ = number of data entries.





b)
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
NH3-N treatment efficiency (%)
0
50
100
150
200
Data number
Measured
Predicted

c)
200
100
0
-100
-200
-300
-400
-500
NO3-N treatment efficiency (%)
0
50
100
150
200
Data number
Measured
Predicted

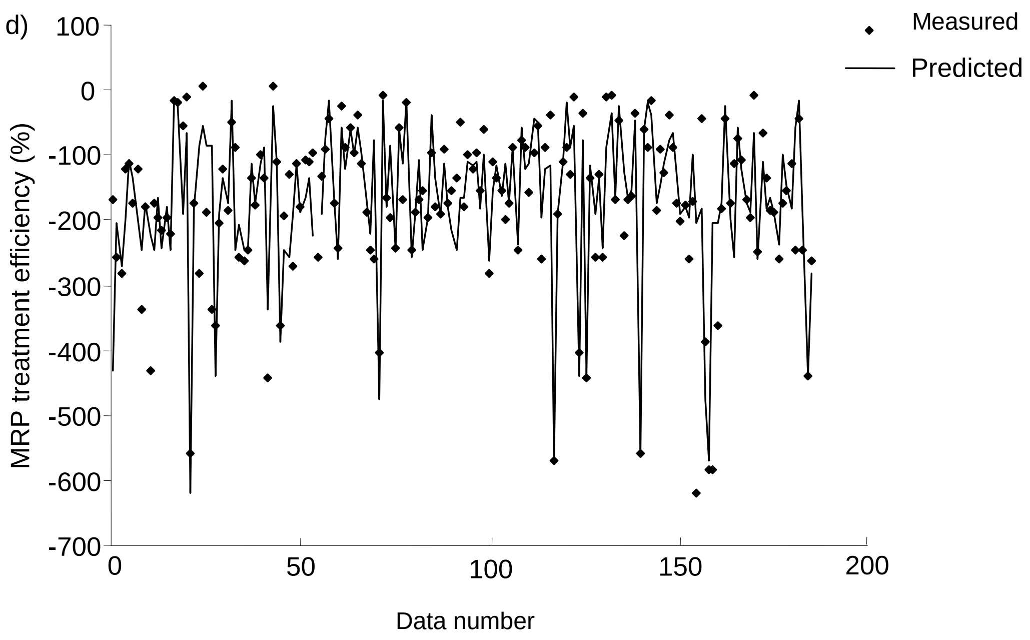



Figure 5-13 Comparison of actual and predicted contaminant treatment efficiency: a) chemical oxygen demand; b) ammonia-nitrogen; c) nitrate-nitrogen; d) molybdate reactive phosphorus. COD, chemical oxygen demand; $NH_3$-N, ammonia-nitrogen; $NO_3$-N, nitrate-nitrogen; MRP, molybdate reactive phosphorus.

## *5.10 Effects of vegetation on contaminant treatment*

Based on literature review, vegetation plays significant roles in CW systems which include providing a substrate for microorganisms, regulating influent flow to created optimal conditions for settlement of suspended solids, uptaking and/or storing nutrients from wastewater, improving hydraulic conductivity of soils, and stabilizing accumulated sediment and substrate.

In experimental period 1, the differences were statistically significant on all sample dates for the comparison of $NH_3$-N (paired t-test, $p$ = 0.00002) and MRP (paired t-test, $p$ = 0.008) treatment efficiencies in two domestic wastewater mesocosms. This suggests that *Phragmites australis* is more efficient than *Agrostis stolonifera* in the prevention of contaminant release. In contrast, there is no significant difference between treatment performances of COD and $NO_3$-N within respective mesocosms. Results of experimental period 2 also indicated that wetland vegetation could influence treatment efficiency of $NH_3$-N. This resulted in lower levels of $NH_3$-N in mesocosm 3 than those in mesocosm 4 (paired t-test, $p = 0.008$). However, the links between wetland vegetation and other contaminants were not obvious. Although, as a whole, contaminants treatment efficiencies of two domestic wastewater mesocosms were not statistically different, the mesocosm planted with *Phragmites australis* performed better than the one planted with *Agrostis stolonifera* in both experimental periods.

There are two possible reasons to explain this finding. First, *Phragmites australis* produces an extensive root and rhizome system within sediment and substrate layers. In addition, it also possesses leaves and aerial stems. These characteristics result in better transportation of oxygen to deeper soils and stimulating organic matter decomposition, the growth of nitrifying bacteria, and the fixation of suspended particles (Brix, 1994). Second, *Agrostis stolonifera*, a typical type of floating vegetation, obtains nearly all nutrients from the water column, while *Phragmites australis* assimilate nutrients directly from the sediment. Considering this particular case, larger number of nutrient was accumulated in sediments rather than in the overlying water column, therefore, the function of the floating plant was generally limited.

Many researchers have tried to investigate the influence of wetland vegetation on the removal of nutrients and other organic matters in experimental and full-scale CW systems. Hijosa-Valsero *et al.* (2010) indicated CW configurations such as vegetation plant were able to impact the treatment performance of the system. They found that *Typha angustifolia* performed better than *Phragmites australis* to remove organic pollutants at the early stage of operation. Lai *et al.* (2011) found that different features of emergent plants have a close relationship with nutrient removal performance in small-scale wetlands. In addition, Gottaschall *et al.* (2007) suggested that *Typha latifolia* L. and *Typha angustifolia* L. might have capacity to store and remove total nitrogen and total phosphorus when influent nutrient loading was not rather high.

## 5.11 Infiltration

As shown in Fig. 4-1, an outlet valve was located on the base plate of each mesocosm to gauge the possibility of groundwater contamination by infiltration of the polluted water. However, no leachate was collected throughout both study periods. This can be explained by the presence of a compact bentonite clay layer, acting as an excellent barrier to prevent pollutants transferring to potential aquifers. Furthermore, biogeochemical processes are taking place within sediments. Some of these play an important role in, for instance, the clogging of the soil matrix, biomass accumulation, and/or biogas (i.e. methane) formation through soil microbes (Tokida *et al.*, 2005; Zhao *et al.*, 2009).

Evidence from full-scale ICW systems supports this finding. As the contaminated influent passes through the ICW system, the suspended matter settles on the soil surface and subsequently slows the infiltration of contaminants through the wetland cells (Mustafa *et al.*, 2009; Scholz, 2006). Moreover, the rearrangement of wetland soil and underlying geological formation also play important role in impending the infiltration of contaminants to groundwater (Mustafa *et al.*, 2009). A comparative study by Karanli *et al.* (2010) showed that there is very low filtration taking place in wetland cells at Glaslough ICW system. Dzakpasu *et al.* (2012) further reported that less than 0.5% of the influent contaminant loading to the first two cells was lost through infiltration in the ICW system.

## 5.12 Limitation

Although the findings are extremely encouraging, the limitations of this study such as mesocosms size, configuration and well-controlled experimental conditions should be considered before the obtained resulted are generalized to full-scale CW systems. In addition, there were some key factors such as realistic hydraulic conditions, weather, and water level fluctuation have not been emulated. However, it is still conceivable that in order to maintain and improve treatment performance in long-term operating ICW systems, attention must be paid to mature sediments and substrates.

Also, the applicability of the obtained statistical results is limited to CW systems with similar configuration and operational conditions. However, these results would provide information on elimination/release mechanisms inside CWs and would simplify wetland monitoring to optimize contaminant removal from farmyard runoff or domestic wastewater.

## 5.13 Summary

This chapter has shown potential release of nutrients and other contaminants from mature sediments. In both periods of experiment, the ICW mesocosms acted rather as nutrient and contaminant sources than sinks since accumulated contaminants remobilized when environmental and chemical conditions have changed. In addition, physico-chemical parameters and type of vegetation have been proven to affect the contaminant treatment efficiency. Although there is no diminution of overall treatment performance has been found in the representative full-scale ICW systems, the results still provide valuable warning hints regarding the decline of contaminant removal efficiency in long-term operating ICW systems.

# Chapter 6

# Impact of Hydraulic Loading Rate and Season on Water Contaminant Removal within Integrated Constructed Wetlands

## *6.1 Introduction*

This chapter investigates the impact of hydraulic rate (HLR) and seasonal temperature on contaminant removal within an integrated constructed wetland (ICW) treating domestic wastewater. It will cover following topics: Section 6.2 and Section 6.3 present the overall water quality improvement performance of the studied ICW system and ICW hydraulic characteristics, respectively. Section 6.4 presents the mass balance computation. Section 6.5 explores relationships between hydraulic loading rates and removal efficiencies. Section 6.5 assesses the impact of seasonal temperature on contaminant removal. The work I am describing in the following has been originally published as an article in Wetlands journal.

## 6.2 Overall performance of the integrated constructed wetland system

The mean influent and effluent concentrations and removal efficiencies of the water quality variables for Glaslough ICW site are presented in Table 6-1. The ICW system demonstrated effective contaminant treatment performances by removing (based on concentrations) approximately 98% biochemical oxygen demand (BOD), 92% chemical oxygen demand (COD), 95% molybdate reactive phosphorus (MRP), 95% total phoshphorus (TP), 97% ammonia-nitrogen ($NH_3$-N), 89% nitrate-nitrogen ($NO_3$-N), 96% total nitrogen (TN), and 96% total suspended solids (TSS) during the study period (May 2008 to December 2011).

Table 6-1 Wastewater quality variables and treatment efficiencies for integrated constructed wetland in Glaslough (Ireland) between May 2008 and December 2011.

| Variable | n | Influent | | Effluent | | TE |
|---|---|---|---|---|---|---|
| | | Mean | SD | Mean | SD | (%) |
| Biochemical oxygen demand (mg $l^{-1}$) | 168 | 334.72 | 148.98 | 5.89 | 5.50 | 98.24 |
| Chemical oxygen demand (mg $l^{-1}$) | 183 | 539.39 | 252.99 | 44.11 | 25.05 | 91.82 |
| Molybdate reactive phosphorus (mg $l^{-1}$) | 177 | 4.92 | 2.98 | 0.27 | 0.45 | 94.51 |
| Total phosphorus (mg $l^{-1}$) | 180 | 7.34 | 3.94 | 0.36 | 0.51 | 95.10 |
| Ammonia-nitrogen (mg $l^{-1}$) | 185 | 42.59 | 18.41 | 1.26 | 2.35 | 97.04 |
| Nitrate-nitrogen (mg $l^{-1}$) | 173 | 3.79 | 3.46 | 0.41 | 0.29 | 89.18 |
| Total nitrogen (mg $l^{-1}$) | 114 | 60.93 | 28.28 | 2.58 | 2.41 | 95.77 |
| Total suspended solids (mg $l^{-1}$) | 170 | 194.95 | 152.03 | 7.62 | 14.98 | 96.09 |

n, sample number; SD, standard deviation; TE, treatment efficiency.

The removal efficiencies for COD, $NH_3$-N, MRP and TP slightly decreased (variation ranges from approximately 4% to 11%) over the study period, whereas reduction for $NO_3$-N showed a drastic decrease (24%) between 2008 and 2011

(Table 6-2). This indicated that treatment efficiency of the ICW system could decline with wetland age due to accumulated impacts of contaminants where sediment becomes saturated. This result agrees with the finding suggested by the mesocosm study present in the previous chapter.

Table 6-2 Comparison of annual treatment efficiencies for integrated constructed wetland in Glaslough between 2008 and 2011. Data are averaged percent removal (and sample number).

| Treatment efficiency (%) | 2008 | 2009 | 2010 | 2011 |
|---|---|---|---|---|
| Biochemical oxygen demand | 98.83 (43) | 98.54 (61) | 96.68 (32) | 98.06 (31) |
| Chemical oxygen demand | 94.04 (45) | 93.31 (66) | 86.73 (34) | 88.76 (38) |
| Molybdate reactive phosphorus | 99.14 (44) | 97.43 (64) | 92.98 (34) | 88.17 (34) |
| Total phosphorus | 98.71 (44) | 97.40 (66) | 93.55 (33) | 88.52 (37) |
| Ammonia-nitrogen | 99.38 (46) | 97.97 (66) | 95.40 (35) | 95.10 (38) |
| Nitrate-nitrogen | 93.01 (46) | 93.85 (57) | 79.05 (35) | 70.79 (35) |
| Total nitrogen | 95.95 (14) | 96.04 (41) | 95.38 (29) | 95.80 (30) |
| Total suspended solids | 95.60 (46) | 98.11 (61) | 94.84 (37) | 93.14 (36) |

## *6.3 Hydraulic characteristics*

HLR and HRT are the most significant operational factors that affect treatment performance of a CW system (Frazer-Williams, 2010). Many studies have been carried out with respect to the relationship between HLR and contaminant removal efficiency. It was suggested that higher HLR may cause decrease in the reduction of contaminants (García *et al.*, 2004; Lin *et al.*, 2005; Tao *et al.*, 2006). The HRT, HLR, and mean daily flow rates for each cell, and the integrated system as a whole are presented in Table 6-3. In general, surface flows from the sludge ponds and precipitation were assumed to be the input, while evapotranspiration and wastewater infiltration were assumed to be lost water. Precipitation and evapotranspiration were measured as the amount of water entering or evaporating from a wetland cell surface. Compared to conventional CWs, the Glaslough ICW system showed relatively low hydraulic loading rates (0.54 cm $d^{-1}$) and long hydraulic retention times (100 d) due to rather large wetland size. Therefore, the results in this study do not necessarily represent the general performances of other CW systems.

Table 6-3 Dimensions, mean hydraulic retention time (HRT), hydraulic loading rate (HLR) and daily flow rate for integrated constructed wetland system in Glaslough.

| ICW section | Area ($m^2$) | Depth (m) | Volume ($m^3$) | Inflow ($m^3$ $d^{-1}$) | | Outflow ($m^3$ $d^{-1}$) | | HRT (d) | HLR (cm $d^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Mean | SD | Mean | SD | | |
| Cell 1 | 4664 | 0.42 | 1958.9 | 104.30 | 73.85 | 110.59 | 64.95 | 19 | 2.46 |
| Cell 2 | 4500 | 0.38 | 1710.0 | 110.59 | 64.95 | 108.83 | 74.83 | 15 | 2.62 |
| Cell 3 | 12660 | 0.32 | 4051.2 | 113.09 | 74.16 | 124.14 | 102.25 | 36 | 1.09 |
| Cell 4 | 9170 | 0.36 | 3301.2 | 124.09 | 102.25 | 137.83 | 122.56 | 27 | 1.56 |
| Cell 5 | 1460 | 0.29 | 423.4 | 137.83 | 122.56 | 152.00 | 174.26 | 3 | 9.65 |
| System | 32454 | N.A. | 11444.7 | 104.30 | 73.85 | 152.00 | 174.26 | 100 | 0.54 |

SD, standard deviation; HRT, hydraulic retention time; HLR, hydraulic loading rate; N.A., not applicable.

## *6.4 Water budget*

In this study, some water transfer mechanisms included in Eq. 2-2 were not encountered due to CW design and site location. Thus, the water budget of this particular ICW system was simply calculated by using following equation:

$$\Delta V = Q_{in} + P - (Q_{out} + E + I) \quad [6\text{-}1]$$

where $\Delta V$ is net change in volume ($m^3\ d^{-1}$), $Q_{in}$ is inflow to system ($m^3\ d^{-1}$), $P$ is precipitation ($m^3\ d^{-1}$), $Q_{out}$ is outflow from system ($m^3\ d^{-1}$), $E$ is evapotranspiration ($m^3\ d^{-1}$), $I$ is infiltration ($m^3\ d^{-1}$).

Rainfall was monitored at the on-site weather station. However, three major disruptions (October 13, 2009 to January 9, 2010; May 11, 2009 to March 17, 2011; and May 12, 2011 to July 21, 2011) were recorded over the study period which caused the discontinuity and gaps in meteorological data and created severe handicaps in water budget analysis. In this case, data collected at the weather station located in Mullingar were used to estimate missing climatic data (Freemeteo, 2012). For instance, where rainfall data are missing, an estimate value will be obtained by using the data from Mullingar's weather station and the linear relationship between rainfall datasets of two weather stations.

The reference evapotranspiration ($ET$) was computed from meteorological data using FAO Penman-Monteith method (Allen *et al.*, 2004). The method is expressed by the following equation:

$$ET = \frac{0.408 \times \Delta \times (R_n - G) + \gamma \times \frac{900}{T + 273} \times u_2 \times (e_s - e_a)}{\Delta + \gamma \times (1 + 0.34 u_2)} \qquad [6\text{-}2]$$

Where $\Delta$ is slope vapour pressure curve (kPa ℃$^{-1}$), $R_n$ is net radiation at the crop surface (MJ $m^{-2}\ d^{-1}$), $G$ is soil heat flux density (MJ $m^{-2}\ d^{-1}$), $\gamma$ is psychrometric (kPa ℃$^{-1}$), $T$ is mean daily air temperature at 2 m height (℃), $u_2$ is wind speed at 2 m height ($m\ s^{-1}$), $e_s$ is saturation vapour pressure (kPa), $e_a$ is actual vapour pressure (kPa), and $(e_s - e_a)$ is saturation vapour pressure deficit (kPa). Wind speed at 2 m height was assumed to be 5 m $s^{-1}$ according to Met Éireann (2012). Radiation data was derived from the air temperature difference and humidity data was estimated from daily minimum air temperature according to Allen *et al.* (2004). The missing *E* data were replaced by the adjusted *ET* calculated from meteorological data. The missing values replacement process is the same as the estimation of missing rainfall data.

Contaminant inflow and outflow loading rates were calculated as follows:

$$L_{in} = \frac{Q_{in} \times C_{in}}{A} \quad [6\text{-}3]$$

where $L_{in}$ is inflow loading rate (g $d^{-1}$ $m^{-2}$), $C_{in}$ is inflow concentration of contaminant (g $m^{-3}$), and *A* is surface area of wetland cells ($m^2$).

$$L_{out} = \frac{Q_{out} \times C_{out}}{A} \quad [6\text{-}4]$$

where $L_{out}$ is outflow loading rate (g $d^{-1}$ $m^{-2}$), $Q_{out}$ is daily outflow from system ($m^3$ $d^{-1}$), $C_{out}$ is outflow concentration of contaminant (g $m^{-3}$).

Removal efficiency of contaminants by ICW was calculated as follow:

$$RE = \frac{(C_{in} - C_{out})}{C_{in}} \times 100\% \quad [6\text{-}5]$$

Contaminant mass removal efficiency, in percentage, was calculated using Eq. 6-6.

$$RE_{mass} = \frac{\left(C_{in} \times Q_{in} - C_{out} \times Q_{out}\right)}{C_i \times Q_{in}} \times 100\% \qquad [6\text{-}6]$$

Hydraulic retention time (HRT) was calculated as:

$$HRT = \frac{V}{Q_{ave}} \qquad [6\text{-}7]$$

Where $V$ is the water volume of the wetland ($m^3$), and $Q_{ave}$ is the mean volumetric flow rate of water through the wetland ($m^3\ d^{-1}$).

Hydraulic loading rate (HLR) was computed with:

$$HLR = \frac{Q_{actual} \times 100}{A} \qquad [6\text{-}8]$$

Where $Q_{actual}$ is the actual flow through the wetland was calculated by taking account of inflow, precipitation, evapotranspiration, and infiltration given as:

$$Q_{actual} = Q_{in} + P - (E + I) \qquad [6\text{-}9]$$

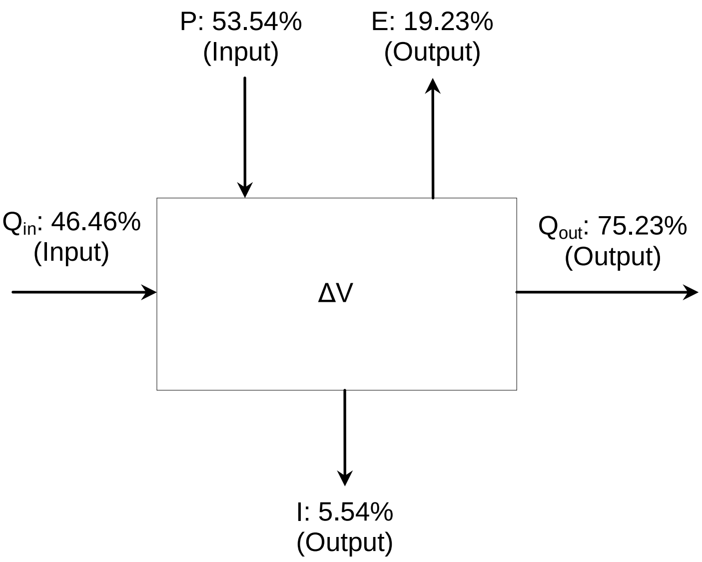


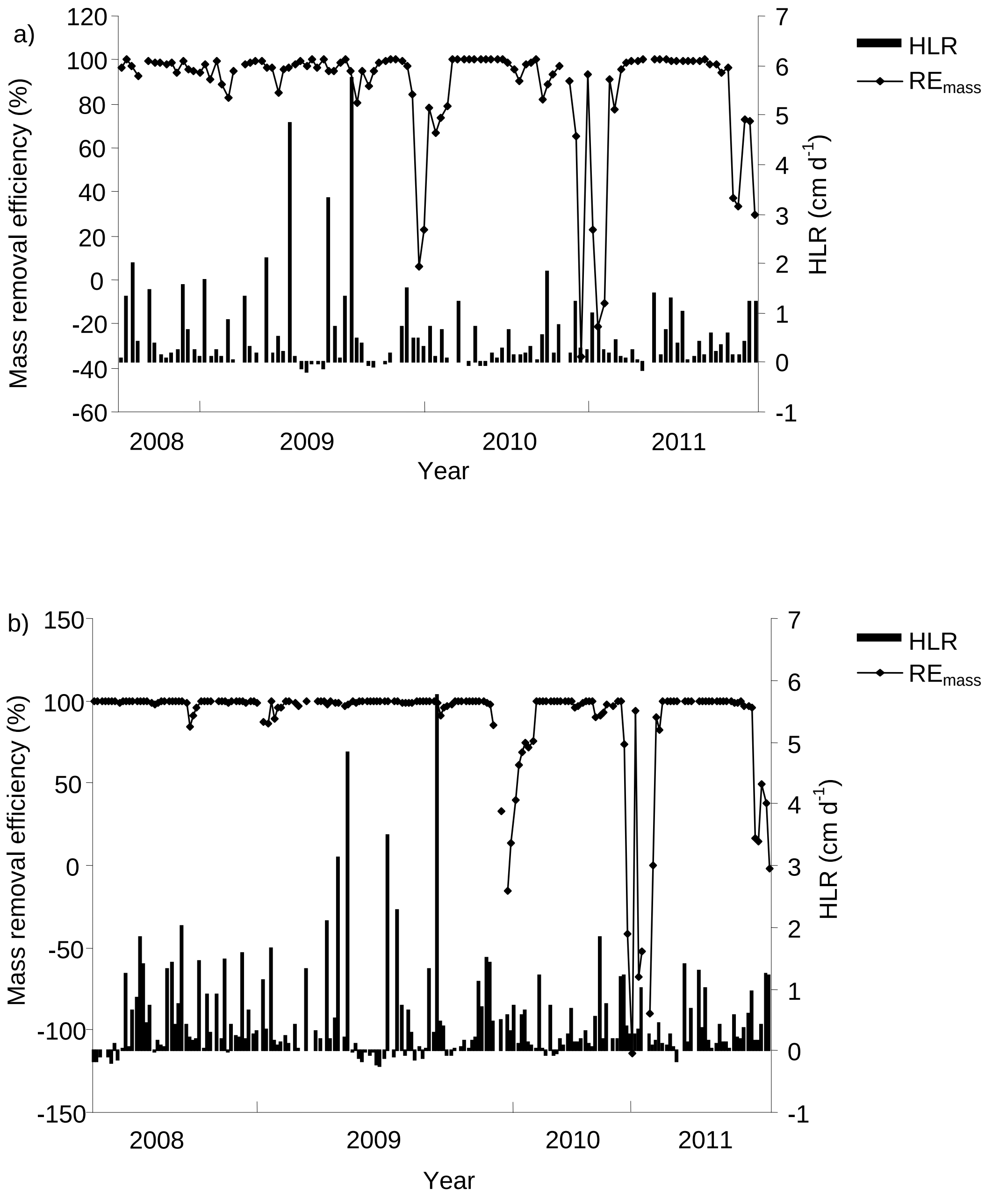

Figure 6-1 Diagram showing water balance calculation of Glaslough integrated constructed wetland system. ΔV, change in storage; $Q_{in}$, wastewater inflow; $Q_{out}$, treated water outflow; P, precipitation; ET, evapotranspiration; I, infiltration.

