Constructed wetlands for the treatment of concentrated stormwater runoff

Design and operation of experimental constructed wetlands applied for gully pot liquor treatment, and application of machine learning techniques to support constructed wetlands management

Byoung-Hwa Lee

A thesis submitted for the degree of doctor of Philosophy
The University of Edinburgh

Declaration

This work has not been submitted for any other degree or professional qualification and the research recorded in this thesis and the thesis itself was composed entirely by myself except where references have been stated.

Byoung-Hwa Lee

Abstract

Research in the area of the constructed wetlands for wastewater treatment has been built up over the years. However, specific design concepts for stormwater runoff treatment systems have not been examined as precisely as for wastewater. Furthermore, the variability of stormwater runoff quality and quantity was a major problem in designing treatment systems. As a consequence, there have been several controversial issues in designing and operating constructed wetlands for stormwater runoff treatment.

The aim of this research was to assess the treatment efficiencies for concentrated stormwater runoff (gully pot liquor) of experimental vertical-flow constructed wetland filters containing common reed and different aggregates, and provide optimal design and operational guidelines of constructed wetlands for stormwater runoff treatment.

Despite highly variable loading, temporarily flooded vertical-flow wetlands showed high treatment performance with respect to BOD, SS, nutrients and heavy metal. High investment costs for more complex filters are not justified by their low contribution to removal performance of pollutants. The sand-gravel based reed beds are recommended as optimal type of wetlands for urban runoff treatment. However, impact of macrophytes on the target heavy metal needs to be examined to avoid adverse effect of macrophytes on the metal removal performance.

A large part of nickel in constructed wetland filters is likely to leach when exposed to a high salt concentration in winter. However, a breakthrough of nickel was not observed since the inflow pH was raised, indicating that conventional pH adjustment

can be successfully applied to constructed wetland systems for urban runoff treatment.

The effluent water quality variables of constructed wetlands are difficult to predict due to the complexity of the processes within the systems. However, it is necessary to monitor and predict the water quality variables to meet environmental policies, and regulatory requirements such as secondary wastewater treatment standards.

Machine learning techniques such as k-nearest neighbours, support vector machine and self-organizing map were applied to predict five-day @ 20 °C N-Allylthiourea biochemical oxygen demand (BOD) and suspended solids (SS), and to demonstrate an alternative method of analyzing water quality indicators.

The results suggest that BOD and SS can be efficiently estimated by applying machine learning techniques with cost-effective input variables such as redox potential and conductivity, which can be monitored in real time. Their performance is encouraging and supports the potential for future use of these models as management tools for the day-to-day process control of constructed wetlands and other 'black box' systems.

Publications

Journals:

Scholz M. and Lee B.-H. (2005), Constructed Wetlands: A Review, *The International Journal of Environmental Studies*, Vol. 62, No. 4, pp. 421-447.

Lee B.-H., Scholz M. and Horn A. (2005), Constructed Wetlands for the Treatment of Concentrated Stormwater Runoff (Part A), *Environmental Engineering Science*, Vol. 23, No. 2, 191-202.

Lee B.-H., Scholz M., Horn A. and Furber A. M. (2005), Prediction of Constructed Treatment Wetland Performance with Case-based Reasoning (Part B), *Environmental Engineering Science*, Vol. 23, No. 2, 203-211.

Lee B.-H. and Scholz M. (2006), A Comparative Study: Prediction of Constructed Treatment Wetland Performance with K-nearest Neighbors and Neural Networks, *Water, Air and Soil Pollution*, accepted for publication.

Scholz M., Lee B.-H. and Härtl J. T. (2006), Design and Operation of Experimental Constructed Treatment Wetlands Applied for Gully Pot Effluent Contaminated with Heavy Metals, *Bioresource Technology*, submitted.

Scholz M., Lee B.-H. and Horn A. (2006), Control of Pollutant Dynamics with Case Based Reasoning in Experimental Constructed Wetlands Treating Gully Pot Liquor, *The Science of the Total Environment*. submitted.

Conferences:

Lee B.-H., Härtl J., Guilbert S. M. A. and Scholz M. (2004), Constructed Wetlands for Gully Pot Effluent Treatment. Poster presentation at the *International Water Association's Young Researchers Conference* (23-24/04/04), International Water Association, Amsterdam, The Netherlands.

Lee B.-H., Scholz M., Horn A. and Furber A. (2005), Prediction of Constructed Treatment Wetland Performance with Case-based Reasoning. A. P. Newman, C. J. Pratt, J. W. Davies and J . M. Blakeman (Eds.). In Proceedings of the *Third National Conference on Sustainable Drainage*. ISBN: 1 84600 007 6. pp. 360-370. Coventry University, Coventry, UK.

Lee B.-H., Scholz M., Horn A. and **Furber A.** (2005), Prediction of Constructed Treatment Wetland Performance with Case-based Reasoning. In proceedings of the *Third National Conference* held by The Chartered Institution of Water and Environmental Management (CIWEM) and Aqua Enviro Technology Transfer in Wakefield (06-08/09/04), Vol. 1, ISBN 1 903958 14 08, pp. 447-457, Aqua Enviro Technology Transfer, Leeds, UK.

Lee B.-H. and **Scholz M.** (2006), Application of Case-based Reasoning to Support Constructed Wetland Management. In Ubertini L. (ed.), Proceedings of the *Second International Association of Science and Technology for Development (IASTED) International Conference on 'Advanced Technology in the Environmental Field'* (06-08/02/06), Lanzarote, Spain, ACTA Press, Calgary, ISBN: 088986-552-3, pp. 100-105.

Scholz M., Lee B.-H. and **Horn A.** (2005), Control of Pollutant Dynamics with Case Based Reasoning in Experimental Constructed Wetlands Treating Gully Pot Liquor. Oral presentation at *WETPOL – International Symposium on Wetland Pollutant Dynamics and Control* (4-8/09/2005), Ghent, Belgium.

Lee B.-H. and **Scholz M.** (2005), Constructed Wetlands Used for Treatment of Urban Runoff Contaminated with Heavy Metals. In *Abstract Booklet of the Institute of Environmental Management and Assessments Seminar on 'Wetlands: Environmental Management and Assesssment'* (15/0905), IEMA, Edinburgh, Scotland, UK.

Scholz M. and **Lee B.-H.** (2005), Design and Operation of Experimental Constructed Wetlands Applied for Gully Pot Effluent Contaminated with Heavy Metals. Proceedings of the 10th *International Conference on Urban Drainage* (21-26/08/05), Copenhagen, Denmark ISBN 87-89220-80-3, p. 54.

Scholz M. and **Lee B.-H.** (2005), Treatment of Gully Pot Liquor Containing Heavy Metals with Constructed Wetlands. *Newsletter of the IWA Specialist Group on Use of Macrophytes in Water Pollution Control*, No. 29, p. 37-44.

Acknowledgements

The author would like to thank his supervisor, Dr Miklas Scholz, for his advice, guidance and support. He also appreciates the scientific advice of Dr. Martin Crapper and Dr. Kate Heal.

Many students have assisted him in the laboratory and the computational work, and he is grateful to all for their great deal of help: Johannes Härtl, Sylvane Guilbert, Frank Mc Gowan, Antje Horn, Alison Furber and Iris Caldwell. He would also like to thank Dr. Peter Anderson and Jim Hutcheson for their assistance in sample analysis and technical support in the laboratory.

He also very much appreciates the invaluable support of his family and would like to dedicate his thesis to his parents and parents-in-law, who always supported and encouraged him during his research study.

Contents

Abbreviations

ANOVA   analysis of variance

BMU   best-matching unit

BOD   five-day @ 20 °C N-Allylthiourea biochemical oxygen demand (mg/l)

COD   chemical oxygen demand (mg/l)

DO   dissolved oxygen (mg/l)

HRT   hydraulic retention time

KNN   k-nearest-neighbors

MAE   mean absolute error

MAPE   mean absolute percentage errors

MASE   mean absolute scaled error

MSE   mean square error

NTU   nephelometric turbidity units

redox   redox potential (mV)

RMSE   root mean square error

SF   surface flow

SOM   self-organizing map

SS   suspended solids (mg/l)

SSF   sub-surface flow

SUDS   sustainable urban drainage system

SVM   support vector machine

TE   topographic error

TDS   total dissolved solids

TS   total solids

TSS   total suspended solids

QE   quantization error

U-matrix   unified distance matrix

Nomenclature

Alphabet characters

A	surface area of wetland
C	regularized constant determining the trade-off between the training error and the model flatness
C_i	influent concentration
C_e	effluent concentration
$f(x)$	decision function
$h_{ci}(t)$	neighborhood kernel around the 'winner unit' c
k_0	zero-order areal rate constant
k_1	first-order areal rate constant
k_{20}	rate constant at 20 °C
k_{BOD}	rate constant for BOD removal
k_N	rate constant for nitrogen removal
k_p	rate constant for phosphorus removal
k_{SS}	rate constant for SS removal
k_T	rate constant at T °C
K	half-saturation constant
$K(x_i, x_j)$	kernel function
L_ε	ε-insensitive loss function
m_i	measured values
$m(t)$	weight vector indicating the output unit's location in the data space at time t
MV_i	mean of variable i found in the case

p_i	predicted values
q	hydraulic loading rate
Q	Volumetric flow rate
$R(C)$	regularized risk function
SDV_i	standard deviation of the values of the case
T	water temperature
V	wetland holding volume
V_i	value of variable i for the case
$V_{norm,ic}$	normalized value of variable i for the past case
$V_{norm,ip}$	normalized value of variable i for the problem case
w_i	the weighting associated with variable i
x_i	input vector
$x(t)$	input vector drawn from the input data set at time t
y_i	desired value

Roman characters

α	tuning parameter to determine the flatness of the smoothing function
$\alpha(t)$	learning rate at time t
γ	kernel parameter
$\phi_i(x)$	non-linear mapping function representing the features of inputs
ω and b	coefficients, which are estimated by minimizing the regularized risk function R(C)

List of figures

List of tables

Chapter 1   Introduction

1.1. Background to the project

Constructed wetlands have been proven to be more economical and energy efficient than traditional centralized treatment systems (Kadlec and Knight, 1996). The experiences and research in the area of the constructed wetlands for wastewater treatment have been built up over the years. However, specific design concepts for stormwater runoff treatment systems have not been examined as precisely as for wastewater.

Stormwater runoff quality is highly unstable due to the flushes of de-icing salts in winter, changes in redox potential (redox) and pH, and seasonal variation in availability of organic leaf litter. The variability of stormwater runoff quality and quantity was a major problem in designing treatment systems. As a consequence, there have been several controversial issues in designing and operating constructed wetlands for stormwater runoff treatment in recent years. The following issues are particularly relevant to this thesis:

Design concept of wetlands. It is well known that the vertical-flow systems have higher removal capacity for organic matters and nutrients than horizontal-flow systems (Cooper et al., 1996). Nevertheless, most of the constructed wetland technologies in common use in the UK and USA have been based on the horizontal-flow systems and remarkable approaches to modify the vertical-flow system were relatively rare.

Recent researches have reported that performance of wetlands could be greatly improved by modifying the operation conditions (Green *et al.*, 1998; IWA, 2000).

One of the innovative modifications is to introduce more oxygen into system by adopting tidal flow (flood and drain), which has shown a great potential for wastewater treatment in recent years (Sun *et al.*, 2005).

Components of wetlands. Although macrophytes are generally considered to be essential constituents in the design of constructed wetlands, their role in treatment processes has been controversial. Concerning the role of filter media in treatment process of the constructed wetlands, special media such as Filtralite and zeolite have shown higher adsorption capacities than normal aggregates. However, there has also been a sceptical view on the role of specific filter media (Scholz and Xu, 2002).

Treatment variability. For constructed wetlands, variability in treatment performance raises capital costs as the treatment system is likely over-designed to compensate for uncertainty of treatment performance. The performance of wetlands is variable depending on variable environmental conditions such as change of the season, variable hydraulic and mass loadings. In particular, performance of wetland systems for stormwater runoff is likely to be more unstable due to variable stormwater quality and quantity.

Prediction of performance. The performance of constructed wetlands needs to be monitored and estimated in real time, if possible, to control treatment processes and meet regulatory requirements. However, performance of constructed wetlands is known to be difficult to model and predict due to the complex processes within the systems.

This thesis addresses these issues particularly relevant for the treatment of urban stormwater runoff. A modified design concept (temporarily flooded vertical-flow wetlands combined with pond) will be applied for urban runoff treatment. The

treatment performance of the wetland will be assessed under various environmental conditions such as dry and wet weather. Design, operation and monitoring guidelines will be optimized to reduce seasonal treatment variability and maintain treatment efficiency.

1.2. Aims of this research

The aim of this thesis can be stated by following statement:

To improve the design and operation guidelines of vertical-flow constructed treatment wetlands to secure a high treatment performance during all seasons in cold climates.

This can be split into following key areas:

1. to propose the temporarily flooded vertical-flow constructed treatment wetland filters, as a more efficient process for concentrated urban runoff treatment;

2. to suggest optimal design and operational guidelines of constructed wetlands to sustain their high level of performance under variable environmental conditions in cold climate;

3. to examine the feasibility of conventional chemical pH adjustment to improve the performance of constructed wetland; and

4. to assess the effectiveness of applying k-nearest-neighbours (KNN), support vector machine (SVM) and self-organizing map (SOM) to predict the outflow water quality of experimental constructed treatment wetlands indirectly.

1.3. Outline of thesis contents

This thesis consists of two parts. While this thesis focuses mainly on the investigation of the experimental constructed wetlands, applications of machine learning techniques for the prediction of wetland performance were also studied.

The brief background and aims of this research are described in Chapter 1.

Chapter 2. Constructed treatment wetlands for urban runoff management.

In this chapter, the brief backgrounds of constructed wetlands including main components, flow-types and the removal mechanisms of pollutants are described. A modified vertical-flow constructed wetlands, which are applied to the present experimental systems are introduced. The findings of recent research into constructed wetlands are also discussed.

Chapter 3. Materials and methods.

This chapter describes the experimental set-up and operation methods applied for experimental study. Filter design and compositions as well as environmental condition of experimental system are also explained.

Chapter 4. Overall treatment performance.

This chapter investigates the treatment mechanisms and potentials for five-day @ 20 °C N-Allylthiourea biochemical oxygen demand (BOD) and suspended solids (SS) in the experimental constructed wetlands. A simple removal model will be applied to evaluate the removal potential of the system. The performance of each filter is also statistically compared to assess the role of design components and operation conditions, and consequently, the optimal design and operation guidelines of constructed wetlands for urban runoff treatment are proposed.

Chapter 5. Nutrient removal performance.

Nutrient removal performance of the experimental system is examined, as demonstrated in chapter 4. The effects of influent water quality and design factors of wetlands on the performance are investigated, and the main mechanism of nutrient removal is identified. Furthermore, the contribution of macrophytes to the nutrient removal is quantified.

Chapter 6. Heavy metal removal performance.

In this chapter, heavy metal removal performance of the system is assessed. Mechanisms of metal removal and impact of environmental conditions on the metal removal performance are also investigated. In particular, the effect of salt and pH on the metal removal is discussed in detail.

After filters are matured, filters are heavily loaded with Cu to investigate the fate of Cu in the long-term. Besides, additional column experiments are implemented to determine the metal removal potential of ochre pellet.

Chapter 7. Application of machine learning techniques to support constructed wetland management.

Machine learning techniques for the indirect prediction of water quality indicator of experimental constructed wetlands are introduced. The KNN, SVM and SOM are applied to predict water quality variables such as BOD, SS, nutrients and metals, which are expensive and labor intensive to estimate. Variables such as redox potential and conductivity, which can be monitored in real time are used as input to models. The possibility of application of machine learning models to support wetland management is discussed.

Finally, this thesis is concluded with recommendations for future work in chapter 8.

Chapter 2   Constructed treatment wetlands

for urban runoff management

2.1. Introduction

The general background of constructed wetlands such as main components, flow-types and the removal mechanisms of pollutants in constructed wetlands are described in this chapter. This chapter introduces a modified vertical-flow constructed wetland, which is highly efficient for pollutant treatment. Later chapters investigate how this relatively new system can be applied for urban runoff treatment.

This chapter is structured as follows. Sections 2.2 and 2.3 give brief descriptions of the main components (substrate and macrophyte) and flow types of constructed wetlands. Section 2.4 describes the removal mechanisms of main pollutants in the constructed wetlands. In each section, relevant research is also discussed. Section 2.5 introduces the constructed wetlands system applied to stormwater runoff treatment and integrated into SUDS.

2.2. Constructed treatment wetlands

Constructed wetlands are man-made systems designed to imitate the optimal treatment conditions found in natural wetlands, which filter out pollutants and act as sinks for nutrients by purifying the water through physical (sedimentation and filtration), physical-chemical (adsorption on plants, soil and organic substrates) and biochemical (biochemical degradation, nitrification, denitrification, decomposition

and plant uptake) processes (Novontny and Olem, 1994).

Constructed wetlands for wastewater treatment have several advantages over conventional treatment methods (Cooper *et al.*, 1996; Moshiri, 2000); e.g., enhanced biodiversity, greater sustainability, low cost of construction and maintenance, low energy requirement, low technology system and less susceptibility to variation in loading rate. Despite such advantages of constructed wetlands, however, many environmental authorities are still skeptical about their use, especially when discharge of high quality effluent is required.

While experience in practical application and research has been built up over the years, a number of fundamental aspects on the exact function of constructed wetlands are not fully understood yet. One reason for this is that constructed wetlands, as compared to other technologies, depend on the interaction of many different components.

2.2.1. Components of a wetland

The term wetland itself describes a wide range of ecosystems. Wetlands are not necessarily flooded all year round, but are areas that are saturated with water for a certain period of the year. Wetlands are transitional areas between uplands where excessive water is not a factor for plant growth, and aquatic ecosystems where flooding excludes rooted emergent vegetation (Kadlec and Knight, 1996).

Wetlands usually have the following components: underlying strata, hydric soil, water, detritus and emergent vegetation. The underlying strata are unaltered organic, mineral or lithic strata which are usually saturated with or impervious to water and are below the active rooting zone of the wetland vegetation (Campbell and Ogden,

1999). The detritus layer is a result of the accumulation of organic material coming from plants, algae, animals and microbes. The soil, water and vegetation are key parameters in the characterization of a wetland.

Substrate. The soil is the main supporting material for plant growth and microbial films in constructed wetlands. Moreover, the soil matrix has a decisive influence on the hydraulic processes (Stottmeister *et al.*, 2003). There are two different types of wetland soil: mineral soil and organic soil. Mineral soil can be silt, sand and gravel. Organic soils are peat, muck and mucky peat.

The filtration media used in constructed wetlands depend on the objectives that need to be attained. Constructed wetlands have been designed and built with substrates ranging from fine texture soil to field stone. A coarse-grained material with high hydraulic conductivity will prevent the filter from getting clogged. A close-grained material will be more efficient in reducing suspended solids and turbidity.

However, some soil beds suffer from surface flow, which leads to poor reed growth, by-passing, and poor overall treatment. As a result of these problems, a mixture of sand and gravel is recommended in terms of hydraulic condition and the removal of contaminants (Stottmeister *et al.*, 2003; IWA, 2000). For vertical-flow constructed wetland, a relatively small range of effective grain size of 0.06 to 0.1 mm has been evaluated, while that for horizontal-flow system was found to be higher at 0.1 mm (Stottmeister *et al.*, 2003).

Several factors of the filter media affect the filtering process, such as the mineral composition, the hydraulic conductivity and the porosity of substrates. A number of specialty media have been studied to increase the adsorption capacity of filter media with different substrates. Mæhlum and Stlnacke (1999) demonstrated that

constructed wetlands including Filteralite removed most organic matter (BOD > 75 %), P (90 > %), N (40 – 80 %) in the cold climate. Zeolite was found to be superior to the other filter-substrate for stormwater treatment (Färm, 2002). Gray et al. (2000) also reported that the P-adsorption capacity of maerl (seaweed) as substrate of constructed wetland is approximately 1200 mg/kg.

However, there have been contradictory views about the function of expensive filter media in the treatment process of constructed wetlands. Scholz and Xu (2002) suggested that there was no additional benefit in using expensive adsorption media like granular activated carbon to enhance filtration performance of constructed wetlands.

Macrophytes. Vegetation is the principal component of a wetland system. Although macrophytes are widely used within treatment wetlands in Europe and Northern America (Cooper et al., 1996; Kadlec and Knight, 1996), the role of macrophytes and the effect of different plant species on the treatment wetland have been controversial.

Several previous studies reported a considerable contribution of macrophytes to the pollutant removal. Karathanasis et al. (2003) reported that the BOD removal efficiency was lower in unplanted systems (63%) than in planted systems (75-70%) and removal efficiency of total suspended solids (TSS) was also significantly lower in unplanted system (46 %) than in planted systems (88-90%) in the sub-surface flow (SSF) wetlands. Gray et al. (2000) also described that planted systems removed more chemical oxygen demand (COD) from sewage than unplanted systems (75% removal compared to 48 %) in the surface flow (SF) wetlands. Furthermore, wetland plants require nutrients for the growth and reproduction. The uptake capacity of

macrophytes is roughly in the range of 30 - 150 kg P/ha/yr and 200 - 2500 kg N/ha/yr (IWA, 2000).

In contrast, some researches did not detect any significant difference between planted and unplanted systems. Baldizon *et al.* (2002) reported that differences in BOD removal performance observed between wetland systems comprising of duckweed, reed and algal was insignificant. Scholz and Xu (2002) also suggested that the BOD removal performance was virtually similar irrespective of planting regimes of constructed wetlands.

Macrophytes can assimilate pollutants in their tissue, and also provide a surface and an environment for microorganisms to grow (Vymazal, 2002). Moreover, the macrophytes create better conditions for sedimentation of SS and prevent erosion by reducing the velocity of the water in the wetland. The growth of roots within filter medium helps to decompose organic matter and prevents clogging by creating channels for the water to pass through in the intermittent loading vertical-flow system. The macrophytes transport approximately 90 % of oxygen available in the rhizosphere which stimulates both aerobic decomposition of organic matter and growth of nitrifying bacteria (Brix, 1997; Reddy *et al.*, 1989). However, despite such an ability of macrophytes, when compared to microorganisms, they only play a secondary role in the degradation of organic matters in wetland systems. (Stottmeister *et al.*, 2003).

Through the annual turnover of plants leaves and shoots, organic matter accretes in wetlands over time. The organic matter serves not only to bind heavy metals directly but also to provide a carbon and energy source for microbial metabolism. Thus plants can be an essential part in the long-term functioning of wetlands (Batty, 2003;

Gladden *et al.*, 2002).

It has become general opinion that the physical function (erosion control and provision of surface area for microorganism) of macrophytes significantly improves the performance of wetlands. In comparison, the metabolism of macrophytes (uptake and oxygen release) affects the treatment process to different extents depending on the design of constructed wetlands (Brix, 1997). While plants significantly affect the removal of pollutants in horizontal SSF systems with long HRT, their role is minor in pollutant removal in periodically loaded vertical-flow filters and SF systems, which usually have short the hydraulic retention time (HRT) in comparison (Karathanasis *et al.*, 2003; Stottmeister *et al.*, 2003).

Previous research has shown that plants have little contribution to heavy metal removal and plants themselves are not important sinks for metals. May and Edwards (2001) reported that Fe and Mn contents in the plant were only 1 and 2 %, respectively, of the annual Fe and Mn loading in the wetlands. Similar findings have been reported for Fe removal (0.07 % of the annual loading) by plants (Mitch and Wise, 1998).

Contradictory results indicating a significant role of plants on the heavy metal removal also have been reported. Batty (2003) reported that *P. australis* took up almost 100 % of Fe supplied at a concentration of 1 mg/l. Fe removal efficiency at Woolley Colliery (West Yorkshire, UK) was also shown to improve from 70 % to 95% when planted (Younger *et al.*, 2002). Cheng *et al.* (2002) found that more than 30 % of Cu and Mn loading were accumulated in *C. alternifolius* in the vertical-flow experimental systems.

The most common plants in wetlands are reed (*Phragmites* sp), cattail (*Typha* sp.), rush (*Juncus* sp.) and bulrush (*Scirpus* sp.). However, the most frequently used plant species worldwide is *P. australis* (IWA specialist, 1999). Densely rooted plants slow the water down and produce a more uniform flow, thus contributing to the stabilization of the sediments.

Aquatic plants also have a negative impact on the wetland management. In autumn, macrophytes loose their leaves so that the BOD concentration will increase due to the increase of nutrients in the litter zone. Furthermore, the overall storage area for water will be reduced due to an accumulation of plant debris. It follows that the retention time of the wastewater in the constructed wetland will decrease if the inflow and outflow rates remain constant.

2.2.2. Hydrology

The hydrology of a wetland is defined by two parameters (Gosselink and Turner, 1978): The hydroperiod and depth of flooding. The hydroperiod is the time during which the soil is flooded or saturated, expressed in percentage. The depth of flooding in a natural wetland varies between +2 m and −1 m relatively to the ground surface, with an average of approximately +1 m. These two parameters highly affect the characteristics (oxygen concentration, pH, nutrients, plants etc.) and stability of the wetlands (Scholz and Lee, 2005).