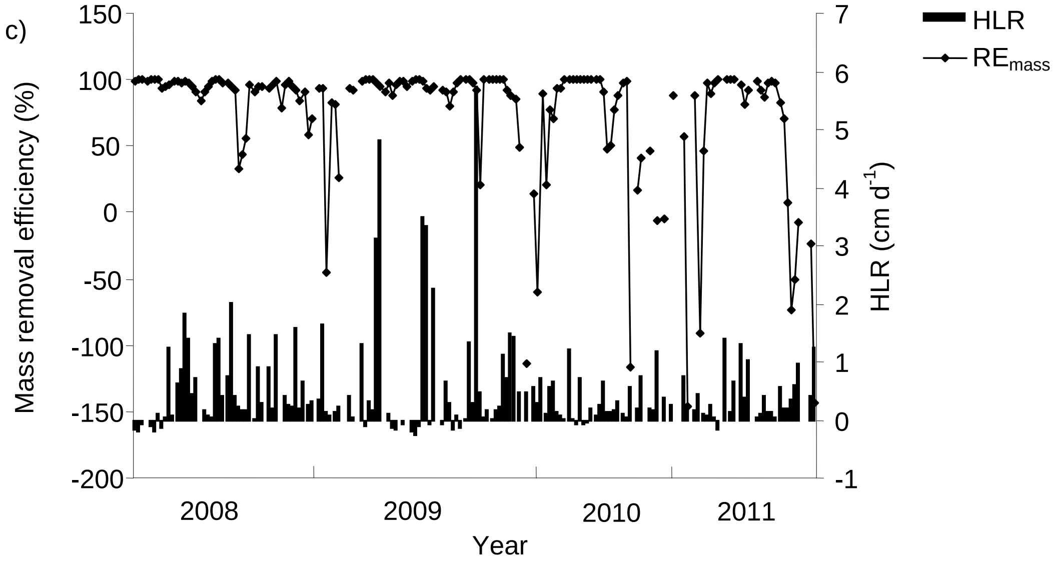
The net change in volume for the monitoring period was 22.51 $m^3$ $d^{-1}$, which represented the water storage within the wetland system at a given time. This change in volume was calculated by using daily monitoring data for rainfall, evapotranspiration, infiltration, wastewater inflow, and the outflow from wetland. As shown in Fig. 6-1, the inflow to the ICW system includes untreated domestic wastewater and precipitation, which contributed approximately 46.46% and53.54%. The percentages for the outflow of the system were as follows: evapotranspiration of 19.23%; infiltration of 5.54%, and outflow of 75.23%. Since the inflow to the system originated from precipitation, it has a considerable influence on the hydraulic loading rate ($R^2$ = 95.99).

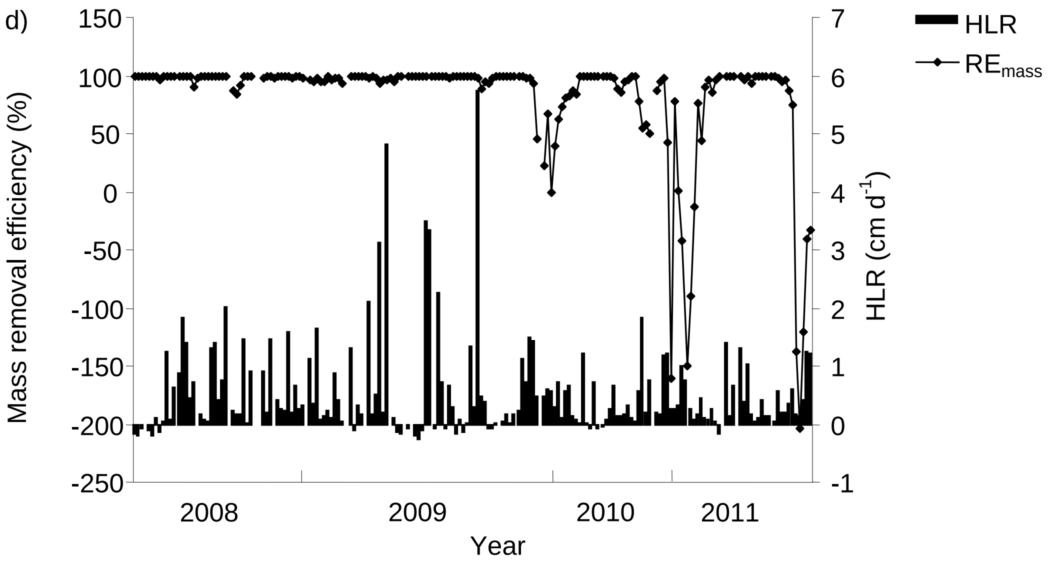
## 6.5 Loading rates and removal efficiencies

As mentioned above, optimal HLR and HRT are important to achieve effective treatment results. At low HLR, the HRT is relative high. In comparison, at high HLR, the wastewater passes rapidly through the wetland, reducing the time available for degradation processes to become effective. However, the result of this particular study seems to contradict previous findings and suggests that mass removal efficiencies for water contaminants have not shown immediate response to the increase of HLR throughout the monitoring period (Fig. 6-2). These observations can probably be explained by the large footprint of the system, which results in a relatively long HRT. The multi-cellular configuration of the ICW system can help control HLR gradient through the whole system. Furthermore, the system is relatively immature, which means the system has high adsorption and storage capacities.

Over monitoring period of this study, the mean influent and effluent $NH_3$-N loading rates were approximately 0.110 and 0.012 g $d^{-1}$ $m^{-2}$ respectively. The mean removal efficiency of $NH_3$-N was 97.04%. The surface inflows brought about a total load of 4700.21 kg $NH_3$-N received by the ICW system, and 88.76% of inputs were retained (Table 6-4). The retention rate was approximately 35.54 g $NH_3$-N $m^{-2}$ $yr^{-1}$. Seasonal hydraulic loading and $NH_3$-N mass removal efficiencies were presented in Figure 6-3a. The decreases of $NH_3$-N mass removal were recorded during winters of 2009/2010 (49.83%); 2010/2011(2.15%), and 2011/2012 (38.20%). However, the overall removal efficiency of $NH_3$-N was comparatively high. Kayranli *et al.* (2010) reported that $NH_3$-N reduction of the Glaslough ICW is higher than that of other microcosm wetlands treating domestic wastewater, which is probably because the system is in an early stage of operation. On the other hand, Boutilier *et al.* (2010) found that treatment efficiencies associated with surface-flow domestic wastewater treatment wetlands decreased during winter. This was probably due to the anaerobic conditions caused by ice cover and lack of flow, thereby decreasing biodegradation.




c)
150
100
50
0
-50
-100
-150
-200
Mass removal efficiency (%)
7
6
5
4
3
2
1
0
-1
HLR (cm d-1)
HLR
REmass
2008
2009
2010
2011
Year


d)
150
100
50
0
-50
-100
-150
-200
-250
Mass removal efficiency (%)
7
6
5
4
3
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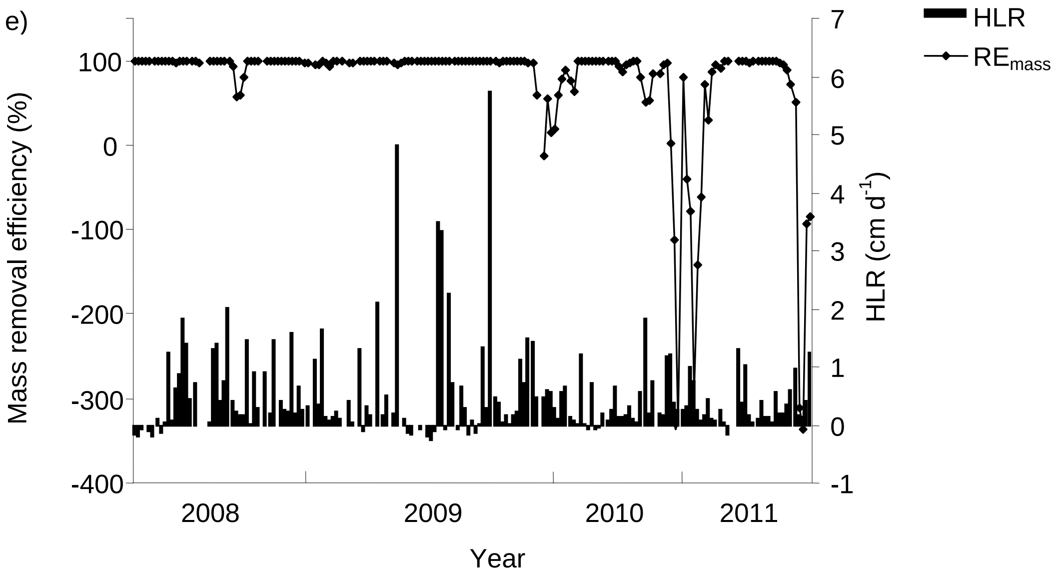
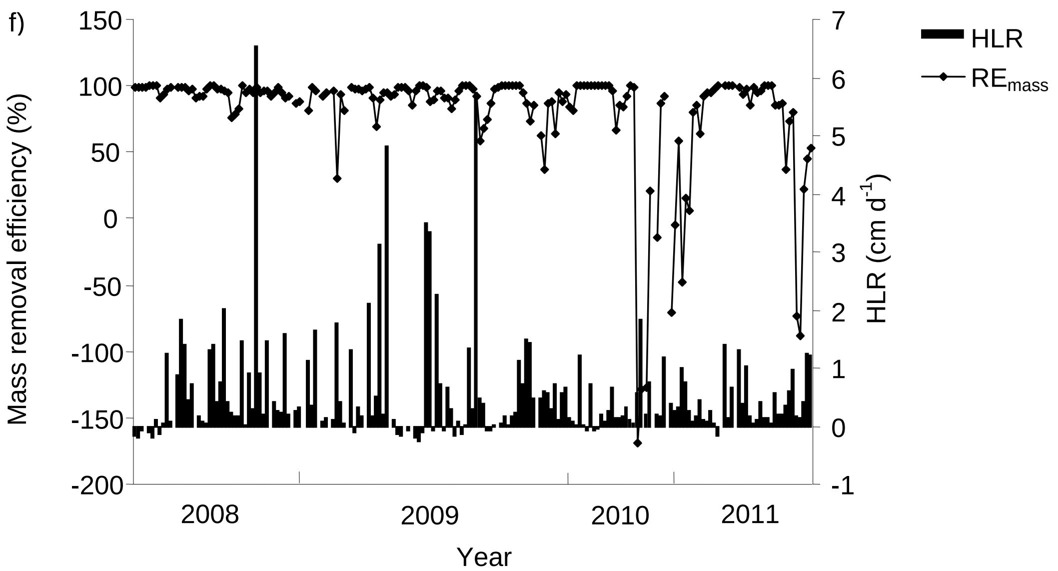
1
0
-1
HLR (cm d-1)
HLR
REmass
2008
2009
2010
2011
Year


e)
HLR
RE$_{mass}$
Mass removal efficiency (%)
HLR (cm d$^{-1}$)
Year
100
0
-100
-200
-300
-400
7
6
5
4
3
2
1
0
-1
2008
2009
2010
2011


f)
HLR
RE$_{mass}$
Mass removal efficiency (%)
HLR (cm d$^{-1}$)
Year
150
100
50
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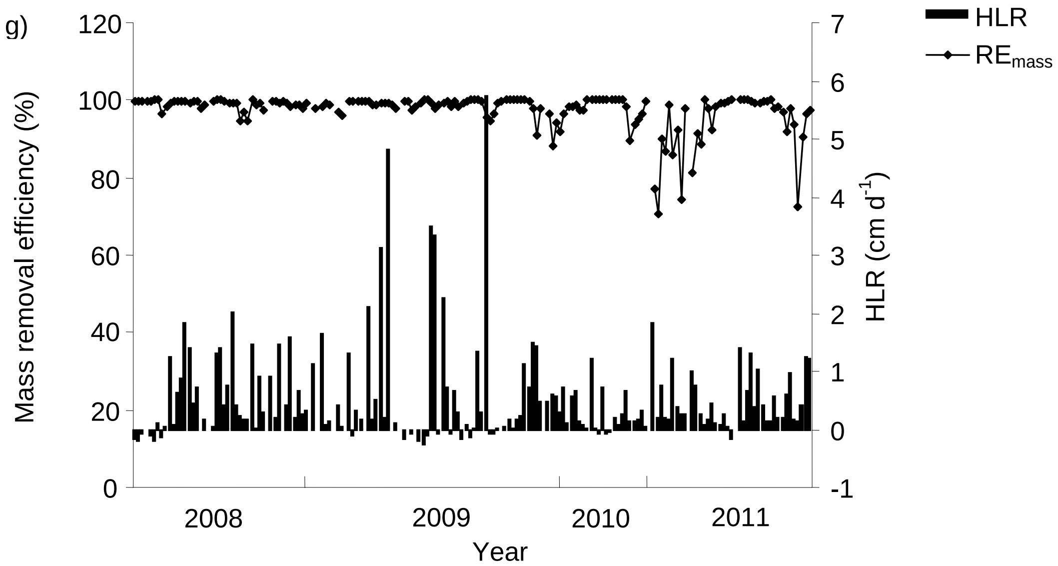


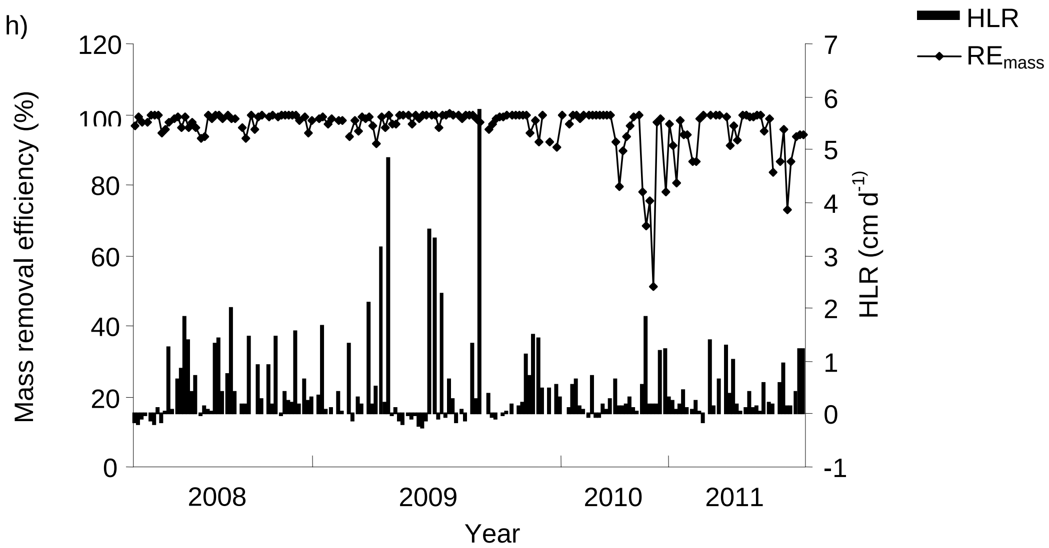



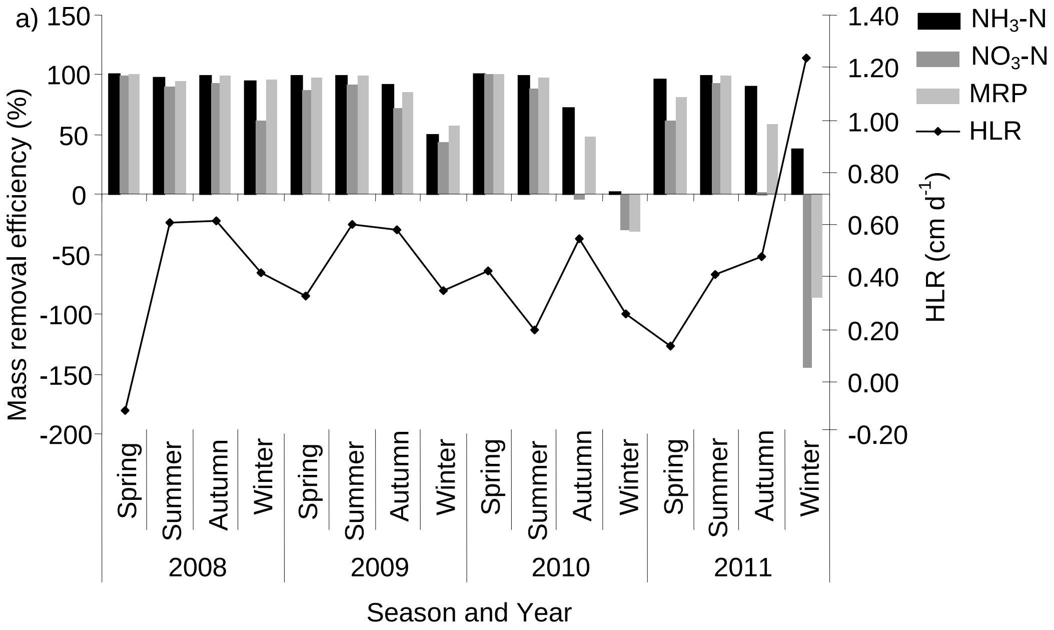

Figure 6-2 Mass removal rates and hydraulic loading rate (HLR) for a) total nitrogen; b) ammonia-nitrogen; c) nitrate-nitrogen; d) total phosphorus; e) molybdate reactive phosphorus; f) chemical oxygen demand; g) biochemical oxygen demand; and h) total suspended solid.

Table 6-4 Total mass loading rates for water quality variables during the monitoring period (May 2008–April 2010).

| Variable | Loadings (kg) | | Mass retained (%) |
|---|---|---|---|
| | Inflow | Outflow | |
| Biochemical oxygen demand | 38859.89 | 865.0754 | 97.77 |
| Chemical oxygen demand | 62533.02 | 7253.424 | 88.40 |
| Total suspended solids | 23600.57 | 771.3949 | 96.73 |
| Molybdate reactive phosphorus | 548.09 | 108.74 | 80.16 |
| Total phosphorus | 8138.52 | 1139.85 | 85.99 |
| Ammonia-nitrogen | 4700.21 | 528.49 | 88.76 |
| Nitrate-nitrogen | 435.25 | 84.12 | 80.67 |
| Total nitrogen | 6434.00 | 838.98 | 86.96 |

The MRP inlet loading rate varied slightly during the study period and the average value was 0.013 g $d^{-1}$ $m^{-2}$. A total load of 548.09 kg MRP was carried into the system, and 80.16% of the inputs were retained (Table 6-4). The mean retention rate over the study period was 4.67 g MRP $m^{-2}$ $yr^{-1}$. The MRP mass removal efficiency varied between -85.59% (winter 2011) and 99.99% (spring 2008 and spring 2010). The low removal efficiency was likely because many plants went dormant during winter time and consequently decreased the capacity to assimilate phosphorous. Holt *et al.* (1998) investigated the year round nitrogen and phosphorus removal performance of wetland plant and reported that the nutrient uptake and biomass production could be largely affected by frost for most species.

The removal of COD, BOD and TSS was generally efficient, and decreased only slightly at relatively higher HLR. The mean inlet and outlet COD loading rates were 1.46 and 0.17 g $d^{-1}$ $m^{-2}$ respectively. The mass removal efficiency of the system was 88.40%. Seasonal hydraulic loading and mass removal efficiency are provided in Figure 6-3b. The relatively high overall COD removal performance (91.82%) might be due to good growth of vegetation, resulting in high concentrations of dissolved oxygen, which can be seen as the electron acceptor for heterotrophs attached to the rhizomes (Avsar *et al.*, 2007). Previous studies also showed that COD removal within CW systems depended on vegetation type and water level (Stottmeister *et al.*, 2003; Sun *et al.*, 2009; Zhu and Sikora, 1995). However, COD reduction showed significant decrease in autumn and winter of 2010 and 2011, particularly in autumn of 2010. This might be attributed to increased hydraulic loading rate and low temperature. The BOD removal rates ranged from 91.67% to 99.77%. The mean mass removal rate for TSS was 96.42%. The relatively consistent BOD and TSS



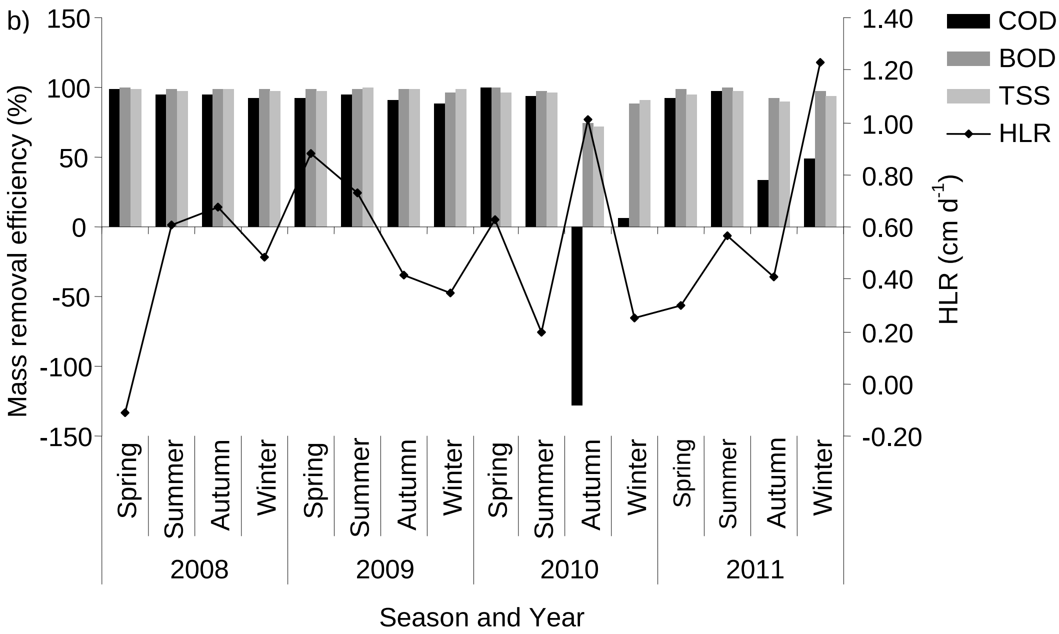



Figure 6-3 Seasonal means of a) ammonia-nitrogen, nitrate-nitrogen and molybdate reactive phosphorus mass removal efficiencies and hydraulic loading rate; and b) chemical oxygen demand, biochemical oxygen demand, and total suspended solids mass removal efficiencies and hydraulic loading rate.

mass removal efficiencies indicated that the reduction of BOD and TSS seemed unaffected either by high hydraulic loading rate or by low temperature.

## *6.6 Temperature and mass removal efficiencies*

The low removal efficiencies recorded were partly a result of the adverse influence of low ambient temperature within the ICW system, reducing microbial activities and diffusion rates (Phipps and Crumpton, 1994; Spieles and Mitsch, 2000). The seasonal mass removal rates of COD were the lowest at -128.0% (Table 6-5). This finding was in contrast to several other studies reporting slight influences of temperature on the removal efficiency of COD within CWs (Dahab *et al.*, 2001; Mæhlum and

Jenssen, 2003; Steinmann *et al.*, 2003; Vymazal, 2001; Züst and Schönborn, 2003). This low COD removal efficiency might be attributed to the absence of sufficient microorganisms attached to the rhizomes at the beginning of the wetland maturation process. Similarly, Table 6-5 shows that nitrogen losses were rather below expectations during the low temperature period. This shortcoming was probably due to the reductions in nitrification and denitrification rates at lower temperatures. Previous research shows that the biological removal of nitrogen is most efficient at temperatures ranging from 25 °C to 30 °C (Hammer and Knight, 1994; Herskowitz *et al.*, 1987; Mitsch *et al.*, 2000; Sutton *et al.*, 1975; Vymazal, 1999). During colder periods, there is little plant uptake of phosphorus, which leads to a decline in MRP mass removal efficiencies, as observed during autumns and winters. However, the system is still relatively immature; therefore, high phosphorus adsorption and storage capacities are to be expected.

## 6.7 Summary

This chapter investigates the effects of season and hydraulic loading rate on contaminant removal in a full-scale integrated constructed wetland. There were slight decreases in removal efficiencies for chemical oxygen demand (COD), ammonia-nitrogen ($NH_3$-N), molybdate reactive phosphorus (MRP) and total phosphorus (TP), whereas a drastic decrease for $NO_3$-N reduction was also recorded. The treatment performance of the ICW system declined with wetland age.

There is no obvious relationship between hydraulic loading rate and contaminant removal efficiency because of large footprint and multi-cellular configuration of ICW system.

Low temperatures in autumn and winter have led to a decrease in biological activity and treatment efficiency. The removal of contaminants in cold climate can be optimized further by increasing the hydraulic retention time and/or by enlarging the wetland system.

In conclusion, the ICW system can be seen as an appropriate, robust, reliable and cost-saving technology that to treat domestic wastewater. However, optimum HLR should be established as to obtain highest removal efficacy in winter time.