In the case of constructed wetlands, however, the hydrological characterization of the wetland is more complex. In wastewater treatment wetlands, the inflow is rather regular and the amount of pollutant brought in is quite constant. In stormwater runoff treatment wetlands, the inflow rate is highly variable and shock loads are likely to occur just after a big rain event. Unless a flow equalization system is installed prior

12

to the wetland, which would therefore induce more maintenance work and higher costs, the hydrological cycle of the wetland is rather complex (Pontier *et al.*, 2001; Shutes *et al.*, 1999).

In this present study, the filters are flooded and drained (temporarily flooded) on a regular basis, allowing oxygen to be regenerated in the lower levels of the filters. When the wetland is drained, the retreating water acts as a passive pump to draw air from the atmosphere into the matrix (Green *et al.*, 1998; Sun *et al.*, 2003). The hydrological regime can therefore be determined with precision (Figure 2-2).

The HRT is considered as one of the most crucial factors in designing and operating a constructed wetland and variable in determining the efficiency of settling solids, biochemical processes, and plant uptake (Kedlec and Knight, 1996).

Existing wetlands are designed with a wide range of HRT, generally ranging from 2 to 20 days. When wetlands are designed for N removal, short HRT is used for nitrate removal and long HRT for removing ammonia. However, wetlands with longer HRT will result in an increase of dissolved organic carbon leached from plant-derived material (Pinney *et al.*, 2000). It is suggested that wetlands should have a minimum retention time of at least 10-15 hours to achieve a high level of removal efficiency for the stormwater runoff treatment (Ellis *et al.*, 2003; Shutes *et al.*, 1999).

2.3. Types of constructed wetlands

Natural wetlands have long been used for wastewater discharge. The technology used for constructed wetlands is based on the observation of the mechanisms that take place in natural wetlands.

2.3.1. Surface-flow system

This type of constructed wetland operates like a natural wetland. The wetland is flooded from the top and water flows horizontally on top of the wetland soil, infiltrates the soil or is evaporated (Figure 2-1).
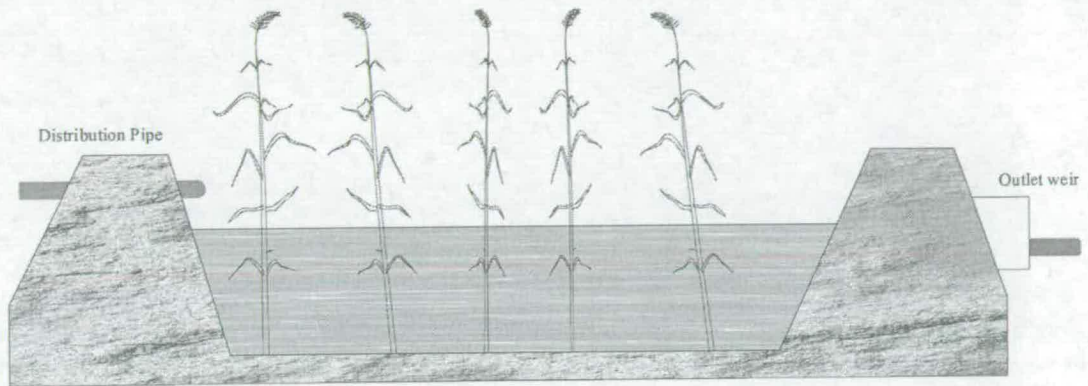
Figure 2-1. Surface-flow wetland containing emergent macrophytes (modified from Kadlec and Knight, 1996)

This kind of system usually has two different strata. The surface water is aerobic and undergoes oxygen-consuming transformations, whereas the deeper zones of the wetland are anaerobic and receive no light.

SF wetlands can be planted with different kinds of macrophytes, such as emergent, free floating, floating-leaved, bottom rooted or submersed macrophytes. The advantages of such systems are that the construction and operation costs are rather low and that the technology is quite simple to use. However, SF systems require a larger area of land and water is exposed to potential human contact (IWA, 2000).

2.3.2. Sub-surface-flow system

SSF wetlands are generally constructed with a porous material (e.q. soil, sand and gravel) as a substrate for growth of rooted wetland plants. The main characteristic of SSF systems is that their surface is not covered with water, even when the soil of the wetland is flooded and substrate provides more surface area for bacterial biofilm growth than SF wetlands, resulting in increased treatment effectiveness (Kedlec and Knight, 1996).

The temperature in SSF wetlands is rather stable, compared to SF systems, as there is no direct solar radiation on the water. The oxygen concentration in the water is usually higher than in SF system, as the roots of the plants are in direct contact with the water and bring oxygen to it.

A SSF wetland combines aerobic, anoxic and anaerobic zones. Water purification, achieved through microbiological, physical a chemical processes, mainly takes place in the aerobic zone, which is situated in the rhizosphere. SSF wetlands have the primary benefit that water is not exposed during the treatment process, minimizing energy losses through evaporation and convection. This makes SSF system more suitable for winter application (Wallace *et al.*, 2000)

The flow in a SSF system can either be horizontal or vertical:

Horizontal-flow systems. Horizontal SSF systems (Figure 2-2) are only used with low flow rates to enable the water to be stagnant in some areas. The depth of a horizontal SSF system is usually not more than 60 cm (Cooper, 1996).

15
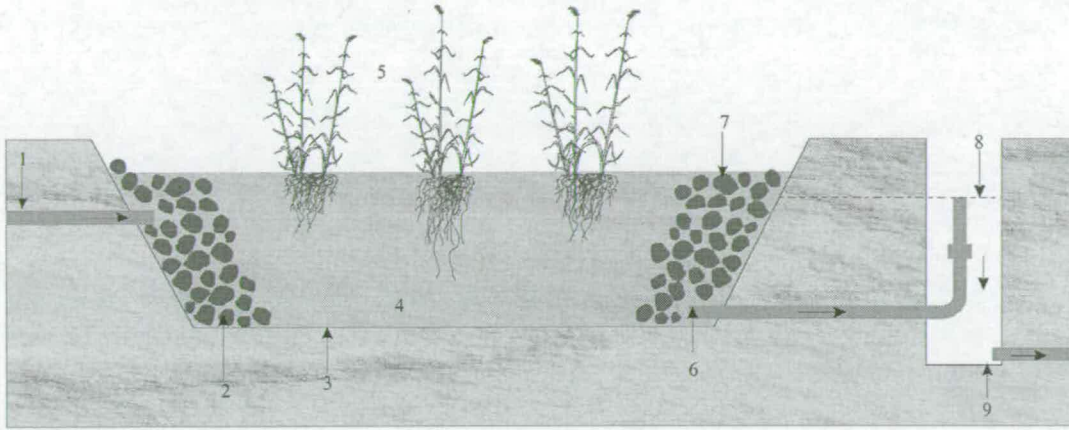
Figure 2-2. Longitudinal section of a constructed wetland with horizontal sub-surface-flow (after Vymazal, 1997). 1: inflows; 2: distribution zone filled with large stones; 3: impermeable layer; 4: filtration medium (e.g. gravel, sand and crushed stones); 5: vegetation; 6: outlet collector; 7: collection zone filled with large stones; 8: water level; 9: outflow.

Vertical-flow systems. Vertical SSF systems (Figure 2-3) are filled with water from the top. The water then flows vertically to the bottom of the wetland where it is evacuated with a drain.

Vertical SSF wetlands can be saturated with water or dried, thus enabling oxygen to be regenerated in all areas of the wetland which is usually anaerobic. This allows more efficient BOD and ammonia-N removal compared to the continuously saturated and generally anaerobic horizontal-flow system (Cooper et al., 1996; Magmedov *et al.,* 1996). In vertical SSF systems, macrophytes will transfer some oxygen down into the rhizosphere, but it will be small in comparison to the oxygen transfer created by the dosing system (IWA, 2000).

Feed dosed intermittently over whole surface

Solid pipe

Perforated pipe
(~110 mm o.d.)

~ 25 cm

~ 8 cm

~ 15 cm

~ 10 cm

~ 15 cm

Sharp sand

6 mm washed
pea-gravel

12 mm round,
washed gravel

30 - 60 mm round,
washed gravel

Free-draining outlet

1 % slope

Network of
agricultural drainage pipes

LDPE liner

Large stones
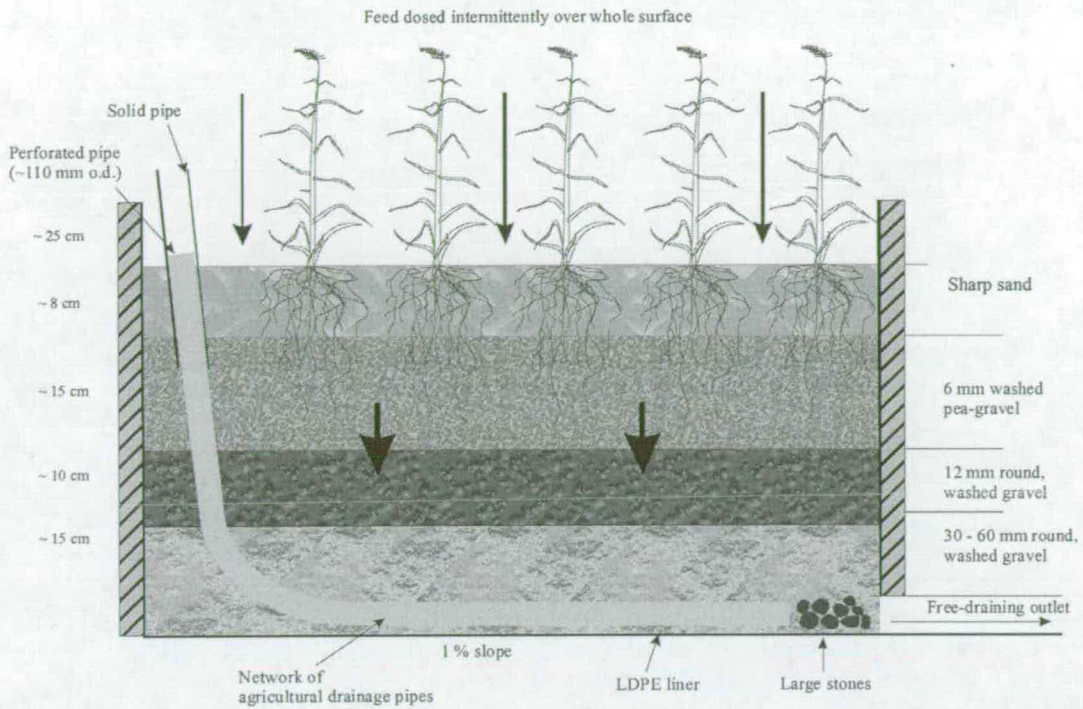
Figure 2-3. Typical arrangement of a vertical flow filter (after Cooper *et al.*, 1996)

2.3.3. Hybrid system

A hybrid system is a combination of two or more different systems. The particular system studied in the present project is a hybrid system: when the filters are filled up to the top, the filter media is covered with water and the top layer of the filters can then be compared to a stabilization pond; the bottom part of the filter acts as vertical-flow wetland (Kedlec and Knight, 1996).

Stabilization ponds can either be anaerobic, both anaerobic and aerobic (facultative pond) or aerobic (maturation pond). An anaerobic pond is usually between 2 and 4 m deep and only the surface is aerated. A maturation pond receives oxygen from natural surface reaeration and from algal photosynthesis. The oxygen released by the algae through photosynthesis is used by the bacteria for the oxidation of organic matter. The nutrients and CO_2 released by the oxidation of organic matter

17

is then used by the algae for photosynthesis.

A facultative pond is made of three different strata: the surface zone, which is aerated naturally; an intermediate zone which is both anaerobic and aerobic; and a bottom layer which is anaerobic. The pond must not be too deep, otherwise light penetration is impeded and the anaerobic zone increases. Considering these characteristics, the particular system designed for this study can be classified as a combination of a vertical-flow wetland system and a facultative pond (i.e. flooded vertical-flow wetland system).

2.4. Removal mechanisms of a constructed wetland

The mechanisms that improve water quality include (IWA, 2000): Settling of suspended particulate matter; Filtration and chemical precipitation through contact of the water with the substrate and litter; Chemical transformation; Adsorption and ion exchange on the surface of plants, substrate, sediment and litter; Breakdown, transformation and uptake of pollutants and nutrients by microorganisms and plants; Predation and natural die-off of pathogens.

2.4.1. Suspended solids removal

SS result from the degradation of macrophytes and the contaminants of the inflow water. In the case of vertical SSF wetland, SS principally settle at the surface of the wetland. SS can also interact with the substrate and stick to the granules. These physical processes are known as granular medium filtration (Tchobanoglous *et al.*, 2003).

Sedimentation of SS is based on flow retardation that leads to gravitational settling of solids in SF wetlands. SS react and bind with various pollutants including organic matter, nutrients, heavy metals and pathogens, and thereby aid their removal (Sundaravadivel and Vigneswaran, 2001). Treatment wetlands are typically efficient in bringing about a net decrease of TSS with removal efficiencies of approximately 80 to 90% (IWA, 2000).

The main problem linked to the sedimentation and filtration of solids is the risk of clogging of the filter, as particulate matter accumulates in voids. This clogging is counteracted by the decomposition of organic matter by microorganisms. The mineral content of the particulate matter, which is not reduced by microorganisms, contributes to the clogging of the filters.

2.4.2. Biochemical processes

Biochemical processes are mechanisms that contribute to the degradation of organic and inorganic matter in the water. Carbon, N and P are the main components that need to be removed from polluted water.

Degradation of organic carbon. The function of constructed wetlands is largely dependent on organic matter accumulation, decomposition and cycling. Organic matter accumulation provides long-term storage of carbon, nutrients and a sustainable supply of carbon for microbial denitrification. However, the accumulated organic matter potentially contributes to the clogging of pore spaces in wetlands and may ultimately leads to a decline in wastewater retention time and reduction in the efficiency of nutrient removal (Nguyen, 2000).

Constructed wetlands usually provide high BOD removal (Vymazal, 1999; Neralla et al., 2000; Leuderitz et al., 2001). Settleable organics are rapidly removed by

deposition and filtration. Degradable carbon compounds are quickly utilized in wetland metabolic process by microorganisms. The uptake of organic matter by the macrophytes is negligible compared to the biological degradation (Cooper *et al.*, 1996).

There are conflicting opinions concerning temperature dependence in BOD removal within constructed wetlands. It is well established that BOD reduction exhibits temperature dependence in other biological treatment processes (Tchobanoglous *et al.*, 2003). Seasonal variations of BOD removal efficiency in the constructed wetlands have been reported by several investigators, with the worst performance occurring during the winter (Leonard, 2000; Karathanasis *et al.*, 2003). It is uncertain whether the poor winter performance is due to low temperatures alone or the combined effect with increased hydraulic loadings. In contrast, several studies have reported negligible temperature dependence for BOD reduction (Harbel *et al.*, 1995; Kadlec and Knight, 1996; Vymazal *et al.*, 1999; Neralla *et al.*, 2000), suggesting that soil microbes in winter still have the capacity to decompose organic matter and that lower temperature can enhance aerobic metabolism through the increase of dissolved oxygen saturation (Kadlec and Knight, 1996).

Nitrogen removal. The mechanisms involved in the removal of N include plants uptake, volatilization and adsorption, but the main process of elimination of N in a constructed wetland is nitrification/denitrification (Figure 2-4).

The nitrification/denitrification mechanisms require both aerobic and anaerobic environments. Nitrifying bacteria are sensitive organisms and are very susceptible to a wide range of parameters such as pH, dissolved oxygen and temperature (IWA, 2000). On the other hand, the enzyme needed for denitrification may be suppressed

in the presence of dissolved oxygen. Nitrification/denitrification can therefore occur simultaneously only in a soil which has both aerobic and anaerobic zones (Cooper *et al.*, 1996).
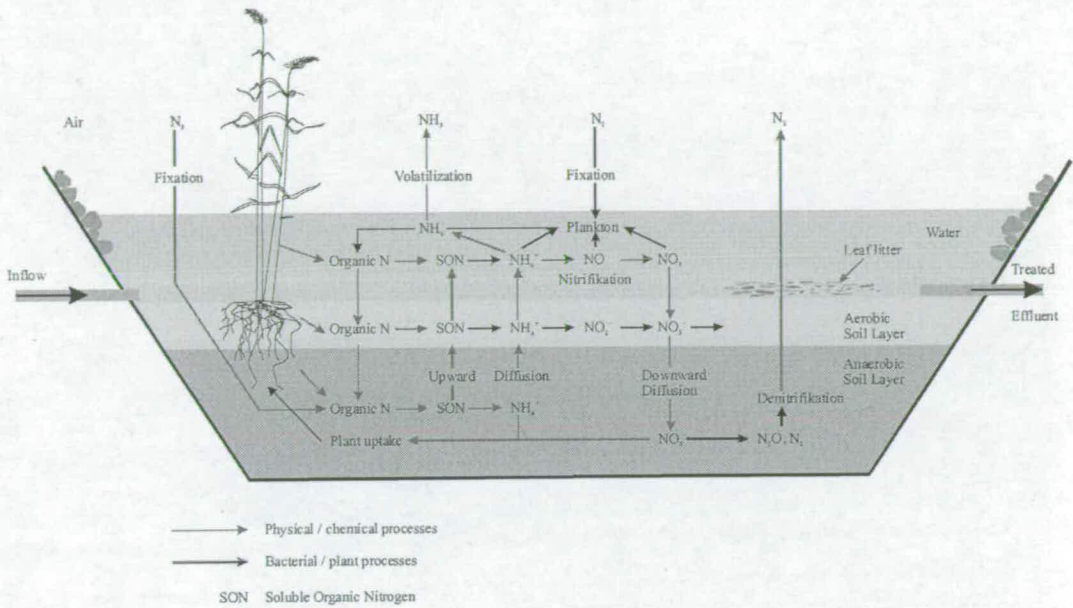
Figure 2-4. Mechanisms of transformation of N in wetland soil (after IWA, 2000).

Neralla *et al.* (2000) described that nitrification was not active in the horizontal SSF system due to its anoxic nature of the wetlands. The nitrification rate in vertical SSF wetlands is rather high, due to the good aeration of the soil through regular bed draining. However, denitrification is lower, as oxygen concentration is higher (Stottmeister *et al.*, 2003; Cooper *et al.*, 1996). Therefore, Luederitz *et al.* (2001) suggested to load the wetlands intermittently, guarantee long flowing distance and supply organic substances necessary for denitrification, to reach high N removal.

Constructed wetlands demonstrated a decreased ability to remove N during the winter months, indicating that N removal processes were temperature dependent (Werker *et al.*, 2002; Kadlec, 1999; Kuschk *et al.*, 2003). Such temperature

dependence can make N removal the determining factor when designing constructed wetlands in cold climates. Because microbes mediate nitrification, the rate of nitrification is directly proportional to the growth of nitrifier bacteria. The nitrifier growth rate increases significantly at higher water temperature.

On the other hand, other authors also described that no clear correlation between seasonal temperature and removal efficiency of nutrient was observed (Harbel et al., 1995; Reed et al., 1995). Nevertheless, constructed wetlands should be assessed as solar powered ecosystems. The removal efficiencies should be affected by annual cycles of numerous parameters such as temperature, humidity, precipitation and vegetation (Kadlec, 1999).

Plant uptake is an important component of N's biogeochemical cycle, since N plays a major role in plant growth. During a period of rapid plant biomass increase, the N removal rate may become significantly higher (Knight et al., 1999; Ellis et al., 2003). Moreover, storage in plant-derived litter is another sustainable mechanism removing N as well as P. Although the litter is relatively low in nutrients just after death, the microbes decaying the litter may take up large amounts of nutrients (Verhoeven and Mæleman, 1999). However, it has also been reported that the amount of N in the harvested plants does not exceed 10% of the total N loading (Stottmeister et al., 2003; Vymazal et al., 1999).

The plant impact on the N removal varies depending on the design of constructed wetlands, as discussed in section 2.2.1. Stottmeister (2003) described that the HRT, including the time the water is in contact with the plant roots, affects the extent to which the plant plays a significant role in the pollutant removal. Haung et al. (2000) also reported that most of the observed variation in N removal could be attributed to

residence time in the wetlands.

Phosphorus removal. The immobilisation of P in constructed wetland systems occurs through chemical precipitation with metals, substrate adsorption of P, bacteria action, plant and algal uptake, and incorporation into organic matter. P interacts strongly with wetland soil and biota, which provides sustainable long-term storage of P (Kedlec and Knight, 1996; Drizo *et al.*, 1997). P removal by planted vertical SSF wetlands occurs through three parallel paths: sorption to substratum, biofilm assimilation and macrophyte uptake (Figure 2-5).
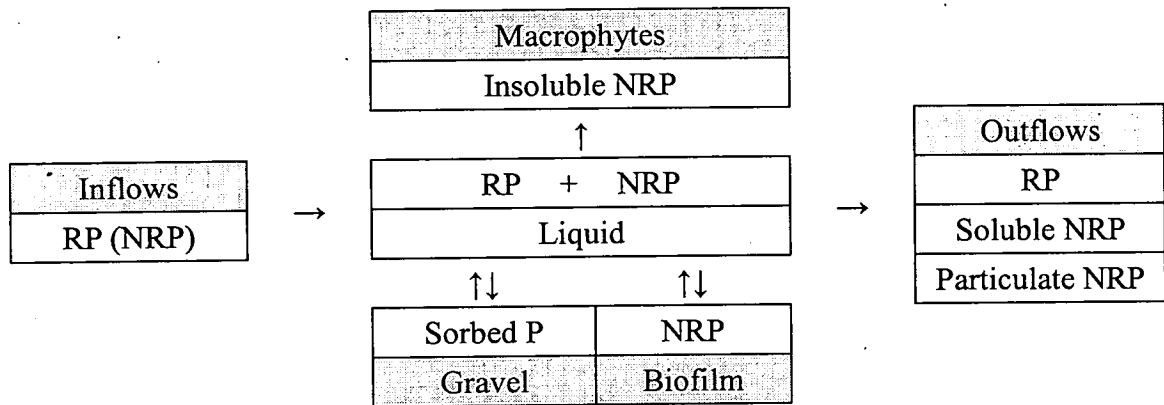
Figure 2-5. Active components, P, and reaction paths in planted wetlands (after Lantzke *et al.*, 1999). RP: reactive P, NRP: non-reactive P.

Lantzke *et al.* (1999) found that the quantity of P removal by the three paths is substratum > macrophyte > biofilm, in the short-term, but macrophyte (70 %) > substratum (20 %) >> biofilm (10 %), in the long-term. Furthermore, it was reported that plant harvesting removed an extra 10 – 20 % of P (Lantzke *et al.*, 1999; Sharma, 1992).

The large plant uptake of P over time probably results from steady uptake, and constant availability of P desorbing from the gravel when the adjacent solution concentration falls below equilibrium. Figure 2-5. illustrates the basic conceptual

model, which shows the reaction paths and the active components of the vertical-flow wetlands (Lantzke *et al.*, 1999).

2.4.3. Metals removal

Metal bioavailability and reduction are controlled by chemical processes including volatile acid sulfide formation and organic carbon binding and sorption in reduced sediments of constructed wetlands (Kadlec, 2002; Obarska-Pempkowiak and Klimkowska, 1999). It follows that metals usually accumulate in the top layer (sediment and litter) of vertical-flow and near the inlet of horizontal-flow constructed wetlands (Scholz and Xu, 2002; Cheng *et al.*, 2002). Main mechanisms of metal removal (Halverson, 2004) are discussed in detail below.

Sorption of metals onto organic matter. In the organic substrate, adsorption seems to be the dominant mechanism for metals removal. Several metals, including Cu and Ni, easily bind to organic matter (Drever, 1988). But over time organic matter can biodegrade and eventually release adsorbed metals. In the present study, barley straw was tested to investigate whether it can improve the removal efficiency of Cu and Ni.

Metals may also be incorporated into the structure of complex humic substances formed during the degradation of organic waste such as SS in both gully pot effluent and macrophyte litter (Norrström and Jacks, 1998). Dissolved and suspended organic material can chelate metals in solution. Although chelated metals such as nickel chelates are effectively retained by filtration processes within the wetland, they are not available biochemically to aquatic plants and microorganisms exposed to the effluent (Kadlec and Knight, 1996).

Formation of metal carbonates and sulfides. Sulfides and carbonates combine

with metals to form relatively insoluble compounds. Specifically, the formation of sulfides provides long-term metal removal, because they will remain permanently in wetland sediments as long as they are not re-oxidized (Sobolewski, 1996). As, Cu, Ph and Zn form highly insoluble sulfide compounds.