Table 6-5 Seasonal comparison of contaminant mass removal efficiencies and results from the Tukey HSD tests.

| MRE | | 2008/2009 | | | | 2009/2010 | | | | 2010/2011 | | | | 2011/2012 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (%) | *F* | Spr. | Sum. | Aut. | Win. | Spr. | Sum. | Aut. | Win. | Spr. | Sum. | Aut. | Win. | Spr. | Sum. | Aut. | Win. |
| $NH_3$-N | 7.09 | 99.9$^{a}$ | 98.4$^{a}$ | 99.6$^{a}$ | 95.1$^{a}$ | 99.2$^{a}$ | 99.3$^{a}$ | 92.2$^{a}$ | 49.8$^{c}$ | 99.9$^{a}$ | 99.3$^{a}$ | 72.7$^{b}$ | 2.2$^{c}$ | 95.8$^{a}$ | 99.9$^{a}$ | 90.8$^{a}$ | 38.7$^{c}$ |
| $NO_3$-N | 8.26 | 99.4$^{a}$ | 89.4$^{a}$ | 92.9$^{a}$ | 62.3$^{a}$ | 87.5$^{a}$ | 92.0$^{a}$ | 72.9$^{a}$ | 44.1$^{a}$ | 99.9$^{a}$ | 89.4$^{a}$ | -3.8$^{b}$ | -28.8$^{b}$ | 61.0$^{a}$ | 93.4$^{a}$ | 0.7$^{b}$ | -144.0$^{c}$ |
| MRP | 7.28 | 99.9$^{a}$ | 94.7$^{a}$ | 99.7$^{a}$ | 96.8$^{a}$ | 98.4$^{a}$ | 99.8$^{a}$ | 85.3$^{a}$ | 56.7$^{b}$ | 99.9$^{a}$ | 97.8$^{a}$ | 47.9$^{b}$ | -31.1$^{c}$ | 81.6$^{a}$ | 99.3$^{a}$ | 58.2$^{ab}$ | -85.6$^{c}$ |
| COD | 25.36 | 99.2$^{a}$ | 95.4$^{a}$ | 94.8$^{a}$ | 91.8$^{a}$ | 92.3$^{a}$ | 94.7$^{a}$ | 90.7$^{a}$ | 88.1$^{a}$ | 99.8$^{a}$ | 94.1$^{a}$ | -128.0$^{c}$ | 6.6$^{b}$ | 91.8$^{a}$ | 97.7$^{a}$ | 33.9$^{b}$ | 48.5$^{ab}$ |
| BOD | 15.18 | 99.9$^{a}$ | 99.0$^{a}$ | 99.1$^{a}$ | 98.7$^{a}$ | 98.9$^{a}$ | 99.1$^{a}$ | 98.2$^{a}$ | 96.7$^{a}$ | 99.9$^{a}$ | 97.9$^{a}$ | 73.8$^{c}$ | 88.5$^{b}$ | 98.8$^{a}$ | 99.6$^{a}$ | 92.4$^{b}$ | 97.0$^{a}$ |
| TSS | 9.47 | 98.3$^{a}$ | 97.5$^{a}$ | 99.2$^{a}$ | 97.7$^{a}$ | 97.2$^{a}$ | 99.4$^{a}$ | 98.1$^{a}$ | 98.1$^{a}$ | 96.5$^{a}$ | 96.3$^{a}$ | 71.9$^{b}$ | 91.2$^{a}$ | 94.4$^{a}$ | 97.6$^{a}$ | 89.1$^{a}$ | 94.2$^{a}$ |

MRE, mass removal efficiency; Spr., spring; Sum., summer; Aut., Autumn; Win., Winter; $NH_3$-N, ammonia-nitrogen; $NO_3$-N, nitrate-nitrogen; MRP, molybdate reactive phosphorus; COD, chemical oxygen demand; BOD, biochemical oxygen demand; TSS, total suspended solids. Different superscript letters indicate significant differences, $a<b<c$.

# Chapter 7

# Long-term Performance of Representative Wildfowl & Wetland Trust Constructed Wetlands

## *7.1 Introduction*

This chapter examines wastewater treatment performance of five Wildfowl & Wetlands Trust (WWT) constructed wetland (CW) systems by analysing water quality monitoring data collected between 2005 and 2009. The obvious trends in seasonal and long-term contaminant removal are also presented.

This study is important because only very few CW systems operated in practice have been undertaken assessments for a sufficiently long period to determine the change of treatment efficiency that will develop as CW systems age. The original research paper has been published in Water and Environment Journal.

## *7.2 Water quality and treatment efficiency*

Table 7-1 summarises the performance data for each wetland system based on results provided by Dr Sally Mackenzie (WWT). These systems had a wide range of operating conditions with hydraulic loading rates (HLR) from 2 to 100 cm $d^{-1}$ and hydraulic retention times (HRT) of 1-25 days (Table 7-2).

It is unfortunate that there was no hydraulic load information on Caerlaverock system. Inflow and outflow water quality monitoring was conducted for 4.5 years at Millennium, Caerlaverock and Llanelli, 3.5 years at Castle Espie and 1 year at Welney.

## 7.3 Nitrogen

Reductions of ammonia-nitrogen ($NH_3$-N) concentrations ranged from 31.9% to 96.8% in five representative CW systems, indicating that nitrification processes occurred in all systems, but the treatment performances were variable. At Castle Espie, the free water surface wetland cell performed better in $NH_3$-N removal (84.4%) than the horizontal sub-surface flow wetland cell (31.9%), supporting the theories that the nitrification process is very oxygen demanding and that the free water surface flow wetland cell can produce more favourable aerobic conditions cell (Tanner and Kadlec, 2003). In addition, almost complete nitrification (96.8%) occurred at the Millennium wetland where relatively higher pH values were recorded in both influent and effluent. This result is consistent with the findings of Lee *et al.* (2009) who indicated that the pH value was an important factor for nitrification process and the nitrification rates swiftly declined when pH drops to values lower than 7.0. These findings also agree with the mesocosm study results obtained from statistical analysis.

Table 7-1 Summary of treatment performance data for the Wildfowl & Wetlands Trust constructed wetland systems.

| | Caerlaverock | Castle Espie | | Llanelli | | Millennium | Welney |
|---|---|---|---|---|---|---|---|
| n | 40 | 28 | | 40 | | 35 | 11 |
| Monitoring period | June/2005 – December/2009 | June/2005 – December/2008 | | June/2005 – December/2009 | | June/2005 – December/2009 | March/2008 – June/2009 |
| | | (G) | (S) | (R) | (L) | | |
| $NH_3$-N | | | | | | | |
| In (mg $l^{-1}$) | 27.2 ±30.3 | 36.4 ±38.9 | | 0.8 ±1.3 | | 28.5 ±18.7 | 10.6 ±1.8 |
| Out (mg $l^{-1}$) | 9.3 ±9.5 | 24.8 ±23.2 | 5.7 ±2.8 | 0.3 ±0.4 | 0.4 ±0.6 | 0.9 ±3.0 | 5.9 ±5.3 |
| TE (%) | 65.8 | 31.9 | 84.4 | 64.6 | 54.4 | 96.8 | 44.7 |
| $NO_3$-N | | | | | | | |
| In (mg $l^{-1}$) | 0.2 ±0.5 | 0.7 ±0.8 | | 3.3 ±1.8 | | 0.3 ±0.5 | 0 |
| Out (mg $l^{-1}$) | 1.6 ±1.4 | 0.4 ±0.5 | 0.6 ±0.7 | 1.1 ±0.7 | 1.1 ±0.9 | 10.7 ±5.2 | 0.9 ±1.9 |
| TE (%) | -710.0 | 37.9 | 13.6 | 67.2 | 66.9 | -3844.4 | N.A. |
| TON | | | | | | | |
| In (mg $l^{-1}$) | 0.2 ±0.5 | 0.7 ±0.8 | | 3.4 ±1.8 | | 0.3 ±0.5 | 0 |
| Out (mg $l^{-1}$) | 1.7 ±1.4 | 0.4 ±0.5 | 0.6 ±0.8 | 1.1 ±0.6 | 1.1 ±0.9 | 11.2 ±5.1 | 0.9 ±2.0 |
| TE (%) | -740.0 | 37.3 | 6.0 | 67.8 | 67.2 | -3765.5 | N.A. |
| $PO_4$-P | | | | | | | |
| In (mg $l^{-1}$) | 7.6 ±2.7 | 8.3 ±5.9 | | 1.3 ±1.3 | | 4.3 ±1.9 | 8.6 ±1.9 |
| Out (mg $l^{-1}$) | 6.3 ±2.5 | 5.7 ±4.3 | 6.3 ±5.2 | 1.5 ±0.8 | 1.1 ±0.7 | 3.7 ±0.9 | 1.1 ±2.2 |
| TE (%) | 17.6 | 31.7 | 24.7 | -10.5 | 16.4 | 14.4 | 87.6 |
| TP | | | | | | | |
| In (mg $l^{-1}$) | 6.8 ±3.3 | 8.4 ±5.9 | | 1.6 ±1.5 | | 5.1 ±2.2 | 7.0 ±1.6 |
| Out (mg $l^{-1}$) | 4.2 ±1.4 | 5.8 ±4.3 | 6.8 ±4.8 | 1.5 ±0.6 | 1.3 ±0.7 | 4.2 ±1.5 | 0.5 ±0.7 |
| TE (%) | 38.5 | 30.9 | 19.0 | 6.9 | 18.8 | 17.7 | 92.5 |

| | Caerlaverock | Castle Espie | | Llanelli | | Millennium | Welney |
|---|---|---|---|---|---|---|---|
| | | (G) | (S) | (R) | (L) | | |
| TSS | | | | | | | |
| In (mg $l^{-1}$) | 14.7 ± 19.5 | 32.2 ± 37.3 | | 14.9 ± 18.0 | | 15.9 ± 17.1 | 26.4 ± 29.2 |
| Out (mg $l^{-1}$) | 9.7 ± 16.9 | 13.7 ± 21.1 | 112.3 ± 189.5 | 13.2 ± 12.9 | 16.0 ± 16.3 | 25.0 ± 32.2 | 28.5 ± 18.7 |
| TE (%) | 33.6 | 57.6 | -249.2 | 11.4 | -7.6 | -57.0 | -7.9 |
| BOD | | | | | | | |
| In (mg $l^{-1}$) | 25.5 ± 15.1 | 34.0 ± 24.7 | | 8.5 ± 6.8 | | 32.7 ± 14.3 | 46.4 ± 9.8 |
| Out (mg $l^{-1}$) | 11.9 ± 11.5 | 9.7 ± 9.5 | 13.2 ± 19.8 | 8.5 ± 6.8 | 8.0 ± 7.7 | 4.1 ± 5.5 | 17.0 ± 13.1 |
| TE (%) | 53.1 | 71.5 | 61.2 | 0 | 5.9 | 87.3 | 63.4 |

n, number of samples; In, inflow; Out, outflow; $NH_3$-N, ammonia-nitrogen; $NO_3$-N, nitrate-nitrogen; TON, total oxidised nitrogen; $PO_4$-P, ortho-phosphate-phosphorus; TP, total phosphorus; TSS, total suspended solids; BOD, biochemical oxygen demand; TE, treatment efficiency; G, effluent from the horizontal sub-surface flow wetland cell with gravel substrate; S, effluent from the free surface flow wetland cell with soil substrate; R, effluent from the right hand secondary free surface flow wetland bed; L, effluent from the left hand secondary free surface flow wetland bed; N.A., not available; standard deviations are indicated by the symbol ±.

Table 7-2 Summary information: design characteristics of the Wildfowl & Wetlands Trust constructed wetland systems.

| Characteristics | Caerlaverock | Castle Espie | Llanelli | Millennium | Welney |
|---|---|---|---|---|---|
| Region | Scotland | Northern Ireland | Wales | England | England |
| Construction | 2001 | 1993 | 2000 | 1999 | 2006 |
| Depth (mm) | N.A. | 500 | 500 | 500 | 500 |
| HRT (days) | N.A. | 0.5 | 25.0 | 4.5 | 0.8 |
| HLR (cm $d^{-1}$) | N.A. | 100.0 | 2.0 | 11.2 | 64.5 |

HRT, hydraulic retention time; HLR, hydraulic loading rate; N.A., not available.

In terms of oxidised nitrogen (TON; $NO_3$-N+$NO_2$-N) and nitrate-nitrogen ($NO_3$-N), the most efficient removals were observed in Llanelli CW with a HRT of 25 days. A decrease in HRT significantly deteriorated the reduction of TON and $NO_3$-N in other wetlands. This correlation between TON and $NO_3$-N removal and HRT has also been observed during previous studies. Trang *et al.* (2010) investigated effects of hydraulic loading rate on the treatment capacity of a pilot scale horizontal subsurface flow CW system. The author reported that removals of total suspended solids (TSS), five-day biochemical oxygen demand ($BOD_5$) and chemical oxygen demand (COD) were efficiency at four controlled hydraulic loading rates, whereas nitrogen and phosphorus reduction decreased with HLRs. Similarly, Chang *et al.* (2007) also showed that the removal efficiencies of ammonium ($NH_4$-N), total phosphate (TP), COD and $BOD_5$ were decreased slightly with an increase in HLR from 20 to 120 cm $d^{-1}$.

## *7.4 Phosphorus*

Except for Welney wetlands, the average TP removal efficiencies of other CW systems ranged from 6.9 to 38.5%, indicating that these wetlands are not an effective method for reducing the concentration of phosphorus in a long run. Wetland systems can usually significantly remove phosphorus during the early stages of operation, however, there is a finite period of effective phosphorus removal after which treatment efficiency declines (Lindstrom and White, 2011; Scholz *et al.*, 2007). This tendency can be illustrated in Caerlaverock wetland (Fig. 7-1), where the initial averaged reduction in $PO_4$-P concentration decreased from 43.8% in 2005 to 3.2% in 2009, though some minor fluctuations were observed. In contrast, better phosphorous removal performance (87.6% in $PO_4$-P and 92.5% in TP) has been recorded for the Welney since the system is relatively young. For Caerlaverock and Welney CW systems, the recorded $PO_4$-P concentrations were greater than those of TP. This might be due to the fact that TP values were measured at Phosyn laboratories which provide more accurate data compared to the Chemets measurements. Nevertheless, records indicated a downward trend in terms of $PO_4$-P and TP reductions over operation time.

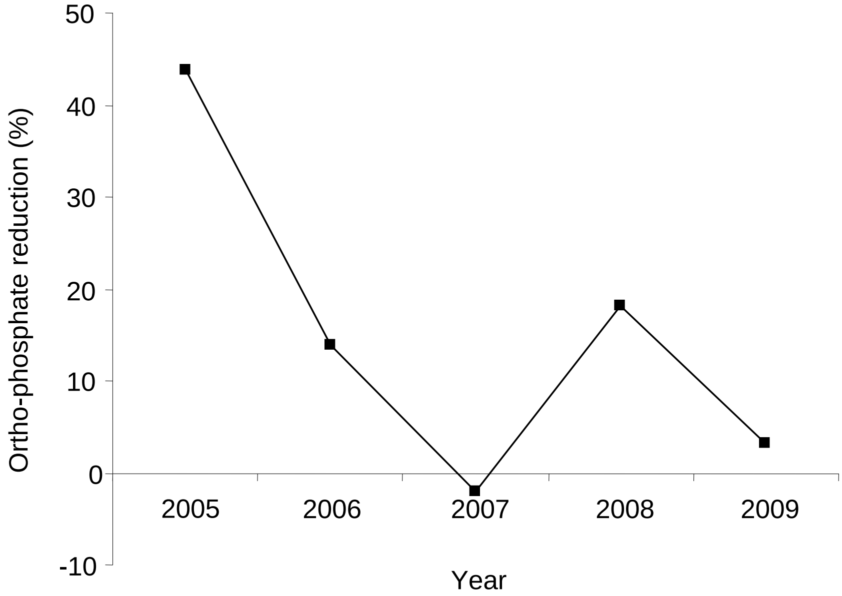



Figure 7-1 Annual mean ortho-phosphate-phosphorus removal efficiency for the Caerlaverock constructed wetland system (2005 – 2009).

## 7.5 Organic strength and solids

Except for the wetland at Llanelli, the reduction in BOD concentration ranged from 53.1% to 87.3%, producing effluent with mean BOD concentrations in the range of 4 to 17 mg $l^{-1}$. At Llanelli, where the BOD level is low for the influent, only 5.9% of the BOD removal was recorded at the right hand outflow point and there was no BOD reduction had been observed in the left hand effluent. This finding is in agreement with previous studies indicating that the BOD is unlikely to be removed completely because of background levels produced within wetland systems (Kadlec and Knight, 1996).

Reductions in TSS concentrations ranged from -249.2% to 57.6% for five wetlands. For some of systems, solids in effluent exceeded those in influent, which suggested that there was a dispersion of soil and clay due to high flow rates and substantial wind action. In addition, the lack of vegetation at the outlet might also contribute to the increase in TSS (Greenway and Wooley, 1999).

## 7.6 Seasonal variations

Seasonal contaminant removals in four constructed wetlands are present in Table 7-3. Welney CW data were not included due to short monitoring period. Microbiological reactions, especially nitrification, can be significantly limited by cold temperature (Kadlec and Knight, 1996). As shown in Fig. 7-2, the reductions of $NH_3$-N were relatively high in summer and autumn for all CW systems. This finding is further supported by Vymazal (2007). The nitrification rates in wetland systems become increasingly inhibited at temperatures of about 10 ℃, and drop rapidly at 6 ℃ (Werker *et al.*, 2002). In contrast, there was no obvious seasonal trend in $NO_3$-N removal, which was probably due to the overall low denitrification rates for the studied wetlands. Since the main removal mechanism of phosphorus in a CW is storage and adsorption (Dunne *et al*., 2005b), temperature showed less limiting effects on phosphorus removal efficiencies.

## 7.7 Reflection on design and management

Most CW system in UK were designed and constructed to treat raw or pre-treated sewage and domestic wastewater. However, few CWs have been studied for a long enough period to determine the change of their treatment performances that might develop as CW systems age. The study of the representative WWT CWs that have been used for long periods of time (> 10 years) showed that $PO_4^{3-}$ removal efficiency declines with age. The wetland has a finite capacity to reduce phosphorus. This study demonstrates the importance of wetland management in particular removal of accumulated sediments as to achieve long-term effectiveness for a CW system. Compared to previously studied ICW systems in Ireland, the HRT of these systems are relatively low. This can be accomplished by adding additional wetland cell or recirculating wastewater within system. In addition, Busnardo *et al.* (1992) reported that the wastewater nutrients could be mainly removed by emergent macrophytes rather than by sediments through designing systems with a high ratio of edge to surface area. According to this research, the removal of $PO_4^{3-}$ can be maintained in a long run by the harvest of aboveground parts. The extra harvesting cost can be offset by recycling the valuable nutrients stored in the plant tissue by applying it as fodder or compost. In addition, nutrient removal can also fluctuate due to variations in boundary conditions such as local climate, contaminant loading rates. Many studies have reported that CW systems might also temporarily release the accumulated nutrients due to flooding or sudden change of environmental conditions. Therefore, hydrological monitoring of CWs is important to modern wetland management.

## 7.8 Limitations

The data in this study was provided by WWT, however, the reliability of data has to be improved by removing potential outliers and suspicious data before conducting further analysis. This might decrease the sample size and cause an obstacle in finding the seasonal performance trend and the meaningful relationship between treatment efficiencies with wetland ageing. In addition, differences in the measurement techniques (Phosyn laboratories and Chemets) may introduce additional uncertainty in the analysis. These limits in the data mean that the study findings are suggestive rather than exact.

Unfortunately, the selected WWT's CW systems are not fully established with hydrological monitoring devices, the accurate inflow and outflow rates, HLR and HRT are unknown. Therefore, this chapter doesn't include the further interpretation of the relationship between HRT and effluent concentration of treated water.

## *7.9 Summary*

Data collected from five representative CWs have been studied to demonstrate the long-term performance of these systems to improve the quality of sewage effluent by reducing nutrient and other contaminants. However, the analysis shows that effective reductions in $NO_3$-N, $PO_4$-P and TSS were not achieved in many CW systems.

The removal of $NH_3$-N has been particularly effective in summer since the nitrification rate is highly temperature dependent.

In general, phosphorous can be greatly reduced at an early stage but the efficiency decreases with time as the wetland site becomes saturated. In contrast, $NH_3$-N removal was effective over long-term operation. There is a potential risk that accumulated nitrogen and phosphorus might be remobilized and released to the water phase as the wetland ages.

Table 7-3 Seasonal comparison of nutrient treatment efficiencies for the Wildfowl & Wetlands Trust constructed wetlands (2005–2009).

| Season | Site | $NH_3$-N % | $NO_3$-N % | $PO_4$-P % | TP % |
|---|---|---|---|---|---|
| Spring | Caerlaverock | 40.90 | N.A. | -3.88 | 22.59 |
| | Castle Espie (G) | -171.32 | N.A. | 25.55 | 25.55 |
| | Castle Espie (S) | -55.04 | 25.00 | -37.27 | -37.27 |
| | Llanelli (R) | 61.29 | 48.68 | 28.68 | 75.28 |
| | Llanelli (L) | 62.90 | 50.57 | 22.67 | 20.50 |
| | Millennium | 97.23 | -3906.67 | -27.78 | N.A. |
| Summer | Caerlaverock | 79.78 | -584.21 | 19.50 | 51.90 |
| | Castle Espie (G) | 47.17 | 41.48 | 32.69 | 32.69 |
| | Castle Espie (S) | 87.28 | 29.94 | 37.45 | 37.45 |
| | Llanelli (R) | 56.82 | 81.18 | -73.61 | -34.72 |
| | Llanelli (L) | 63.64 | 80.19 | -8.87 | -14.61 |
| | Millennium | 98.59 | -3350.00 | 3.23 | 4.32 |
| Autumn | Caerlaverock | 67.08 | -260.00 | 23.21 | 29.75 |
| | Castle Espie (G) | 17.87 | 19.79 | 39.26 | 39.26 |
| | Castle Espie (S) | 88.67 | -58.00 | 30.64 | 30.64 |
| | Llanelli (R) | 80.23 | 69.01 | 10.48 | 18.83 |
| | Llanelli (L) | 50.14 | 65.79 | 24.22 | 31.27 |
| | Millennium | 98.79 | -2461.54 | 30.03 | 32.53 |
| Winter | Caerlaverock | 21.55 | -148.37 | -5.79 | 29.51 |
| | Castle Espie (G) | -166.67 | N.A. | -11.11 | -11.11 |
| | Castle Espie (S) | -233.33 | N.A. | -22.22 | -22.22 |
| | Llanelli (R) | 52.17 | 34.22 | 25.76 | 36.70 |
| | Llanelli (L) | 50.36 | 40.54 | 46.83 | 45.25 |
| | Millennium | 82.31 | -5735.00 | 4.26 | N.A. |

$NH_3$-N, ammonia-nitrogen removal efficiency; $NO_3$-N, nitrate-nitrogen removal efficiency; $PO_4$-P, ortho-phosphate-phosphorus removal efficiency; TP, total phosphorus removal efficiency; G, effluent from the horizontal sub-surface flow wetland cell with gravel substrate; S, effluent from the free surface flow wetland cell with soil substrate; R, effluent from the right hand secondary free surface flow wetland cell; L, effluent from the left hand secondary free surface flow wetland cell; N.A., not available.

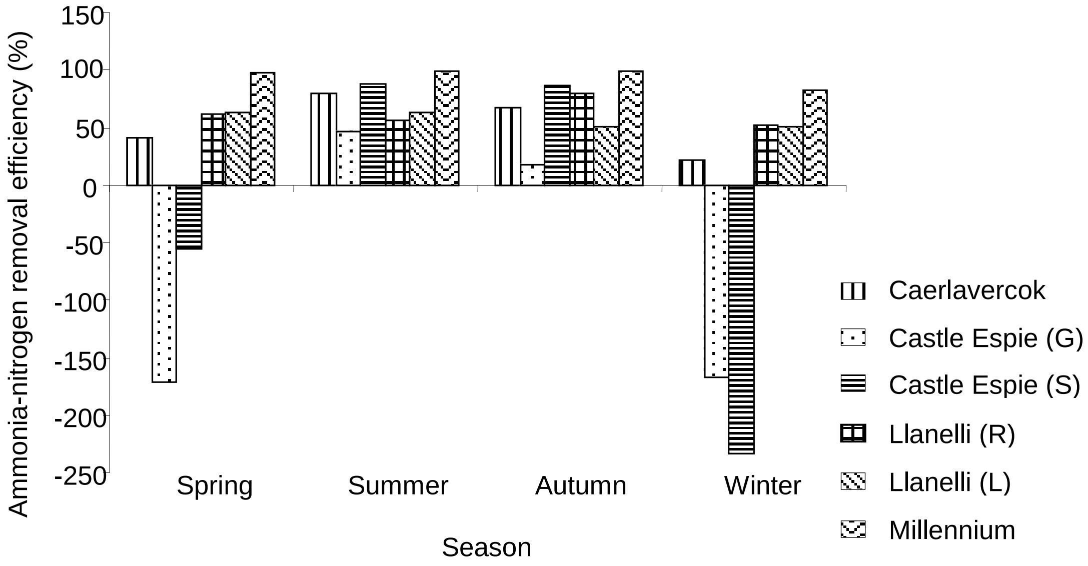



Figure 7-2 Seasonal mean ammonia-nitrogen removal efficiencies for the Caerlaverock, Castle Espie, Llanelli and Millennium constructed wetland systems.