Figure 2-6 presents Eh-pH relationships describing interactions between Cu and potential inorganic ligands such as oxides, hydroxides, carbonates and sulfides (Gladden, 2003). According to the diagram, CuS and Cu_2S would be the dominant Cu species at given sufficiently negative redox (<-100) and circumneutral pH.
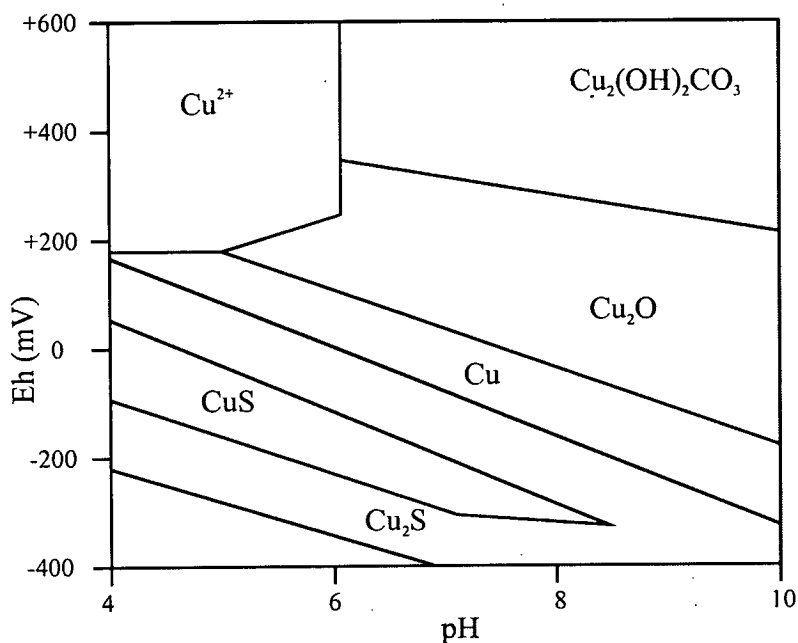
Figure 2-6. Eh-pH diagram for the Cu-C-S-O-H system (after Gladden, 2002)

Oxidation and hydrolysis of metals. Al, Fe and Mn can form insoluble compounds such as oxides, oxyhydroxides and hydroxides (Karathanasis and Thompson 1995). In this case, macrophytes species with high plant surface area have been shown to be very effective at retaining metal hydroxide particles (IWA, 2000).

The residual concentration of hydroxides is also linked to the pH of the water. Ni and Cu are likely to come into solution if environmental conditions are optimal.

25

Nickel hydroxide ($Ni(OH)_2$) and copper hydroxide ($Cu(OH)_2$) in a concentration of 1 mg/l (inflow concentration) precipitate at pH 6.9 and pH 9.1, and in a concentration of 10 mg/l (estimated concentration in the litter zone) at pH 6.4 and pH 8.5. If pH is maintained between 7.5 and 8.0, hydroxides are less likely to precipitate (Figure 2-7). The possibility of pH adjustment to prevent metal breakthrough was investigated in this study during the second year (section 6.3).
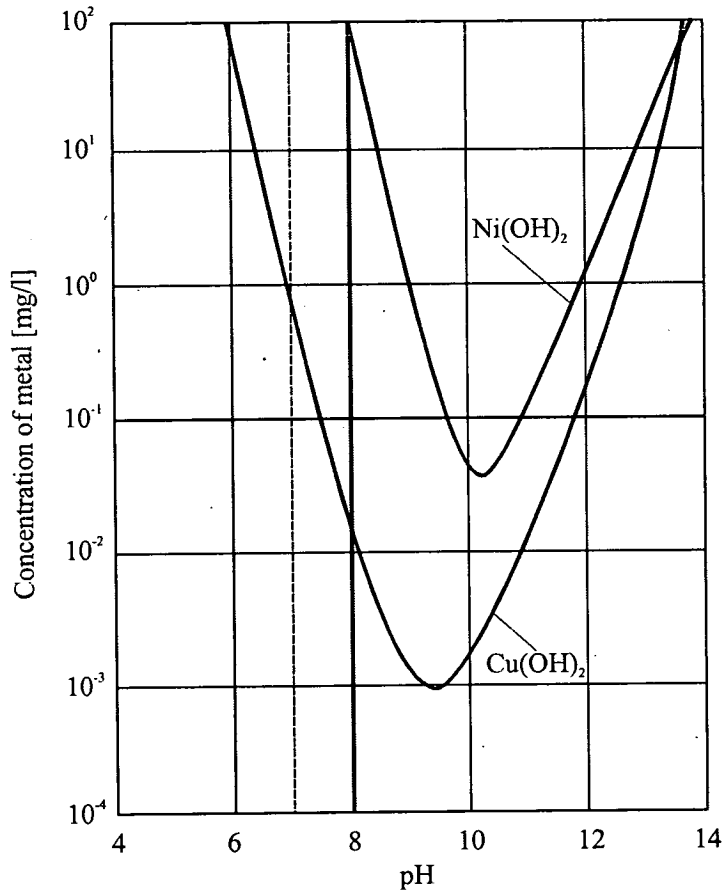
Figure 2-7. Metal solubility and pH (after Tchobanoglous *et al.*, 2003)

Binding of metals to iron and manganese oxides. Metals may bind with the iron and manganese oxides via adsorption or co-precipitation processes. These redox sensitive oxides may redissolve with change of oxygen concentration.

Table 2-1 summarizes the metal removal mechanisms and efficiencies regarding

Cu and Ni obtained from the previous researche.

Table 2-1. Copper and nickel removal in wetland treatment system (modified from Halverson, 2004).

Metal	Removal mechanism	Removal (%)	Case study	references
Cu	• Sorption onto organic matter • Formation of insoluble sulfides • Binding to iron and manganese oxides • Reduction to nonmobile form by bacterial activity	68	SSF and SF wetlands treating stormwater, Brentwood, UK	Scholes *et al.*, 1998
		81.7-91.8	Experimental SSF wetland treating surface runoff	Munger *et al.*, 1998
		53	SF system designed for domestic sewage treatment, Poland	Obarska-Pempkowiak and Klimkowska, 1999.
		79.4	Horizontal SSF reed beds treating dairy parlor effluents	Mantovi *et al.*, 2003
		99	Vertical-flow system fed with artificial wastewater	Cheng *et al.*, 2002
		4	SSF wetland with balancing pond for the highway runoff treatment, UK	Revitt *et al.*, 2004
Ni	• Sorption onto organic matter • Formation of carbonates • Binding to iron and manganese oxides	48	SSF and SF wetlands treating stormwater, Brentwood, UK	Scholes *et al.*, 1998
		63	SF constructed wetland treating coal combustion by-product leachate, Pennsylvania	Ye *et al.*, 2001b
		58.6	Horizontal SSF reed beds treating dairy parlor effluents	Mantovi *et al.*, 2003
		72.6	SSF wetland with balancing pond for the highway runoff treatment, UK	Revitt *et al.*, 2004

2.5. Constructed wetlands for urban runoff treatment

2.5.1. Urban runoff treatment

Stormwater runoff from urban areas has been recognized as a major contributor to pollution of the receiving urban watercourses. The principal pollutants in urban runoff are BOD, SS, heavy metals, hydrocarbons, de-icing salts, faecal coliforms, and particulate pollution. These pollutants originate from vehicle emissions and corrosion; road corrosion and erosion; animal faeces; litter, leaves and grass residues; and spills (Butler and Davies, 2004; Scholes *et al.*, 1998).

Pollutants carried by runoff are very varied and are mainly non-point source pollutants, i.e. diffuse pollutants whose origin cannot be defined with precision. The variability of urban runoff quality and the complexity of the different processes involved in pollutant removal present a major problem in standardizing the design of treatment systems (Munger *et al.*, 1995; Pontier *et al.*, 2004).

Various conventional methods have been applied to treat stormwater runoff. However, most technologies are not cost-effective or too complex. In contrast to standard domestic wastewater treatment technologies, stormwater runoff treatment systems have to be robust to highly variable flow rates and water quality variations. The stormwater runoff quality depends on the load of pollutants present on the road, and the corresponding dilution by each storm event (Scholz, 2003a).

2.5.2. Integration of constructed wetlands into sustainable urban drainage system

Sustainable urban drainage system (SUDS) are an individual or series of management structures and associated processes designed to drain surface water

runoff in a sustainable approach by mimicking the drainage patterns of the natural watershed. SUDS include filter strips and swales, filer drains and permeable surface, infiltration systems as well as basins, ponds and wetlands (CIRIA, 2000; Butler and Davies, 2004; Jefferies et al, 1999). The use of SUDS has been instrumental in reducing both the detrimental impact of polluted runoff to the watercourses, and flooding caused by increased urbanization and traditional stormwater drainage systems.

In recent years, constructed wetlands have gained much attention as cost-effective SUDS systems for pollution control of urban stormwater runoff (Shutes *et al.*, 2001; EA, 2003). Constructed wetlands can be categorized as systems which store and treat received stormwater before releasing it at a reduced rate once the peak flow has passed (Revitt *et al.*, 2004). Furthermore, wetland can not only attenuate stormwater runoff flow, but also significantly improve water quality (Butler and Davies, 2004).

Nevertheless, applications of constructed wetlands for stormwater runoff control and treatment were relatively rare. Only 39 constructed wetlands were found to be used in the management of urban surface runoff in the UK (EA, 2003). Furthermore, specific design criteria for urban runoff treatment have not been established yet.

EA (2003) suggested an ideal design concept of constructed wetlands for highway runoff treatment (Figure 2-8). This system includes the following structures: oil separator and silt trap; spillage containment; settlement pond; constructed wetlands; final settlement tank; outfall into receiving watercourse and access.
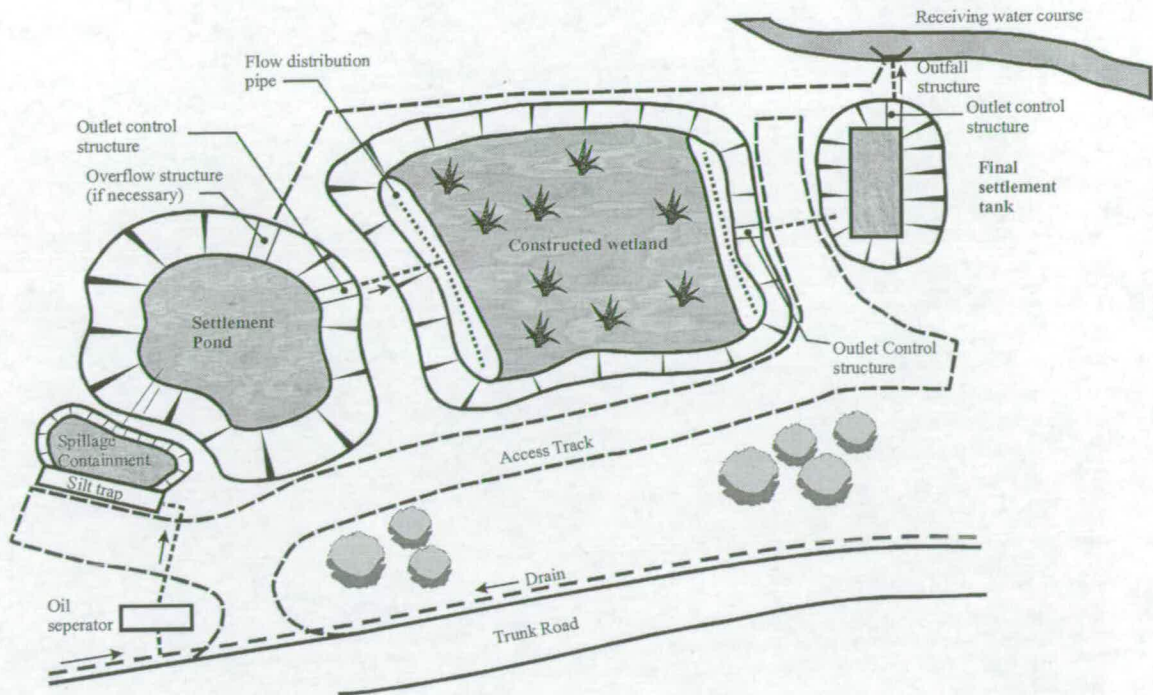
Figure 2-8. Layout of constructed wetland for highway runoff treatment (after EA, 2003).

2.5.3. Gully pot liquor treatment

Gully pot liquor is concentrated surface runoff that is detained in the wet gully pot until it overflows into the sewer due to incoming surface runoff from new rainfall events. Gully pots can be viewed as simple physical, chemical and biological reactors. Gully pots are particularly effective in retaining SS and reduce the annual loads for most pollutants except ammonia. However, in the absence of regular cleaning, gully pots can be expected to act as grit chambers and consequently, highly concentrated pollutants during the storm events may be released (Morrison et al., 1995; Osborne *et al.*, 1998). Currently, gully pot emptying is undertaken on an annual or twice annual cleaning frequency and extracted liquor is transported for treatment at sewage works or landfill disposal (Butler *et al.*, 1995; Memon *et al.*, 2002).

An option to treat gully pot liquor locally in constructed wetlands would be more sustainable. This can reduce transport and treatment costs. The cost can be further reduced by re-using the water treated from the constructed wetlands during cleaning of gully pot. Furthermore, a constructed wetland can be a much more feasible alternative in the area, where sewer connection system is not available. Figure 2-9 shows the developed full-scale constructed wetlands to treat locally gully pot liquor in Fife, Scotland.
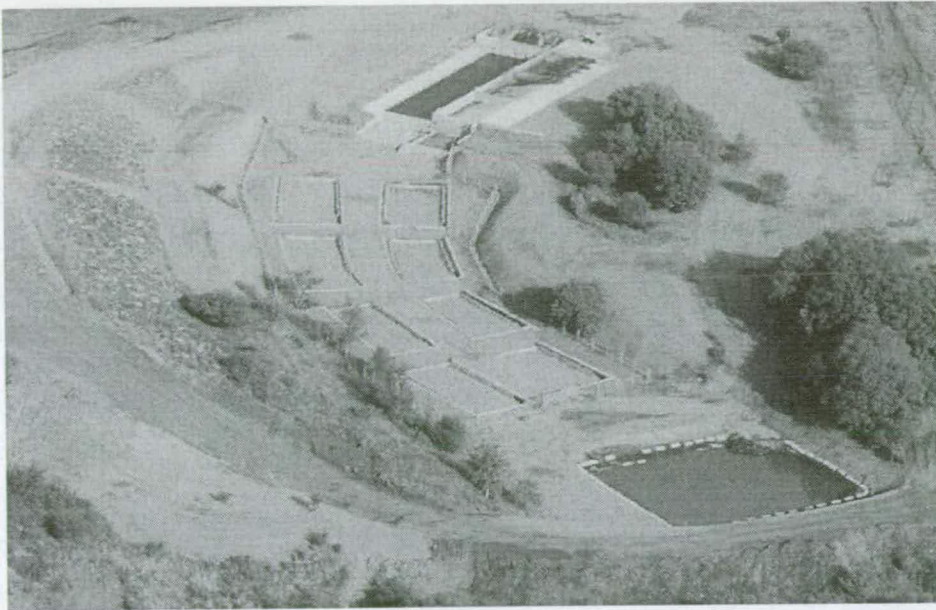
Figure 2-9. Sub-surface flow constructed wetlands treating gully pot liquor in Fife, Scotland (Photo was obtained from Dr. Cunningham).

2.5.4. Application of temporarily flooded vertical-flow wetlands

Over the last decades, several studies have shown much progress in the performance and reliability of treatment wetlands by developing novel treatment wetlands, which are tidal flow system (Green *et al.*, 1998; Sun *et al.*, 2005), aerated systems (Bezbaruah and Zhang, 2003) and combination of constructed wetland with other treatment systems (Obarska-Pempkowiak and Klimkowska,, 1999). Overall, the performance of these systems was improved by providing more oxygen into

system through passive or mechanical aeration.

In particular, the tidal (temporarily flooded) vertical-flow design has recently attracted significant attention due to its highly efficient treatment potential and relatively low operation cost. Tidal vertical-flow constructed wetlands have potential to enhance the removal of BOD through aerobic decomposition and removal of ammonium-N through nitrification, as maximum pollutant-biofilm contact is established and the rate of oxygen transfer increased during the operation (Sun *et al.*, 2005).

However, these innovative systems have been mostly applied to wastewater treatment and their applications were focused on the strong effluent such as dairy farm wastewater and landfill leachate. Contrary to wastewater treatment, stormwater runoff (gully pot liquor and effluent) treatment systems must take into account a variable flow and the quality of the water being treated.

It is therefore required to examine the possibility of applying advanced wetland systems for stormwater runoff treatment and establish design guidelines. The main design concept of the present system is a temporarily flooded (tidal flow) vertical-flow wetland combined with a facultative pond. A combination of both systems is considered to be potentially efficient for stormwater runoff treatment. In addition to the enhanced oxygen transfer by temporary flooding, a pond on a top of matrix provides high hydraulic buffer capacity, a high density of habitats for microorganisms and desirable environmental conditions (aerobic and anaerobic) for nutrient removal.

2.5.5. Heavy metal removal from urban runoff

Heavy metals within urban runoff are associated with fuel additives, car body corrosion, and tyre and brake wear. Common metal pollutants from cars include Pb, Zn, Cu, Cr, Ni and Cd. Freshwater quality standards are most likely to be exceeded by Cu (IWA, 2000; Scholz *et al.*, 2002; Tchobanoglous *et al.*, 2003).

A detention pond has usually been used as stormwater runoff treatment facility. This system can remove effectively metals associated with particulate through the settlement. However, metals can be re-suspended from the sediments in the following storm events (Pitcher *et al.*, 2004). Compared to the traditional detention pond, constructed wetlands have been found to be a more effective and sustainable option for heavy metal removal (Munger *et al.*, 1995; Scholes *et al.*, 1998; Shutes *et al.*, 2001).

A possible combination of bed filter media with constructed wetlands was also investigated to improve the metal removal performance of the systems. Recent studies have focused on the filter media such as peat, blast furnace slag, zelolite, opoka and granular activated carbon (Färm, 2002; Kietliñska and Renman, 2005; Pitcher *et al.*, 2004; Scholz *et al.*, 2002).

Ochre could also be used as filter material to remove heavy metal from urban runoff. Ochre is produced through mine water treatment. Mine water treatment plants accumulate large quantities of $Fe(OH)_3$ and $FeO \cdot OH$ precipitate, collectively known as ochre. While ochre is currently considered waste, the usage in wastewater and sewage treatment and phosphate removal are under consideration (Heal *et al.*, 2004).

Iron oxide and hydroxides were shown to have high removal capacity for heavy metal in previous researches (Lai and Chen, 2001; Møller *et al*, 2002). Furthermore, Heal *et al.* (2004) demonstrated that pelletised ochre successfully removed phosphate from wastewater by sorption to iron oxide and hydroxide within ochre. In the present study, the pelletised ochre filters in combination with constructed wetlands were tested particularly for Cu and Ni removal.

Heavy metals can also be leached from the sediments due to the changing environmental conditions such as pH and salts concentrations. Increased salts concentration due to the loading of salt during the winter can cause some metals to become more soluble and bioavailable by forming soluble chloride complexes (Warren and Zimmerman, 1994). Influence of change of pH as well as salts concentration on the metal removal processes is investigated and the possibility of applying conventional pH control to the constructed wetland systems is also examined in a later chapter.

2.6. Summary

This chapter has documented the components and types of wetlands, as well as the removal mechanisms of pollutants in the constructed wetlands. This information will be used in the following chapters.

It was noted that new design concepts of constructed wetlands for wastewater treatment have been developed to improve treatment performance and to mitigate the treatment variability. However, sustainable design and operational guidelines have not been established particularly for the urban runoff treatment. Furthermore, the roles of filter media and macrophytes are still controversial and the removal

mechanisms in the processes were not fully identified. Temporarily flooded vertical-flow wetland combined with a pond is developed to investigate the treatment mechanism and optimize the composition and operation conditions of constructed wetlands for urban runoff treatment in the cold climate.

Chapter 3   Materials and methods

3.1. Introduction

This chapter gives brief description of the systems and analysis used in the experiment. Section 3.2 describes the experimental set-up including filter design and media compositions. Operation conditions such as hydraulic cycle, addition of heavy metal and aeration are also documented in the section 3.3. Section 3.4 describes the ochre filter set-up for heavy metal treatment.

3.2. Experimental set-up description

3.2.1. Site study

Twelve pilot scale wetland filters (Figure 3-1) treating pre-treated gully pot liquor were located outdoors at The King's Buildings campus (The University of Edinburgh, Scotland) to assess the system performance in a cold climate (09/09/02 to 21/09/04). Scholz and his research team operated the experimental system during the first year (Scholz *et al.*, 2005).

The first twelve days of operation were not analyzed because the water quality was not representative. Gully pot liquor was collected from randomly selected gully pots on the campus, the nearby predominantly housing estates and two major roads. After mixing both the sediment and the water phase within the gully pot, water was collected by manual abstraction with a 2 l beaker.

3.2.2. Filter design and media composition.

Round drainage pipes were used to construct the filters. All twelve vertical-flow wetland filters were designed with the following dimensions: height = 830 mm and diameter = 100 mm. Different packing order arrangements of filter media and plant roots were used in the wetland filters (Figure 3-1).

Figure 3-1. Constructed wetland filters (May, 2004)

The applied materials are stones (37.5-75 mm), large gravel (10-20 mm), medium gravel (5-10 mm), small gravel (1.2-5 mm), Filtralite, sand (0.6-1.2 mm) and barley straw. The outlet of each constructed wetland comprised a valve at the center of the bottom plate of each filter and the diameter of outlet is 10mm..

All filters simulate wetlands. Different wetland filters are similar to various other natural treatment processes. For example, filters 1 and 2 (controls) are similar to wastewater stabilization ponds or gully pots (extended storage) without a significant amount of filter media (Figure 3-2). In comparison, Filters 3, 5, 7 and 9 are similar to gravel and slow sand filters, and Filters 4, 6, 8 and 10 are typical reed bed filters. The composition of Filter 11 and 12 is discussed in detail in the following section. The reed bed filters contain gravel and sand substrate and native *P. australis*, all of similar total biomass weight during planting and from the same local source.
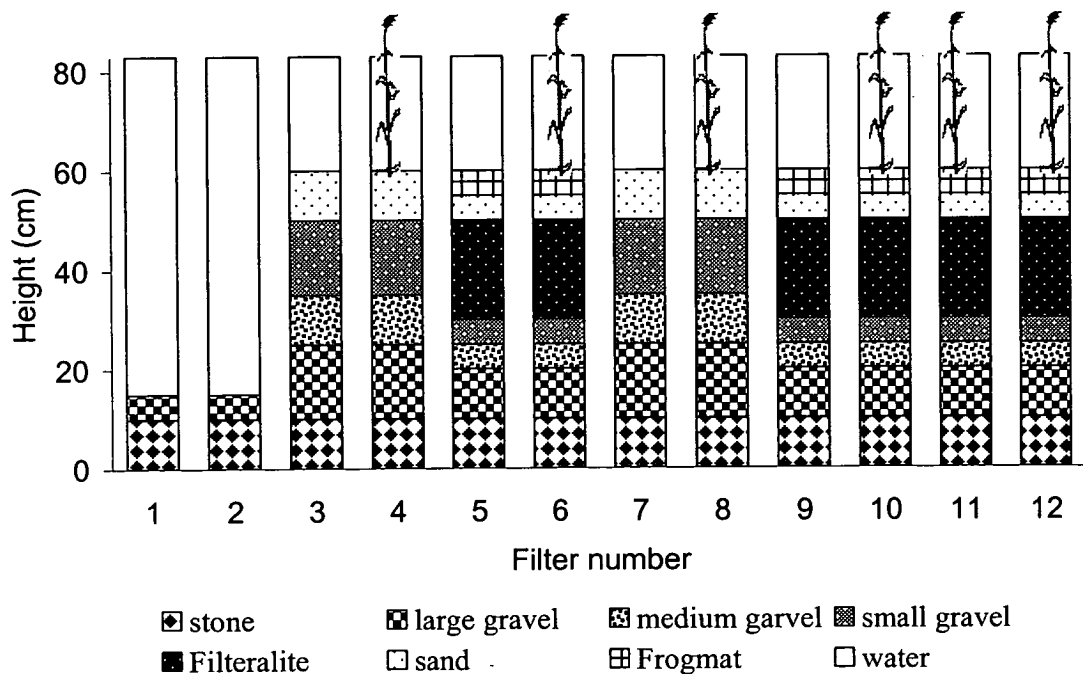
Figure 3-2. Packing order of filters

Filters 5, 6, 9 and 10 also contain adsorption media. Additional natural adsorption media (Filtralite and Frogmat) were used. Filtralite (containing 3% of calcium oxide (CaO)) with diameters between 1.5 and 2.5 mm is associated with enhanced metal and nutrient reduction (Brix *et al.*, 2001; Scholz and Xu, 2002). Furthermore, Frogmat (natural product based on raw barley straw) has a high adsorption area and

is therefore likely to be associated with a high heavy metal reduction potential. The use of other filter media with high adsorption capacities such as activated carbon (Scholz and Martin 1998; Scholz *et al.*, 2002) and oxide-coated sand (Sansalone, 1999) has been discussed elsewhere.