Future analysis of hydraulic data would permit an accurate quantification of CW treatment performance and aid further wetland system design and management efforts for WWT. However, the determination of loads and fluxes as part of a complex nutrient balance model for each wetland would be rather costly and can not be justified in the present economic climate.

The findings can be seen as rather rare evidence that CW have a limited life span. Therefore, proper wetland management plans (e.g., sediment removal) need to be implemented after wetland system construction to allow for a long operation period.

Table 7-4 Annual nutrient concentrations (mean ± standard deviation) for the Wildfowl & Wetlands Trust constructed wetlands.

| Site | Year | $NH_3$-N (mg $l^{-1}$) | | | $NO_3$-N (mg $l^{-1}$) | | | $PO_4$-P (mg $l^{-1}$) | | | TP (mg $l^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Inflow | Outflow | | Inflow | Outflow | | Inflow | Outflow | | Inflow | Outflow | |
| Caerlaverock | 2005 | 63.5±37.3 | 17.7±9.1 | | 1.3±0.7 | 0.7±0.3 | | 8.1±2.8 | 4.6±0.8 | | 8.6±2.7 | 5.0±1.2 | |
| | 2006 | 43.5±24.5 | 13.4±9.3 | | 0 | 0.8±1.0 | | 9.5±1.5 | 8.2±2.3 | | 5.7±1.9 | 3.9±1.4 | |
| | 2007 | 21.1±30.9 | 11.0±11.7 | | 0 | 2.0±1.2 | | 6.6±2.9 | 6.7±3.3 | | 6.4±3.3 | 3.7±1.0 | |
| | 2008 | 10.2±6.8 | 3.7±2.1 | | 0 | 2.7±1.6 | | 7.2±2.2 | 5.9±1.4 | | 5.1±1.3 | 4.4±1.5 | |
| | 2009 | 7.3±3.3 | 2.0±1.9 | | 0 | 1.1±0.9 | | 7.8±4.7 | 7.5±4.8 | | 9.3±4.1 | 5.3±2.1 | |
| Castle Espie | | | (G) | (S) | | (G) | (S) | | (G) | (S) | | (G) | (S) |
| | 2005 | 75.5±40.3 | 44.4±23.3 | 6.5±2.1 | 1.2±0.8 | 0.8±0.4 | 1.1±0.8 | 8.1±4.6 | 4.2±2.2 | 1.6±0.9 | 8.6±4.5 | 4.8±2.7 | 3.8±2.5 |
| | 2006 | 30.5±18.0 | 24.2±14.3 | 7.0±3.6 | 0.2±0.2 | 0.1±0.1 | 0.1±0.2 | 13.2±8.5 | 10.3±5.2 | 13.2±4.0 | 13.2±8.5 | 10.3±5.2 | 13.2±4.0 |
| | 2007 | 3.2±2.8 | 2.0±0.9 | 3.5±1.0 | 0.1±0.1 | 0.1±0.6 | 0 | 5.4±2.3 | 6.0±2.5 | 6.7±1.5 | 5.4±2.3 | 6.0±2.5 | 6.7±1.5 |
| | 2008 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | 6.1±3.8 | 2.3±0.1 | 3.7±2.4 | 6.1±3.8 | 2.3±0.1 | 3.7±2.4 |
| Llanelli | | | (R) | (L) | | (R) | (L) | | (R) | (L) | | (R) | (L) |
| | 2005 | 1.1±1.4 | 0.2±0.1 | 0.3±0.2 | 5.3±2.5 | 1.1±0.6 | 1.8±1.5 | 1.3±1.6 | 1.5±0.4 | 1.3±0.8 | 1.7±1.9 | 1.7±0.4 | 1.5±0.9 |
| | 2006 | 0.2±0.0 | 0.2±0.1 | 0.2±0.1 | 3.3±1.5 | 1.5±0.7 | 1.0±0.1 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| | 2007 | 0.7±1.1 | 0.4±0.3 | 0.4±0.3 | 2.6±0.8 | 0.8±0.6 | 0.9±0.6 | 2.1±1.3 | 1.2±0.5 | 1.2±0.6 | 2.2±1.3 | 1.3±0.6 | 1.3±0.6 |
| | 2008 | 1.7±2.1 | 0.3±0.3 | 0.5±1.0 | 2.7±2.1 | 0.6±0.5 | 0.5±0.4 | 0.7±0.5 | 1.7±1.4 | 0.7±0.4 | 0.9±0.6 | 1.4±0.8 | 1.0±0.5 |
| | 2009 | 0 | 0.6±1.1 | 0.6±1.3 | 3.5±0.9 | 1.5±0.5 | 1.8±0.7 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| Millennium | 2005 | 27.7±20.7 | 0.5±0.2 | | 0.9±0.5 | 12.0±6.8 | | 4.3±1.9 | 3.7±0.9 | | 5.1±2.2 | 4.2±1.5 | |
| | 2006 | 29.8±18.3 | 0.5±0.9 | | 0 | 9.7±4.9 | | 9.2±3.6 | 9.6±3.0 | | N.A. | N.A. | |
| | 2007 | 28.6±20.8 | 2.6±6.2 | | 0.1±0.2 | 11.0±4.4 | | 7.6±2.0 | 6.1±1.0 | | N.A. | N.A. | |
| | 2008 | 34.5±20.3 | 0.2±0.2 | | N.A. | N.A. | | 10.4±6.3 | 7.7±0.8 | | N.A. | N.A. | |
| | 2009 | 17.0±11.1 | 0.5±0.8 | | N.A. | N.A. | | 6.4±2.5 | 6.2±2.0 | | N.A. | N.A. | |
| Welney | 2008 | 10.0±0.0 | 4.6±4.2 | | 0 | 1.2±2.2 | | 8.8±1.8 | 0.1±0.1 | | 6.6±1.3 | 0.2±0.1 | |
| | 2009 | 15.0±0.0 | 15.0±0.0 | | 0 | 0 | | 8.0±2.8 | 1.0±0.0 | | 8.2±2.5 | 1.5±1.1 | |

$NH_3$-N, ammonia-nitrogen; $NO_3$-N, nitrate-nitrogen; $PO_4$-P, ortho-phosphate-phosphorus; TP, total phosphorus; G, effluent from the horizontal sub-surface flow wetland cell with gravel substrate; S, effluent from the free surface flow wetland cell with soil substrate; R, effluent from the right hand secondary free surface flow wetland cell; L, effluent from the left hand secondary free surface flow wetland cell; N.A., not available.

# Chapter 8

# Conclusions and Recommendations

## *8.1 Conclusions*

Based on the findings of the present study and foregoing discussion, the main conclusions can be summarised as follows:

- Both mesocosm-scale and full-scale integrated constructed wetland (ICW) studies showed that contaminants (i.e. nitrogen and phosphorus) accumulated in wetland sediments and substrates could release back to overlying water column and the system acted as contaminant sources rather than sinks. The treatment performance of ICWs (in particular the first cell) declines after 10 years of operation.
- The relationships between physico-chemical parameters and contaminant treatment efficiency were sequentially investigated using four advanced statistical tools (MRA, PCA, RDA, and SOM). The obtained results offered complementary information for the estimation of the treatment efficiency of contaminants. The statistical analysis results indicated that electrical conductivity (EC) and redox potential (RP) values affect chemical oxygen demand treatment efficiency. Chloride (Cl) concentration and RP value have an impact on ammonia-nitrogen treatment performance. Nitrate-nitrogen removal is influenced by dissolved oxygen (DO) concentration and RP value. Molybdate reactive

phosphorus treatment efficiency is related to DO concentration and EC value. The SOM model was validated successfully used to predict water quality variables in ICWs. The application of SOM can minimize the costs of water quality monitoring and support management decisions in real-time.

- The use of two different common used wetland plants was also evaluated in mesocosm study. In experimental period 1, the treatment efficiencies of $NH_3$-N and MRP were statistically significant on all sample dates. In addition, $NH_3$-N concentrations in mesocosm 3 were significantly lower than those in mesocosm 4 in the second experimental period. Even though no obvious difference between the performances of vegetation was recorded for other studied parameters, *Phragmites australis* outperformed *Agrostis stolonifera*. The experimental results showed that *Phragmites australis* enhanced the oxygen diffusion to sediment and substrate layers due to the extensive root and rhizome system. On the other hand, since *Agrostis stolonifera* can only obtain nutrients from the water column which limited their function in this particular study.
- No leachate could be collected from outlet valves at bottom of each mesocosm throughout both experimental periods. Furthermore, the monitoring data of groundwater and surface water indicated that full-scale ICW applications had neither contaminated groundwater nor recipient aquatic systems. Although the absence of artificial liners, the compact bentonite layer functions as an excellent barrier to reduce infiltration of wastewater and minimize groundwater contamination. In addition, the biogeochemical processes taking place within sediments play a significant role in clogging soil matrix and in providing impedance to infiltration.

- The mass removal efficiencies of contaminants have not shown immediate response to the increase of HLR throughout the study period in Glaslough ICW. These results contradict previous studies which had suggested that high HLR might reduce the effectiveness of contaminant degradation processes. The large footprint and multi-cellular configuration of the studied can help regulate HLR gradient through the system.
- Glaslough ICW showed significantly poor ammonia-nitrogen removal in winter, 2010 (2.2%) and winter, 2011 (38.7%). Negative removals of nitrate-nitrogen had also been recorded in autumn, 2010 (-3.8%), winter, 2010 (-28.8%) and winter 2011 (-144.0%). Molybdate reactive phosphorus removal was ineffective in winter, 2010 (-31.1%) and winter, 2011 (-85.6%). Similarly, the system showed lower chemical oxygen demand treatment performances in autumns and winters. No significant seasonal differences were observed for biochemical oxygen demand and total suspended solids reduction. Moreover, the reductions of ammonia-nitrogen were relatively higher in summers for four representative WWT constructed wetland system. These findings illustrated that the effects of temperatures on treatment effectiveness of CWs resulted from the changes in both chemistry and microbial activity. In fact, the contaminants removal of CWs in cold climate can be optimized further by increasing the hydraulic retention time and/or by enlarging the wetland system.
- Appropriate sediment management (in particular the first cell) is paramount to maintain treatment performances of CWs and to protect receiving watercourses though very few evidence indicating decreased contaminant removal efficiencies of constructed wetland systems has been published.

## 8.2 Recommendations

The results from preliminary mesocosm study demonstrated contaminant release from wetland sediments. This can be the first step toward explicitly investigating wetland sediments that act as a source of nutrients and contaminants. In addition, these obtained results are in good agreement with full-scale ICW treatment performance. According to the findings and discussion of this study, possible extensions of the research are as follows:

- The mesocosm based study was carried out under well controlled operational conditions which might limit the application of findings derived from statistical analysis. Thus, the full-scale ICW dataset should be further analysed to improve the tested techniques and models.
- It is not clear understanding of key biotic and abiotic variables, their interactions at temporal and spatial scales, and their effects on nutrient retention and/or release by wetland sediments. Further study on sediment and soil microbial community should be conducted.
- It is important to quantify the role of wetland plants in treatment wetlands.
- The tracer study was not performed to confirm hydraulic retention time of Glaslough ICW system.
- Wetlands have the potential to sequester atmospheric carbon via the accretion of new sediments and substrates. On the other hand, they can also emit greenhouse

gases ($CO_2$, $CH_4$ and $N_2O$). Factors such as hydrologic conditions affecting greenhouse gases release from wetlands need to be investigated.

- Given the tropical locations for many developing countries, the performance of ICW and establishment of plant species in tropical climates should be examined.

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# Appendix A

***Selected experimental data***

Table A1 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 1).

| Date | Temperature (℃) | | | | | pH | | | | | Electrical conductivity (μS $cm^{-1}$) | | | | | Redox potential (mV) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III |
| 19/02/2009 | 16.7 | 16.6 | 17.1 | 16.4 | 16.4 | 7.70 | 7.02 | 7.20 | 6.95 | 6.75 | 1466 | 565 | 2381 | 2136 | 3100 | 150 | 164 | 144 | 194 | 190 |
| 26/02/2009 | 16.4 | 17.0 | 16.5 | 16.8 | 16.5 | 7.39 | 6.14 | 6.67 | 6.60 | 6.49 | 1576 | 868 | 1743 | 2128 | 3148 | 174.2 | 164 | 32 | 76 | 65 |
| 19/03/2009 | 16.8 | 17.0 | 16.8 | 16.9 | 16.8 | 7.57 | 7.67 | 6.65 | 6.50 | 6.50 | 970 | 596 | 1379 | 1272 | 3014 | 121.3 | 131 | 10 | 33 | 33 |
| 26/03/2009 | 17.4 | 18.0 | 16.5 | 17.0 | 16.7 | 7.03 | 6.15 | 6.25 | 6.33 | 6.45 | 446 | 444 | 219 | 722 | 3024 | 80 | 173 | 11 | 9 | 25 |
| 02/04/2009 | 16.5 | 18.0 | 16.6 | 17.5 | 17.5 | 7.34 | 6.28 | 6.53 | 6.30 | 6.54 | 687 | 508 | 511 | 539 | 3044 | 51.2 | 21 | 10 | 12 | 19 |
| 09/04/2009 | 16.2 | 18.0 | 16.8 | 17.5 | 16.9 | 7.50 | 6.80 | 6.37 | 6.13 | 6.48 | 742 | 840 | 1235 | 864 | 2054 | 66.1 | 82 | -15 | 13 | 42 |
| 16/04/2009 | 16.5 | 19.0 | 17.0 | 16.2 | 16.8 | 7.21 | 6.38 | 6.23 | 6.24 | 6.61 | 871 | 185 | 792 | 906 | 1848 | 24 | 51 | -43 | -49 | 45 |
| 23/04/2009 | 17.1 | 19.0 | 17.0 | 16.8 | 17.1 | 7.30 | 6.49 | 6.33 | 6.02 | 6.62 | 893 | 199 | 438 | 798 | 1264 | 27 | 78 | -49 | -31 | 38 |
| 30/04/2009 | 16.9 | 18.5 | 17.0 | 17.0 | 17.2 | 7.56 | 6.08 | 6.32 | 6.08 | 6.49 | 768 | 98 | 469 | 629 | 1275 | 38.8 | 70 | -59 | -60 | 35 |
| 07/05/2009 | 16.5 | 19.5 | 17.1 | 18.0 | 17.2 | 7.50 | 6.30 | 5.85 | 5.97 | 6.26 | 948 | 129 | 411 | 638 | 1710 | 29.5 | 70 | -37 | -20 | 45 |
| 14/05/2009 | 16.5 | 19.5 | 17.2 | 17.3 | 17.1 | 7.56 | 6.54 | 5.90 | 6.08 | 6.32 | 1050 | 184 | 627 | 650 | 1790 | 31 | 76 | -29 | -56 | 49 |
| 21/05/2009 | 16.4 | 20.0 | 17.0 | 17.2 | 17.1 | 7.43 | 6.25 | 6.10 | 6.39 | 6.39 | 983 | 203 | 547 | 697 | 1787 | 30.1 | 53 | -34 | -45 | 44 |
| 28/05/2009 | 17.3 | 22.0 | 18.1 | 17.1 | 17.5 | 7.35 | 6.46 | 6.12 | 5.89 | 6.34 | 1137 | 339 | 512 | 1174 | 1708 | 24 | 41 | -26.4 | -43 | 32 |
| 04/06/2009 | 17.7 | 22.0 | 18.1 | 16.5 | 17.0 | 7.72 | 6.51 | 6.53 | 6.02 | 6.52 | 1038 | 238 | 744 | 1078 | 1788 | 36.5 | 45 | -23 | -38 | 29 |
| 11/06/2009 | 16.2 | 20.0 | 17.3 | 17.0 | 16.5 | 7.64 | 6.88 | 6.46 | 5.65 | 6.83 | 830 | 386 | 326 | 1120 | 1710 | 40 | 38 | -65 | -45 | 10 |
| 18/06/2009 | 16.0 | 18.4 | 17.0 | 16.5 | 16.5 | 7.50 | 6.65 | 6.34 | 6.00 | 6.68 | 1237 | 117 | 679 | 868 | 1260 | 48 | 35 | -80 | -42 | 12 |
| 25/06/2009 | 17.5 | 22.0 | 17.9 | 17.8 | 16.2 | 7.68 | 6.45 | 6.41 | 6.55 | 6.70 | 1151 | 234 | 636 | 815 | 1738 | 45 | 30 | -96 | -55 | -25 |
| 02/07/2009 | 16.5 | 22.0 | 16.6 | 16.3 | 17.0 | 7.80 | 6.60 | 6.61 | 5.88 | 6.52 | 1117 | 230 | 620 | 742 | 1750 | 172 | 33 | -52 | -43 | -22 |
| 09/07/2009 | 16.7 | 22.5 | 17.7 | 17.3 | 16.7 | 7.80 | 6.98 | 6.57 | 5.89 | 6.36 | 1148 | 189 | 587 | 772 | 1615 | 120 | 72 | -87 | -49 | 10 |

Table A2 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 1).

| Date | Temperature (°C) | | | | | pH | | | | | Electrical conductivity (µS $cm^{-1}$) | | | | | Redox potential (mV) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III |
| 16/07/2009 | 17.3 | 22.0 | 17.0 | 17.7 | 17.8 | 7.51 | 6.84 | 6.19 | 5.88 | 6.40 | 1194 | 170 | 540 | 742 | 1674 | 175 | 92 | -77 | -47 | -51 |
| 23/07/2009 | 16.3 | 22.0 | 16.1 | 16.7 | 17.2 | 7.76 | 6.62 | 6.42 | 6.17 | 6.52 | 1123 | 137 | 563 | 651 | 1656 | -12 | 40 | -74 | -66 | -45 |
| 30/07/2009 | 17.1 | 21.5 | 17.5 | 17.1 | 17.6 | 7.65 | 6.55 | 6.50 | 5.81 | 6.39 | 1171 | 145 | 512 | 633 | 1670 | -12 | 35 | -81 | -53 | -34 |
| 06/08/2009 | 16.9 | 22.0 | 17.2 | 17.1 | 17.6 | 7.44 | 6.73 | 6.33 | 5.95 | 6.41 | 1170 | 122 | 474 | 645 | 1725 | -22 | 25 | -87 | -65 | -46 |
| 13/08/2009 | 17.0 | 22.0 | 17.2 | 17.3 | 17.2 | 7.52 | 6.41 | 6.62 | 6.01 | 6.46 | 1104 | 213 | 460 | 657 | 1795 | -21 | 22 | -89 | -71 | -48 |
| 20/08/2009 | 16.2 | 19.0 | 17.2 | 17.1 | 16.5 | 7.60 | 6.63 | 6.53 | 6.06 | 6.44 | 1120 | 150 | 450 | 684 | 1752 | -31 | 35 | -93 | -180 | -55 |
| 27/08/2009 | 16.5 | 22.0 | 17.1 | 17.3 | 17.2 | 7.67 | 6.47 | 6.64 | 6.08 | 6.58 | 1184 | 153 | 419 | 656 | 1768 | -38 | 28 | -145 | -120 | -44 |
| 03/09/2009 | 17.0 | 18.0 | 17.5 | 17.2 | 17 | 7.58 | 6.06 | 6.53 | 5.99 | 6.44 | 1212 | 168 | 400 | 621 | 1802 | -31 | 30 | -168 | -184 | -58 |
| 10/09/2009 | 16.5 | 20.0 | 17.3 | 17.6 | 17.1 | 7.65 | 6.50 | 6.63 | 5.91 | 6.55 | 1220 | 315 | 370 | 675 | 1730 | -35 | 24 | -370 | -331 | -66 |
| 17/09/2009 | 16.0 | 20.2 | 17.2 | 17.3 | 16.9 | 7.58 | 6.67 | 6.64 | 6.15 | 6.37 | 1312 | 149 | 358 | 699 | 1873 | -27 | 10 | -360 | -350 | -95 |
| 24/09/2009 | 16.2 | 18.0 | 16.8 | 16.7 | 16.8 | 7.66 | 6.17 | 6.71 | 6.02 | 6.28 | 1403 | 122 | 376 | 663 | 1739 | -48 | 12 | -379 | -323 | -98 |
| 01/10/2009 | 15.6 | 18.4 | 16.4 | 16.3 | 16.3 | 7.51 | 6.45 | 6.58 | 5.96 | 6.75 | 1181 | 152 | 416 | 614 | 1825 | -37 | 14 | -345 | -312 | -105 |
| 20/10/2009 | 16.0 | - | 16.4 | 16.4 | 16.9 | 7.27 | - | 6.23 | 6.32 | 6.08 | 1333 | - | 433 | 636 | 1915 | 22 | - | -32 | -26 | -40 |
| 06/11/2009 | 15.5 | 15.2 | 15.6 | 16.1 | 15.9 | 6.83 | 6.68 | 6.03 | 6.24 | 6.76 | 1125 | 224 | 480 | 654 | 2120 | -180 | -106 | -179 | -398 | -295 |
| 13/11/2009 | 15.2 | 15.2 | 15.4 | 15.1 | 15.9 | 7.24 | 7.09 | 6.31 | 6.03 | 6.73 | 1050 | 163 | 437 | 627 | 2092 | -243 | -186 | -242 | -467 | -355 |
| 20/11/2009 | 17.2 | 17.4 | 16.8 | 17.4 | 16 | 7.23 | 6.00 | 6.40 | 5.85 | 6.93 | 1201 | 148 | 423 | 645 | 2150 | -340 | -216 | -112 | -320 | -209 |
| 27/11/2009 | 15.0 | 14.5 | 15.3 | 15.2 | 15.3 | 7.15 | 6.68 | 6.35 | 5.95 | 6.59 | 1228 | 138 | 383 | 586 | 2225 | -411 | -333 | -284 | -358 | -270 |
| 02/12/2009 | 13.8 | 13.6 | 14.6 | 14.8 | 15.2 | 7.18 | 6.50 | 6.63 | 6.24 | 6.63 | 1092 | 215 | 377 | 515 | 2051 | -351 | -388 | -185 | -395 | -242 |
| 11/12/2009 | 14.2 | 14.8 | 14.3 | 13.5 | 14.00 | 7.45 | 7.04 | 6.68 | 6.38 | 6.74 | 1092 | 224 | 392 | 538 | 2222 | -243 | -122 | -128 | -307 | -208 |

Table A3 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 1).