3.3. Environmental conditions

3.3.1. Operation conditions

The filtration system was designed to operate in batch flow mode to reduce pumping and computer control costs. The influents of Filter 2 and Filters 7 to 12 were dosed with hydrated copper nitrate ($Cu(NO_3)_2.3H_2O$) and hydrated nickel nitrate ($Ni(NO_3)_2.6H_2O$). As illustrated in Figure 3-3, Filters 11 and 12 are more complex in their design and operation. The top water layer of both filters is aerated (with air supplied by air pumps) to enhance oxidation (minimizing zones of reducing conditions) and nitrification (Green *et al.* 1998; Cheng *et al.* 2002).
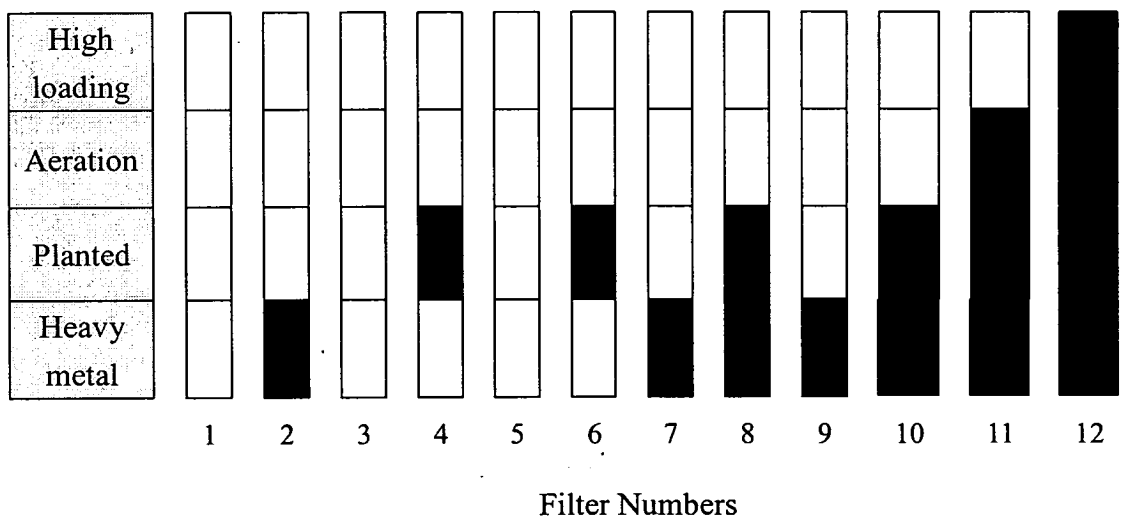
Figure 3-3. Operational conditions (black = applied) of experimental filters.

The hydraulic regime of Filter 12 differs from that of Filters 1 to 11 (Table 3-1) to identify the best filtration performance. A higher hydraulic load should result in greater stress on *P. australis* and biomass.

According to Table 3-1, all filters were periodically inundated (100 %) with pre-treated inflow gully pot liquor and partially drained (50 %) or entirely drained (0 %) to encourage air penetration through the aggregates. When the filters are flooded, air is removed from the matrix and consequently a pond is formed on the top of the matrix. When the filters are drained, the retreating water acts as a passive pump to draw air from the atmosphere into the matrix (Green et al., 1998; Scholz and Xu, 2002; Sun *et al.*, 2005).

Table 3-1. Systematic regime for manually controlled filling and emptying (expressed as % drainage volume) of the experimental filters (25/09/02 - 09/10/02). The first periodic cycle for Filters 1 to 11 is the duration from 25/09/02 to 14/10/02. The first periodic cycle for Filter 12 is the duration from 25/09/02 to 04/10/02. One and two complete cycles for Filters 1 to 11, and Filter 12 are shown, respectively.

num-ber	date	day	filter 1 to 11	filter 12	num-ber	date	day	filter 1 to 11	filter 12
1-16	09-24/09/02	...	...	...	27	05/10/02	Sa	100	100
17	25/09/02	We	100	100	28	06/10/02	Su	100	100
18	26/09/02	Th	100	100	29	07/10/02	Mo	100	100→50
19	27/09/02	Fr	100	100→50	30	08/10/02	Tu	100	50
20	28/09/02	Sa	100	50	31	09/10/02	We	100	50→100
21	29/09/02	Su	100	50	32	10/10/02	Th	100	100
22	30/09/02	Mo	100	50→100	33	11/10/02	Fr	100→0	100→0
23	01/10/02	Tu	100	100	34	12/10/02	Sa	0	0
24	02/10/02	We	100→50	100→0	35	13/10/02	Su	0	0
25	03/10/02	Th	50	0	36	14/10/02	Mo	0→100	0→100
26	04/10/02	Fr	50→100	0→100	37	15/10/02-21/09/04	...	...	...

Raw gully pot liquor was sieved (pore size of 2.5 mm) to simulate preliminary and primary treatment. This procedure is in line with common practice in the wastewater industry (Tchobanoglous *et al.*, 2003). Sieving resulted in a mean annual reduction of BOD and SS by approximately 11 and 23 %, respectively.

Since 22 September 2003, the pH value of the inflow has been artificially raised by addition of sodium hydroxide (NaOH) to the sieved gully pot liquor. As a consequence, the inflow pH increased from a mean of pH 6.7 to pH 8.1 (Table 4-1).

Plant weights were measured regularly. In November 2003 and December 2004, overall plant weights were estimated for stems after drying the harvested plants at 105 °C for 24 hours. This helped assess biomass development.

3.3.2. Metal nitrate addition

Cu and Ni were selected as additional heavy metals for investigation because they are commonly occurring contaminants from road vehicles and are not easily bio-available (Kadlec and Knight, 1996; Scholz and Xu, 2002). It follows that these metals are likely to accumulate within the sediment and debris of constructed wetlands. As the build-up continues, metal toxicity increases as does the risk of severe pollution due to leaching (Scholz *et al.*, 2002).

Some heavy metals do accumulate easily in constructed wetlands but may be released if environmental conditions change; e.g., road gritting (containing salt) in winter. Such transformation processes are not well understood (Norrström and Jacks, 1998).

Hydrated copper nitrate ($Cu(NO_3)_2.3H_2O$) and hydrated nickel nitrate ($Ni(NO_3)_2.6H_2O$) were added to the inflow water of Filter 2 and Filters 7 to 12 to

give total concentrations of dissolved Cu and Ni of approximately 1 mg/l for each metal, comparable to figures reported for urban water heavily contaminated with heavy metals and mine wastewater (Mungur *et al.*, 1997; Scholz and Xu, 2002).

Concerning the dosed inflow water, the background concentration for nitrate-N (including nitrite-N) was only approximately 0.499 mg/l. Therefore, introduced nitrate-N (see above) contributed to 65% (or approximately 0.917 mg/l) of the overall nitrate-N (including nitrite-N) load.

The volumes available for the influent water differ among the filters due to different filter media compositions (Figure 3-2) and hydraulic regimes (Table 3-1). For example, the mean annual total loading rates for the Filter 8 were therefore 143 and 140 mg for Ni and Cu, respectively.

In autumn 2004 (24 September) 1g Cu as copper nitrate ($Cu(NO_3)_2$) was added to filters 1, 3, 4, 5, 6 and 12 to investigate the long-term trend of Cu retention performance of wetland filters. Furthermore, it is examined whether a breakthrough of Cu takes place in heavily contaminated wetlands with Cu (toxic shock). The added copper nitrate contains 1.95 g nitrate. Considering the annual amount of Cu loaded in these filters (153 and 127 mg/year in Filter 8 during first and second year, respectively), 1 g of Cu loaded in Filters is the amount which could be loaded approximately for 7 years in the present system.

3.4. Ochre filters set-up

Heavy metal retention performance using ochre media were monitored from September 2004 to March 2005. The pelletised ochre (Figure 3-4) with diameter between 2 and 4 mm from the Silkstone mine wastewater treatment scheme (Yorkshire, UK) was used in this experiment.

Figure 3-4. Ochre pellets

As shown in Figure 3-5, Cylinders packed with ochre pellets were designed with the following dimensions: height = 200 mm and diameter = 15 mm and attached to the bottom of wetland filters. Effluents of wetland filters were filtered through the ochre cylinders with hydraulic loading rate of 20.6 to 28.8 m/h. Cu and Ni concentrations were analyzed before and after filtration for ochre cylinders connected to Filters 3, 4, 7 and 8.

43
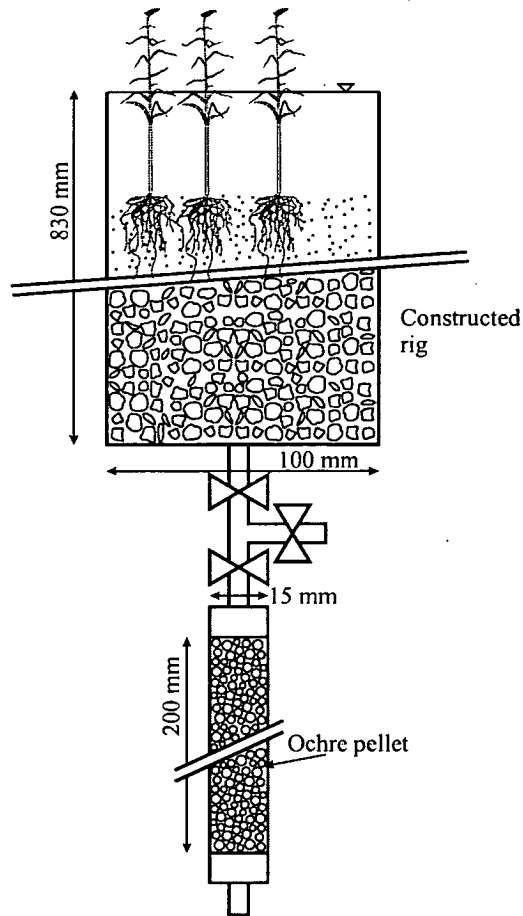
Figure 3-5. Ochre cylinder attached to the constructed rig

3.5. Analysis

3.5.1. Metal determinations

Metal concentrations were determined in the raw gully pot liquor, sieved (pore size of 0.25 mm) gully pot liquor (partially used as actual inflow water for Filters 1, 3, 4, 5 and 6), contaminated (added metal nitrates) sieved gully pot liquor (partially used as actual inflow water for Filters 2, 7, 8, 9, 10, 11 and 12) and the effluent waters from the experimental rig. Less than 2 l were taken for effluent water samples.

Samples were taken randomly from well-mixed water and three sample replicates were taken from pre-filtered (applying whatman 1.2 μm cellulose nitrate membrane filters) sub-samples.

Macrophytes were also taken into account for metal determination. To prepare acid digests, samples were dried at 105°C overnight in a drying oven (UM500, Memmert) prior to being ashed at 400°C for 12 hours in a muffle furnace (ELF 11/14, Carbolite). Ashed samples (0.7 g; standard deviation: 0.28 g) were then digested under reflux in *aqua regia* for 2 hours, cooled, filtered through Whatman No. 5412 filter papers and made up to 100 mL with deionised water ready for analysis.

A Varian Spectr 11 400 Atomic Absorption Spectrophotometer with a GTA-96 graphite furnace tube atomiser was used for the standard analysis of copper and nickel. Notched GTA partition tubes (coated) were applied, and the carrier gas was nitrogen for analyses before 9th November 2002 and argon thereafter. The change of the carrier gas had no significant influence on the results (data not shown). Argon is the standard carrier gas in most national analytical laboratories (Scholz, 2003).

The Spectrophotometer was calibrated with standards of 0, 0.01, 0.02, 0.03, 0.04 and 0.05 ppm nickel, and 0, 0.0005, 0.01, 0.015, 0.020 and 0.025 ppm copper made up from 1000 mg/L stock solutions (BDH Spectrosol). Some samples (e.g. contaminated inflow water) were diluted accordingly. The calibration curves were calculated by least squares linear regression analysis. The coefficients of determination (r^2) were generally above 0.99 for both nickel and copper standards.

An Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was used for selected samples only. The purpose was to economically screen the inflow

45

and outflow in order to determine various trace concentrations such as zinc. There were no significant differences between data obtained by atomic absorption spectrophotometry and ICP-OES (data not shown) (Scholz, 2003). Multi-element calibration standards with concentrations 0, 0.1, 1, and 10 mg/L were used and the emission intensity measured at appropriate wavelengths. For all elements, analytical precision (relative standard deviation) was typically 5-10% for three individual aliquots.

3.5.2. BOD, nutrient and other determinations

The BOD was determined in all water samples with the OxiTop IS 12-6 system, a manometric measurement device, supplied by the Wissenschaftlich-Technische Werkstätten (WTW), Weilheim, Germany. Nitrification was suppressed by adding 0.05 ml of 5 g/l N-Allylthiourea (WTW Chemical Solution No. NTH 600) solution per 50 ml of sample water.

SS and total solids (TS) were measured on every sampling day. Well-mixed samples of 100 ml were filtered through Whatman 1.2 μm cellulose nitrate membrane filters previously weighed; glass bottles were also weighed before and after pouring water samples. Paper filters and glass bottles were dried overnight in a drying oven at 105°C and were then weighed to measure SS and TS, respectively.

Nitrate was reduced to nitrite by cadmium and determined as an azo dye at 540 nm (using a Perstorp Analytical EnviroFlow 3000 flow injection analyzer) following diazotisation with sulfanilamide and subsequent coupling with N-1-naphthylethylendiamine dihydrocloride (Allen, 1974).

Ammonia-N and ortho-phosphate-P were determined by automated colorimetry in all water samples from reaction with hypochlorite and salicylate ions in solution in the presence of sodium nitrosopentacyanoferrate (nitroprusside), and reaction with acidic molybdate to form a phosphomolybdenum blue complex, respectively (Allen, 1974). The colored complexes formed were measured spectrometrically at 655 and 882 nm, respectively, using a Bran and Luebbe autoanalyzer (Model AAIII).

A Hanna HI 9142 portable waterproof dissolved oxygen (DO) meter, a HACH 2100N turbidity meter and a Mettler Toledo MPC 227 conductivity, total dissolved solids (TDS) and pH meter were used to determine DO, turbidity, and conductivity, TDS and pH, respectively. An ORP HI 98201 redox meter with a platinum tip electrode HI 73201 was used. Composite water samples were analyzed on Mondays, Wednesdays and Fridays. All other analytical procedures were performed according to the American standard methods (APHA, 1995).

3.5.3. Data analysis

Wilcoxon signed-rank analysis. A Wilcoxon signed-rank analysis is a nonparametric, paired-sample test. The main difference between parametric and non-parametric techniques is that parametric techniques make distributional assumptions, usually that data follows a normal distribution.

This test gives greater weight to pairs with larger differences than to pairs with smaller differences. The differences are ranked with respect to their absolute values (i.e., -1 has a lower values than either +2 or -2), but the sign of the difference is retained with the rank. The pairs in which there is no difference are dropped from the sample, and sample size is reduced accordingly. H_o in this test is that the sum of the positive ranks in a population is equal to the sum of the negative ranks in the

population (Hampton, 1994).

In the present study, the Wilcoxon signed-rank analysis was selected because urban runoff and outflow samples do not followed a specific statistical distribution such as the normal or log-normal distributions and therefore, a nonparametric test was required (Clark and Pitt, 1999). A Wilcoxon signed-rank analysis was used to test whether the different filter media and operation condition would significantly affect the performance of the filter system. P values less than 0.05 are considered significant and lead to the conclusion that performance of the filters is different depending on the filters.

3.6. Summary

Twelve experimental filters, which were temporarily flooded vertical-flow systems, were operated for two years. Each filter had different filter compositions. Some filters were planted to investigate the contribution of macrophytes to the performance. Different operational conditions such as hydraulic loading rate and aeration were applied. The pH of the influents was increased to prevent metal leaching during the second year of operation.

Influents of six out of twelve filters were contaminated with heavy metal. After two year operation, excessive Cu was loaded to investigate the long-term trend of metal removal. Ochre filters in combination with constructed wetlands were operated to investigate the metal removal performance in the final experimental stage.

Chapter 4   Overall treatment performance

4.1. Introduction

This chapter investigates treatment potentials and mechanisms for BOD and SS in experimental constructed wetlands. Seasonal and annual variations of influent and effluent water quality are presented and the performance of filters is assessed by evaluating the mass loading and removal rates of filters. Simple removal models are applied to estimate the removal potentials of the wetland filters.

The SOM (neural network model) is used to elucidate the effect of influent water quality on the BOD and SS removal. The performance of each filter is also statistically compared to examine the impact of design components and operation conditions on the removal performance of wetland filters.

The major objectives of this chapter are to assess the performance of temporarily flooded vertical-flow wetland filters treating high loads of BOD and SS, and to establish the design and operation guideline for efficient and sustainable constructed treatment wetlands.

4.2. Inflow water quality

Table 4-1 summarizes the water quality of the inflow to those filters artificially contaminated with heavy metals after the first and second year of operation. The pH of the inflow was artificially raised to assess its influence on the treatment performance and particularly on the potential breakthrough of heavy metals during the second winter (Table 4-1).

49

Table 4-1. Primary treated gully pot liquor: water quality variables after contamination with hydrated cooper nitrate and hydrated nickel nitrate

		22/09/02-21/09/03				
Variable	Unit	Number of samples	Mean	SD[a]	Mean (winter)	Mean (summer)
BOD[b]	mg/l	58	61	49	44	87
Suspended solids	mg/l	70	336	378	748	161
Total solids	mg/l	66	2996	6793	9404	377
TDS[c]	mg/l	72	2622	7231	7909	208
Turbidity	NTU	71	311.7	479.6	690.6	162.1
Dissolve oxygen	mg/l	68	4.7	2.5	5.7	3.2
pH	-	71	6.7	0.4	6.9	6.7
Redox potential	mV	62	142.5	112.7	165.5	2.7
Conductivity	μS	71	5273.1	11182.2	15890.2	448.5
Temperature	°C	69	10.7	5.8	4.8	18.0
		22/09/03-21/09/04 (artificial increase of pH after 21/09/03)				
Variable	Unit	Number of samples	Mean	SD[a]	Mean (winter)	Mean (summer)
BOD[b]	mg/l	73	89	55	90	67
Suspended solids	mg/l	75	854	1421	1955	367
Total solids	mg/l	71	2142	3220	5296	795
TDS[c]	mg/l	77	1126	2336	3115	202
Turbidity	NTU	78	274.5	358.6	546.2	143.6
Dissolved oxygen	mg/l	78	3.1	1.5	3.4	3.2
pH	-	78	8.1	1.1	8.3	8.7
Redox potential	mV	78	44.4	93.4	31.8	64.1
Conductivity	μS	78	2227.2	4620.8	6191.7	403.6
Temperature	°C	75	12.0	5.6	6.0	18.9

[a]standard deviation; [b]five-day @20 °C N-Allylthiourea biochemical oxygen demand; [c]total dissolved solids.

The inflow data set was divided into two sub-sets (winter and summer) to assess the effect of seasonal variations (e.g., temperature) and road management (e.g., road gritting and salting) on the water quality. Most variables including BOD (except for

the first year of operation), SS, TS, turbidity and conductivity are high in winter compared to summer (Table 4-1).

In particular, high levels of TDS in winter suggest that it was mostly attributed to chloride from de-icing agents, as reported in previous research (Viklander *et al.*, 2003). Regarding the variation of influent water quality, high standard deviation values of TS and TDS indicate that these concentrations are highly variable through the season (Table 4-1).

4.3. Comparison of annual effluent water qualities

The overall filtration performance figures are summarized in Table 4-2 and Table 4-3. The influence of metal addition, the presence of macrophytes, filter aeration and increased loading rate on the performance was observed.

Removal efficiencies for BOD and SS were high in all filters (except for filter 1 and 2; extended storage) and relatively lower in winter than in summer during the first year, but increased over time (Table 4-2 and Table 4-3). However, all filters with the exception of Filters 1 and 2 showed high BOD removal figures (>94 %) in the second winter. The temperature in the second winter was 6.0 °C on average (Table 4-2). This suggests that soil microbes have the capacity to decompose organic matter during mild winter and that moderately low temperatures can enhance aerobic metabolism because of DO saturation (Kadlec and Knight 1996).

Furthermore, the artificial increase of pH after the first year of operation had no apparent influence on the BOD treatment performance. Despite the artificial increase of pH in the inflow, the pH of the outflow was comparable to the first year of

operation. Moreover, the pH of the outflow was relatively stable in the second year (standard deviation of approximately 0.18). Interestingly, effluent pH values of the planted and unplanted filters were slightly acidic and slightly alkaline, respectively (Table 4-2).

Table 4-2. Mean and standard deviation of effluent water quality variables

Mean (22/09/02-21/09/03)							
Variable	Unit	Filter 1	Filter 2	Filter 3	Filter 4	Filter 5	Filter 6
BOD[a]	mg/l	37	43	16	31	23	34
SS[b]	mg/l	175	189	121	130	132	127
Total Solids	mg/l	2773	3602	2939	3266	2949	3990
pH	-	6.8	7.0	7.1	6.7	7.0	6.7
Conductivity	μS	5148.5	6827.7	5920.8	5392.6	5809.9	5797.7
Variable	Unit	Filter 7	Filter 8	Filter 9	Filter 10	Filter 11	Filter 12
BOD[a]	mg/l	13	22	22	38	20	20
SS[b]	mg/l	97	93	86	79	73	164
Total Solids	mg/l	2376	2118	1717	1809	1779	2942
pH	-	7.2	6.7	7.1	6.6	6.8	6.8
Conductivity	μS	4912.2	4346.8	3808.8	3667.8	3528.5	5941.4
Mean (22/09/03-21/09/0404; artificial increase of pH after 21/09/03)							
Variable	Unit	Filter 1	Filter 2	Filter 3	Filter 4	Filter 5	Filter 6
BOD[a]	mg/l	30	30	3	2	4	4
SS[b]	mg/l	435	908	77	66	130	83
Total Solids	mg/l	1690	1932	1380	1399	1373	1431
pH	-	7.3	7.5	7.3	6.9	7.3	6.9
Conductivity	μS	2268.2	2356.0	2339.9	2260.3	2220.0	2507.6
Variable	Unit	Filter 7	Filter 8	Filter 9	Filter 10	Filter 11	Filter 12
BOD[a]	mg/l	2	3	3	4	4	8
SS[b]	mg/l	147	78	83	72	90	103
Total Solids	mg/l	1390	1497	1509	1805	1579	1647
pH	-	7.3	7.0	7.3	6.9	7.0	7.1
Conductivity	μS	2199.2	2484.2	2450.6	2459.6	2534.5	2495.3

[a]five-day @ 20 °C N-Allylthiourea biochemical oxygen demand; [b]suspendid solids

Table 4-3. Removal (%) per wetland filter[a] of outflow variables

22/09/02-21/09/03

Vari-able	Filter 1			Filter 2			Filter 3			Filter 4			Filter 5			Filter 6		
	b	c	d	b	c	d	b	c	d	b	c	d	b	c	d	b	c	d
BOD[e]	43	13	82	32	3	80	76	59	85	51	40	84	65	49	88	49	44	86
SS[f]	52	40	81	44	25	78	67	53	92	65	54	86	64	54	92	66	52	88
TS[g]	9	N	N	N	N	21	4	N	6	N	1	N	3	N	N	N	N	N
Turb[h]	78	86	65	71	86	51	96	98	95	90	94	94	90	96	91	93	95	93
Cond[i]	2	N	N	N	N	2	N	N	N	N	N	N	N	N	N	N	N	N

Vari-able	Filter 7			Filter 8			Filter 9			Filter 10			Filter 11			Filter 12		
	b	c	d	b	c	d	b	c	d	b	c	d	b	c	d	b	c	d
BOD[e]	79	53	94	66	32	92	67	51	93	43	2	89	69	68	89	69	65	84
SS[f]	72	60	98	73	62	91	75	71	95	77	70	92	78	71	88	51	35	86
TS[g]	20	15	25	29	32	N	42	48	19	39	45	2	40	43	N	2	N	28
Turb[h]	96	97	99	93	95	96	91	94	98	89	90	93	94	96	94	86	85	92
Cond[i]	4	N	N	15	11	N	26	36	N	28	32	N	31	29	N	N	N	N

22/09/03-21/09/0404 (artificial increase of pH after 21/09/03)

Vari-able	Filter 1			Filter 2			Filter 3			Filter 4			Filter 5			Filter 6		
	b	c	d	b	c	d	b	c	d	b	c	d	b	c	d	b	c	d
BOD[e]	66	69	76	63	44	71	97	100	96	97	99	94	95	99	96	95	99	93
SS[f]	49	74	52	15	N	76	91	91	98	92	92	98	85	91	97	90	91	97
TS[g]	25	36	37	15	23	56	38	40	65	38	42	58	39	50	64	36	38	49
Turb[h]	57	77	48	61	68	62	98	99	95	98	99	98	97	97	96	98	99	98
Cond[i]	N	7	18	N	8	N	N	12	N	N	18	N	0	22	N	N	9	N

Vari-able	Filter 7			Filter 8			Filter 9			Filter 10			Filter 11			Filter 12		
	b	c	d	b	c	d	b	c	d	b	c	d	b	c	d	b	c	d
BOD[e]	97	99	95	97	99	91	97	99	96	96	99	90	96	98	90	91	94	88
SS[f]	81	89	99	90	91	96	91	90	99	91	91	98	89	87	97	87	87	98
TS[g]	39	42	72	34	46	50	34	43	71	21	22	53	31	36	56	28	24	34
Turb[h]	97	98	99	98	98	98	97	99	98	98	99	99	98	97	99	93	93	97
Cond[i]	3	16	N	N	17	N	N	16	N	N	15	N	N	9	N	N	2	N

[a] Change $(\%) = \frac{(in - out) \times 100\ (\%)}{in}$, where in=inflow and out=outflow; [b]overall mean; [c]mean of the winter; [d]mean of the summer; [e]five-day @ 20 °C N-Allylthiourea biochemical oxygen demand (mg/l); [f]suspended solids (mg/l); [g]total solids (mg/l); [h]turbidity (NTU); [i]conductivity (μS); in italics: BOD>20 mg/l and SS>30 mg/l (outflow values). Abbreviation: N=negative removal (i.e. more output than input).

The reductions in BOD were satisfactory for most filters if compared to minimum American and European standards (<20 mg/l) for the secondary treatment of effluent (Figure 4-1). Furthermore, BOD levels in effluents of Filter 3 through 11 were less than or close to a minimum wetland background level of 3.5 mg/l, reported by Kadlec and Knight (1996) (Table 4-2).
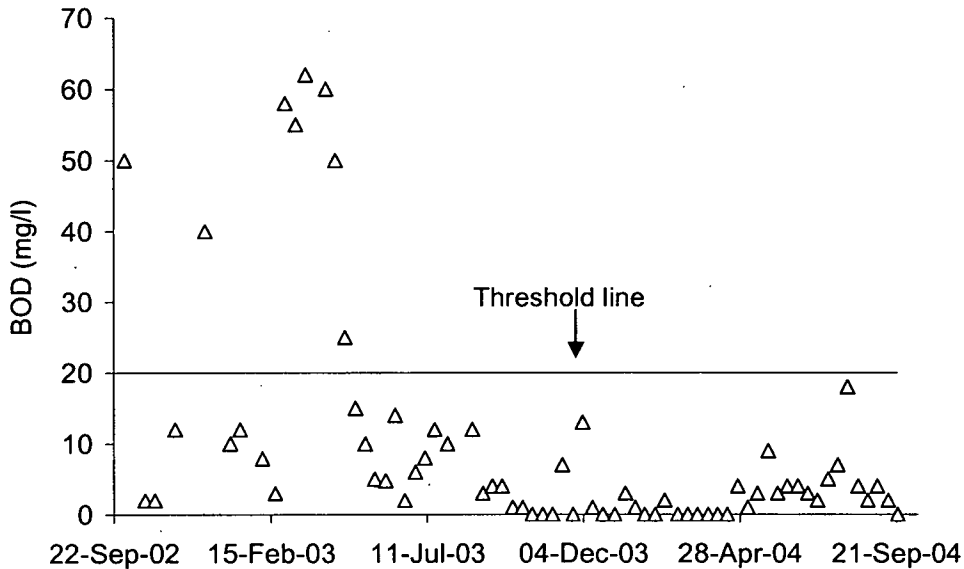
Figure 4-1. Effluent BOD concentrations in Filter 8. Solid line represents minimum American and European standards (<20 mg/l) for the secondary treatment of effluent.

The parameter in Figure 4-2 is presented as ratio of effluent BOD concentrations (BOD_e) to influent ones (BOD_i) of Filter 8 to highlight the removal changes of BOD. The BOD ratios were relatively high and unstable in the first winter. This suggests that biomass was not matured enough to treat organic matter in the beginning of operation. In addition to that, lower pH and higher salt concentrations during the first winter season deteriorated the filtration performance. Similar findings are reported in previous research (Clark and Pitt, 1999). However, BOD ratios decreased over time and filters showed the high treatment potential during the second year.
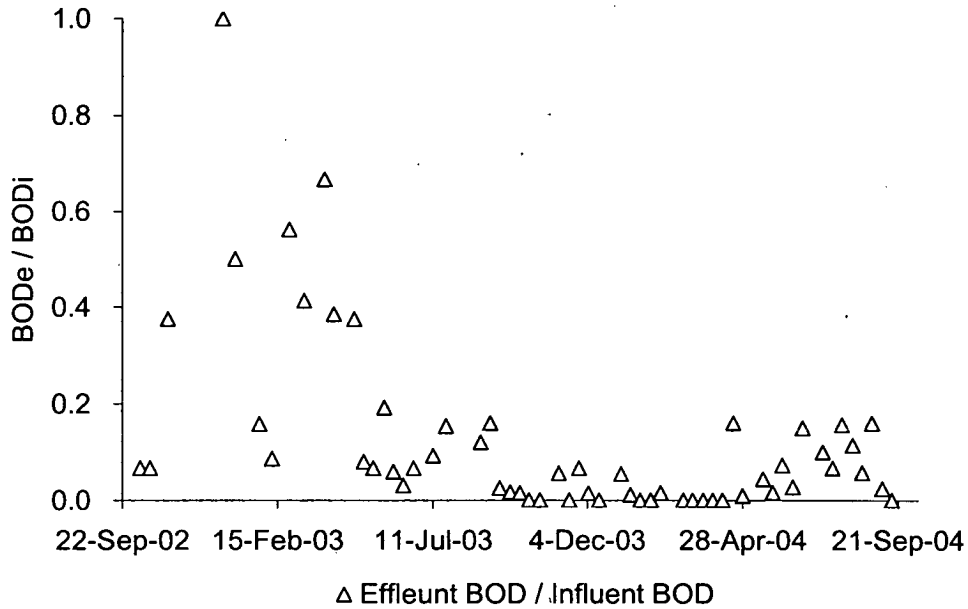
Figure 4-2. BOD removal ratios in Filter 8. BOD_e/BOD_i is the ratio of effluent BOD concentrations to influent BOD concentrations.

As illustrated in Figure 4-3, the effluent SS concentrations were high in winter and frequently exceeded the threshold of 30 mg/l throughout the year except for summer.
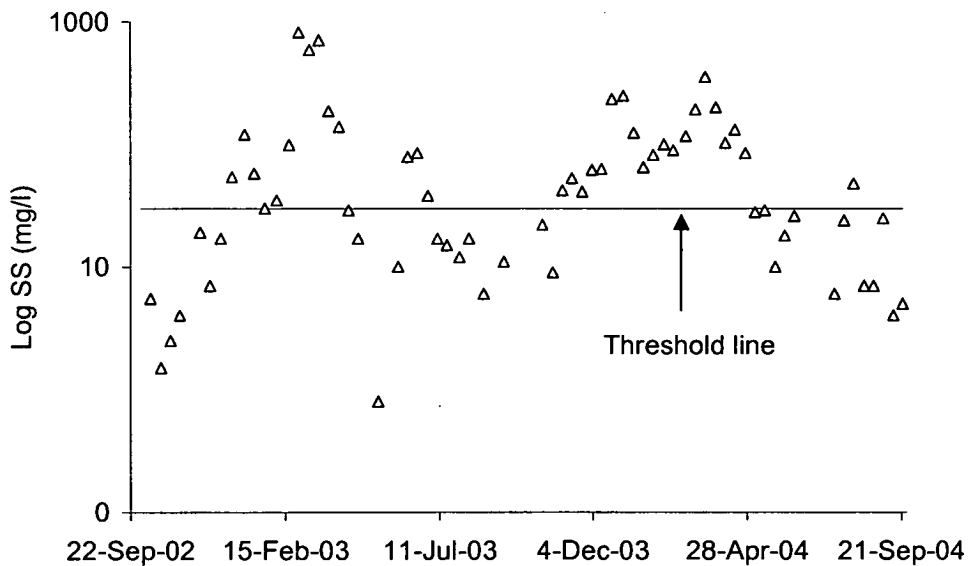
Figure 4-3. Effluent suspended solids (SS) concentrations in Filter 8. Solid line represents minimum American and European standards (<30 mg/l) for the secondary treatment of effluent.

55

However, ratio of the effluent SS concentrations (SS_e) over the influent SS concentrations (SS_i) decreased consistently throughout the operation periods (Figure 4-4). During the first year, influent SS in Filter 8 averaged 335.7 mg/l and was reduced to 92.5 mg/l resulting in an average removal efficiency of 73 %. Increased SS removal efficiency of 90 % was recorded during the second year (Table 4-2 and Table 4-3).
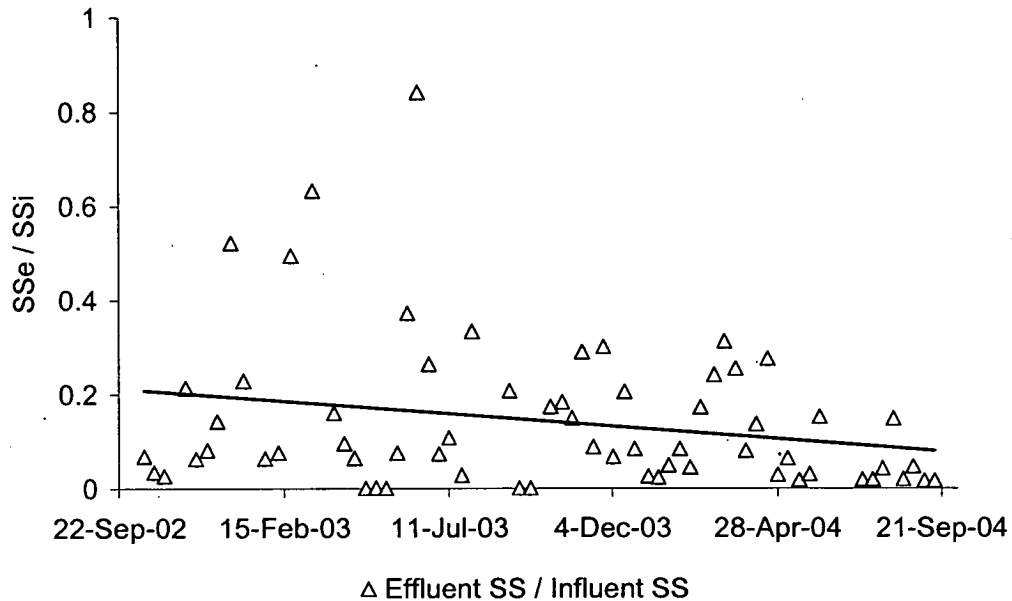
Figure 4-4. Suspended solids (SS) removal ratios in Filter 8. SS_e/SS_i is the ratio of the effluent SS concentrations over the influent SS concentrations. Solid line represents the trend line fitted to the data.

Negative reduction rates for TS and conductivity were predominantly caused by road salting in late autumn and winter (Table 4-1). Any conventional filter system including constructed wetlands is unable to retain salts in high concentrations. As shown in Figure 4-5, the filters did not reduce the TDS concentrations frequently, showing increasing removal ratios (effluent TDS over influent TDS concentrations) gradually. Salts can not be retained after a certain loading threshold that is associated

with a lag period is exceeded. The lag period is predominantly a function of the buffering capacity of the biomass and the batch-flow operational mode. It follows that after an initial positive removal period, the removal efficiencies become negative (Norrström and Jacks, 1998). Furthermore, the dissolved solids fraction increases as microbial biomass mineralizes the organic contaminants. Conductivity correlates well with dissolved solids that contribute to a large proportion of the TS mass (Cooper *et al.*, 1996; Scholz *et al.*, 2002).
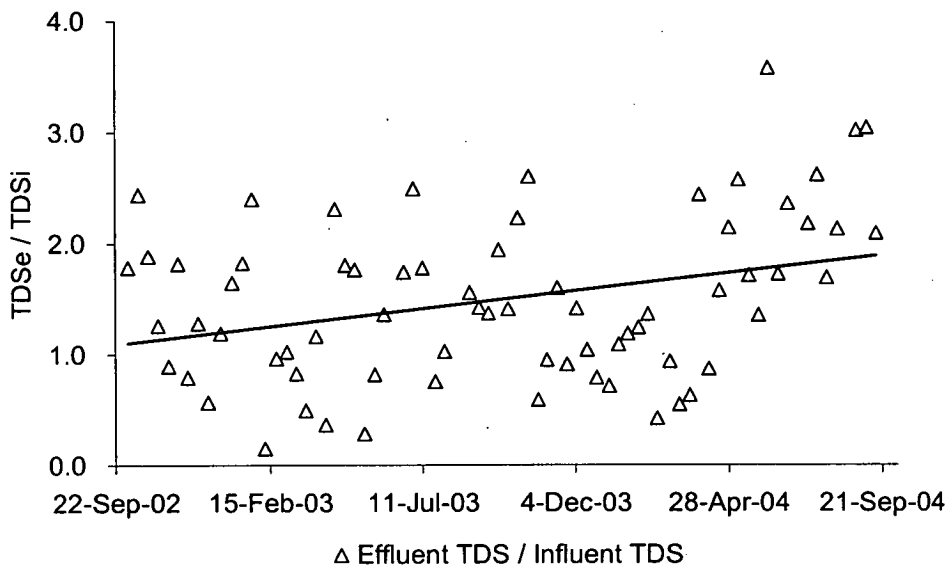
Figure 4-5. Total dissolved solids (TDS) removal ratios in Filter 8. TDS_e/TDS_i is the ratio of the effluent TDS concentrations over the influent TDS concentrations. Solid line represents the trend line fitted to the data.

4.4. Change of inflow water volume

The inflow water volumes were measured three times by draining the filters entirely during the operation periods (Table 4-4). The inflow water volumes of all filters decreased during the operation time. The accumulated sediment including macrophytes litter and solids reduces the inflow water volume.

Trends of inflow water volume changes were estimated using a regression equation as illustrated in Figure 4-6. These volume data were used to calculate mass loading and removal rates in the following sections.

Table 4-4. Change of inflow water volume

Date	September 2002	January 2004		February 2005	
Filter Number	Volume (l)	Volume (l)	Reduction (%)	Volume (l)	Reduction (%)
3	4.0	3.3	17.5	1.8	55.0
4	4.1	2.8	31.7	2.0	51.2
5	3.8	3.6	5.3	2.0	47.4
6	4.1	4.1	0.0	3.6	12.2
7	3.8	3.7	2.6	1.9	50.0
8	4.0	3.3	17.5	2.3	42.5
9	3.8	3.4	10.5	2.0	47.4
10	4.0	3.8	5.0	2.4	40.0
11	4.0	3.8	5.0	3.3	17.5
12	4.0	3.3	17.5	2.9	27.5

$y = -1E-06x^2 + 0.0918x - 1701.9$
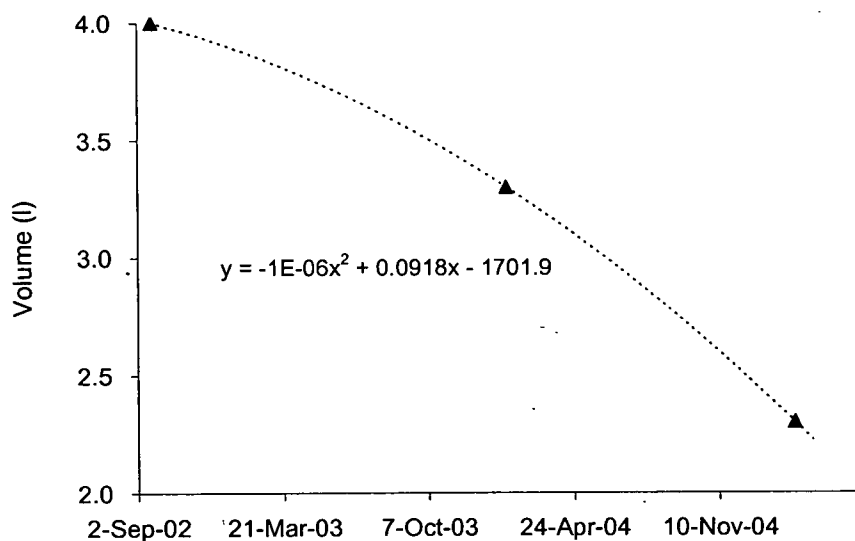
Figure 4-6. Change of inflow water volume in Filter 8. The curve represents trend line fitted to the data.

4.5. BOD removal

4.5.1. Removal performance

Figure 4-7 illustrates the variation of mass inflows and outflows of BOD in Filter 8. Mass inflows and outflows of BOD were calculated by multiplying BOD concentration with water volume (see section 4.4). It should be noticed that organic loading in the present study were highly variable (Figure 4-7 and Table 4-1). Despite highly variable organic loading, mass outflows of BOD were low and steady throughout the seasons, particularly during the second year.
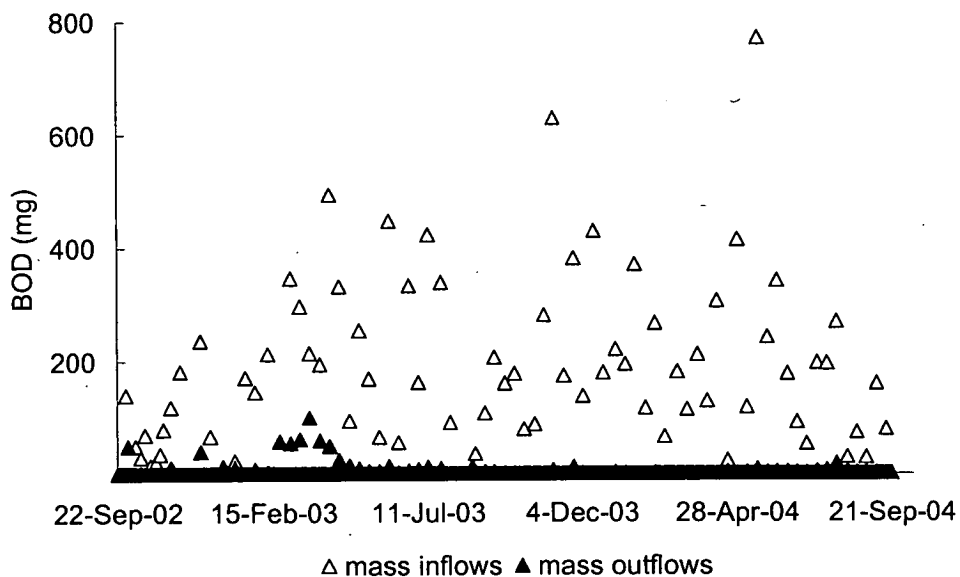
Figure 4-7. Variation of mass inflows and outflows of BOD in Filter 8. 60 out of 88 data sets are under 5 mg BOD.

Karathanasis et al. (2003) reported that the apparent seasonal variations in BOD removal performance of SSF systems were observed and declining performance during the winter was due to the decayed aboveground biomass, which contributes additional BOD to water. Newman et al. (2000) also described that reduced performance of wetland during the winter was likely the results of several seasonal

59

differences such as evapotranspiration rates, temperature and plant senescence. However, despite distinct seasonal pattern of environmental conditions, the present system was shown to be robust to the seasonal change and highly efficient in a cold climate. Harvesting macrophytes in late autumn was also likely to contribute to sustain the performance during the winter in the present study.

Table 4-5 presents the loading rates of Filters 3 through 12 for each year. The organic loading rate of Filter 12 ranged from 0.86 to 49.73 $g/m^2 \cdot d$ (Table 4-5). The average BOD loading rate (= 11.97 and 14.32 $g/m^2 \cdot d$ for each year) of Filter 12 is much higher than the loading rate of 3.35 $g/m^2 \cdot d$ and 5.0 $g/m^2 \cdot d$ for horizontal SSF wetlands in Czech (Vymazal, 1999), and in Denmark, respectively (Brix, 1998).

Table 4-5. Mass loading rates of BOD

Filter Number	Mass loading rate ($g/m^2 \cdot d$)			
	First year		Second year	
	mean	range	mean	range
3	6.03	1.15-12.78	5.20	0.77-16.88
4	5.64	1.03-11.85	4.74	0.75-51.02
5	6.38	1.24-13.11	5.90	0.93-18.60
6	6.82	1.34-13.91	7.11	1.30-21.71
7	6.28	1.01-13.37	5.79	0.65-20.59
8	5.85	0.92-12.58	5.44	0.61-19.67
9	5.91	1.01-12.65	5.45	0.61-19.50
10	6.32	1.01-13.57	5.82	0.65-20.73
11	5.90	0.99-13.15	6.21	0.71-22.91
12	11.97	0.86-42.13	14.32	1.00-49.73

Furthermore, the maximum BOD loading rate (= 49.73 $g/m^2 \cdot d$) of Filter 12 is much higher than maximum loading of 13.3 $g/m^2 \cdot d$ for a SSF system and 11.2 $g/m^2 \cdot d$ for SF system recommended by USEPA (1988), based on ultimate oxygen demand

(Table 4-5).

Considerable organic matter was removed efficiently in all the filters except for filter 1 and 2; extended storage (Table 4-5 and Table 4-6). Mass removal rate of BOD in the Filter 12 was 9.19 $g/m^2 \cdot d$ on average, ranging between 0.12 and 35.75 $g/m^2 \cdot d$ with loading rates of 11.97 $g/m^2 \cdot d$ during the first year. Furthermore, BOD removal rate increased to mass removal rate of 13.23 $g/m^2 \cdot d$ with mass loading rate of 14.32 $g/m^2 \cdot d$ during the second year. These values are much higher than the removal rate of 2.87 $g/m^2 \cdot d$ for horizontal SSF systems in Czech (Vymazal, 1999) and 5.05 $g/m^2 \cdot d$ in Poland (Kowalik and Obarska-Pempkowiak, 1998).

This result suggests that a temporarily flooded vertical-flow system is highly efficient for organic matter removal, compared to other systems. Temporarily flooding (i.e. Intermittent flooding and draining) is likely to supply more oxygen required for degradation of organic matter. Drainage causes suction of fresh air through the aeration tubes installed in low the layer, and flooding pushes the exhausted air out of filters. During drying periods, accumulated suspended organic matter is degraded, reduced clogging. In addition, the ponding on top of the filter media zone ensures uniform distribution of influents across the media and provides high hydraulic buffer capacity (Luederitz et al., 2001; Green et al., 1998).

Table 4-6. Mass removal rate[a] of BOD

| Filter Number | Mass removal rate ($g/m^2 \cdot d$) | | | |
| | First year | | Second year | |
	mean	range	mean	range
3	5.08	0.82-11.31	5.02	0.71-16.18
4	4.07	0.66-7.47	4.61	0.69-14.40
5	5.40	0.75-10.59	5.59	0.90-16.66
6	4.80	0.27-8.38	6.73	1.15-20.86
7	5.41	0.81-11.32	5.63	0.56-20.25
8	4.49	0.78-8.16	5.25	0.45-18.94
9	5.02	0.86-9.24	5.29	0.41-19.03
10	4.28	0.86-8.88	5.57	0.59-19.80
11	4.82	0.61-10.62	5.94	0.42-21.69
12	9.19	0.12-35.75	13.23	0.80-45.23

[a](in – out)/area · retention time, where in = mass inflow, out = mass outflows

Differences in mass removal rates of all filters except Filters 12 were not considerable particularly during the second year, implying that BOD removal performance of filters was comparable irrespective of filter composition and operation conditions. However, the removal rates of unplanted systems (Filters 3, 5, 7 and 9) during the first year were consistently higher than those of corresponding planted systems (Filters 4, 6, 8 and 10). This suggests that an unplanted system is more efficient for BOD removal in the relatively new wetland systems. Performance of filters was further compared via Wilcoxon signed-rank analysis in section 4.5.3.

Figure 4-8 and Figure 4-9 show well correlated linear regressions that display the capability of the filters with given loading rates. Previous studies have also reported that BOD removal rates increased with increasing influent loading rates (Knight and Knight, 1996; Klomjek and Nitisoravut, 2005)).
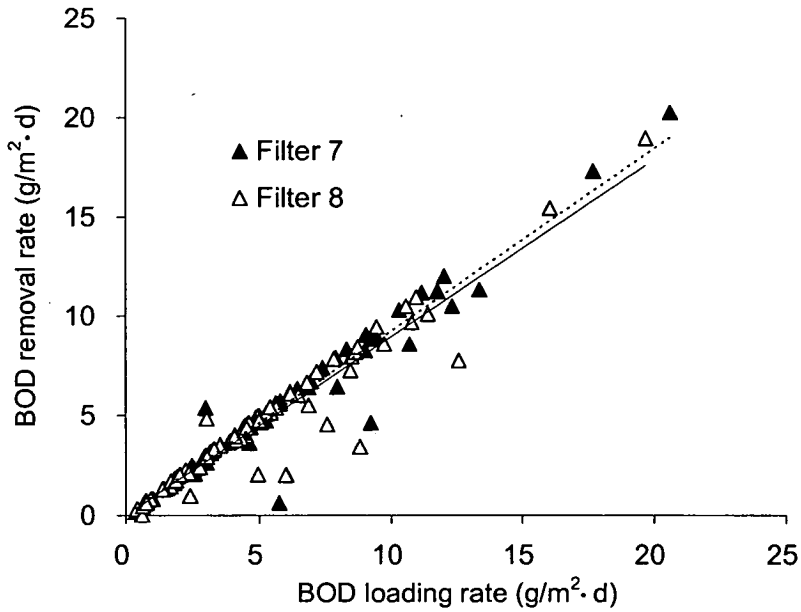
Figure 4-8. Mass loading and removal rate of BOD in Filters 7 and 8.
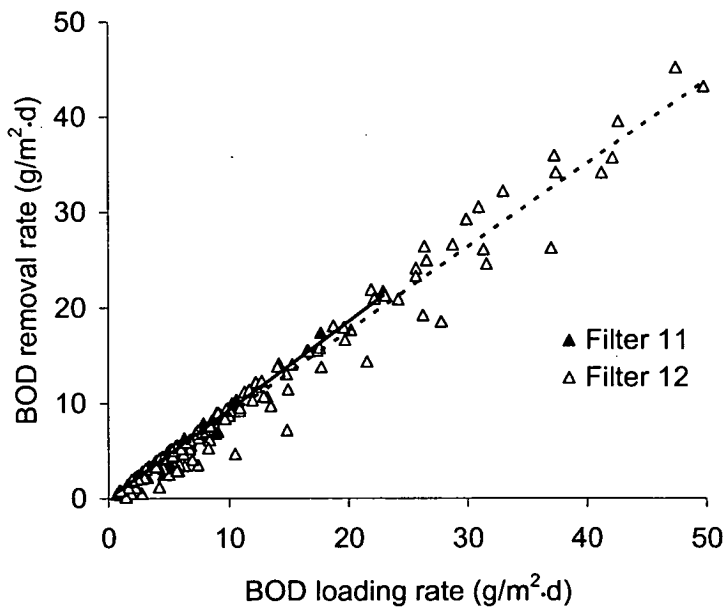
Figure 4-9. Mass loading and removal rate of BOD in Filters 11 and 12

As given in Figure 4-8, the unplanted system (Filter 7) showed slightly better performance in comparison to planted system (Filter 8). The gradient (= 0.88) of the

regression line of Filter 12 slightly reduced compared to that (= 0.93) of Filter 11, indicating that the BOD treatment performance was degraded at a lower retention time. Nevertheless, the system exhibited great potential for BOD removal under high loading rates (Figure 4-9).