| Date | Temperature (℃) | | | | | pH | | | | | Electrical conductivity (μS $cm^{-1}$) | | | | | Redox potential (mV) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III |
| 18/12/2009 | 13.4 | 14.1 | 12.7 | 12.7 | 13.7 | 7.58 | 6.76 | 6.39 | 6.15 | 6.74 | 1115 | 149 | 368 | 584 | 2114 | -155 | -52 | -186 | -302 | -276 |
| 15/01/2010 | 14.5 | 14.4 | 14.5 | 15.3 | 14.9 | 7.49 | 6.60 | 6.53 | 5.96 | 6.80 | 1209 | 180 | 375 | 520 | 2290 | -174 | -183 | -132 | -328 | -194 |
| 22/01/2010 | 16.2 | 16.5 | 16.3 | 16.5 | 16.4 | 7.45 | 6.76 | 6.29 | 6.28 | 6.79 | 1305 | 190 | 384 | 570 | 2126 | -189 | -156 | -184 | -358 | -226 |
| 29/01/2010 | 15.1 | 15.3 | 15.1 | 15.1 | 15.4 | 7.20 | 6.64 | 6.45 | 6.35 | 6.81 | 1240 | 158 | 382 | 540 | 2071 | -165 | -128 | -192 | -324 | -235 |
| 05/02/2010 | 14.9 | 15.6 | 15.2 | 15.2 | 15.0 | 7.28 | 6.65 | 6.42 | 6.29 | 6.95 | 1305 | 211 | 333 | 574 | 2165 | -160 | -120 | -185 | -345 | -227 |
| 11/02/2010 | 14.3 | 14.9 | 14.5 | 15.3 | 14.2 | 7.23 | 6.67 | 6.37 | 6.03 | 6.98 | 1240 | 191 | 304 | 527 | 2046 | -184 | -109 | -178 | -329 | -232 |
| 18/02/2010 | 14.3 | 14.9 | 14.5 | 14.8 | 14.9 | 7.02 | 6.66 | 6.22 | 5.93 | 6.86 | 1292 | 181 | 295 | 538 | 2042 | -175 | -112 | -183 | -315 | -229 |
| 25/02/2010 | 14.8 | 14.6 | 15.2 | 15.3 | 15.2 | 7.28 | 6.68 | 6.42 | 6.24 | 6.89 | 1208 | 191 | 292 | 528 | 1988 | -180 | -125 | -179 | -325 | -243 |
| 04/03/2010 | 14.7 | 15.4 | 15.3 | 15.6 | 15.8 | 7.15 | 6.61 | 6.46 | 5.97 | 6.95 | 1149 | 252 | 312 | 518 | 1936 | -186 | -118 | -176 | -311 | -212 |
| 11/03/2010 | 17.1 | 16.6 | 16.1 | 16.7 | 16.4 | 6.98 | 6.55 | 6.38 | 5.98 | 6.89 | 1148 | 208 | 299 | 513 | 2004 | -180 | -105 | -150 | -304 | -243 |
| 19/03/2010 | 16.2 | 17.2 | 16.4 | 16.9 | 16.6 | 6.93 | 6.62 | 6.21 | 5.93 | 6.90 | 1410 | 250 | 409 | 577 | 2022 | -170 | -192 | -215 | -352 | -232 |
| 25/03/2010 | 16.6 | 16.8 | 17.7 | 18.2 | 16.7 | 6.86 | 6.60 | 6.30 | 5.98 | 7.03 | 1277 | 290 | 376 | 532 | 1885 | -155 | -138 | -206 | -300 | -253 |
| 30/03/2010 | 15.4 | 15.8 | 16.2 | 16.6 | 15.5 | 7.08 | 6.34 | 6.01 | 5.81 | 7.09 | 1398 | 284 | 394 | 588 | 2059 | -164 | -125 | -207 | -265 | -186 |
| 09/04/2010 | 17.3 | 18.0 | 18.2 | 17.4 | 16.5 | 7.77 | 6.80 | 6.28 | 5.87 | 7.20 | 1437 | 204 | 402 | 565 | 1983 | -152 | -109 | -177 | -291 | -185 |
| 15/04/2010 | 16.8 | 17.6 | 17.5 | 18.3 | 16.6 | 7.84 | 6.76 | 6.36 | 5.98 | 7.57 | 1287 | 246 | 409 | 580 | 2433 | -135 | -115 | -217 | -276 | -187 |
| 22/04/2010 | 16.4 | 16.1 | 16.4 | 17.5 | 16.8 | 7.80 | 6.64 | 6.29 | 5.74 | 7.61 | 1495 | 399 | 403 | 598 | 1954 | -128 | -107 | -216 | -264 | -163 |
| 06/05/2010 | 18.4 | 18.1 | 18.4 | 18.5 | 18.0 | 7.88 | 7.07 | 6.21 | 5.74 | 7.31 | 1558 | 358 | 503 | 604 | 2214 | -120 | -104 | -140 | -184 | -70 |
| 13/05/2010 | 17.4 | 17.6 | 18.4 | 18.4 | 16.9 | 7.86 | 7.07 | 6.20 | 5.68 | 7.25 | 1564 | 296 | 482 | 602 | 2270 | -82 | -105 | -136 | -165 | -37 |
| 20/05/2010 | 18.9 | 18.8 | 19.7 | 19.4 | 18.8 | 7.99 | 7.32 | 6.30 | 5.81 | 7.45 | 1565 | 398 | 509 | 682 | 2204 | -64 | -85 | -129 | -170 | -32 |

Table A4 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 1).

| Date | Temperature (℃) | | | | | pH | | | | | Electrical conductivity (μS cm$^{-1}$) | | | | | Redox potential (mV) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III |
| 27/05/2009 | 18.4 | 18.6 | 19.0 | 19.4 | 18.8 | 7.75 | 6.95 | 6.44 | 5.87 | 7.79 | 1666 | 396 | 525 | 684 | 3111 | -125 | -92 | -80 | -153 | -29 |
| 04/06/2010 | 20.8 | 21.9 | 18.8 | 18.7 | 18.2 | 7.83 | 6.64 | 6.56 | 6.06 | 7.38 | 1690 | 322 | 718 | 722 | 2257 | -76 | -120 | -126 | -172 | -39 |
| 10/06/2010 | 19.6 | 18.9 | 19.5 | 18.7 | 17.3 | 7.78 | 6.56 | 6.36 | 5.71 | 7.35 | 1598 | 356 | 670 | 735 | 2434 | -86 | -94 | -128 | -160 | -40 |
| 24/06/2010 | 20.9 | 17.8 | 19.7 | 21.7 | 19.5 | 7.9 | 7.33 | 6.33 | 5.85 | 7.08 | 1606 | 289 | 600 | 760 | 2119 | -119 | -74 | -92 | -108 | -37 |
| 01/07/2010 | 22.6 | 22.4 | 21.2 | 20.3 | 17.5 | 7.76 | 7.12 | 6.39 | 5.92 | 7.13 | 1647 | 343 | 606 | 769 | 2640 | -109 | -70 | -91 | -130 | -45 |
| 08/07/2010 | 19.5 | 21.3 | 20.3 | 23.3 | 18.3 | 7.55 | 6.98 | 6.36 | 5.98 | 7.60 | 1375 | 370 | 586 | 689 | 2500 | -100 | -85 | -124 | -109 | -39 |
| 15/07/2010 | 19.9 | 20.0 | 19.4 | 21.1 | 16.8 | 7.65 | 7.25 | 6.43 | 5.87 | 7.02 | 1563 | 479 | 601 | 737 | 2187 | -86 | -60 | -124 | -102 | -26 |
| 22/07/2010 | 17.8 | 18.3 | 18.6 | 18 | 17 | 7.78 | 7.20 | 6.78 | 6.27 | 7.34 | 1447 | 531 | 630 | 719 | 2067 | -63 | -68 | -83 | -105 | -40 |
| 28/07/2010 | 16.8 | 17.7 | 18.2 | 18.8 | 17.2 | 7.53 | 7.26 | 6.59 | 5.95 | 7.24 | 1727 | 671 | 738 | 823 | 2478 | -26 | -63 | -71 | -117 | -75 |
| 09/08/2010 | 20.1 | 18.6 | 19.7 | 20.9 | 18.1 | 8.17 | 7.41 | 6.67 | 6.16 | 7.26 | 1596 | 409 | 746 | 834 | 2216 | -31 | -31 | -114 | -106 | -29 |
| 13/08/2010 | 17.4 | 19.6 | 18.7 | 18.0 | 17.3 | 7.86 | 7.04 | 6.61 | 6.17 | 7.16 | 1574 | 412 | 719 | 863 | 2348 | -61 | -42 | -50 | -110 | -47 |
| 19/08/2010 | 17.4 | 18.1 | 19.4 | 20.1 | 17.3 | 7.92 | 7.44 | 6.40 | 6.31 | 6.96 | 1572 | 504 | 644 | 667 | 2370 | -40 | -64 | -67 | -110 | -39 |
| 24/08/2010 | 16.7 | 16.9 | 18.1 | 18.8 | 16.8 | 8.13 | 7.08 | 6.70 | 6.17 | 6.90 | 1643 | 428 | 761 | 738 | 2490 | -26 | -37 | -76 | -106 | -32 |
| 03/09/2010 | 17.6 | 18.2 | 18.5 | 19.8 | 18.7 | 7.75 | 7.27 | 6.34 | 5.95 | 7.24 | 1574 | 458 | 585 | 695 | 2287 | -85 | -89 | -85 | -120 | -48 |
| 09/09/2010 | 17.5 | 18.1 | 18.6 | 19.2 | 18.9 | 7.97 | 7.34 | 6.46 | 6.13 | 6.97 | 1643 | 574 | 742 | 854 | 2355 | -64 | -78 | -110 | -115 | -69 |
| 16/09/2010 | 17.8 | 18.6 | 19.3 | 20.1 | 19.5 | 7.61 | 7.46 | 6.74 | 6.21 | 7.34 | 1527 | 493 | 606 | 735 | 2141 | -56 | -87 | -118 | -107 | -71 |
| 23/09/2010 | 16.9 | 17.8 | 18.2 | 19.6 | 18.2 | 7.84 | 7.41 | 6.57 | 6.04 | 7.18 | 1715 | 617 | 724 | 865 | 2453 | -107 | -96 | -98 | -110 | -39 |
| 30/09/2010 | 17.2 | 18.3 | 18.9 | 20.8 | 19.3 | 7.63 | 7.37 | 6.45 | 5.98 | 7.26 | 1476 | 535 | 647 | 785 | 2521 | -75 | -84 | -95 | -124 | -40 |
| 07/10/2010 | 16.8 | 17.2 | 18.4 | 21.3 | 20.1 | 7.87 | 7.15 | 6.61 | 6.17 | 7.12 | 1684 | 652 | 748 | 789 | 2384 | -84 | -101 | -97 | -118 | -37 |

Table A5 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 1).

| Date | Temperature (°C) | | | | | pH | | | | | Electrical conductivity (μS $cm^{-1}$) | | | | | Redox potential (mV) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III |
| 14/10/2009 | 17.3 | 17.6 | 18.6 | 19.5 | 18.3 | 7.82 | 7.35 | 6.84 | 6.25 | 7.24 | 1587 | 506 | 675 | 823 | 2495 | -78 | -68 | -105 | -120 | -35 |
| 21/10/2010 | 17.0 | 17.3 | 18.7 | 20.3 | 19.1 | 7.79 | 7.42 | 6.78 | 6.19 | 7.18 | 1623 | 549 | 712 | 845 | 2508 | -95 | -49 | -99 | -115 | -40 |
| 28/10/2010 | 15.8 | 15.2 | 17.3 | 16.1 | 17.9 | 7.83 | 6.68 | 6.03 | 6.22 | 6.75 | 1425 | 326 | 680 | 654 | 2320 | -115 | -67 | -112 | -124 | -75 |
| 04/11/2010 | 15.3 | 15.2 | 16.8 | 15.1 | 15.4 | 7.24 | 7.09 | 6.31 | 6.07 | 6.78 | 1550 | 463 | 637 | 823 | 2195 | -106 | -90 | -96 | -132 | -87 |
| 11/11/2010 | 15.1 | 16.4 | 15.6 | 16.4 | 16.2 | 7.23 | 6.04 | 6.4 | 5.87 | 6.91 | 1501 | 585 | 723 | 642 | 2340 | -84 | -77 | -108 | -109 | -62 |
| 18/11/2010 | 15.6 | 14.5 | 15.6 | 15.1 | 15.3 | 7.75 | 6.68 | 6.45 | 5.85 | 6.52 | 1628 | 429 | 763 | 763 | 2135 | -75 | -102 | -102 | -114 | -79 |
| 25/11/2010 | 14.9 | 15.6 | 14.6 | 14.2 | 15.0 | 7.81 | 6.38 | 6.67 | 6.24 | 6.73 | 1483 | 513 | 616 | 814 | 2278 | -80 | -95 | -97 | -125 | -59 |
| 02/12/2010 | 15.0 | 13.8 | 14.5 | 13.5 | 14.3 | 7.45 | 7.04 | 6.69 | 6.38 | 6.84 | 1592 | 516 | 592 | 736 | 2122 | -76 | -88 | -86 | -111 | -42 |
| 09/12/2010 | 14.4 | 14.3 | 12.9 | 14.7 | 13.9 | 7.58 | 6.76 | 6.39 | 6.14 | 6.54 | 1615 | 449 | 568 | 634 | 2104 | -95 | -78 | -91 | -104 | -53 |
| 16/12/2010 | 13.8 | 14.7 | 14.5 | 15.3 | 14.9 | 7.49 | 6.60 | 6.43 | 5.94 | 6.52 | 1709 | 508 | 675 | 629 | 2230 | -90 | -62 | -105 | -112 | -62 |
| 11/02/2011 | 14.1 | 14.5 | 14.8 | 15.2 | 14.3 | 7.43 | 6.77 | 6.38 | 6.03 | 6.94 | 1640 | 491 | 704 | 627 | 2046 | -104 | -89 | -108 | -129 | -72 |
| 18/02/2011 | 14.2 | 14.8 | 14.9 | 15.0 | 14.7 | 7.42 | 6.86 | 6.49 | 5.93 | 6.87 | 1592 | 518 | 695 | 638 | 2142 | -95 | -92 | -93 | -114 | -69 |
| 25/02/2011 | 14.5 | 14.7 | 15.1 | 15.3 | 15.0 | 7.33 | 6.68 | 6.41 | 6.24 | 6.88 | 1608 | 491 | 692 | 625 | 2084 | -88 | -105 | -97 | -105 | -63 |

Table A6 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 1).

| Date | Dissolved oxygen (mg $l^{-1}$) | | | | | Total suspended solids (mg $l^{-1}$) | | | | | COD (mg $l^{-1}$) | | | | | Ammonia-nitrogen (mg $l^{-1}$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III |
| 19/02/2009 | 3.5 | 6.5 | 5.3 | 6.8 | 6.5 | - | - | - | - | - | 105 | 110 | 60 | 65 | 85 | - | - | - | - | - |
| 26/02/2009 | 3.3 | 6.6 | 2.2 | 2.5 | 2.3 | - | - | - | - | - | 104 | 92 | 45 | 68 | 89 | - | - | - | - | - |
| 19/03/2009 | 3.3 | 4.9 | 1.7 | 2.3 | 3.3 | 10 | 10 | 15 | 10 | 20 | 106 | 85 | 58 | 71 | 104 | - | - | - | - | - |
| 26/03/2009 | 3.5 | 5.2 | 2.6 | 4 | 3.1 | 10 | 20 | 10 | 10 | 20 | 95 | 76 | 60 | 62 | 95 | 0.422 | 0.419 | 1.380 | 2.771 | 219.390 |
| 02/04/2009 | 4.0 | 4.8 | 3.6 | 3.4 | 3.3 | 10 | 20 | 15 | 20 | 20 | 98 | 88 | 62 | 64 | 98 | 0.383 | 0.351 | 1.061 | 3.885 | 178.031 |
| 09/04/2009 | 5.2 | 6.9 | 2.5 | 4.3 | 3.9 | 10 | 20 | 10 | 20 | 20 | 102 | 95 | 66 | 72 | 138 | 3.445 | 0.325 | 0.187 | 18.903 | 322.738 |
| 16/04/2009 | 5.7 | 5.5 | 1.7 | 2.8 | 4.8 | 10 | 10 | 15 | 20 | 15 | 108 | 94 | 68 | 74 | 135 | 1.094 | - | 1.437 | 16.554 | 231.448 |
| 23/04/2009 | 5.6 | 5.1 | 3.1 | 3.6 | 4.4 | 10 | 10 | 15 | 20 | 10 | 100 | 85 | 70 | 78 | 158 | 0.193 | 0.874 | 0.970 | 10.256 | 102.611 |
| 30/04/2009 | 5.7 | 4.9 | 3 | 3.7 | 4.3 | 10 | 20 | 10 | 10 | 10 | 94 | 75 | 54 | 76 | 154 | 0.130 | 0.224 | 0.867 | 9.803 | 101.152 |
| 07/05/2009 | 5.6 | 6.3 | 2.9 | 4.9 | 4.8 | 10 | 20 | 10 | 10 | 20 | 112 | 108 | 84 | 82 | 180 | 0.080 | 0.177 | 1.014 | 12.126 | 104.211 |
| 14/05/2009 | 5.5 | 5.1 | 2.4 | 4.5 | 4.2 | 10 | 10 | 10 | 10 | 10 | 116 | 95 | 100 | 80 | 165 | 0.225 | 0.796 | 2.222 | 16.792 | 97.669 |
| 21/05/2009 | 5.3 | 5.5 | 2.7 | 4.1 | 3.2 | 10 | 20 | 10 | 10 | 10 | 114 | 95 | 82 | 78 | 175 | 0.126 | 2.48 | 7.454 | 23.582 | 93.718 |
| 28/05/2009 | 6.0 | 5.4 | 2.6 | 4.3 | 4.1 | 10 | 30 | 15 | 10 | 10 | 124 | 100 | 84 | 82 | 185 | 0.114 | 1.414 | 9.310 | 22.234 | 89.332 |
| 04/06/2009 | 5.9 | 4.7 | 3.2 | 4.4 | 4.5 | 10 | 20 | 10 | 10 | 10 | 118 | 86 | 73 | 84 | 187.5 | 0.114 | 1.414 | 9.310 | 22.234 | 89.332 |
| 11/06/2009 | 6.0 | 4.5 | 2.9 | 4.1 | 3.8 | 10 | 20 | 10 | 10 | 10 | 125 | 84 | 85 | 94 | 192 | 0.110 | 4.906 | 9.784 | 28.097 | 67.054 |
| 18/06/2009 | 5.7 | 5.3 | 2.9 | 4.0 | 3.9 | 10 | 30 | 10 | 10 | 10 | 132 | 90 | 115 | 105 | 195 | 0.090 | 0.349 | 8.475 | 19.838 | 87.539 |
| 25/06/2009 | 5.6 | 5.3 | 1.8 | 3.7 | 3.2 | 10 | 30 | 10 | 10 | 10 | 135 | 92 | 132 | 138 | 215 | 0.100 | 2.456 | 6.282 | 20.577 | 73.438 |
| 02/07/2009 | 5.4 | 5.1 | 1.5 | 2.9 | 4.0 | 10 | 20 | 10 | 10 | 10 | 100 | 58 | 112 | 125 | 160 | 0.100 | 2.748 | 4.779 | 16.53 | 67.160 |
| 09/07/2009 | 5.2 | 4.3 | 1.6 | 3.3 | 3.2 | 10 | 30 | 10 | 10 | 10 | 155 | 100 | 145 | 230 | 160 | 0.103 | 1.589 | 6.150 | 20.607 | 79.823 |

Table A7 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 1).

| Date | Dissolved oxygen (mg $l^{-1}$) | | | | | Total suspended solids (mg $l^{-1}$) | | | | | COD (mg $l^{-1}$) | | | | | Ammonia-nitrogen (mg $l^{-1}$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III |
| 16/07/2009 | 5.3 | 5.2 | 1.7 | 3.9 | 3.1 | 10 | 30 | 10 | 10 | 10 | 145 | 86 | 130 | 160 | 240 | 0.092 | 0.493 | 4.807 | 17.128 | 92.163 |
| 23/07/2009 | 4.8 | 5.0 | 1.8 | 2.4 | 3.0 | 12 | 26 | 10 | 12 | 10 | 150 | 96 | 135 | 154 | 225 | 0.102 | 0.701 | 5.626 | 12.063 | 71.655 |
| 30/07/2009 | 4.6 | 4.8 | 1.6 | 2.9 | 3.0 | 12 | 30 | 8 | 12 | 10 | 165 | 90 | 110 | 130 | 230 | 0.060 | 0.815 | 4.789 | 14.664 | 102.043 |
| 06/08/2009 | 4.8 | 4.2 | 1.4 | 2.4 | 3.1 | 10 | 30 | 12 | 10 | 10 | 170 | 120 | 140 | 150 | 240 | 0.089 | 0.832 | 4.731 | 19.836 | 101.228 |
| 13/08/2009 | 4.4 | 4.4 | 1.5 | 2.5 | 3.4 | 8 | 20 | 8 | 12 | 8 | 150 | 90 | 110 | 130 | 240 | 0.073 | 3.202 | 4.848 | 17.85 | 104.451 |
| 20/08/2009 | 4.5 | 4.3 | 1.4 | 2.6 | 3.3 | 10 | 24 | 10 | 10 | 10 | 98 | 88 | 64 | 86 | 154 | 0.095 | 1.121 | 5.449 | 19.025 | 75.235 |
| 27/08/2009 | 4.9 | 4.6 | 1.5 | 3.2 | 3.5 | 8 | 28 | 10 | 10 | 8 | 86 | 78 | 76 | 128 | 146 | 0.030 | 0.759 | 3.893 | 21.53 | 85.384 |
| 03/09/2009 | 4.7 | 4.9 | 1.7 | 3 | 3.4 | 8 | 24 | 12 | 8 | 10 | 75 | 74 | 72 | 140 | 126 | 0.122 | 1.641 | 4.671 | 16.051 | 84.277 |
| 10/09/2009 | 4.8 | 4.6 | 1.8 | 3.5 | 3.4 | 10 | 26 | 12 | 10 | 10 | 82 | 76 | 68 | 138 | 135 | 0.307 | 7.687 | 4.548 | 22.011 | 72.102 |
| 17/09/2009 | 4.2 | 4.7 | 1.4 | 3.1 | 2.3 | 12 | 28 | 14 | 12 | 10 | 84 | 65 | 76 | 128 | 142 | 0.141 | 1.144 | 8.02 | 20.858 | 89.974 |
| 24/09/2009 | 4.4 | 4.5 | 1.4 | 3.3 | 2.0 | 12 | 26 | 14 | 12 | 10 | 86 | 62 | 69 | 135 | 139 | 0.406 | 1.763 | 4.601 | 21.436 | 79.141 |
| 01/10/2009 | 4.5 | 4.1 | 1.5 | 2.8 | 2.2 | 8 | 24 | 12 | 10 | 8 | 95 | 54 | 64 | 142 | 144 | 0.099 | 2.754 | 3.332 | 18.711 | 87.194 |
| 20/10/2009 | 5.6 | - | 3.9 | 3.3 | 4.8 | 40 | - | 60 | 160 | 160 | 105 | | 115 | 104 | 30 | 0.105 | - | 3.936 | 22.012 | 82.688 |
| 06/11/2009 | 5.0 | 5.1 | 4 | 3.5 | 4.7 | 60 | 20 | 60 | 220 | 160 | 92 | 85 | 78 | 69 | 45 | 0.186 | 1.038 | 2.998 | 19.626 | 85.877 |
| 13/11/2009 | 5.8 | 6.4 | 3.5 | 4 | 5.3 | 40 | 60 | 20 | 160 | 60 | 110 | 33 | 145 | 115 | 67 | 0.142 | 0.563 | 3.894 | 18.863 | 79.219 |
| 20/11/2009 | 5.4 | 5.0 | 3.0 | 3.5 | 5.5 | 60 | 40 | 20 | 200 | 60 | 101 | 32 | 120 | 100 | 81 | 0.139 | 1.203 | 3.829 | 20.665 | 82.44 |
| 27/11/2009 | 5.4 | 5.9 | 2.9 | 4.7 | 4.6 | 60 | 20 | 20 | 160 | 160 | 110 | 45 | 105 | 96 | 110 | 0.061 | 0.077 | 3.818 | 19.01 | 93.359 |
| 02/12/2009 | 5.7 | 5.5 | 3.2 | 4.4 | 4.7 | 40 | 40 | 20 | 120 | 60 | 85 | 28 | 110 | 85 | 65 | 0.118 | 4.848 | 3.871 | 6.931 | 67.326 |
| 11/12/2009 | 4.7 | 4.9 | 2.7 | 3.6 | 4.7 | 20 | 80 | 40 | 120 | 60 | 102 | 34 | 89 | 101 | 65 | 2.669 | 5.206 | 3.441 | 6.334 | 71.252 |

Table A8 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 1).