4.5.2. Removal kinetics

First-order model. The first-order degradation approach has been widely used to predict removal performance for all pollutants such as organic matter, SS and nutrients in constructed wetlands. Although there is no convincing evidence that the rate of organic matter removal is first-order, it is still seen as most appropriate equation in the light of present knowledge (IWA, 2000; Sun *et al.*, 2005).

However, it is inappropriate to apply the first-order model to the temporarily flooded vertical-flow system for the design of a wetland because of periodic character of the process. Nevertheless, a first-order equation can be applied to compare the treatment performance of temporarily flooded vertical-flow systems with those of other systems. The rate of organic matter removal is evaluated using the following Kickuth equation, which is widely applied for constructed wetlands (Sun *et al.*, 2005).

$$A = Q \ln(C_i / C_e) / k_{BOD} \qquad \qquad 4\text{-}1$$

Where :

Q =   average daily flow rate (m^3 / d);

C_i =   influent BOD (g / m^3);

C_e =   effluent BOD (g / m^3);

A =   surface area (m^2); and

k_{BOD} =   rate constant (m/d).

As shown in Table 4-7, Average k_{BOD} values of Filter 12 are 0.26 and 0.49 (m/d) in the first and second year of operation respectively. This indicates that a temporarily flooded vertical-flow wetland system is highly efficient for BOD removal, considering the typical k_{BOD} value of 0.07 – 0.10 (m/d) obtained in UK systems (Cooper et al., 1996), and 0.06 (m/d) derived from USA wetland systems (Knight et al., 2000).

All k_{BOD} values for the second year are double those of the first year, indicating treatment performance improved consistently. Furthermore, the BOD removal performance of filters did not deteriorate under high pH condition during the second year (Table 4-1).

Table 4-7. BOD removal rate constants

Filter Number	k_{BOD} (m/d)	
	First year	Second year
3	0.14	0.28
4	0.09	0.25
5	0.13	0.25
6	0.14	0.30
7	0.16	0.32
8	0.12	0.28
9	0.12	0.25
10	0.09	0.27
11	0.13	0.29
12	0.26	0.49

BOD removal has found to be temperature dependent in other water treatment processes. This effect on the performance of wetlands can be modeled as a modified Arrhenius equation as follows (Kadlec and Knight, 1996);

$$k_T = k_{20}\theta^{(T-20)} \qquad\qquad 4-2$$

Where :

k_{20} = k at 20 °C (m/d);

k_T = k at T °C (m/d);

θ = theta value (dimensionless); and

T = water temperature (°C).

The θ values for BOD removal in Filter 12, derived by regression analysis, were 1.00 and 0.99 during first and second year, respectively, indicating that temperature had little effect on the first-order rate constant. Corresponding k_{20} were 0.35 and 0.39 (m/d) during first and second year, respectively. Kadlec and Knight (1996) also reported that θ was 1.00 for treatment wetlands in the North America Treatment Wetland Database.

Monod kinetics. The Monod equation can be used to compare the maximum treatment capacity of a vertical-flow system with others, as demonstrated in the application of the first-order model (see above).

In biochemical treatment systems, the removal rate will eventually cease to be first-order and become zero-order with increasing influent loading. Such a transition can be represented by the Monod (1949) equation (Equation 4-3).

$$r = k_{0,v} V \frac{C_i}{K + C_i}$$ 4-3

Where:

r = rate of biological degradation (g/d);

$k_{0,v}$ = zero-order volumetric rate constant (g/m³·d);

V = holding volume (m³);

66

K = half-saturation constant (g/m^3); and

C_i = influent concentration (g/m^3).

In other words, the removal rates are limited by pollutant availability at relatively low pollutant concentrations, and saturated at relatively high pollutant concentrations (Mitchell and McNevin, 2001). The removal equation can be expressed as follows;

First-order equation; $\ln(C_i/C_e) = k_1 A/Q = k_1/q$ 　　　　　　　　4-4

Zero-order equation; $C_i - C_e = k_0/q$ 　　　　　　　　4-5

Where :

C_i = influent concentration (g/m^3);

C_e = effluent concentration (g/m^3);

k_1 = first-order areal rate constant (m/d);

k_0 = zero-order areal rate constant ($g/m^2\cdot d$);

A = surface area (m^2);

Q = volumetric flow rate (m^3/d); and

q = hydraulic loading rate (m/d).

To model the transition from first to zero-order BOD removal kinetics in the present study, normalized organic loading and removal rates against the maximum possible mass removal rate were defined (Mitchell and McNevin, 2001).

Normalized loading rate; $R_L = C_iQ/k_{0,v}V = C_iq/k_{0,A}$ 　　　　4-6

Normalized removal rate; $R_R = (C_i - C_e)Q/k_{0,v}V = (C_i - C_e)q/k_{0,A}$ 　　4-7

Where :

C_i = influent concentration (g/m^3);

C_e = effluent concentration (g/m^3);

$k_{0,V}$ = zero-order volumetric rate constant ($g/m^3 \cdot d$);

$k_{0,A}$ = zero-order areal rate constant ($g/m^2 \cdot d$);

Q = volumetric flow rate (m^3/d);

q = hydraulic loading rate (m/d); and

V = wetland holding volume (m^3).

For a particular influent concentration, as flow rate increases, the removal rate increases until a maximum removal rate is achieved. Since the removal rate reached the maximum, further increase of flow rate (i.e. normalized loading rate is greater than one) will cause a higher effluent concentration, resulting in failure of the system with the excess loading.

In Monod kinetics, a zero-order saturated constant, representing the absolute maximum removal rate can be found. This eliminates the possibility of oversizing a wetland that operates in the first-order regime and undersizing a wetland that operates in the zero-order regime (Mitchell and McNevin, 2001).

At the maximum removal rate, the normalized loading rate (= R_L) is equal to unity. Therefore, the following equation can be deduced from the equation 4-6;

$$C_i q = k_0 \qquad\qquad 4\text{-}8$$

The maximum possible removal rate for BOD achieved in Filter 12 was approximately 37 $g/m^2/d$, as given in Figure 4-10. Thus, design criteria based on the Monod equation for Filter 12 can be obtained as follows; $C_i q = 37$ $g/m^2 \cdot d$. Although it is inappropriate to apply this model to a temporarily flooded vertical-flow system, the removal rate obtained can be used to compare the system capacity with other systems and to give a useful operation guideline for the system. This maximum

removal rate is much higher than the 8 $g/m^2/d$ obtained in performance data of the SSF constructed wetlands surveyed by US EPA (1994), showing the great removal capacity of the system.
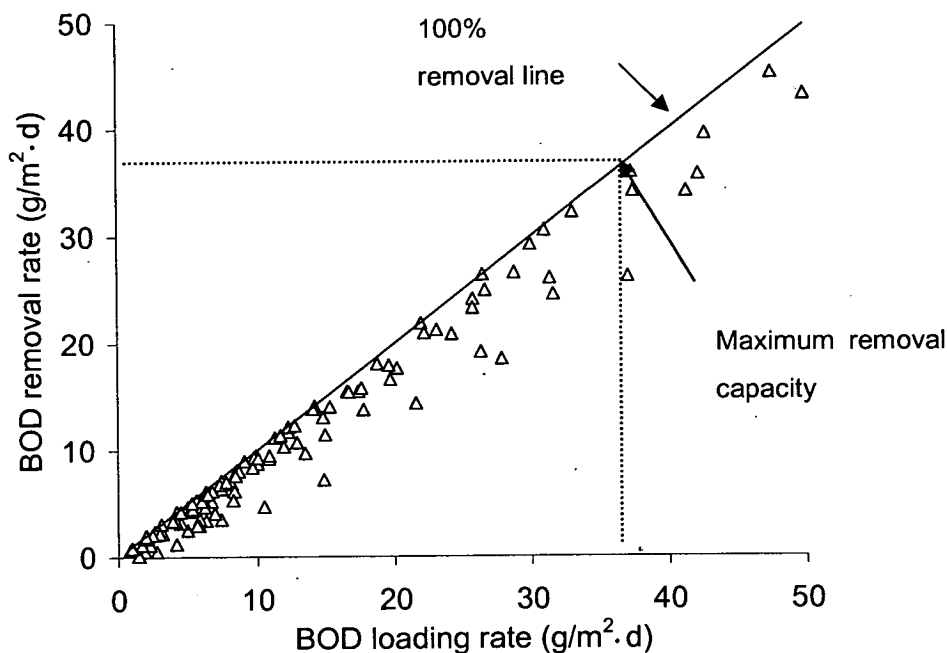
Figure 4-10. Maximum removal capacity of BOD in Filter 12

4.5.3. Factors affecting BOD removal

Effect of influent water quality. The SOM model developed by Kohonen (2001) was applied using the data obtained in Filter 12 to identify the relationship between the influent water quality variables and BOD treatment efficiencies (Figure 4-11). The SOM model shows its high performance in visualization of relationship for non-linear and complex biochemical data sets (Lu and Lo, 2002; Garcia and González, 2004). Visualization gives better understanding of the relationships between most variables in biochemical processes. The SOM model is described in detail in section 7.3.5.

The unified distance matrix (U-matrix) visualizes distances between neighboring map units, and helps to identify the cluster structures of the map. Each component plane shows values for each variable with its corresponding unit. Figure 4-11 presents that high effluent BOD concentrations (> 20 mg/l), shown in the low and right part in the map, are associated with relatively low pH (< 7) and high influent BOD concentrations (> 100 mg/l). However, the relationship between the effluent BOD concentrations and conductivity, and temperature are unclear in the SOM map. From the U-matrix, it can be seen that these data units are not clustered.
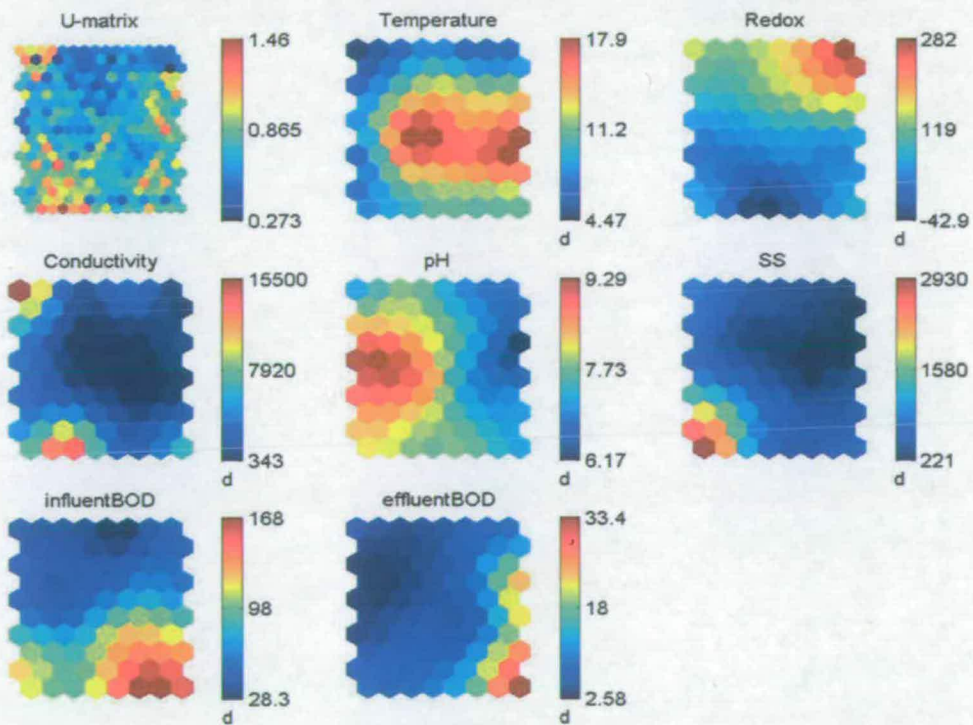
Figure 4-11. Visualization of relationship between influent water quality indicators and effluent BOD concentrations in Filter 12. U-matrix on top left, then component planes. The eight figures are linked by position: in each figure, the hexagon in a certain position corresponds to the same map unit.

As shown in the SOM map, the relatively high influent pH did not link to the high effluent BOD concentrations. This clearly indicates that high pH did not harm the

microorganisms responsible for BOD reduction during the processes.

Regarding the effect of high salt on the BOD treatment, Klomjek and Nitisoravut (2005) reported that high salt concentration is a major factor causing poor BOD treatment by leading to plant stress and affecting the metabolism function of the organism. However, it was shown that high salt concentration, presented by conductivity did not have significant effect on BOD treatment performance in the present study.

As to the temperature dependence for BOD reduction, temperature did not show any significant relation with the effluent BOD concentrations in the map (Figure 4-11). Negative effect of cold climate on the performance of wetlands has been reported in previous studies (Leonard, 2000; Karathanasis et al., 2003). At the same time, several studies of SSF wetlands have suggested negligible temperature dependence for BOD removal (Baver et al., 1987; Kadlec and Knight, 1996).

Theories to explain the non-effect of temperature have been described by Kedlec and Knight (1996). The net BOD removal is the difference between the generation and consumption process. Therefore, the difference between the slowed BOD production and slowed BOD removal in winter season may not differ considerably from that observed in more biologically active warmer months.

Furthermore, it is known that soil microbes still have the capacity to decompose organic matter in low temperature conditions, even though dormant vegetation and a slow reaction for microbes may reduce the biological removal process within the wetland. Inherent bed insulation can also serve to maintain a moderate removal rate in the wetland (Werker et al., 2002).

In addition, not all of the BOD removal mechanism may slow with decreasing temperature. Physical and chemical processes would facilitate BOD removal within wetland even though biological activity slows in winter. For example, the solubility of some organic compounds can be decreased and some fraction of BOD may be colloidal and be susceptible to removal by filtration at low temperature (Kedlec and Knight, 1996).

Design and operation conditions. Wilcoxon signed-rank analysis p values of less than 0.05 are considered significant and lead to the conclusion that performance of the filters is different depending on the filters.

The Wilcoxon signed-rank analysis p values between planted and unplanted filters are given in Table 4-8. During the first year, all the p values were less than 0.05 under the hypothesis that effluent BOD values of planted filters are similar or lower compared to the BOD values of unplanted ones, indicating that effluent BOD values of planted systems are higher than unplanted systems.

This is compatible with the presence of red *Tubifex tubifex* (Sludgeworm) worms in planted filters. *T. tubifex* is known as an indicator for organically polluted water including high BOD_5 and low DO concentrations (Kadlec *et al.*, 1996). Effluent water from planted filters had a mean number of 1.0 (SD: 0.74) *T. tubifex* worms per liter. In contrast, unplanted filters contained on average 0.1 (SD: 0.86) *T. tubifex* worms per liter. This provides further evidence that *P. australis* adversely affected the effluent water quality in the present study. However, *T. tubifex* were virtually absent in all filters since spring 2003.

Another possible reason for lower effluent BOD concentrations in the unplanted

system may be due to the lack of vegetation cover, which may results in extra aeration and oxidation of the organic load (Thomas *et al.*, 1995). Furthermore, plant debris was returned and decayed within system and increased organic loading in planted system during the winter season.

However, p values, greater than 0.05 during the second year, indicate that macrophytes did not affect significantly the removal performance of organic matter, as reported in elsewhere (Lim *et al.*, 2001). This result suggests that developed biofilm substrate offset the negative impact of macrophytes on the treatment during the second year. In addition to that, it is attributed to the developed root of macrophytes enhancing the capacity of transporting the oxygen to substrate and providing larger surface area for microorganisms.

Table 4-8. Comparison of effluent BOD concentrations for planted and unplanted filters.

Filter Number	Wilcoxon p values	
	First year	Second year
3 and 4	0.01	0.51
5 and 6	0.01	0.66
7 and 8	0.00	0.36
9 and 10	0.00	0.19

As shown in Table 4-9, expensive filter media such as Filteralite did not contribute to the reduction of BOD significantly. The p values between filter 8 and 10 indicates that additional filter media still deteriorated the filtration performance of filters.

It has been reported that sand media have only a limited ability to removal organic material due to its limited capacity for substrate growth and a subsequent small microbial population, while it is highly effective in removing suspended particles

including bacteria and virus (Collins *et al.*,1992; Selim and Wang, 1994). However, basic sand-gravel filters showed high BOD removal efficiencies after biomass is matured (for example, BOD removal efficiency of Filters 7 and 8 is 97% in the second year of operation) and similar performance to those of modified filter media such as Filtralite in the present systems.

Table 4-9. Comparison of effluent BOD concentrations for different filter media.

Filter Number	Wilcoxon p values	
	First year	Second year
3 and 5	0.25	0.51
4 and 6	0.92	0.00
7 and 9	0.25	0.63
8 and 10	0.00	0.02

Wilcoxon p values between contaminated and uncontaminated filters with heavy metal were greater than 0.05 in most filters except for Filters 4 and 8. P values between Filters 4 and 8 during first year reveals that effluent concentrations of Filter 4 were higher than those of Filter 8. Therefore, it can be inferred that toxicity of heavy metal did not affect BOD removal performance (Table 4-10). Lim et al. (2003) also reported that COD removal efficiency was practically independent of increasing metal loading.

Table 4-10. Comparison of effluent BOD concentrations for contamination of heavy metal

Filter Number	Wilcoxon p values	
	First year	Second year
3 and 7	0.06	0.58
4 and 8	0.01	0.19
5 and 9	0.13	0.11
6 and 10	0.75	0.24

Wilcoxon p values between Filters 11 and 12 were 0.77 and 0.02 during first year and second year, respectively. The p value of 0.02 during second year indicates that the effluent BOD concentrations of Filter 12 were higher than those of Filter 11 due to the high loading rate, even though k_{BOD} (m/d) of Filter 12 was greater than that of Filter 11 (Table 4-7).

Wilcoxon p values between Filters 10 and 11 indicate the effect of aeration in the BOD removal. Wilcoxon p value in the first year was 0.00, implying that artificial aeration improved the BOD removal efficiency in the new filter system. However, p value (= 0.09) in the second year indicates aeration did not contribute significantly to the BOD removal in the matured system.

From the Wilcoxon signed-rank analysis, it can be summarized that macrophytes as well as expensive filter media did not contribute significantly to the organic matter treatment, whereas loading rate had a serious impact on it. In other words, a performance for organic matter removal was mainly controlled by operation condition rather than filter design in the highly loaded vertical-flow system.

4.6. Suspended solids removal

4.6.1. Removal performance

. Figure 4-12 illustrates the variation of mass inflows and outflows of SS during the two years in Filter 8. It is evident that mass inflows and outflows of SS were relatively high in winter. This shows clearly a seasonal dependence of SS, comparable to previous studies (Newman et al., 2000).

Experimental filters were heavily loaded with SS (i.e. loading rate of Filter 12 was 135.59 g/m^2·d during the second year) compared to the other wetland system and

loading rates were highly variable ranging from 1.09 to 1024.51 $g/m^2 \cdot d$ in Filter 12

(Table 4-11). Loading rates of most of SSF wetland system were reported as between

3 and 5 $g/m^2 \cdot d$ (Kadlec and Knight, 1996; Brix, 1994).
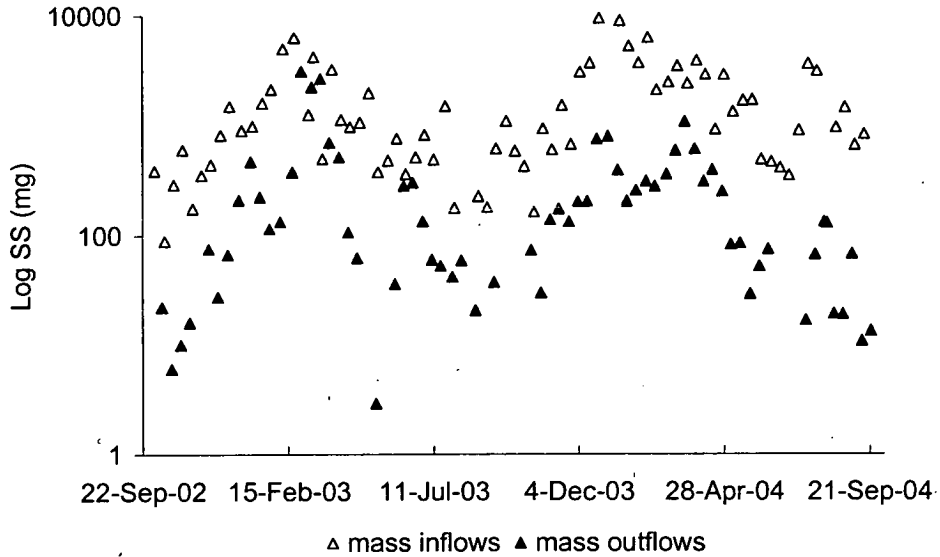
Figure 4-12. Mass inflows and outflows of suspended solids (SS) in Filter 8

Table 4-11. Mass loading rate of suspended solids (SS)

Filter Number	Mass loading rate ($g/m^2 \cdot d$)			
	First year		Second year	
	mean	range	mean	range
3	23.41	0.41-90.73	43.22	1.98-168.33
4	22.04	0.41-85.55	39.14	1.90-150.24
5	23.73	0.39-91.58	49.16	2.37-188.71
6	25.24	0.42-96.99	59.24	3.24-218.94
7	24.14	0.39-93.16	49.51	2.32-191.49
8	23.11	0.40-89.35	46.34	2.35-175.52
9	23.02	0.39-88.94	46.51	2.26-178.29
10	24.63	0.41-95.15	49.69	2.37-191.49
11	23.99	0.41-92.40	52.92	2.82-197.42
12	51.66	2.76-205.93	135.59	1.09-1024.51

Bavor and Schulz (1993) reported that solids accumulation leading to clogging

76

problems appeared at a loading rate corresponding to 10 to 40 $g/m^2 \cdot d$ and slightly below these loading rate, operation was possible for more than 6 months in sand filters. They suggested that a sustainable solids loading rate for gravel-based macrophytes systems would be on the order of 40 $g/m^2 \cdot d$ using domestic sewage effluent input. However, despite high SS loading rate, clogging problems were not observed during operation periods in most systems except the unplanted systems (i.e. clogging was observed in Filters 5, 7 and 9 on 3 and 12 December 2003). This suggests that macrophytes provide good filtration conditions, by preventing the filters from clogging (Brix, 1997).

Table 4-12 presents the mass removal rates of SS for each year. Mass removal rate of SS in the Filter 12 was 35.70 $g/m^2 \cdot d$ averagely with loading rate of 51.66 $g/m^2 \cdot d$ during the first year and increased greatly to a mass removal rate of 121.13 $g/m^2 \cdot d$ with loading rates of 135.59 $g/m^2 \cdot d$ during the second year (Table 4-12).

Table 4-12. Mass removal rate[a] of suspended solids (SS)

Filter Number	Mass removal rate ($g/m^2 \cdot d$)			
	First year		Second year	
	mean	range	mean	range
3	16.16	-0.40-43.74	38.66	-2.34-161.91
4	14.34	-0.28-39.90	35.57	1.84-144.21
5	16.12	-0.75-45.12	43.67	2.03-178.19
6	16.62	0.21-48.37	52.97	2.62-208.13
7	19.66	0.39-76.32	43.50	2.13-178.85
8	18.51	0.28-70.62	41.42	2.08-168.48
9	19.35	0.02-78.23	41.06	2.15-171.41
10	20.92	0.00-78.82	44.78	1.95-185.12
11	20.10	0.33-70.82	46.88	2.45-186.71
12	35.70	-3.90-125.23	121.13	-5.34-971.05

[a](in – out)/area · retention time, where in = mass inflow, out = mass outflows

These values were higher than removal rate of 26.7 $g/m^2 \cdot d$ obtained from SF

wetlands (Lin *et al.*, 2005) and 30 to 68 g/m^2·d in SSF systems (Lee *et al.*, 2004), indicating that SS mass removal capacity of the temporarily flooded vertical-flow system is greater than those of SF and SSF system.

The SS mass removal rates linearly increased as SS loading rates increased from 1.09 to 1024.51 g/m^2·d and removal rates were highly correlated with loading rates, as given in Figure 4-13, indicating that the applied load had not yet reached its maximum allowable capacity. Furthermore, as illustrated in Figure 4-13, the gradient (= 0.87) of trend line of Filter 12 was not reduced significantly in comparison to that (= 0.89) of Filter 11. This suggests that filter was responding well at given higher loading rates.
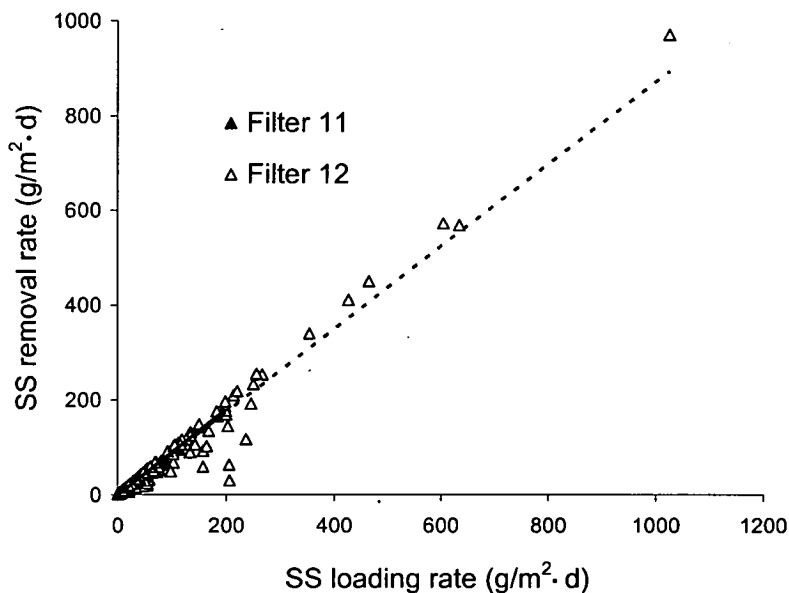
Figure 4-13. Mass loading and removal rates of suspended solids (SS) in Filters 11 and 12

Figure 4-14 show that the SS removal performance between planted and unplanted systems was virtually similar, indicating that the contribution of macrophytes to the SS removal was negligible. This is further discussed in section 4.6.3.
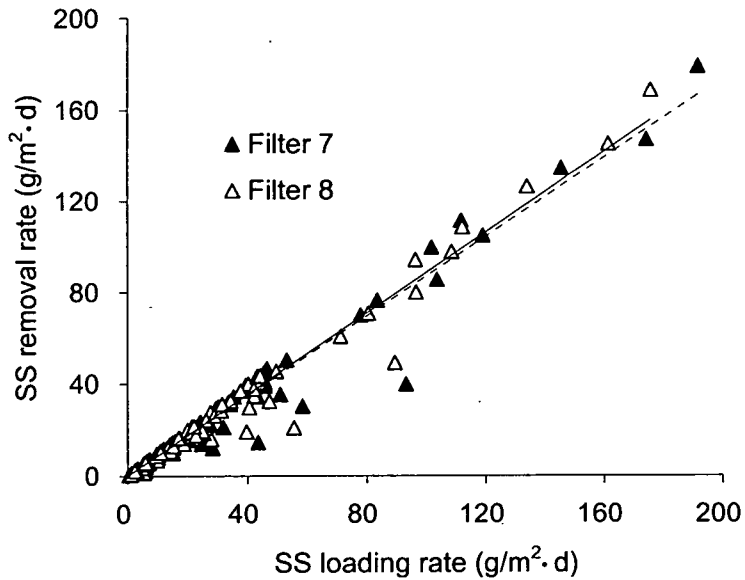
Figure 4-14. Mass loading and removal rates of suspended solids (SS) in Filters 7 and 8

4.6.2. Removal kinetics

The SS removal rate constants are evaluated using the first-order removal equation (see section 4.5.2). The average k_{SS} value was 0.46 m/d, showing the maximum value of 1.58 m/d during the second year in Filter 12 (Table 3.3). This is much higher than removal rate of 0.06 m/d obtained from a livestock wastewater treatment database (Knight *et al.*, 2000) and 0.119 m/d in SSF wetlands in Czech Republic (IWA, 2000).

During the first operation, the theta $(=\theta)$ value was 0.99 and k_{20} was 0.32, suggesting that temperature has little effect on the SS removal performance. Similar values were reported by Kadlec and Knight (1996) (θ = 1.00) and Knight (2000) (θ = 1.01). However, k_{SS} value was affected by temperature during second year (θ = 1.06, k_{20} = 0.68).

79

Table 4-13. Suspended solids (SS) removal rate constants

Filter Number	k_{SS} (m/d)	
	First year	Second year
3	0.20	0.15
4	0.14	0.15
5	0.17	0.17
6	0.19	0.22
7	0.25	0.18
8	0.19	0.15
9	0.17	0.16
10	0.19	0.18
11	0.19	0.18
12	0.33	0.46

As demonstrated in removal kinetics for BOD (section 4.5.2), SS removal rates can also be applied to Monod kinetics to estimate the SS removal potential from correlations between SS loading and removal rates (Figure 4-15). The maximum possible removal rate of SS in Filter 12 was approximately 500 $g/m^2 \cdot d$, much higher, compared to 13 $g/m^2 \cdot d$ based on USEPA data in SSF constructed wetland (1994).
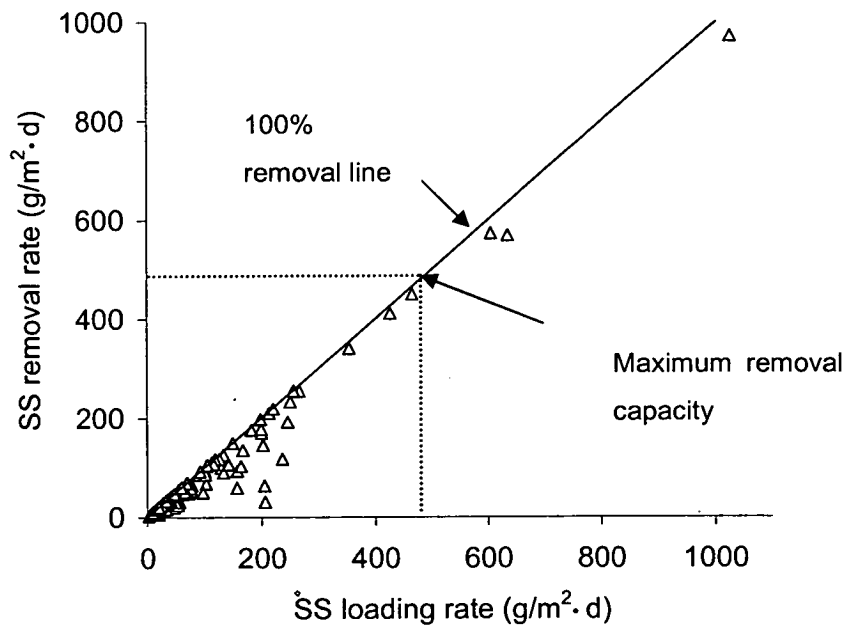
Figure 4-15. Maximum removal capacity of suspended solids (SS) in Filter 12

4.6.3. Factors affecting suspended solids removal

Effect of influent water quality. Figure 4-16 presents a SOM map elucidating the relationship between SS treatment efficiency and influent water quality. High effluent SS concentrations (> 350 mg/l) are apparently related to relatively low temperature (< 10 °C) and high conductivity (> 17,000 μS).
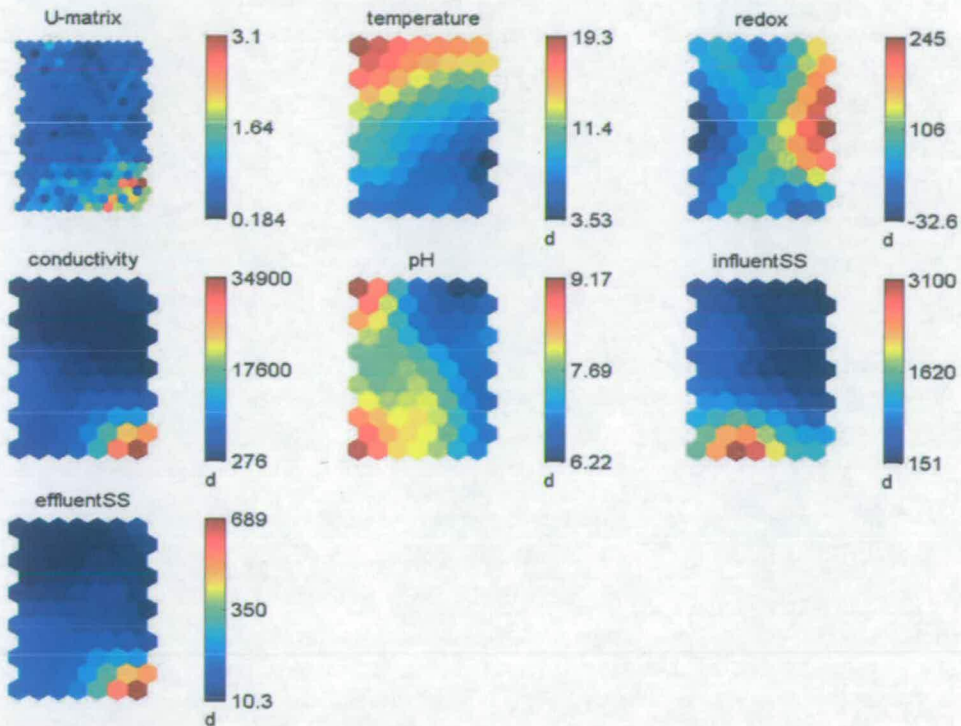
Figure 4-16. Visualization of relationship between influent water quality indicators and effluent suspended solids (SS) concentrations in Filter 8

Multiple linear regression analysis was carried out to identify the important influent water quality variables for SS reduction, and the derived regression equations revealed that influent conductivity and influent SS concentration were statistically significant on the SS removal performance and accounted for 29 - 93 % of variation in effluent SS concentrations (Table 4-14).

Table 4-14. Relationship between influent water quality and effluent suspended solids (SS) concentrations

Filter Number	Regression Equation[a]	R^2
3	$C_e = 0.020CON + 11.174$	0.93
4	$C_e = 0.020CON + 15.062$	0.94
5	$C_e = 0.018CON + 32.315$	0.87
6	$C_e = 0.022CON + 18.375$	0.89
7	$C_e = 0.014CON + 35.920$	0.56
8	$C_e = 0.012CON + 32.947$	0.60
9	$C_e = 0.007CON + 48.491$	0.29
10	$C_e = 0.008CON + 38.743$	0.39
11	$C_e = 0.035C_i + 0.010CON$	0.53
12	$C_e = 0.028C_i + 0.024CON$	0.92

[a] C_e = effluent SS concentration, C_i = influent SS concentration, CON = influent conductivity

Kedlec and Knight (1996) also produced the following regression equations for 22 SSF wetlands from the North American Database;

$$C_e = 0.063C_i + 7.8 \quad (R^2 = 0.09) \quad\quad\quad 4\text{-}9$$

Similarly, a better regression equation was found for 77 Danish soil-based wetlands (Brix, 1994), indicating that the influent SS loading had significant impact on the SS removal performance;

$$C_e = 0.09C_i + 4.7 \quad (R^2 = 0.67) \quad\quad\quad 4\text{-}10$$

In the present study, however, influent SS concentrations had no significant effect on the treatment performance except Filters 11 and 12, whereas SS treatment performance was considerably affected by influent conductivity in all filters. The

accompanying salts represented by conductivity are likely to cause an elevated internal SS production. Similar findings were reported in previous researches (Clark and Pitt, 1999; Kedlec and Knight, 1996). Revitt *et al.* (2003) also reported that de-icing activity increased the SS concentrations in sewer during the winter. However, it is known that moderate increases of salt concentrations do usually increase flocculation within the filter and therefore decrease SS and turbidity outflow values.

Design and operation conditions. The Wilcoxon signed-rank analysis p values for effluent SS concentrations between planted and unplanted filters are given in Table 4-15. All the p values except the case of Filters 3 and 4 during the first year were higher than 0.05, revealing that the SS removal performance of most of filters was virtually similar. In the case of Filters 3 and 4, the effluent SS concentrations of Filter 4 (planted system) were even higher statistically than those of Filter 3 (unplanted).

These results clearly show that SS removal performance is not affected by macrophytes, contradicting the results of Karathanasis *et al.* (2003), who reported that the vegetated systems exhibited nearly twice as high a removal efficiency as the unplanted system. Brix (1997) indicated that the higher SS removal performance in a planted system is attributed to a larger surface area, reduced water velocity and reinforced settling and filtration by the root network.

The small differences in the SS removal performance between systems with and without macrophytes indicate that the contribution of macrophytes to the physical SS removal processes were not significant in the temporarily flooded vertical-flow system. Similar findings were also reported elsewhere (Thomas *et al.*, 1995; Tanner *et al.*, 1995).

Table 4-15. Comparison of effluent suspended solids (SS) concentrations for planted and unplanted filters.

Filter Number	Wilcoxon p values	
	First year	Second year
3 and 4	0.00	0.07
5 and 6	0.34	0.15
7 and 8	0.23	0.49
9 and 10	0.87	0.11

Concerning the effluent TDS concentrations, effluent TDS concentrations were statistically higher in planted system than unplanted system except in the case of Filters 9 and 10 (Table 4-16). This is likely due to the release of nutrients back into the water as a result of plant decay, increasing the dissolved ions content (Mashauri *et al.*, 1999).

Table 4-16. Comparison of effluent total dissolved solids (TDS) concentrations for planted and unplanted filters.

Filter Number	Wilcoxon p values	
	First year	Second year
3 and 4	0.02	0.36
5 and 6	0.01	0.00
7 and 8	0.07	0.00
9 and 10	0.96	0.11

As shown in Table 4-17, there was no considerable difference on SS removal performance between different filter media in most filters. It could be stated that the differences in the size, compositions and porosities of the substrate did not show significant effects on the SS removal performance of vertical-flow wetland system, as given previous study (Krokusuz *et al.*, 2005). However, in the case of filter 3 and 5, basic sand-gravel filters exhibit better performance than modified filters during the first year.

Table 4-17. Comparison of effluent suspended solids (SS) concentrations for different filter media

Filter Number	Wilcoxon p values	
	First year	Second year
3 and 5	0.01	0.10
4 and 6	0.13	0.09
7 and 9	0.10	0.66
8 and 10	0.93	0.08

The SS removal efficiencies of Filter 12 were lower during the first year (p value : 0.00), but similar to those of Filter 11 during second year (p value : 0.53). This suggests that the filter's potential for SS removal increased over time and these systems responded well at a high loading rate. In summary, it can be concluded that that macrophytes and filter media did not have significant impact on solids removal in the vertical-flow system, likewise BOD removal performance.

4.7. Summary

This chapter has demonstrated that temporarily flooded vertical-flow wetlands were highly efficient for BOD and SS removal, in comparison to other types of wetlands. Despite highly variable loading, the BOD removal performance in the wetland filters was satisfactory and stable throughout the seasons, whereas the SS treatment performance deteriorated particularly in the late autumn and winter.

The BOD removal performance was not significantly affected by the variation of heavy metal loadings, salt and temperature. In particular, the artificial increase of pH after the first year of operation had no apparent influence on the BOD treatment processes. Furthermore, wetland systems showed significant buffer capacity for pH.

This suggests that the temporarily flooded vertical-flow wetland systems could be well adapted to highly variable environmental conditions. However, the SS removal efficiency decreased with increasing salt content.

The maximum possible removal rates of the systems for BOD and SS were estimated as 37 $g/m^2 \cdot d$ and 500 $g/m^2 \cdot d$, respectively, showing high removal potentials in comparison to other types of constructed wetlands. This also indicates that the applied loading rates in the present study did not reach their maximum.

Removal performance for BOD and SS was mainly controlled by operational condition such as loading rates rather than filter compositions. The presence of macrophytes and Filteralite in selected filters did not result in an obvious reduction of BOD and SS. Moreover, macrophytes gave a negative impact on the BOD removal processes in the present study, even though macrophytes provided good filtration conditions by preventing the filter from clogging. Artificial aeration improved the BOD removal efficiencies in the new filter systems, whereas its effect was not apparent in the matured systems.

Chapter 5   Nutrient removal performance

5.1. Introduction

Nutrient removal performance of the temporarily flooded system is assessed and their removal mechanisms are also investigated in this chapter. As demonstrated in Chapter 4 for BOD and SS, nutrient removal efficiencies of wetland filters in terms of areal mass loading and removal are evaluated. A simple first-order model is also applied to estimate the potential for nutrient removal.

Statistical models using multiple linear regression analysis and the SOM model were used to assess the effect of influent water quality, and the main mechanism of nutrient removal was identified. Wilcoxon signed-rank analysis was carried out to investigate the role of macrophytes and filter media in the nutrient removal processes. Furthermore, the contributions of macrophytes to the nutrient removal were quantified by measuring the nutrient content in the harvested macrophytes.

5.2. Nitrogen removal

5.2.1. Removal performance

Figure 5-1 shows the effluent nitrate-N and ammonia-N concentrations in Filter 8. The ammonia-N concentrations were relatively high in the winter season, but significantly decreased over time. This reflects a temperature dependence of N removal performance and increased nutrient release from decaying macrophyte material during the winter. Similar seasonal variations of N removal were reported elsewhere (Werker *et al.*, 2002).
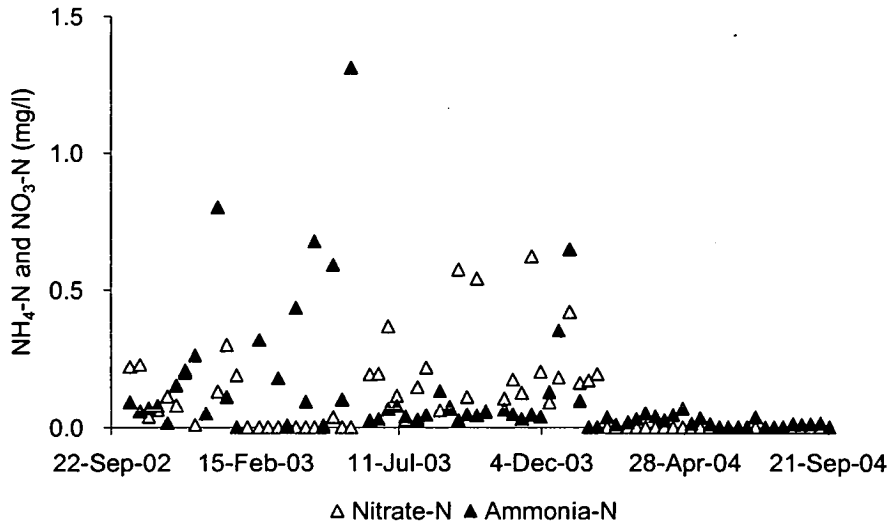
Figure 5-1. Effluent nitrate-nitrogen and ammonia- nitrogen concentrations in Filter 8. Outliers (3.541, 7-Feb-03; 3.541, 28 Feb-03) are not shown.

As given in Figure 5-2, mass inflows of ammonia-N were highly variable throughout two years. Mass outflows of ammonia-N were relatively high in winter, but decreased considerably over time, showing a stable performance for ammonia-N removal during the second year.

Mass outflows of nitrate-N were relatively low and stable in the planted system (Filter 8), showing high removal potential of temporarily flooded systems for nitrate-N removal (Figure 5-3).
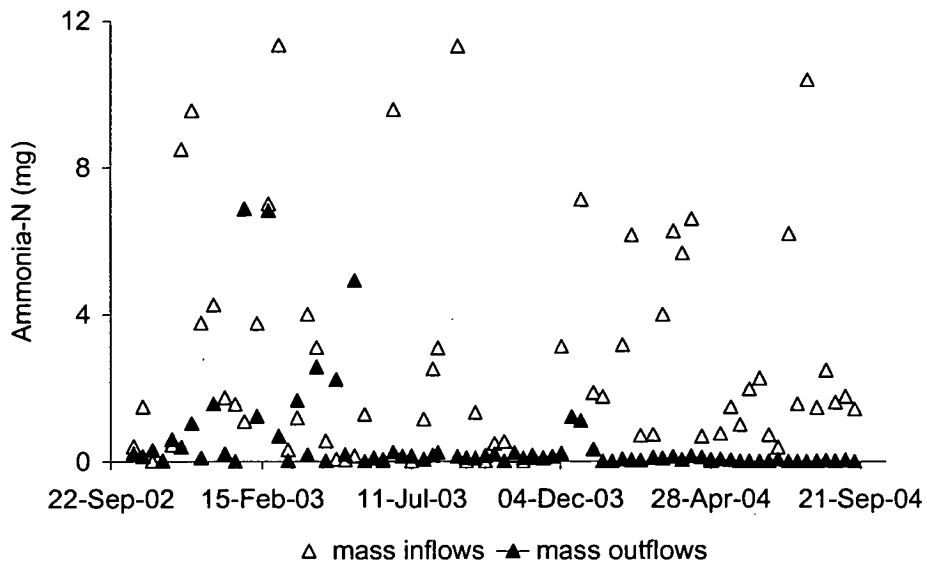
Figure 5-2. Mass inflows and outflows of ammonia- nitrogen in Filter 8. Outlier (25.8, 15- Dec-03) is not shown.
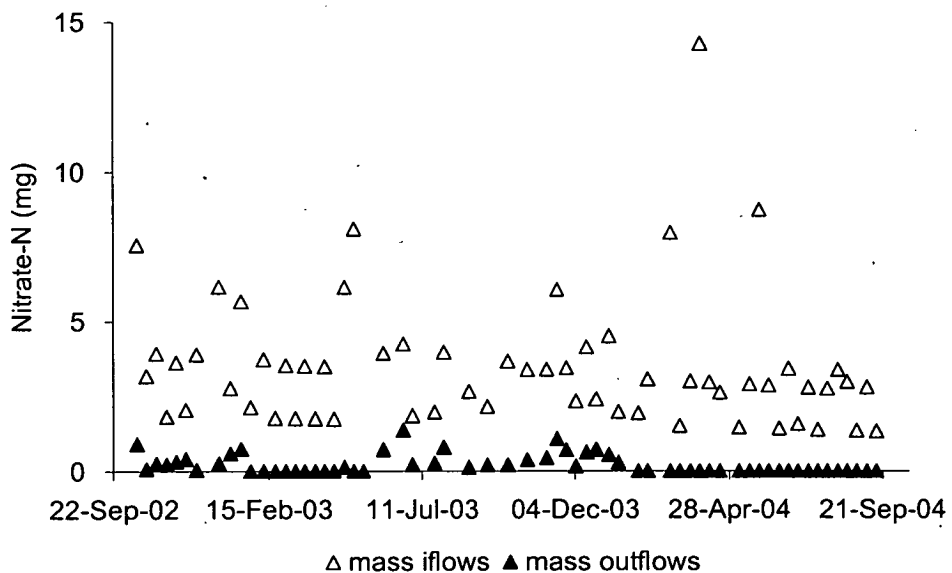
Figure 5-3. Mass inflows and outflows of nitrate- nitrogen in Filter 8. Outlier (21, 16-May-03) is not shown.

Average loading rate of ammonia-N for Filter 8 was 0.105 $g/m^2 \cdot d$ ranging 0.000-0.906 $g/m^2 \cdot d$ during the fist year. Corresponding mass removal rate was 0.082,

resulting in reduction rate of 78.7 % (Table 5-1). Loading and removal rate of nitrate-N in Filter 8 was 0.106 and 0.099, respectively during the same period.

Ammonia-N reduction efficiencies for planted filters (Filter 8) were always higher than for comparable unplanted filters (Filter 7). Furthermore, nitrate-N reduction efficiencies for planted filters were much higher than those for unplanted filters. In particular, the nitrate-N concentrations increased through the treatment process in unplanted system during the second year (Filter 7).