| Date | Dissolved oxygen (mg $l^{-1}$) | | | | | Total suspended solids (mg $l^{-1}$) | | | | | COD (mg $l^{-1}$) | | | | | Ammonia-nitrogen (mg $l^{-1}$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III |
| 18/12/2009 | 4.9 | 4.9 | 2.2 | 3.4 | 4.7 | 60 | 40 | 40 | 120 | 40 | 105 | 45 | 101 | 89 | 148 | 0.306 | 2.667 | - | 6.288 | 5.953 |
| 15/01/2010 | 4.6 | 4.4 | 2.3 | 3.2 | 4.7 | 60 | 40 | 80 | 200 | 120 | 102 | 36 | 96 | 101 | 125 | 0.209 | 5.972 | 2.053 | 5.965 | 68.828 |
| 22/01/2010 | 4.6 | 4.6 | 2.3 | 3.9 | 4.9 | 60 | 40 | 80 | 160 | 120 | 115 | 46 | 118 | 95 | 85 | 0.115 | 2.552 | 1.670 | 6.919 | 67.886 |
| 29/01/2010 | 4.8 | 4.9 | 3.1 | 3.9 | 4.6 | 60 | 40 | 80 | 160 | 120 | 110 | 30 | 85 | 102 | 110 | - | 0.741 | 68.594 | 6.277 | - |
| 05/02/2010 | 4.7 | 4.8 | 2.9 | 3.5 | 4.2 | 60 | 60 | 80 | 200 | 120 | 120 | 48 | 78 | 92 | 97 | 0.420 | - | - | 6.777 | 68.156 |
| 11/02/2010 | 4.9 | 4.6 | 3.1 | 3.4 | 4.4 | 60 | 60 | 80 | 140 | 120 | 115 | 72 | 65 | 100 | 135 | 0.052 | 0.368 | 1.254 | 19.880 | 46.73 |
| 18/02/2010 | 4.9 | 4.5 | 2.8 | 3.2 | 4.7 | 60 | 40 | 80 | 160 | 120 | 114 | 76 | 50 | 72 | 87 | 0.093 | 1.659 | 1.546 | 18.076 | 78.316 |
| 25/02/2010 | 4.5 | 4.4 | 2.7 | 3.3 | 4.9 | 60 | 40 | 80 | 180 | 120 | 101 | 49 | 42 | 71 | 103 | 0.084 | 0.141 | 1.285 | 18.216 | 52.888 |
| 04/03/2010 | 4.7 | 4.2 | 2.8 | 2.8 | 4.9 | 60 | 40 | 80 | 160 | 120 | 96 | 67 | 43 | 81 | 104 | 0.928 | 7.635 | 2.052 | 16.462 | 56.137 |
| 11/03/2010 | 4.7 | 4.4 | 2.7 | 3.2 | 4.2 | 60 | 60 | 100 | 160 | 100 | 93 | 49 | 42 | 69 | 101 | 0.120 | 0.310 | 1.659 | 14.192 | 84.141 |
| 19/03/2010 | 4.1 | 3.7 | 2.5 | 2.8 | 3.7 | 60 | 40 | 120 | 200 | 100 | 104 | 71 | 62 | 81 | 125 | 0.104 | 4.228 | 2.353 | 20.499 | 58.676 |
| 25/03/2010 | 4.0 | 4.5 | 2.4 | 2.4 | 4 | 60 | 60 | 100 | 200 | 80 | 107 | 67 | 57 | 72 | 97 | 0.086 | 0.223 | 1.711 | 18.951 | 80.125 |
| 30/03/2010 | 3.7 | 3.9 | 1.4 | 3.1 | 4.1 | 60 | 60 | 120 | 200 | 120 | 107 | 74 | 68 | 75 | 128 | 0.020 | 1.343 | 1.381 | 18.823 | 82.401 |
| 09/04/2010 | 3.9 | 4.1 | 1.7 | 3.0 | 4.1 | 60 | 60 | 120 | 180 | 120 | 104 | 76 | 64 | 70 | 127 | 0.053 | 1.16 | 0.965 | 12.409 | 76.508 |
| 15/04/2010 | 3.5 | 3.9 | 1.4 | 2.2 | 3.6 | 60 | 40 | 120 | 180 | 120 | 109 | 84 | 71 | 93 | 117 | 0.105 | 0.242 | 1.385 | 16.505 | 83.741 |
| 22/04/2010 | 3.6 | 3.5 | 0.9 | 2.0 | 3.7 | 60 | 60 | 160 | 120 | 80 | 125 | 95 | 75 | 69 | 129 | 0.066 | 0.086 | 1.445 | 18.303 | 57.94 |
| 06/05/2010 | 3.3 | 3.8 | 1.5 | 2.0 | 3.6 | 60 | 40 | 120 | 160 | 80 | 135 | 103 | 107 | 93 | 104 | 0.119 | 0.224 | 1.411 | 9.227 | 85.232 |
| 13/05/2010 | 3.6 | 3.8 | 1.5 | 2.0 | 3.7 | 60 | 40 | 120 | 200 | 120 | 130 | 102 | 94 | 74 | 127 | 0.077 | 0.16 | 1.314 | 17.566 | 79.573 |
| 20/05/2010 | 3.3 | 2.2 | 1.4 | 1.7 | 3.4 | 40 | 40 | 120 | 200 | 60 | 140 | 97 | 102 | 89 | 115 | 0.092 | 10.886 | 1.249 | 20.443 | 73.285 |

Table A9 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 1).

| Date | Dissolved oxygen (mg $l^{-1}$) | | | | | Total suspended solids (mg $l^{-1}$) | | | | | COD (mg $l^{-1}$) | | | | | Ammonia-nitrogen (mg $l^{-1}$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III |
| 27/05/2009 | 3.1 | 2.5 | 1.4 | 1.8 | 3.5 | 60 | 20 | 80 | 200 | 40 | 150 | 109 | 106 | 52 | 115 | 0.078 | 1.811 | 2.514 | 19.958 | 73.706 |
| 04/06/2010 | 3.2 | 2.8 | 1.6 | 2 | 3.5 | 60 | 20 | 80 | 200 | 40 | 150 | 110 | 102 | 95 | 105 | 0.212 | 0.09 | 1.163 | 17.758 | 75.157 |
| 10/06/2010 | 3.5 | 2.4 | 1.9 | 2.3 | 3.4 | 40 | 20 | 100 | 200 | 40 | 150 | 101 | 115 | 99 | 130 | 0.114 | 0.478 | 1.121 | 14.404 | 73.156 |
| 24/06/2010 | 3.4 | 2.6 | 2.0 | 2.4 | 3.6 | 40 | 20 | 100 | 200 | 40 | 148 | 102 | 109 | 130 | 95 | 0.545 | 0.314 | 2.578 | 18.752 | 71.044 |
| 01/07/2010 | 3.5 | 3.0 | 1.2 | 1.6 | 2.8 | 40 | 20 | 80 | 160 | 40 | 150 | 120 | 135 | 105 | 145 | 0.158 | 0.185 | 0.956 | 16.574 | 80.474 |
| 08/07/2010 | 3.6 | 2.4 | 1.4 | 2.5 | 3.0 | 40 | 20 | 80 | 200 | 20 | 150 | 120 | 124 | 129 | 148 | 0.864 | 0.087 | 2.252 | 12.725 | 77.535 |
| 15/07/2010 | 3.4 | 2.6 | 1.4 | 2.4 | 2.8 | 60 | 40 | 60 | 180 | 20 | 150 | 110 | 125 | 120 | 149 | 0.095 | 0.285 | 1.564 | 10.942 | 84.121 |
| 22/07/2010 | 3.8 | 2.3 | 1.8 | 2.0 | 3.0 | 80 | 20 | 120 | 200 | 60 | 150 | 142 | 135 | 110 | 146 | 0.534 | 0.147 | 1.702 | 15.138 | 86.778 |
| 28/07/2010 | 2.9 | 2.1 | 2.3 | 2.6 | 2.9 | 40 | 40 | 80 | 160 | 40 | 150 | 143 | 125 | 115 | 110 | 0.078 | 1.785 | 2.245 | 9.214 | 72.654 |
| 09/08/2010 | 2.9 | 2.5 | 2.7 | 2.4 | 2.6 | 20 | 20 | 160 | 140 | 20 | 150 | 140 | 142 | 120 | 137 | 0.252 | 0.574 | 2.458 | 22.434 | 65.445 |
| 13/08/2010 | 3.0 | 2.2 | 2.4 | 1.8 | 3.2 | 0 | 20 | 80 | 160 | 20 | 150 | 145 | 130 | 98 | 130 | 0.272 | 0.263 | 1.345 | 19.447 | 59.014 |
| 19/08/2010 | 2.8 | 2.6 | 2.2 | 2.1 | 2.8 | 20 | 20 | 40 | 80 | 20 | 155 | 148 | 123 | 131 | 130 | 0.147 | 1.789 | 2.874 | 12.858 | 76.74 |
| 24/08/2010 | 2.2 | 2.3 | 2.1 | 2.3 | 2.4 | 20 | 20 | 40 | 100 | 20 | 155 | 149 | 128 | 125 | 130 | 0.081 | 8.541 | 1.457 | 21.625 | 60.585 |
| 03/09/2010 | 3.6 | 2.6 | 1.9 | 2.4 | 2.8 | 20 | 20 | 60 | 180 | 20 | 125 | 102 | 120 | 112 | 135 | 0.073 | 1.789 | 1.740 | 20.465 | 59.456 |
| 09/09/2010 | 3.2 | 2.3 | 1.8 | 2.3 | 2.9 | 0 | 20 | 80 | 160 | 20 | 135 | 109 | 114 | 108 | 132 | 0.068 | 0.577 | 2.014 | 17.474 | 74.978 |
| 16/09/2010 | 2.9 | 2.5 | 2 | 2.5 | 3.2 | 40 | 20 | 80 | 140 | 20 | 128 | 112 | 125 | 125 | 112 | 0.153 | 0.658 | 1.255 | 17.803 | 83.585 |
| 23/09/2010 | 3.2 | 2.1 | 1.6 | 2.1 | 2.9 | 40 | 40 | 100 | 160 | 40 | 132 | 110 | 124 | 117 | 129 | 0.189 | 0.471 | 2.891 | 21.485 | 76.495 |
| 30/09/2010 | 3.4 | 2.4 | 1.8 | 2.3 | 3.4 | 60 | 40 | 120 | 200 | 20 | 127 | 101 | 111 | 104 | 134 | 0.069 | 0.563 | 1.956 | 18.384 | 56.841 |
| 07/10/2010 | 3.3 | 2.6 | 1.9 | 2.0 | 3.2 | 60 | 40 | 60 | 140 | 20 | 128 | 106 | 119 | 114 | 128 | 0.077 | 0.784 | 1.245 | 10.797 | 86.737 |

Table A10 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 1).

| Date | Dissolved oxygen (mg $l^{-1}$) | | | | | Total suspended solids (mg $l^{-1}$) | | | | | COD (mg $l^{-1}$) | | | | | Ammonia-nitrogen (mg $l^{-1}$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III |
| 14/10/2009 | 3.5 | 2.7 | 2.2 | 2.4 | 3.6 | 40 | 40 | 100 | 120 | 20 | 130 | 105 | 119 | 105 | 127 | 0.158 | 1.258 | 2.356 | 13.458 | 65.258 |
| 21/10/2010 | 3.2 | 2.4 | 1.8 | 2.2 | 3.3 | 60 | 20 | 80 | 140 | 20 | 125 | 117 | 124 | 110 | 135 | 0.096 | 0.568 | 1.874 | 15.864 | 73.215 |
| 28/10/2010 | 3.6 | 3.4 | 2 | 2.2 | 3.7 | 60 | 20 | 60 | 180 | 160 | 121 | 92 | 120 | 100 | 121 | 0.031 | 0.039 | 1.351 | 13.91 | 56.88 |
| 04/11/2010 | 3.6 | 3.6 | 2.4 | 2.9 | 2.9 | 40 | 60 | 40 | 160 | 60 | 130 | 105 | 11 5 | 96 | 110 | 0.069 | 1.469 | 1.468 | 12.046 | 53.32 |
| 11/11/2010 | 3.8 | 2.9 | 2.1 | 2.9 | 3.4 | 40 | 40 | 20 | 140 | 60 | 125 | 108 | 119 | 107 | 115 | 0.029 | 0.858 | 1.365 | 14.382 | 60.44 |
| 18/11/2010 | 3.7 | 2.7 | 1.9 | 2.4 | 3.2 | 60 | 20 | 20 | 120 | 160 | 102 | 114 | 124 | 101 | 120 | 0.056 | 4.246 | 1.622 | 11.692 | 55.27 |
| 25/11/2010 | 3.9 | 2.6 | 2.1 | 2.7 | 3.1 | 20 | 40 | 20 | 160 | 40 | 105 | 95 | 101 | 119 | 142 | 0.047 | 2.665 | 1.724 | 10.736 | 57.25 |
| 02/12/2010 | 3.9 | 2.2 | 1.8 | 2.2 | 2.9 | 20 | 80 | 40 | 120 | 60 | 102 | 106 | 106 | 101 | 135 | 0.073 | 3.483 | 2.175 | 11.660 | 56.990 |
| 09/12/2010 | 3.5 | 3.4 | 2.7 | 2.4 | 2.8 | 60 | 20 | 40 | 140 | 60 | 115 | 96 | 118 | 105 | 116 | 0.041 | 0.083 | 1.399 | 11.572 | 55.260 |
| 16/12/2010 | 3.7 | 3.2 | 1.8 | 2.6 | 2.9 | 40 | 40 | 100 | 160 | 40 | 110 | 112 | 112 | 103 | 110 | 0.041 | 0.069 | 1.278 | 13.564 | 54.200 |
| 11/02/2011 | 3.9 | 3.6 | 2.1 | 2.4 | 3.4 | 60 | 40 | 80 | 160 | 80 | 105 | 102 | 115 | 102 | 125 | 0.042 | 0.116 | 1.09 | 12.644 | 54.290 |
| 18/02/2011 | 3.6 | 3.5 | 2.3 | 2.7 | 3.7 | 60 | 60 | 60 | 140 | 100 | 117 | 96 | 110 | 107 | 130 | 0.048 | 7.220 | 0.801 | 8.176 | 39.540 |
| 25/02/2011 | 3.5 | 2.9 | 2 | 2.8 | 3.2 | 60 | 40 | 80 | 180 | 120 | 105 | 99 | 112 | 101 | 113 | 0.049 | 0.146 | 1.086 | 10.200 | 37.980 |

Table A11 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 1).

| Date | Nitrate-nitrogen (mg $l^{-1}$) | | | | | Nitrite-nitrogen (mg $l^{-1}$) | | | | | Molybdate reactive phosphorus (mg $l^{-1}$) | | | | | Chloride (mg $l^{-1}$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III |
| 19/02/2009 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 26/02/2009 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 19/03/2009 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 26/03/2009 | 2.958 | 0.337 | 0.413 | 0.375 | 0.500 | 0.019 | 0.009 | 0.027 | 0.005 | 0.025 | 1.187 | 0.244 | 0.273 | 1.411 | 16.564 | 50.702 | 24.935 | 29.229 | 11.360 | 312.311 |
| 02/04/2009 | 6.309 | 0.387 | 0.500 | 0.446 | 1.230 | 0.034 | 0.013 | 0.032 | 0.013 | 0.018 | 1.482 | 0.170 | 0.151 | 3.503 | 19.491 | 94.503 | 9.309 | 30.561 | 18.451 | 213.294 |
| 09/04/2009 | 0.083 | 0.460 | 10.023 | 0.325 | 0.818 | 0.006 | 0.009 | 0.027 | 0.004 | 0.013 | 2.262 | 0.204 | 2.038 | 4.001 | 18.897 | 31.997 | 7.991 | 138.491 | 51.092 | 374.042 |
| 16/04/2009 | 1.268 | - | 0.313 | 0.336 | 0.848 | 0.016 | - | 0.004 | 0.015 | 0.015 | 0.517 | - | 1.95 | 7.04 | 15.636 | 27.949 | - | 36.375 | 83.593 | 320.256 |
| 23/04/2009 | 9.101 | 0.478 | 0.34 | 0.407 | 1.004 | 0.005 | 0.001 | 0.001 | 0.002 | 0.003 | 2.53 | 0.716 | 0.693 | 2.657 | 13.654 | 111.214 | 7.627 | 29.519 | 30.303 | 114.276 |
| 30/04/2009 | 9.101 | 0.478 | 0.34 | 0.407 | 1.004 | 0.002 | 0.019 | 0.019 | 0.004 | 0.008 | 2.004 | 0.303 | 0.779 | 2.456 | 19.526 | 84.360 | 1.310 | 30.379 | 32.587 | 107.819 |
| 07/05/2009 | 12.138 | 0.588 | 0.302 | 0.482 | 0.633 | 0.003 | 0.008 | 0.007 | 0 | 0.019 | 2.538 | 0.626 | 0.704 | 3.483 | 13.416 | 158.571 | 9.070 | 64.438 | 26.340 | 99.042 |
| 14/05/2009 | 13.756 | 0.751 | 0.352 | 0.329 | 0.863 | 0.003 | 0.019 | 0.019 | 0.019 | 0.051 | 2.768 | 0.471 | 1.107 | 3.585 | 12.56 | 180.167 | 9.550 | 30.318 | 29.609 | 98.609 |
| 21/05/2009 | 13.156 | 0.504 | 0.329 | 0.385 | 0.576 | 0.02 | 0.019 | 0.002 | 0.019 | 0.002 | 2.495 | 0.461 | 2.746 | 4.574 | 13.064 | 167.169 | 11.201 | 50.668 | 34.623 | 91.669 |
| 28/05/2009 | 16.071 | 0.641 | 0.985 | 1.219 | 3.762 | 0.004 | 0.014 | 0.025 | 0.019 | 0.08 | 2.784 | 1.795 | 4.535 | 6.011 | 10.29 | 173.397 | 32.951 | 91.093 | 54.844 | 81.947 |
| 04/06/2009 | 15.64 | 0.605 | 0.727 | 1.172 | 2.899 | 0.009 | 0.003 | 0.007 | 0.019 | 0.135 | 2.523 | 0.553 | 2.952 | 5.587 | 10.581 | 164.578 | 28.786 | 54.962 | 45.459 | 77.938 |
| 11/06/2009 | 19.579 | 0.461 | 0.614 | 1.106 | 3.313 | 0.006 | 0.019 | 0.02 | 0.002 | 0.016 | 2.923 | 0.369 | 4.070 | 5.380 | 10.141 | 211.061 | 40.998 | 62.752 | 49.159 | 79.534 |
| 18/06/2009 | 17.700 | 0.384 | 0.369 | 0.595 | 0.86 | 0.014 | 0.026 | 0.036 | 0.031 | 0.048 | 2.517 | 0.512 | 2.654 | 3.497 | 12.382 | 204.238 | 9.126 | 79.531 | 63.835 | 98.950 |
| 25/06/2009 | 16.458 | 0.36 | 0.456 | 0.565 | 0.841 | 0.013 | 0.031 | 0.035 | 0.034 | 0.043 | 1.694 | 0.743 | 2.085 | 4.051 | 9.108 | 192.017 | 30.663 | 75.004 | 65.477 | 107.822 |
| 02/07/2009 | 15.237 | 0.428 | 0.309 | 0.542 | 0.939 | 0.012 | 0.015 | 0.019 | 0.023 | 0.034 | 2.181 | 0.379 | 3.934 | 4.105 | 9.086 | 180.036 | 29.828 | 77.702 | 68.233 | 86.005 |
| 09/07/2009 | 16.925 | 0.434 | 0.272 | 0.521 | 0.83 | 0.013 | 0.006 | 0.015 | 0.021 | 0.03 | 2.085 | 0.446 | 3.331 | 4.54 | 11.26 | 194.930 | 18.922 | 72.299 | 68.352 | 83.966 |

Table A12 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 1).

| Date | Nitrate-nitrogen (mg $l^{-1}$) | | | | | Nitrite-nitrogen (mg $l^{-1}$) | | | | | Molybdate reactive phosphorus (mg $l^{-1}$) | | | | | Chloride (mg $l^{-1}$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III |
| 16/07/2009 | 18.722 | 0.417 | 0.339 | 0.557 | 1.262 | 0.012 | 0.004 | 0.018 | 0.014 | 0.079 | 2.459 | 0.63 | 2.771 | 3.691 | 13.701 | 214.425 | 11.536 | 69.663 | 62.045 | 107.793 |
| 23/07/2009 | 17.945 | 0.361 | 0.308 | 0.572 | 1.192 | 0.01 | 0.019 | 0.012 | 0.015 | 0.044 | 2.177 | 1.019 | 3.812 | 3.486 | 9.064 | 191.477 | 9.925 | 63.063 | 57.454 | 91.488 |
| 30/07/2009 | 18.656 | 0.597 | 0.298 | 0.543 | 1.12 | 0.007 | 0.004 | 0.012 | 0.013 | 0.064 | 2.53 | 1.056 | 3.295 | 3.508 | 14.151 | 199.941 | 11.316 | 56.874 | 51.963 | 135.342 |
| 06/08/2009 | 19.798 | 0.446 | 0.307 | 0.568 | 1.858 | 0.006 | 0.005 | 0.019 | 0.018 | 0.176 | 2.898 | 0.871 | 3.819 | 3.725 | 14.074 | 206.367 | 9.765 | 52.670 | 50.161 | 145.325 |
| 13/08/2009 | 18.606 | 0.433 | 0.343 | 0.56 | 1.235 | 0.008 | 0.004 | 0.027 | 0.015 | 0.035 | 3.134 | 0.469 | 4.436 | 4.34 | 15.005 | 201.179 | 21.697 | 50.252 | 47.128 | 142.255 |
| 20/08/2009 | 19.114 | 0.495 | 0.335 | 0.558 | 0.970 | 0.008 | 0.005 | 0.01 | 0.016 | 0.028 | 3.077 | 0.637 | 4.63 | 4.484 | 9.266 | 191.425 | 9.623 | 46.973 | 43.955 | 105.367 |
| 27/08/2009 | 20.300 | 0.494 | 0.558 | 1.013 | 1.291 | 0.014 | 0.012 | 0.044 | 0.085 | 0.112 | 3.285 | 0.836 | 3.894 | 5.366 | 10.927 | 204.399 | 10.535 | 41.853 | 37.179 | 103.821 |
| 03/09/2009 | 22.321 | 0.411 | 0.442 | 0.885 | 1.174 | 0.016 | 0.014 | 0.042 | 0.074 | 0.107 | 3.626 | 2.727 | 4.063 | 5.675 | 9.960 | 220.555 | 10.244 | 37.876 | 35.876 | 114.045 |
| 10/09/2009 | 21.438 | 0.291 | 0.435 | 2.317 | 3.651 | 0.016 | 0.005 | 0.042 | 0.085 | 0.167 | 4.247 | 1.175 | 4.271 | 5.109 | 9.418 | 207.975 | 69.090 | 35.548 | 35.328 | 121.210 |
| 17/09/2009 | 22.395 | 0.617 | 1.163 | 2.352 | 3.207 | 0.02 | 0.007 | 0.04 | 0.066 | 0.108 | 4.336 | 0.484 | 4.395 | 5.314 | 10.853 | 245.431 | 14.471 | 69.747 | 49.157 | 123.986 |
| 24/09/2009 | 21.372 | 0.608 | 1.232 | 2.264 | 2.94 | 0.017 | 0.008 | 0.038 | 0.058 | 0.087 | 3.973 | 1.338 | 2.767 | 5.155 | 10.595 | 225.469 | 7.114 | 57.874 | 47.448 | 109.708 |
| 01/10/2009 | 20.815 | 0.088 | 1.165 | 2.282 | 16.138 | 0.018 | 0.009 | 0.041 | 0.067 | 0.124 | 3.902 | 1.987 | 2.720 | 4.829 | 12.831 | 204.394 | 9.840 | 47.550 | 45.993 | 136.449 |
| 20/10/2009 | 26.766 | - | 0.01 | 0.01 | 0.066 | 0.017 | - | 0.024 | 0.046 | 0.093 | 4.805 | - | 1.94 | 4.305 | 9.257 | 247.267 | - | 44.498 | 40.88 | 175.158 |
| 06/11/2009 | 17.506 | 0.133 | 0.01 | 0.01 | 0.01 | 0.095 | 0.019 | 0.025 | 0.047 | 0.061 | 4.387 | 1.823 | 1.281 | 3.142 | 9.733 | 180.391 | 21.025 | 50.246 | 45.572 | 190.898 |
| 13/11/2009 | 17.632 | 0.22 | 0.01 | 0.573 | 0.01 | 0.034 | 0.161 | 0.026 | 0.057 | 0.079 | 4.504 | 1.487 | 4.194 | 4.626 | 9.131 | 182.256 | 13.959 | 47.428 | 49.773 | 187.236 |
| 20/11/2009 | 20.675 | 0.776 | 0.01 | 0.01 | 0.01 | 0.011 | 1 | 0.029 | 0.054 | 0.101 | 5.118 | 1.749 | 3.968 | 4.458 | 10.488 | 217.743 | 10.316 | 42.829 | 44.152 | 207.097 |
| 27/11/2009 | 21.512 | 1.044 | 0.01 | 0.01 | 0.01 | 0.011 | 2.35 | 0.023 | 0.051 | 0.086 | 5.324 | 1.768 | 3.718 | 4.348 | 11.318 | 227.151 | 10.896 | 37.788 | 39.217 | 219.386 |
| 02/12/2009 | 16.65 | 0.193 | 0.122 | 0.1 | 0.126 | 0.039 | 0.22 | 0.011 | 0.014 | 0.087 | 4.811 | 2.512 | 4.341 | 1.666 | 8.303 | 201.061 | 25.669 | 39.528 | 40.758 | 211.634 |
| 11/12/2009 | 18.314 | 0.505 | 0.1 | 0.003 | 0.299 | 0.04 | 0.297 | 0.016 | 0.020 | 0.055 | 1.35 | 2.309 | 3.928 | 3.963 | 9.703 | 251.554 | 22.678 | 43.736 | 41.497 | 237.682 |

Table A13 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 1).

| Date | Nitrate-nitrogen (mg $l^{-1}$) | | | | | Nitrite-nitrogen (mg $l^{-1}$) | | | | | Molybdate reactive phosphorus (mg $l^{-1}$) | | | | | Chloride (mg $l^{-1}$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III |
| 18/12/2009 | 18.165 | 0.352 | - | 0.1 | 0.198 | 0.181 | 0.031 | - | 0.016 | 0.119 | 1.733 | 1.557 | - | 3.805 | 11.249 | 231.606 | 16.395 | - | 45.982 | 94.379 |
| 15/01/2010 | 19.453 | 0.247 | 0.1 | 0.1 | 1.388 | 0.034 | 0.043 | 0.016 | 0.017 | 0.045 | 5.397 | 0.127 | 3.123 | 3.31 | 9.364 | 253.429 | 77.056 | 43.543 | 41.728 | 290.305 |
| 22/01/2010 | 19.14 | 0.481 | 0.1 | 0.1 | 0.245 | 0.026 | 0.141 | 0.015 | 0.015 | 0.14 | 5.333 | 1.144 | 1.903 | 3.06 | 5.93 | 251.798 | 17.27 | 40.522 | 48.806 | 256.825 |
| 29/01/2010 | - | 3.661 | 0.1 | - | - | - | 0.159 | 0.056 | 0.014 | - | - | 1.169 | 9.659 | 3.601 | - | - | 18.207 | 257.975 | 44.828 | - |
| 05/02/2010 | 20.524 | - | - | 0.1 | 0.793 | 0.054 | - | - | 0.015 | 0.166 | 5.572 | - | - | 2.697 | 12.13 | 248.08 | - | - | 41.617 | 261.774 |
| 11/02/2010 | 22.318 | 4.908 | 0 | 0 | 0.404 | 0.008 | 0.027 | 0.008 | 0.001 | 0.132 | 4.989 | 1.328 | 1.538 | 3.041 | 5.544 | 236.33 | 16.264 | 41.62 | 44.456 | 228.406 |
| 18/02/2010 | 22.335 | 0.256 | 0 | 0 | 0.281 | 0.019 | 0.062 | 0.001 | 0.005 | 0.015 | 5.068 | 1.468 | 2.322 | 2.935 | 8.276 | 237.365 | 13.474 | 36.839 | 43.135 | 246.966 |
| 25/02/2010 | 22.845 | 2.958 | 0 | 0.009 | 0.351 | 0.017 | 0.015 | 0.006 | 0.009 | 0.05 | 5.211 | 1.613 | 2.261 | 2.063 | 7.791 | 246.721 | 14.395 | 34.913 | 46.392 | 145.806 |
| 04/03/2010 | 22.283 | 0.708 | 0 | 0 | 0.09 | 0.062 | 0.045 | 0.004 | 0.006 | 0.059 | 5.092 | 1.816 | 2.401 | 3.087 | 9.157 | 241.205 | 26.399 | 37.744 | 41.287 | 158.698 |
| 11/03/2010 | 22.692 | 8.676 | 0 | 0 | 0.408 | 0.009 | 0.032 | 0.006 | 0.020 | 0.018 | 5.218 | 2.591 | 2.426 | 2.937 | 9.377 | 228.573 | 31.958 | 39.592 | 36.349 | 258.287 |
| 19/03/2010 | 21.703 | 3.886 | 0 | 0 | 0.313 | 0.015 | 0.06 | 0.003 | 0.004 | 0.024 | 5.107 | 1.914 | 5.628 | 3.173 | 8.865 | 211.157 | 33.804 | 53.215 | 42.558 | 163.148 |
| 25/03/2010 | 26.72 | 12.272 | 0 | 0 | 0.22 | 0.006 | 0.01 | 0.002 | 0.003 | 0.049 | 5.297 | 2.631 | 3.188 | 2.871 | 11.813 | 257.735 | 37.204 | 51.597 | 47.271 | 239.081 |
| 30/03/2010 | 26.662 | 0.107 | 0.028 | 0.046 | 0.556 | 0.032 | 0.019 | 0.003 | 0.005 | 0.014 | 5.433 | 0.708 | 3.256 | 2.512 | 12.584 | 249.002 | 18.365 | 49.957 | 50.494 | 241.876 |
| 09/04/2010 | 20.203 | 0.175 | 0.011 | 0.014 | 0.475 | 0.018 | 0.022 | 0 | 0.003 | 0.005 | 4.762 | 0.233 | 2.679 | 2.785 | 9.246 | 199.077 | 10.915 | 23.187 | 38.058 | 240.534 |
| 15/04/2010 | 24.149 | 0.954 | 0.03 | 0.025 | 0.937 | 0.068 | 2.495 | 0.004 | 0.002 | 0.044 | 4.864 | 0.442 | 3.102 | 2.964 | 11.562 | 238.506 | 25.342 | 45.171 | 48.421 | 324.097 |
| 22/04/2010 | 23.89 | 0.01 | 0.01 | 0.01 | 0.204 | 0.06 | 6.39 | 0.005 | 0.004 | 0.006 | 4.894 | 0.936 | 3.355 | 4.229 | 10.935 | 239.834 | 43.282 | 49.872 | 46.793 | 149.19 |
| 06/05/2010 | 27.272 | 0.533 | 0.01 | 0.01 | 0.253 | 0.008 | 2.084 | 0.003 | 0.006 | 0.025 | 5.067 | 0.474 | 2.827 | 1.373 | 6.642 | 261.536 | 42.687 | 43.285 | 21.649 | 292.079 |
| 13/05/2010 | 24.642 | 0.732 | 0.01 | 0.01 | 0.296 | 0.011 | 1.712 | 0.005 | 0.012 | 0.015 | 3.689 | 0.431 | 2.725 | 2.734 | 14.529 | 259.042 | 37.54 | 70.068 | 56.772 | 290.416 |
| 20/05/2010 | 24.875 | 0.23 | 0.01 | 0.01 | 0.606 | 0.008 | 0.263 | 0.006 | 0.006 | 0.041 | 2.143 | 0.719 | 2.035 | 2.846 | 5.562 | 263.838 | 89.94 | 70.825 | 62.318 | 274.914 |

Table A15 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 1)

| Date | Nitrate-nitrogen (mg $l^{-1}$) | | | | | Nitrite-nitrogen (mg $l^{-1}$) | | | | | Molybdate reactive phosphorus (mg $l^{-1}$) | | | | | Chloride (mg $l^{-1}$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III |
| 27/05/2009 | 26.451 | 3.532 | 0.01 | 0.01 | 1.123 | 0.029 | 5.383 | 0.007 | 0.012 | 0.055 | 4.331 | 1.467 | 2.475 | 2.419 | 15.104 | 279.059 | 129.812 | 81.402 | 73.416 | 476.048 |
| 04/06/2010 | 28.633 | 1.409 | 0.285 | 0.01 | 0.759 | 0.014 | 1.112 | 0.194 | 0.008 | 0.028 | 4.156 | 0.931 | 2.046 | 2.008 | 10.533 | 289.318 | 21.389 | 66.379 | 78.105 | 235.431 |
| 10/06/2010 | 22.524 | 0.445 | 0.719 | 0.343 | 1.230 | 0.052 | 0.027 | 0.038 | 0.018 | 0.185 | 2.517 | 0.522 | 2.654 | 3.687 | 12.382 | 193.238 | 12.146 | 73.501 | 63.835 | 102.750 |
| 24/06/2010 | 20.785 | 0.432 | 0.181 | 0.722 | 0.815 | 0.074 | 2.495 | 0.041 | 0.017 | 0.044 | 1.694 | 0.523 | 2.045 | 4.051 | 9.037 | 199.017 | 30.563 | 76.904 | 65.477 | 107.822 |
| 01/07/2010 | 27.365 | 0.797 | 0.408 | 0.258 | 0.832 | 0.045 | 1.654 | 0.023 | 0.022 | 0.037 | 2.191 | 0.389 | 3.324 | 4.405 | 9.086 | 178.636 | 24.828 | 74.702 | 68.034 | 83.035 |
| 08/07/2010 | 24.147 | 0.492 | 0.157 | 0.872 | 1.207 | 0.085 | 0.075 | 0.034 | 0.023 | 0.123 | 2.185 | 0.467 | 3.054 | 4.302 | 10.264 | 194.930 | 28.942 | 72.048 | 66.252 | 73.906 |
| 15/07/2010 | 26.586 | 0.35 | 0.924 | 0.542 | 0.902 | 0.004 | 2.286 | 0.025 | 0.007 | 0.128 | 2.454 | 0.642 | 2.078 | 3.692 | 14.607 | 213.425 | 1.405 | 64.612 | 62.045 | 127.793 |
| 22/07/2010 | 28.752 | 0.296 | 0.346 | 0.467 | 0.923 | 0.071 | 1.985 | 0.023 | 0.041 | 0.156 | 4.834 | 0.429 | 4.052 | 2.435 | 11.862 | 228.508 | 29.342 | 43.124 | 46.231 | 314.197 |
| 28/07/2010 | 23.324 | 0.614 | 0.078 | 0.563 | 0.666 | 0.015 | 0.034 | 0.027 | 0.056 | 0.107 | 4.894 | 0.886 | 3.056 | 3.298 | 10.634 | 239.834 | 53.292 | 49.874 | 46.593 | 154.192 |
| 09/08/2010 | 25.257 | 0.608 | 0.277 | 0.657 | 0.571 | 0.007 | 0.098 | 0.012 | 0.032 | 0.096 | 5.087 | 0.435 | 2.474 | 2.114 | 6.662 | 275.536 | 44.383 | 43.791 | 21.049 | 307.079 |
| 13/08/2010 | 23.854 | 0.057 | 0.317 | 1.813 | 2.562 | 0.012 | 1.364 | 0.028 | 0.024 | 0.058 | 5.092 | 0.403 | 2.385 | 2.634 | 12.075 | 229.842 | 36.541 | 70.068 | 46.682 | 290.416 |
| 19/08/2010 | 28.857 | 0.607 | 0.144 | 0.784 | 0.451 | 0.024 | 7.351 | 0.021 | 0.019 | 0.117 | 2.583 | 0.473 | 2.952 | 5.587 | 12.581 | 165.578 | 28.886 | 57.822 | 44.409 | 77.948 |
| 24/08/2010 | 20.451 | 9.624 | 0.464 | 1.955 | 0.094 | 0.071 | 0.062 | 0.038 | 0.02 | 0.043 | 2.922 | 1.369 | 2.272 | 5.380 | 13.041 | 211.061 | 40.798 | 62.702 | 41.059 | 84.534 |
| 03/09/2010 | 22.781 | 2.885 | 0.651 | 2.587 | 0.434 | 0.034 | 0.045 | 0.027 | 0.005 | 0.033 | 2.517 | 0.502 | 1.354 | 2.697 | 12.303 | 204.238 | 6.176 | 78.541 | 63.835 | 98.853 |
| 09/09/2010 | 21.235 | 5.473 | 0.422 | 2.047 | 0.217 | 0.047 | 0.145 | 0.019 | 0.004 | 0.042 | 1.694 | 0.947 | 2.035 | 4.081 | 9.191 | 194.017 | 30.663 | 79.054 | 64.477 | 103.822 |
| 16/09/2010 | 27.757 | 0.106 | 1.708 | 1.344 | 0.726 | 0.078 | 0.182 | 0.022 | 0.006 | 0.017 | 2.081 | 0.379 | 3.324 | 5.105 | 9.054 | 179.036 | 30.878 | 76.602 | 69.233 | 82.005 |
| 23/09/2010 | 23.457 | 0.285 | 1.405 | 0.01 | 0.258 | 0.089 | 0.156 | 0.008 | 0.007 | 0.022 | 2.085 | 0.496 | 3.231 | 4.405 | 11.26 | 194.930 | 19.823 | 70.213 | 68.352 | 82.966 |
| 30/09/2010 | 26.0475 | 0.844 | 0.785 | 0.01 | 0.374 | 0.042 | 0.189 | 0.007 | 0.002 | 0.028 | 2.489 | 0.63 | 3.711 | 3.892 | 13.701 | 212.423 | 10.956 | 62.163 | 63.045 | 137.793 |
| 07/10/2010 | 27.447 | 0.015 | 0.478 | 0.457 | 0.988 | 0.004 | 2.445 | 0.014 | 0.006 | 0.036 | 2.177 | 1.089 | 3.812 | 3.486 | 9.064 | 190.478 | 9.975 | 63.063 | 57.754 | 91.788 |

Table A16 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 1).

| Date | Nitrate-nitrogen (mg $l^{-1}$) | | | | | Nitrite-nitrogen (mg $l^{-1}$) | | | | | Molybdate reactive phosphorus (mg $l^{-1}$) | | | | | Chloride (mg $l^{-1}$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III | Control | Influent | Tap I | Tap II | Tap III |
| 14/10/2009 | 24.658 | 0.658 | 0.541 | 1.546 | 0.842 | 0.032 | 1.028 | 0.036 | 0.029 | 0.189 | 3.687 | 0.875 | 3.698 | 5.974 | 12.564 | 201.248 | 25.687 | 62.598 | 39.265 | 268.971 |
| 21/10/2010 | 23.756 | 0.524 | 0.398 | 0.982 | 0.597 | 0.079 | 0.754 | 0.029 | 0.012 | 0.087 | 2.924 | 0.498 | 4.011 | 4.235 | 11.685 | 196.357 | 17.886 | 70.364 | 64.875 | 154.697 |
| 28/10/2010 | 21.619 | 6.29 | 0.01 | 0.01 | 0.46 | 0.001 | 0.007 | 0 | 0.008 | 0.46 | 3.346 | 0.622 | 2.142 | 1.832 | 10.202 | 256.731 | 43.544 | 93.925 | 91.476 | 317.224 |
| 04/11/2010 | 22.569 | 0.182 | 0.01 | 0.01 | 0.316 | 0.004 | 0.008 | 0.001 | 0.01 | 0.03 | 3.076 | 0.684 | 1.65 | 1.652 | 12.64 | 276.489 | 31.641 | 79.674 | 77.852 | 329.670 |
| 11/11/2010 | 23.144 | 0.281 | 0.01 | 0.01 | 3.83 | 0.006 | 0.1 | 0.003 | 0.01 | 0.05 | 3.61 | 0.826 | 2.017 | 1.774 | 11.69 | 286.742 | 41.028 | 89.624 | 90.560 | 374.660 |
| 18/11/2010 | 22.169 | 0.365 | 0.01 | 0.01 | 0.35 | 0.006 | 0.005 | 0.001 | 0.012 | 0.08 | 3.578 | 0.671 | 2.075 | 2.036 | 13.12 | 276.113 | 49.235 | 82.175 | 60.092 | 448.040 |
| 25/11/2010 | 20.934 | 0.484 | 0.01 | 0.01 | 0.14 | 0.005 | 0.104 | 0 | 0.016 | 0.04 | 3.336 | 0.912 | 2.131 | 2.04 | 12.17 | 259.885 | 61.293 | 89.532 | 68.160 | 319.600 |
| 02/12/2010 | 16.504 | 0.765 | 0.01 | 0.01 | 1.22 | 0.011 | 2.432 | 0.001 | 0.016 | 0.04 | 3.023 | 0.577 | 2.166 | 1.532 | 12.3 | 187.868 | 72.734 | 94.626 | 73.660 | 290.360 |
| 09/12/2010 | 22.237 | 2.811 | 0.229 | 0.01 | 0.07 | 0.082 | 8.198 | 0.469 | 0.012 | 0.08 | 3.364 | 0.79 | 1.612 | 1.676 | 11.06 | 276.123 | 84.562 | 103.106 | 93.904 | 333.030 |
| 16/12/2010 | 20.109 | 2.375 | 0.01 | 2.312 | 0.056 | 0.004 | 5.439 | 0.001 | 0.016 | 0.04 | 3.37 | 0.418 | 2.252 | 1.144 | 11.83 | 243.197 | 48.837 | 112.865 | 103.288 | 290.820 |
| 11/02/2011 | 19.893 | 2.068 | 0.009 | 0.01 | 0.012 | 0.051 | 3.972 | 0.001 | 0.02 | 0.04 | 2.962 | 0.891 | 1.855 | 1.48 | 9.23 | 231.450 | 43.010 | 81.086 | 110.496 | 317.420 |
| 18/02/2011 | 19.062 | 5.306 | 0.01 | 0.01 | 0.01 | 0.005 | 2.867 | 0.001 | 0.028 | 0.04 | 2.786 | 4.65 | 0.36 | 1.388 | 10.18 | 222.295 | 103.262 | 70.784 | 95.676 | 147.900 |
| 25/02/2011 | 24.664 | 3.681 | 0.01 | 0.036 | 0.19 | 0.003 | 0.13 | 0.002 | 0.016 | 0.04 | 5.046 | 2.912 | 1.705 | 1.456 | 9.16 | 294.883 | 42.552 | 95.539 | 94.892 | 191.750 |

Table A17 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 2).

| Date | Temperature (℃) | | | | pH | | | | Conductivity (μS $cm^{-1}$) | | | | Redox potential (mV) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III |
| 08-Jul-11 | 19.9 | 20.1 | 19.4 | 16.8 | 8.06 | 7.57 | 7.06 | 6.31 | 2273 | 273 | 983 | 3644 | -103 | -60 | -62 | -270 |
| 15-Jul-11 | 17.8 | 18.3 | 18.6 | 17.5 | 8.23 | 7.44 | 6.95 | 6.45 | 1982 | 384 | 1014 | 3767 | -81 | -56 | -72 | -268 |
| 22-Jul-11 | 17.5 | 17.7 | 18.2 | 17.7 | 8.13 | 7.68 | 7.27 | 6.75 | 2068 | 451 | 952 | 3599 | -107 | -76 | -83 | -227 |
| 29-Jul-11 | 20.1 | 18.6 | 19.7 | 18.1 | 8.04 | 7.73 | 7.43 | 6.61 | 1795 | 347 | 1012 | 3822 | -94 | -78 | -155 | -248 |
| 05-Aug-11 | 17.4 | 19.6 | 18.7 | 17.3 | 8.15 | 7.48 | 6.77 | 6.33 | 2377 | 326 | 914 | 3634 | -102 | -67 | -84 | -229 |
| 12-Aug-11 | 17.4 | 18.1 | 19.4 | 17.7 | 8.20 | 7.58 | 7.47 | 6.60 | 2486 | 524 | 1185 | 3424 | -74 | -83 | -46 | -256 |
| 19-Aug-11 | 17.6 | 16.9 | 18.1 | 17.9 | 8.13 | 7.34 | 7.39 | 6.51 | 2010 | 303 | 984 | 3890 | -102 | -80 | -85 | -226 |
| 26-Aug-11 | 17.6 | 18.2 | 18.5 | 18.7 | 8.18 | 7.25 | 6.74 | 6.27 | 1648 | 432 | 1015 | 3999 | -108 | -99 | -94 | -247 |
| 02-Sep-11 | 17.5 | 18.1 | 18.6 | 18.9 | 8.07 | 7.39 | 7.16 | 6.84 | 2528 | 327 | 1206 | 3999 | -103 | -78 | -73 | -254 |
| 09-Sep-11 | 16.4 | 16.0 | 16.8 | 16.2 | 8.01 | 7.19 | 6.52 | 5.87 | 2941 | 382 | 1224 | 3999 | -63 | -124 | -156 | -264 |
| 16-Sep-11 | 16.6 | 15.5 | 17.2 | 16.3 | 8.32 | 7.43 | 6.65 | 6.23 | 3410 | 570 | 1129 | 3999 | -219 | -275 | -219 | -246 |
| 23-Sep-11 | 16.6 | 15.9 | 16.5 | 15.9 | 8.24 | 8.40 | 6.78 | 6.3 | 3004 | 388 | 1120 | 3999 | -188 | -278 | -161 | -256 |
| 30-Sep-11 | 17.4 | 15.8 | 16.6 | 16.6 | 7.86 | 7.28 | 6.95 | 6.24 | 2778 | 524 | 1234 | 3933 | -203 | -94 | -115 | -277 |
| 07-Oct-11 | 16.3 | 16.2 | 16.0 | 16.3 | 8.18 | 7.2 | 7.01 | 6.5 | 2522 | 248 | 1056 | 3210 | -134 | 20 | -105 | -234 |
| 14-Oct-11 | 16.9 | 16.2 | 16.7 | 16.6 | 8.24 | 7.04 | 6.98 | 6.42 | 2380 | 302 | 1218 | 3557 | -155 | -74 | -200 | -262 |
| 21-Oct-11 | 17.4 | 15.7 | 17.2 | 16.7 | 8.09 | 7.55 | 6.82 | 6.33 | 2414 | 410 | 1172 | 3188 | -158 | -80 | -125 | -248 |
| 28-Oct-11 | 16.5 | 16.3 | 16.6 | 17.5 | 8.18 | 7.31 | 6.89 | 6.41 | 2278 | 230 | 1118 | 2948 | -115 | -120 | -159 | -237 |
| 04-Nov-11 | 17.9 | 16.4 | 16.9 | 17.6 | 8.07 | 7.34 | 6.98 | 6.45 | 2208 | 300 | 1135 | 2981 | -220 | -96 | -74 | -285 |
| 11-Nov-11 | 16.3 | 17.0 | 16.3 | 16.4 | 8.01 | 7.53 | 7.20 | 6.50 | 2223 | 325 | 1076 | 2857 | -168 | -68 | -122 | -218 |

Table A18 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 2).

| Date | Temperature (°C) | | | | pH | | | | Conductivity (μS $cm^{-1}$) | | | | Redox potential (mV) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III |
| 25-Nov-11 | 16.9 | 16.1 | 17.4 | 17.4 | 8.48 | 7.68 | 8.11 | 6.98 | 2467 | 244 | 1081 | 2200 | -179 | -75 | -73 | -220 |
| 02-Dec-11 | 16.4 | 15.7 | 17 | 17.7 | 8.23 | 7.78 | 7.00 | 6.5 | 1978 | 323 | 967 | 2378 | -88 | -83 | -78 | -225 |
| 09-Dec-11 | 16.2 | 15.7 | 16.3 | 17.0 | 8.18 | 7.14 | 7.06 | 6.49 | 2230 | 261 | 966 | 2313 | -79 | -74 | -59 | -260 |
| 16-Dec-11 | 16.2 | 16.7 | 16.8 | 16.9 | 8.43 | 7.44 | 7.35 | 6.53 | 1691 | 360 | 907 | 2240 | -65 | -40 | -53 | -244 |
| 22-Dec-11 | 17.5 | 16.3 | 16.5 | 17.6 | 8.05 | 7.63 | 7.15 | 6.45 | 1672 | 464 | 874 | 2298 | -40 | -44 | -33 | -255 |
| 06-Jan-12 | 17.0 | 17.0 | 16.5 | 17.5 | 8.25 | 8.42 | 7.32 | 6.62 | 1674 | 391 | 973 | 2176 | -37 | -85 | -42 | -267 |
| 13-Jan-12 | 17.2 | 16.4 | 16.8 | 17.5 | 8.36 | 7.5 | 7.32 | 6.55 | 2144 | 602 | 1024 | 2129 | -73 | -63 | -64 | -275 |
| 20-Jan-12 | 17.2 | 16.2 | 17.3 | 17.3 | 8.24 | 7.71 | 7.39 | 6.55 | 1667 | 361 | 923 | 2035 | -50 | -47 | -69 | -295 |
| 30-Jan-12 | 16.6 | 16.5 | 17.2 | 16.8 | 8.43 | 7.52 | 7.53 | 6.6 | 2576 | 574 | 964 | 1877 | -74 | -43 | -60 | -255 |
| 06-Feb-12 | 16.6 | 16.6 | 16.7 | 16.9 | 8.38 | 7.50 | 7.47 | 6.66 | 2253 | 457 | 968 | 1734 | -62 | -57 | -55 | -248 |
| 13-Feb-12 | 16.6 | 16.6 | 16.7 | 16.9 | 8.08 | 7.24 | 7.31 | 6.67 | 1692 | 663 | 923 | 1759 | -51 | -45 | -36 | -255 |
| 20-Feb-12 | 16.4 | 16.8 | 17 | 17.4 | 8.18 | 8.39 | 7.4 | 6.73 | 2009 | 284 | 991 | 1658 | -60 | -68 | -56 | -258 |
| 05-Mar-12 | 15.5 | 15.4 | 15.8 | 15.8 | 8.18 | 7.64 | 7.42 | 6.69 | 1834 | 249 | 988 | 1653 | -60 | -65 | -45 | -247 |
| 12-Mar-12 | 16.3 | 16.5 | 16.5 | 16.6 | 8.01 | 8.04 | 7.33 | 6.60 | 1536 | 271 | 893 | 1604 | -55 | -61 | -50 | -233 |
| 19-Mar-12 | 16.3 | 16.2 | 16.4 | 16.7 | 8.06 | 7.26 | 7.22 | 6.57 | 1592 | 374 | 910 | 1537 | -54 | -49 | -41 | -226 |
| 26-Mar-12 | 16.6 | 16.5 | 16.9 | 17.1 | 8.10 | 7.43 | 7.44 | 6.64 | 1460 | 294 | 851 | 1502 | -52 | -48 | -43 | -245 |
| 09-Apr-12 | 15.9 | 15.8 | 16.0 | 16.5 | 8.13 | 7.66 | 7.38 | 6.65 | 1494 | 264 | 812 | 1491 | -57 | -50 | -39 | -255 |
| 16-Apr-12 | 16.0 | 15.6 | 16.2 | 16.2 | 7.97 | 8.49 | 7.49 | 6.65 | 1491 | 246 | 801 | 1339 | -54 | -90 | -43 | -254 |
| 23-Apr-12 | 16.3 | 16.3 | 16.6 | 16.6 | 8.01 | 7.37 | 7.3 | 6.64 | 1429 | 370 | 780 | 1325 | -52 | -55 | -47 | -245 |

Table A19 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 2).

| Date | Temperature (℃) | | | | pH | | | | Conductivity (μS $cm^{-1}$) | | | | Redox potential (mV) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III |
| 07-May-12 | 16.9 | 16.1 | 17.4 | 17.4 | 8.48 | 7.68 | 8.11 | 6.98 | 2467 | 244 | 1081 | 2200 | -179 | -75 | -73 | -220 |
| 14-May-11 | 16.4 | 15.7 | 17.0 | 17.7 | 8.23 | 7.78 | 7.00 | 6.5 | 1978 | 323 | 967 | 2378 | -88 | -83 | -78 | -225 |
| 21-May-11 | 16.2 | 15.7 | 16.3 | 17.0 | 8.18 | 7.14 | 7.06 | 6.49 | 2230 | 261 | 966 | 2313 | -79 | -74 | -59 | -260 |
| 28-May-11 | 16.2 | 16.7 | 16.8 | 16.9 | 8.43 | 7.44 | 7.35 | 6.53 | 1691 | 360 | 907 | 2240 | -65 | -40 | -53 | -244 |

Table A20 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 2).

| Date | Dissolved oxygen (mg $l^{-1}$) | | | | Total suspended solids (mg $l^{-1}$) | | | | COD (mg $l^{-1}$) | | | | Ammonia-nitrogen (mg $l^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III |
| 08-Jul-11 | 3.4 | 3.2 | 1.3 | 1.2 | 100 | 0 | 0 | 320 | 126 | 88 | 137 | 120 | 0.141 | 0.695 | 3.237 | 60.129 |
| 15-Jul-11 | 3.2 | 2.9 | 1.4 | 1.2 | 120 | 60 | 0 | 340 | 108 | 98 | 153 | 135 | 0.153 | 0.941 | 4.703 | 52.802 |
| 22-Jul-11 | 3.1 | 3.3 | 1.3 | 1.3 | 140 | 0 | 40 | 460 | 140 | 106 | 114 | 126 | 0.134 | 1.226 | 4.825 | 56.638 |
| 29-Jul-11 | 2.9 | 3.1 | 1.1 | 0.9 | 80 | 40 | 40 | 320 | 132 | 93 | 136 | 145 | 0.182 | 0.485 | 5.594 | 61.243 |
| 05-Aug-11 | 2.5 | 2.9 | 1.4 | 1.3 | 60 | 0 | 20 | 420 | 128 | 76 | 122 | 147 | 0.186 | 0.872 | 4.389 | 63.571 |
| 12-Aug-11 | 2.9 | 3.3 | 1.3 | 1.2 | 80 | 20 | 0 | 240 | 134 | 115 | 150 | 175 | 0.095 | 1.253 | 5.713 | 54.746 |
| 19-Aug-11 | 3.1 | 3.4 | 1.2 | 1.1 | 180 | 80 | 20 | 260 | 142 | 98 | 133 | 156 | 0.15 | 0.734 | 4.382 | 57.295 |
| 26-Aug-11 | 2.8 | 3.1 | 1.2 | 1.1 | 140 | 60 | 0 | 320 | 138 | 78 | 162 | 169 | 0.173 | 0.973 | 5.356 | 51.957 |
| 02-Sep-11 | 3.0 | 3.2 | 1.2 | 1.0 | 120 | 0 | 0 | 420 | 142 | 89 | 145 | 146 | 0.144 | 1.368 | 3.468 | 75.184 |
| 09-Sep-11 | 3.2 | 3.3 | 1.3 | 1.4 | 140 | 0 | 20 | 200 | 158 | 71 | 87 | 108 | 0.656 | 1.587 | 2.007 | 93.501 |
| 16-Sep-11 | 3.3 | 3.4 | 1.3 | 1.3 | 120 | 0 | 0 | 320 | 155 | 70 | 84 | 111 | 0.163 | 3.101 | 3.582 | 52.043 |
| 23-Sep-11 | 3.1 | 3.0 | 1.4 | 1.3 | 100 | 0 | 0 | 280 | 153 | 65 | 83 | 110 | 0.171 | 1.827 | 3.922 | 93.296 |
| 30-Sep-11 | 2.6 | 3.1 | 1.9 | 1.4 | 120 | 80 | 40 | 80 | 154 | 82 | 87 | 109 | 0.188 | 0.944 | 4.338 | 72.521 |
| 07-Oct-11 | 2.5 | 2.5 | 2.4 | 1.7 | 120 | 0 | 40 | 640 | 152 | 54 | 89 | 115 | 0.147 | 1.197 | 2.189 | 76.209 |
| 14-Oct-11 | 2.3 | 2.4 | 0.9 | 0.9 | 180 | 0 | 0 | 320 | 156 | 70 | 92 | 110 | 0.138 | 1.096 | 4.59 | 62.707 |
| 21-Oct-11 | 1.4 | 0.5 | 1.0 | 0.6 | 80 | 20 | 40 | 200 | 156 | 103 | 85 | 110 | 0.124 | 0.16 | 4.737 | 55.699 |
| 28-Oct-11 | 2.8 | 3.0 | 1.8 | 1.4 | 120 | 60 | 0 | 320 | 157 | 50 | 82 | 84 | 0.133 | 0.663 | 4.926 | 52.249 |
| 04-Nov-11 | 3.5 | 1.0 | 2.3 | 0.8 | 80 | 0 | 20 | 380 | 157 | 71 | 72 | 110 | 0.155 | 0.93 | 4.472 | 44.09 |
| 11-Nov-11 | 3.2 | 2.3 | 2.5 | 1.2 | 20 | 0 | 40 | 580 | 157 | 88 | 95 | 105 | 0.199 | 0.719 | 5.842 | 6.228 |

Table A21 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 2).

| Date | Dissolved oxygen (mg $l^{-1}$) | | | | Total suspended solids (mg $l^{-1}$) | | | | COD (mg $l^{-1}$) | | | | Ammonia-nitrogen (mg $l^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III |
| 25-Nov-11 | 3.2 | 3.8 | 2.2 | 1.1 | 60 | 0 | 0 | 460 | 142 | 55 | 143 | 83 | 0.22 | 0.308 | 5.753 | 45.966 |
| 02-Dec-11 | 2.9 | 3.6 | 2.0 | 0.6 | 40 | 60 | 0 | 280 | 142 | 81 | 125 | 114 | 0.135 | 0.297 | 0.061 | 42.256 |
| 09-Dec-11 | 3.2 | 4.0 | 2.4 | 0.6 | 100 | 60 | 0 | 280 | 142 | 42 | 123 | 114 | 0.086 | 0.2 | 5.751 | 42.097 |
| 16-Dec-11 | 3.9 | 3.4 | 1.9 | 0.5 | 60 | 0 | 0 | 360 | 80 | 137 | 119 | 112 | 0.132 | 0.389 | 5.208 | 28.751 |
| 22-Dec-11 | 3.2 | 3.7 | 2.2 | 0.8 | 180 | 0 | 0 | 400 | 118 | 156 | 142 | 54 | 0.117 | 0.252 | 5.268 | 29.371 |
| 06-Jan-12 | 3.6 | 3.8 | 2.1 | 1.1 | 120 | 60 | 40 | 260 | 132 | 142 | 156 | 108 | 0.127 | 0.436 | 5.552 | 31.029 |
| 13-Jan-12 | 3.9 | 3.2 | 1.9 | 1.0 | 120 | 0 | 80 | 200 | 139 | 204 | 178 | 122 | 0.051 | 0.228 | 5.916 | 36.061 |
| 20-Jan-12 | 4.4 | 4.3 | 2.5 | 1.0 | 280 | 0 | 160 | 200 | 141 | 103 | 160 | 117 | 0.038 | 2.867 | 5.639 | 33.116 |
| 30-Jan-12 | 4.7 | 3.9 | 2.7 | 1.0 | 340 | 0 | 220 | 200 | 135 | 141 | 163 | 129 | 0.062 | 0.05 | 5.926 | 24.475 |
| 06-Feb-12 | 5.0 | 3.7 | 1.8 | 1.4 | 300 | 80 | 60 | 380 | 137 | 126 | 163 | 145 | 0.089 | 0.044 | 5.338 | 29.133 |
| 13-Feb-12 | 4.5 | 3.5 | 2.7 | 1.6 | 220 | 120 | 140 | 260 | 140 | 252 | 177 | 147 | 0.084 | 2.295 | 4.532 | 28.663 |
| 20-Feb-12 | 4.4 | 5.0 | 2.4 | 1.0 | 100 | 140 | 220 | 240 | 136 | 84 | 213 | 173 | 0.083 | 1.542 | 5.008 | 25.297 |
| 05-Mar-12 | 4.9 | 5.2 | 2.6 | 0.8 | 180 | 220 | 0 | 240 | 137 | 62 | 216 | 198 | 0.094 | 0.663 | 4.303 | 21.814 |
| 12-Mar-12 | 5.0 | 6.2 | 2.6 | 1.8 | 200 | 20 | 80 | 260 | 140 | 65 | 195 | 167 | 0.074 | 0.465 | 1.566 | 20.93 |
| 19-Mar-12 | 4.6 | 5.6 | 2.3 | 1.2 | 400 | 0 | 140 | 180 | 110 | 116 | 201 | 160 | 0.159 | 0.095 | 0.938 | 14.391 |
| 26-Mar-12 | 4.3 | 3.9 | 2.0 | 0.9 | 260 | 40 | 140 | 200 | 141 | 77 | 199 | 158 | 0.092 | 0.081 | 0.23 | 19.376 |
| 09-Apr-12 | 4.7 | 5.1 | 2.6 | 1.2 | 200 | 20 | 80 | 220 | 141 | 33 | 169 | 161 | 0.514 | 1.767 | 0.287 | 21.266 |
| 16-Apr-12 | 6.4 | 6.8 | 3.5 | 2.7 | 220 | 20 | 0 | 120 | 140 | 73 | 154 | 156 | 0.194 | 0.15 | 0.224 | 17.358 |
| 23-Apr-12 | 6.0 | 6.3 | 3.4 | 2.2 | 300 | 80 | 0 | 160 | 136 | 130 | 160 | 142 | 0.097 | 1.005 | 0.115 | 20.147 |

Table A22 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 2).

| Date | Dissolved oxygen (mg $l^{-1}$) | | | | Total suspended solids (mg $l^{-1}$) | | | | COD (mg $l^{-1}$) | | | | Ammonia-nitrogen (mg $l^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III |
| 07-May-12 | 5.2 | 5.8 | 3.3 | 4.1 | 440 | 20 | 0 | 20 | 138 | 97 | 199 | 141 | 0.088 | 0.369 | 0.092 | 16.956 |
| 14-May-11 | 5.8 | 5.1 | 3.3 | 3.6 | 260 | 0 | 80 | 120 | 143 | 72 | 152 | 145 | 0.107 | 0.544 | 0.16 | 16.046 |
| 21-May-11 | 6.5 | 6.2 | 4.5 | 3.5 | 500 | 40 | 0 | 160 | 136 | 46 | 134 | 131 | 0.089 | 0.832 | 0.19 | 13.001 |
| 28-May-11 | 5.6 | 5.4 | 3.3 | 3.2 | 380 | 0 | 0 | 120 | 126 | 16 | 110 | 114 | 0.099 | 0.853 | 0.151 | 13.187 |

Table A23 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 2).

| Date | Nitrate-nitrogen (mg $l^{-1}$) | | | | Nitrite-nitrogen (mg $l^{-1}$) | | | | Molybdate reactive phosphorous (mg $l^{-1}$) | | | | Chloride (mg $l^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III |
| 08-Jul-11 | 19.18 | 0.36 | 0.10 | <0.02 | 0.36 | 0.12 | 0.01 | <0.003 | 4.63 | 0.45 | 1.41 | <0.02 | 301.09 | 34.50 | 112.09 | 212.01 |
| 15-Jul-11 | 27.01 | 0.76 | <0.02 | <0.02 | 0.27 | 0.07 | <0.003 | <0.003 | 3.70 | 1.13 | 0.62 | <0.02 | 276.10 | 24.38 | 107.22 | 244.61 |
| 22-Jul-11 | 21.72 | 0.54 | <0.02 | <0.02 | 0.48 | 0.07 | 0.01 | <0.003 | 3.63 | 0.91 | 0.47 | <0.02 | 317.03 | 52.12 | 92.25 | 184.32 |
| 29-Jul-11 | 20.47 | 0.78 | 0.15 | <0.02 | 0.42 | 0.13 | <0.003 | <0.003 | 4.40 | 1.28 | 1.23 | <0.02 | 423.08 | 27.43 | 95.98 | 201.51 |
| 05-Aug-11 | 22.24 | 0.39 | <0.02 | <0.02 | 0.48 | 0.08 | <0.003 | <0.003 | 4.48 | 0.72 | 0.84 | <0.02 | 314.70 | 43.10 | 115.32 | 157.93 |
| 12-Aug-11 | 24.28 | 0.47 | 0.16 | <0.02 | 0.54 | 0.10 | 0.00 | <0.003 | 3.64 | 0.69 | 0.85 | <0.02 | 410.60 | 33.76 | 107.28 | 168.36 |
| 19-Aug-11 | 23.44 | 0.68 | <0.02 | <0.02 | 0.78 | 0.05 | 0.00 | <0.003 | 4.85 | 0.55 | 0.59 | <0.02 | 309.74 | 47.60 | 89.62 | 125.47 |
| 26-Aug-11 | 18.60 | 0.88 | 0.13 | <0.02 | 0.61 | 0.05 | <0.003 | <0.003 | 4.74 | 0.47 | 1.73 | <0.02 | 218.54 | 58.17 | 91.05 | 240.09 |
| 02-Sep-11 | 24.95 | 0.43 | <0.02 | <0.02 | 0.69 | 0.03 | <0.003 | <0.003 | 3.85 | 0.68 | 1.17 | <0.02 | 326.85 | 29.71 | 120.95 | 256.44 |
| 09-Sep-11 | 26.50 | 0.37 | <0.02 | <0.02 | 1.92 | 0.02 | 0.00 | <0.003 | 3.49 | 1.10 | 0.94 | <0.02 | 634.57 | 40.72 | 213.13 | 313.39 |
| 16-Sep-11 | 23.62 | <0.02 | 1.53 | <0.02 | 0.87 | 0.14 | 0.00 | <0.003 | 4.95 | 0.49 | 0.29 | <0.02 | 412.24 | 62.39 | 98.47 | 213.07 |
| 23-Sep-11 | 27.68 | <0.02 | <0.02 | <0.02 | 0.73 | 0.02 | <0.003 | <0.003 | 4.51 | 0.35 | 0.77 | <0.02 | 396.13 | 24.59 | 112.30 | 267.35 |
| 30-Sep-11 | 27.31 | 0.21 | <0.02 | <0.02 | 0.11 | 0.13 | <0.003 | <0.003 | 4.40 | 0.38 | 1.06 | <0.02 | 547.91 | 61.54 | 123.53 | 232.02 |
| 07-Oct-11 | 28.13 | 0.12 | <0.02 | <0.02 | 0.03 | 0.01 | <0.003 | <0.003 | 4.04 | 0.32 | 0.59 | <0.02 | 526.27 | 24.93 | 50.89 | 239.32 |
| 14-Oct-11 | 20.35 | 0.21 | <0.02 | <0.02 | 0.01 | 0.17 | <0.003 | <0.003 | 3.75 | 0.46 | 0.88 | <0.02 | 323.74 | 30.47 | 92.01 | 225.74 |
| 21-Oct-11 | 19.35 | 0.79 | <0.02 | <0.02 | 0.00 | 1.69 | <0.003 | <0.003 | 3.86 | 0.54 | 0.42 | <0.02 | 300.39 | 42.68 | 111.60 | 204.56 |
| 28-Oct-11 | 18.48 | 0.06 | <0.02 | <0.02 | 0.01 | 0.04 | 0.00 | 0.09 | 3.90 | 0.45 | 0.52 | <0.02 | 287.60 | 25.79 | 95.09 | 197.94 |
| 04-Nov-11 | 25.79 | 0.20 | <0.02 | <0.02 | 0.01 | 0.12 | 0.00 | <0.003 | 4.16 | 0.63 | 0.46 | <0.02 | 433.76 | 34.86 | 57.69 | 164.81 |
| 11-Nov-11 | 21.05 | 0.18 | 0.12 | 0.12 | 0.02 | 0.10 | 0.01 | 0.00 | 4.02 | 0.46 | 0.73 | 0.01 | 330.34 | 36.86 | 92.67 | 99.50 |

Table A24 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 2).

| Date | Nitrate-nitrogen (mg $l^{-1}$) | | | | Nitrite-nitrogen (mg $l^{-1}$) | | | | Molybdate reactive phosphorous (mg $l^{-1}$) | | | | Chloride (mg $l^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III |
| 25-Nov-11 | 26.46 | 0.42 | <0.02 | 0.03 | 0.47 | 0.02 | 0.01 | 0.03 | 6.12 | 0.54 | 2.63 | 0.02 | 534.23 | 27.91 | 128.23 | 196.12 |
| 02-Dec-11 | 23.20 | 1.06 | <0.02 | <0.02 | 0.01 | 1.08 | 0.00 | 0.02 | 4.77 | 0.67 | 2.10 | 0.01 | 422.27 | 35.86 | 91.48 | 182.82 |
| 09-Dec-11 | 22.78 | 0.89 | <0.02 | 0.05 | 0.01 | 0.68 | 0.00 | 0.02 | 3.62 | 0.47 | 2.23 | 0.01 | 402.42 | 26.67 | 99.01 | 179.91 |
| 16-Dec-11 | 20.41 | 0.35 | <0.02 | 0.10 | 0.02 | 0.12 | 0.00 | 0.01 | 3.88 | 0.35 | 2.07 | 0.01 | 349.49 | 27.70 | 72.36 | 137.48 |
| 22-Dec-11 | 19.63 | 1.02 | <0.02 | 0.22 | 0.02 | 0.10 | 0.00 | 0.03 | 4.11 | 0.47 | 2.01 | 0.01 | 350.22 | 31.08 | 79.57 | 137.35 |
| 06-Jan-12 | 17.24 | 0.85 | <0.02 | 0.28 | 0.01 | 0.04 | 0.00 | 0.02 | 3.70 | 1.50 | 3.27 | 0.02 | 286.45 | 38.60 | 124.51 | 154.66 |
| 13-Jan-12 | 23.35 | 5.77 | 0.10 | 0.40 | 0.19 | 0.01 | <0.003 | 0.02 | 5.31 | 2.90 | 3.80 | 0.04 | 434.95 | 70.12 | 94.66 | 184.55 |
| 20-Jan-12 | 13.86 | 1.64 | <0.02 | <0.02 | 0.01 | 0.01 | 0.00 | 0.01 | 3.50 | 0.86 | 3.72 | 0.02 | 220.81 | 37.67 | 119.37 | 173.67 |
| 30-Jan-12 | 26.76 | 7.62 | 0.07 | <0.02 | 0.01 | 0.02 | 0.00 | 0.02 | 7.76 | 2.36 | 4.66 | 0.04 | 558.37 | 60.50 | 131.03 | 133.08 |
| 06-Feb-12 | 25.34 | 7.19 | <0.02 | <0.02 | 0.01 | 0.02 | 0.03 | 0.03 | 6.52 | 0.54 | 2.61 | 0.02 | 463.08 | 51.94 | 68.90 | 174.16 |
| 13-Feb-12 | 16.99 | 7.06 | <0.02 | 0.06 | 1.20 | 0.16 | 0.00 | 0.03 | 3.36 | 0.45 | 2.97 | 0.02 | 236.88 | 93.67 | 76.75 | 180.84 |
| 20-Feb-12 | 21.80 | 0.15 | <0.02 | <0.02 | 0.00 | 0.02 | <0.003 | 0.03 | 4.39 | 0.11 | 3.27 | 0.02 | 351.25 | 23.55 | 140.55 | 182.37 |
| 05-Mar-12 | 20.59 | 0.12 | <0.2 | 0.23 | 0.02 | 0.12 | 0.05 | 0.04 | 4.34 | 0.64 | 4.71 | 0.06 | 386.63 | 32.85 | 149.74 | 191.92 |
| 12-Mar-12 | 18.75 | 0.21 | <0.2 | <0.2 | 0.04 | 0.21 | 0.03 | 0.01 | 4.04 | 0.25 | 3.52 | 0.04 | 331.39 | 25.41 | 92.87 | 134.05 |
| 19-Mar-12 | 16.68 | 1.22 | <0.2 | <0.2 | 0.02 | 2.90 | 0.03 | 0.01 | 3.68 | 0.42 | 2.72 | 0.04 | 266.96 | 55.00 | 92.63 | 97.69 |
| 26-Mar-12 | 18.25 | 0.80 | 1.16 | <0.2 | 0.02 | 1.15 | 0.05 | 0.01 | 3.46 | 0.20 | 2.88 | 0.09 | 300.40 | 39.32 | 165.08 | 118.82 |
| 09-Apr-12 | 19.70 | 0.95 | 0.20 | <0.2 | 0.89 | 0.12 | 0.05 | 0.02 | 3.86 | 0.28 | 2.36 | 0.18 | 315.79 | 29.61 | 134.14 | 180.41 |
| 16-Apr-12 | 21.04 | 0.04 | 0.12 | <0.2 | 0.00 | 0.12 | 0.01 | 0.01 | 3.63 | 0.16 | 2.45 | 0.24 | 310.92 | 15.32 | 120.68 | 127.98 |
| 23-Apr-12 | 20.94 | 0.47 | 0.06 | <0.2 | 0.09 | 0.03 | 0.01 | 0.01 | 3.31 | 0.29 | 1.82 | 0.31 | 298.36 | 50.54 | 123.45 | 172.28 |

Table A25 Water quality variables for farmyard runoff mesocosms 1 and 2 (Experimental period 2).

| Date | Nitrate-nitrogen (mg $l^{-1}$) | | | | Nitrite-nitrogen (mg $l^{-1}$) | | | | Molybdate reactive phosphorous (mg $l^{-1}$) | | | | Chloride (mg $l^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III | Control | Influent | Tap I | Tap III |
| 07-May-12 | 23.78 | 0.73 | 0.07 | 0.88 | 0.02 | 0.11 | 0.00 | 0.03 | 4.33 | 0.63 | 2.08 | 0.68 | 355.19 | 52.03 | 105.71 | 223.80 |
| 14-May-11 | 21.68 | 0.42 | 0.06 | <0.2 | 0.01 | 0.14 | 0.00 | 0.01 | 4.14 | 1.02 | 1.91 | 0.79 | 331.73 | 29.95 | 107.12 | 148.45 |
| 21-May-11 | 18.10 | 0.35 | 0.08 | <0.2 | 0.07 | 0.02 | 0.00 | 0.01 | 4.09 | 1.54 | 2.84 | 0.91 | 259.59 | 26.30 | 102.98 | 110.47 |
| 28-May-11 | 24.10 | 0.37 | 0.11 | <0.2 | 0.02 | 0.30 | 0.01 | 0.01 | 4.10 | 1.70 | 2.32 | 1.36 | 364.34 | 18.18 | 92.03 | 129.70 |

# Appendix B

## *Publications involved in this thesis:*

**Dong, Y.**, Wiliński, P., Dzakpasu, M., Scholz, M. (2011). Impact of hydraulic loading rate and season on water contaminant reductions within integrated constructed wetlands. Wetlands 31(3), 499–509.

**Dong, Y.**, Scholz, M., Harrington, R. (2012). Statistical modelling of contaminants removal in mature integrated constructed wetland sediments. Journal of Environmental Engineering 138, 1009–1017.

**Dong, Y.**, Scholz, M., Mackenzie, S. (2012). Performance evaluation of representative Wildfowl & Wetlands Trust (WWT) constructed wetlands treating sewage. Water and Environment Journal (Article first published online: 20 Sep 2012).

**Dong, Y.**, Kayranli, B., Scholz, M., Harrington, R. (2012). Nutrient release from integrated constructed wetlands sediment receiving farmyard runoff and domestic wastewater. Water and Environment Journal (Article first published online: 8 Oct 2012).