Table 5-1. Mass loading and removal rates of ammonia-nitrogen and nitrate-nitrogen

Filter Number	First year			Second year		
	Loading $(g/m^2 \cdot d)$	Removal[a] $(g/m^2 \cdot d)$	Reduction rate (%)	Loading $(g/m^2 \cdot d)$	Removal[a] $(g/m^2 \cdot d)$	Reduction rate (%)
Ammonia-N						
7	0.111	0.052	46.9	0.085	0.070	81.7
8	0.105	0.082	78.7	0.081	0.077	95.8
12	0.310	0.214	69.0	0.230	0.170	73.8
Nitrate-N						
7	0.110	0.029	26.6	0.093	-0.039	-41.7
8	0.106	0.099	93.7	0.088	0.084	95.5
12	0.270	0.199	73.7	0.222	0.179	80.6

[a](in – out)/area · retention time, where in = mass inflow, out = mass outflows

As plotted in Figure 5-4 and Figure 5-5, there is a linear relationship between the loading and removal rate of ammonia-N in both filters. Higher removal rate and more consistent removal performance in Filter 8 were observed, compared to Filter 7. However, the reduced gradient (= 0.82) of regression line of Filter 12, compared to that (= 0.96) of Filter 8, implies that ammonia–N removal performance of the system becomes degraded at given higher loading rates (Figure 5-5).
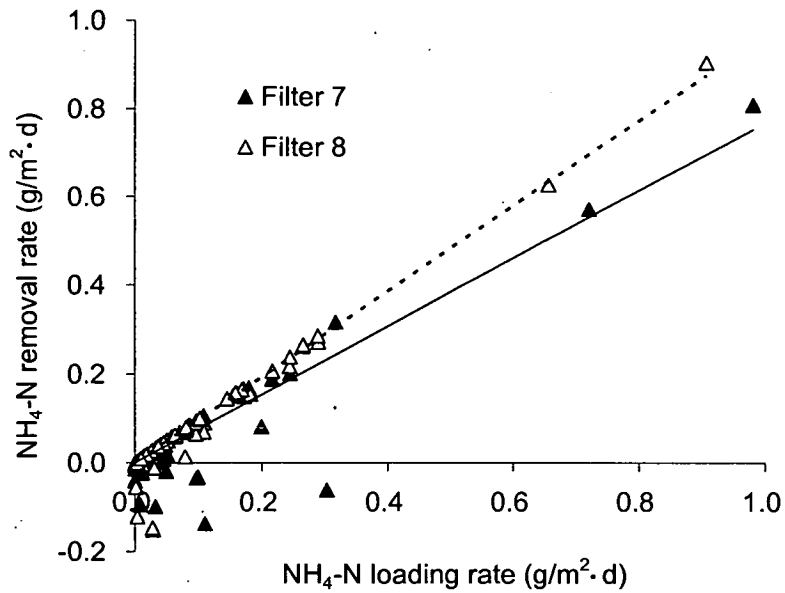
Figure 5-4. Mass loading and removal rates of ammonia-nitrogen in Filters 7 and 8
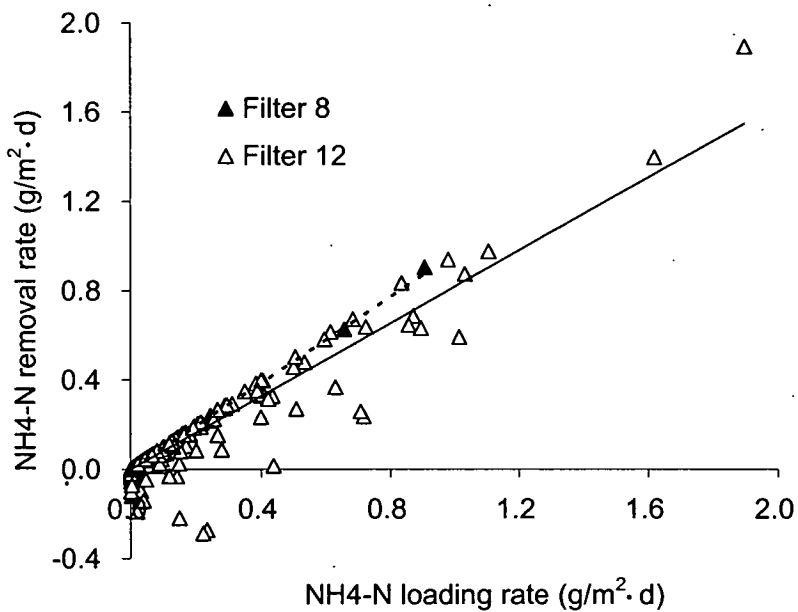
Figure 5-5. Mass loading and removal rates of ammonia-nitrogen in Filters 8 and 12

Regarding mass loading and removal rates of nitrate-N, linear relationship between both rates was not shown in Filter 7, whereas both rates were linearly

related in Filter 8 (Figure 5-6). This suggests that the unplanted system was not capable of reacting efficiently to influent nitrate-N loading.
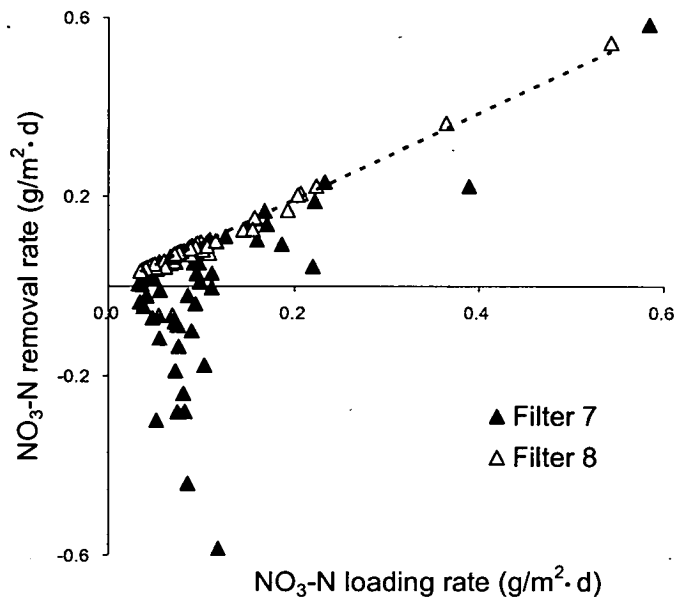
Figure 5-6. Mass loading and removal rates of nitrate-nitrogen in Filters 7 and 8.

A Wilcoxon signed-rank analysis for effluent N concentrations also confirmed the · result of comparison of removal rates for planted and unplanted systems (Table 5-1, Figure 5-4 and Figure 5-6). All p values between unplanted (Filter 7) and planted (Filter 8) system are 0.00 for ammonia-N and nitrate-N, suggesting that effluent N concentrations in planted system were apparently lower than those of unplanted system.

5.2.2. Removal model

First-order removal model. As demonstrated in sections 4.5.2 and 4.6.2, the rates of ammonia-N and nitrate-N removal are evaluated using the first-order removal equation. The average k_N value for Ammonia-N removal was 0.355 (m/d), showing

the maximum value of 0.907 (m/d) during the second year in Filter 12 (Table 5-2). This value is much higher, compared to k of 0.049 (m/d) in SF system and 0.093 (m/d) in SSF system reported by Kedlec and Knight (1996), 0.027 (m/d) obtained from LWDB (Knight *et al.*, 2000) and k_{TN} of 0.028 in Czech SSF systems (IWA, 2000).

In the case of nitrate-N removal rates, the average k_N value of Filter 12 was 0.837 (m/d) during the second year, showing higher value than 0.164 (m/d) described by Kadlec and Knight (1996). This result suggests that temporarily flooded and planted systems were highly efficient for N removal.

In particular, the k_N values in the second year were significantly higher than those in the first year. This is likely due to increased pH of influents during the second year. Such a pH impact on the ammonia-N removal is discussed in detail in section 5.2.3.

Table 5-2. Removal rate constants of ammonia-nitrogen and nitrate-nitrogen

Filter Number	k_N (m/d)	
	First year	Second year
Ammonia-N		
7	0.071	0.143
8	0.120	0.262
12	0.264	0.355
Nitrate-N		
7	0.205	0.050
8	0.366	0.428
12	0.616	0.837

The theta ($= \theta$) values of Filter 8 and 12 were 1.01 and 1.05 respectively, for both ammonia-N and nitrate-N, indicating that higher temperature enhanced the activities of nitrifying bacteria and subsequently increased a removal rate of ammonia-N (Table 5-3).

Table 5-3 Temperature factor and k_{20} values

	θ	k_{20}
Ammonia-N		
8	1.01	0.578
12	1.05	0.652
Nitrate-N		
8	1.01	0.674
12	1.05	0.893

Furthermore, high theta ($=\theta$) value of Filter 12 indicates that temperature had great effect on the removal performance in the highly loaded system. Such a temperature dependence for ammonia and nitrate-N removal ($\theta = 1.05$) were also reported in previous researches (Kedlec and Knight, 1996; Knight *et al.*, 2000).

Statistical models. The main presumptions for using the first-order model are that k-values do not depend on the hydraulic loading rate and influent concentrations, and that plug flow is a reasonable approximation of the hydraulic conditions in the wetlands. However, these presumptions are not valid for temporarily flooded system, as discussed in section 4.5.2.

Statistical models for ammonia-N reduction can be an alternative way to the first-order model. These models are capable of predicting reduction rate, as well as explaining factors important for reduction (Braskerud, 2002), as demonstrated in section 4.6.3. Multiple linear regression analysis was carried out as statistical models, including hydraulic loading rate and influent water quality variables such as ammonia-N and nitrate-N concentrations, temperature, conductivity, pH, DO and redox. As a result, influent ammonia-N concentration, conductivity and temperature were selected as the optimal regressors (Table 5-4).

Table 5-4. Statistical models for ammonia-nitrogen reductions

Filter Number	Regression Equation[a]	R^2
7	$C_e = 0.185C_i + 4.18*10^{-5}CON - 0.052Temp$	0.38
8	$C_e = 3.00*10^{-5}CON$	0.15
12	$C_e = 0.145C_i + 4.53*10^{-5}CON - 0.035Temp$	0.52

[a] C_e = effluent ammonia-N concentration, C_i = influent ammonia-N concentration, CON = influent conductivity, Temp = influent water temperature

As given in Table 5-4, ammonia-N concentrations were increased with increasing conductivity. This is attributed to an adverse effect of salt on the microorganisms. Such a salt inhibition effect on nutrient removal was reported in previous studies. Uygur and Kargi (2004) found that ammonia-N removal efficiency decreased from 96 % to 39 % when salt content increased form 0 to 6 % in sequencing batch reactor.

As expected, the ammonia-N concentrations are likely to decrease under high temperature conditions. The effect of temperature on the N removal performance was quantified by estimating the theta value (Table 5-3). Tseng and Wu (2004) also derived the following equations which indicate that the ammonia removal rates of biofilters are positively affected by temperature and influent ammonia concentration but negatively by SS in an exponential manner in the submerged biofilter experiment.

$$SNR = 165.75T^{0.228}SS^{-16}TAN^{0.71} \quad (R^2 = 0.95) \qquad\qquad 5-1$$

Where:

SNR = Specific ammonia removal rate (mg TAN/m^2/d)

T = Influent water temperature

SS = Influent suspended solids concentrations (mg/l)

TAN = Influent total ammonia concentrations (mg/l)

The hydraulic loading rate was not selected, suggesting that hydraulic loading had no significant influence on the performance of ammonia-N removal (Table 5-4). This result contradicts the first-order model theory that N reduction decreases as the hydraulic loading increases. Little impact of hydraulic loading on the N reduction is probably due to the low hydraulic loading rate for detecting statistically significant effects in the present system.

Similarly, Braskerud (2002) reported no significant effect of hydraulic load on the N reduction, introducing the following statistical model for N retention derived from SF constructed wetlands in the cold climate:

$$C_e = 0.008 + 0.93C_i \qquad\qquad 5\text{-}2$$

Contradicting results were produced by Kadlec and Knight (1996) and Knight *et al.* (2000) in SF wetlands systems;

$$C_e = 0.336C_i^{0.728}q^{0.745} \quad (R^2 = 0.44) \qquad\qquad 5\text{-}3$$

$$C_e = 0.682C_i^{0.874}q^{0.319} \quad (R^2 = 0.87) \qquad\qquad 5\text{-}4$$

The low value of R^2 (= 0.15) of Filter 8 indicates that input information is unable to sufficiently account for the degree of N removal. This is partially attributed to lack of information on organic and total N changes. Nevertheless, considering the relatively high R^2 value of Filter 7 compared to Filter 8, it can be concluded that N removal performance of unplanted systems was more susceptible to influent water quality than that of planted systems. In addition, the relatively high R^2 (= 0.50) value of Filter 12 implies that N removal performance of a highly loaded system (Filter 12) was more affected by influent water quality than that of other systems (Filters 7 and 8).

The relationship between ammonia-N concentration and other variables are also presented in the SOM map organized by performance data from Filter 12 (Figure 5-7). High effluent ammonia-N concentrations (> 1.4 mg/l) are apparently linked to high conductivity (> 17,300 μS), high influent concentrations (> 4.2 mg/l), and low temperature (< 10 °C).
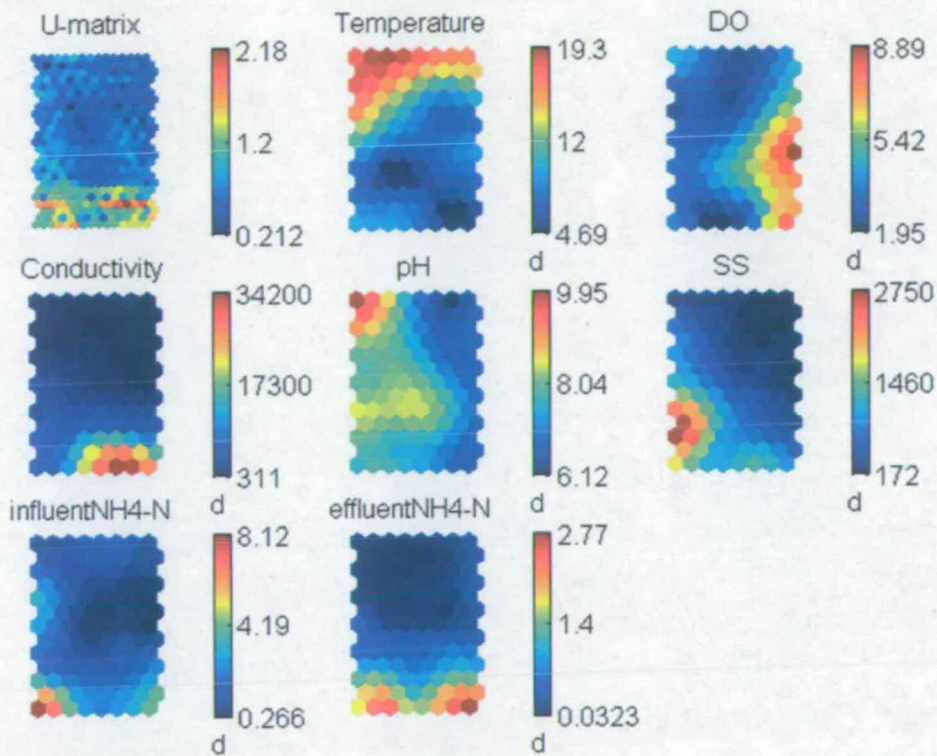
Figure 5-7. Visualization of relationship between influent water quality indicators and effluent ammonia-nitrogen concentrations in Filter 12.

In the case of regression analysis for nitrate-N removal, Temperature and influent ammonia-N were selected as significant regressors (regression equation is not shown). However, R^2 value (= 0.09) of this regression equation is extremely low. Further investigation on the N-species change including organic N is needed to modify this model. Contrary to the SOM map of ammonia-N, the SOM map organized with nitrate-N data sets did not present any apparent relationships between

effluent nitrate-N concentration and influent water quality indictors (Figure 5-8).
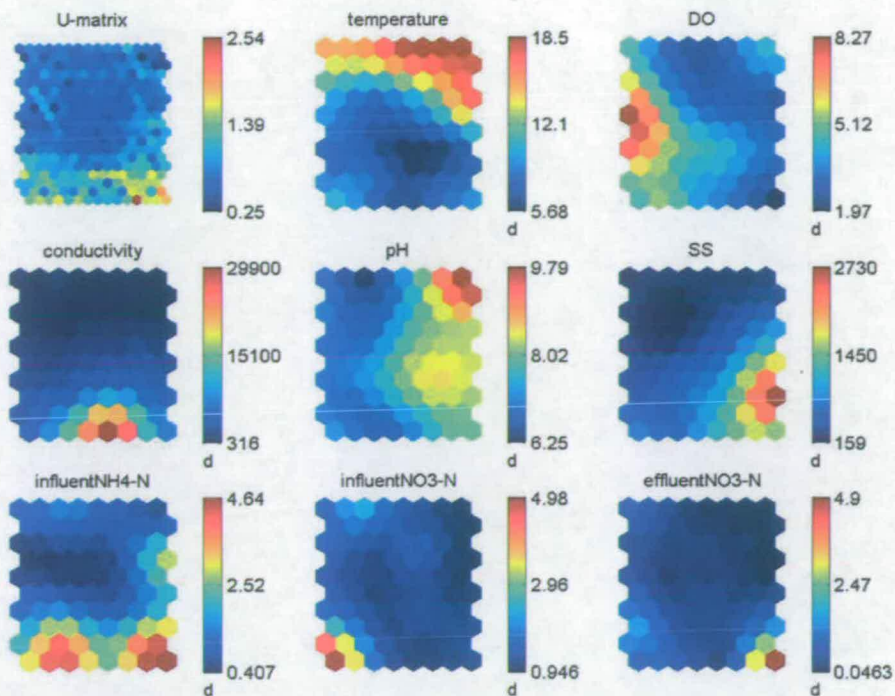
Figure 5-8. Visualization of relationship between influent water quality indicators and effluent nitrate-nitrogen concentrations in Filter 12.

5.2.3. Mechanism of nitrogen removal

Main removal mechanism. It is well known that microbial nitrification and denitrification are the main removal processes in most constructed wetlands, as proven in previous studies (Green *et al*., 1998; Kedlec and Knight, 1996). Nitrification, the conversion of ammonium-N to nitrate-N, is important because *P. australis* takes up nitrate-N preferentially to ammonia-N. The uptake capacity of macrophytes is roughly in the range 20 to 250 g/m^2/year and this amount can be removed if the biomass is harvested (Brix, 1994).

Immobilization into microbial cells is also major process of ammonia-N removal in the constructed wetlands, because a large amount of organic matter is removed by

growth of microorganisms in wetlands system. 0.074 g ammonia-N can be immobilized for 1 g BOD removal by biomass assimilation (Sun *et al.*, 2005).

The temporarily flooded (intermittently loaded) vertical-flow system is known to be efficient in providing oxygen for nitrifying bacteria. Intermittent loading facilitates oxygen transfer by drawing the water table down periodically to allow oxygen to penetrate into the deeper zones of the filters. Furthermore, air pipes were installed to ventilate the lower media layer in the present system. Oxygenation in intermittently loaded vertical-flow system increases several fold over that in horizontal SSF systems, resulting in efficient nitrification process (Green *et al.*, 1998).

In addition to that, it is well documented that macrophytes release oxygen from roots into the rhizosphere and this oxygen leakage stimulates growth of nitrifying bacteria (Brix, 1997). Thus, in the present system, considering higher removal rates of N in the planted systems compared to unplanted systems, it can be concluded that oxygen release and N uptake by macrophytes significantly contributed to N removal (Table 5-1).

Denitrification is the process in which nitrate-N is reduced to gaseous N (data were not collected). This transformation is supported by facultative anaerobes. These organisms are capable of breaking down oxygen-containing compounds such as nitrate-N to obtain oxygen in an anoxic environment that is dominant during the long periods of filter flooding. This anoxic condition was periodically provided by temporarily flooding in this system.

Ammonification, the conversion of organic N to ammonia-N, is slower in

anaerobic than in aerobic soils due to the reduced efficiency of heterotrophic decomposition in anaerobic environments. Therefore, it can be inferred the ammonification process was also facilitated by increased oxygenation in the temporarily flooded system. Moreover, Filters 11 and 12 were aerated.

In contrast, N removal performance of SSF constructed wetlands treating ammonia-rich wastewater is often relatively poor (IWA, 2000). Neralla *et al.* (2000) also reported that 40% of ammonia-N was reduced, indicating that nitrification was not active in SSF system.

Sun *et al.* (2005) also found that less than 10 % of ammonia-N was removed due to the nitrification in tidal-flow system treating high loads of wastewater. It is believed that high loads of organic matter may have inhibited the nitrification process because oxygen is primarily used by heterotrophic microbes to remove organic matter and significant nitrification can not take place until BOD drops to 200mg/l or below (Korkusuz *et al.*, 2005; Su and Ouyang, 1996).

However, in the present study, nitrification is considered as a major mechanism of N removal. This is supported by the fact that nitrate-N concentration increased concurrently when effluent ammonia-N concentration significantly decreased in the unplanted filter during the summer (Figure 5-9). Furthermore, influent BOD concentrations (61-90 mg/l) were not so high as to inhibit the nitrification process.
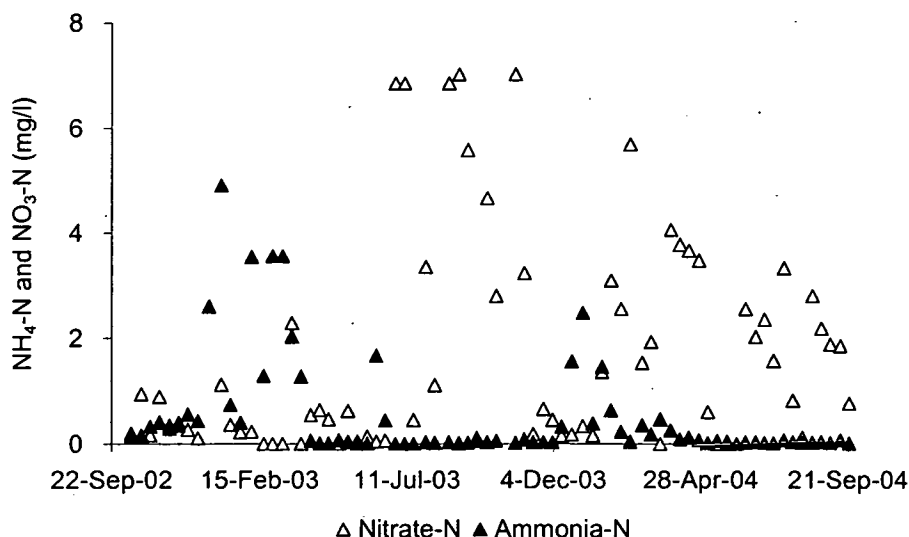
Figure 5-9. Effluent nitrate-nitrogen and ammonia-nitrogen concentrations in Filter 7

Table 5-5 presents the mass balance for ammonia-N in Filter 7 during the second year. Removal amount of ammonia-N by nitrification was estimated by the net increase of nitrate-N in the process. The considerable amount (= 112 mg) of ammonia-N removed by nitrification, indicates that nitrification significantly contributed to ammonia-N removal. Furthermore, considering that the nitrate-N could be removed by other processes such as denitrification, removal percentage by the nitrification may be higher than that (= 46 %) estimated in the present study. Other processes such as plant uptake, adsorption and biomass assimilation explain 36 % of ammonia-N removal.

Table 5-5. Mass balance for ammonia-nitrogen in Filter 7

	Total loads	exports	Removal by nitrification	Removal by other process
Ammonia-N (mg)	244	43 (18 %)	112 (46 %)	89 (36 %)

However, the further analysis for total N and total Kjeldahl N are needed to quantify the mass transformation of N and to identify the exact mechanism of N

removal in the constructed wetlands. N removal by plant uptake is further discussed in the following sections.

Role of macrophytes and filter media. The contribution by macrophytes also could be considered significant as plant uptake and oxygen transfer increased by the root system were likely to improve the reduction of ammonia-N. This explains the higher reduction of ammonia-N for planted (79 - 96%) filters in comparison to those of unplanted (47 - 82%) filters (Table 5-1). Furthermore, considering the difference of removal rates of nitrate-N for planted (94–96 %) and unplanted (-42-27 %) system (Table 5-1), macrophytes were likely to play a key role in removing nitrate-N.

Ammonia-N originates from decomposed macrophytes such as *P. australis* and animals such as bacteria and protozoa. It was therefore important to harvest *P. australis* in autumn. Macrophytes were harvested three times during the operation periods, each time at the end of autumn. Dry weights of the macrophytes were determined for all planted filters (Table 5-6). These data show that the dry weights for all filters increased consistently. The amount of nutrients removed through harvesting is therefore likely to have increased as well.

Table 5-6. Weight of macrophytes for all planted filters

Filter Numbers	Dry weight (g)		
	2002	2003	2004
4	8.0	20.6	23.8
6	4.7	23.9	32.2
8	1.0	28.5	29.6
10	1.1	21.7	48.4
11	1.5	19.5	40.2
12	6.0	23.5	33.3

Amounts of total N removed by harvesting macrophytes were estimated. These values were calculated from the concentration of total N and weight of harvested macrophytes in November of 2004. Amounts of total N accumulated in stem and leaf of macrophytes were 88.7, 79.4, 81.0, 139.3, 130.6 and 120.0 mg for Filters 4, 6, 8, 10, 11 and 12, respectively. Considering the total removed amount of ammonia-N (221 mg) and nitrate-N (241 mg) in Filter 8 during the second year, substantial amount (17.5 %) of N could be removed by harvest.

With respect to the pH effect on growth of macrophytes, considering the macrophyte biomass harvested in 2004, high pH is unlikely to inhibit the growth of macrophytes. Furthermore, the filters loaded with heavy metal contaminated water produced more macrophyte biomass, indicating that development of macrophytes was not inhibited when exposed to high concentration of metals (Table 5-6), which is agreed with previous researches (Ye et al., 2003; McCabe et al., 2001). Considering the systematic and stratified experimental set-up, there seems to be no logical explanation for obvious differences in macrophyte biomass (except for the possibility of random variation).

According to previous findings (Cooper et al., 1996), the maximum salinity tolerance value for P. australis is about 45 g/l. Considering that the measured conductivity and TS inflow values are approximately 5.1 mS and 3.0 g/l (Table 4-1), respectively, the presence of salts should not significantly affect the macrophyte development negatively.

To investigate the effect of filter media on the N removal, the Wilcoxon signed-rank analysis between different filter media was carried out (Table 5-7). P values, higher than 0.05, indicates that expensive filter media such as Filteralite did not

contribute significantly to the nutrient reduction. The p values between Filters 3 and 5, and Filters 8 and 10 suggest that additional filter media still degraded the filtration performance of filters. Higher ammonia-N concentration in Filters 5 and 10 is likely attributed to barley straw, which was added to improve heavy metal removal performance of filters.

Table 5-7. Comparisons of effluent nitrogen concentrations for different filter media.

Filter Number	Wilcoxon p values	
	Ammonia-N	Nitrate-N
3 and 5	0.02	0.17
4 and 6	0.57	0.96
7 and 9	0.50	0.10
8 and 10	0.00	0.08

Data collected from 21-Sep-02 to 27-Feb-03 were used.

P value (= 0.04) for ammonia-N between Filters 10 (without aeration) and 11 (with aeration) indicates that artificial aeration facilitated nitrification, resulting in lowering ammonia-N concentration of Filter 11.

Ammonia-nitrogen removal and pH. Figure 5-10 illustrates the changes of the influent and effluent pH for planted and unplanted system. The pH of the outflow is relatively constant for all filters. All filters acted as pH buffers during operation periods. Therefore, it can be stated that the buffering capacity of the system was greatly enhanced by the presence of active biomass rather than macrophytes. The buffering capacity is slightly lower for the simple filters (1 and 2, data not shown) in comparison to other filters, suggesting that more complex filters have a better ability to buffer the pH because they have higher amount of active biomass.
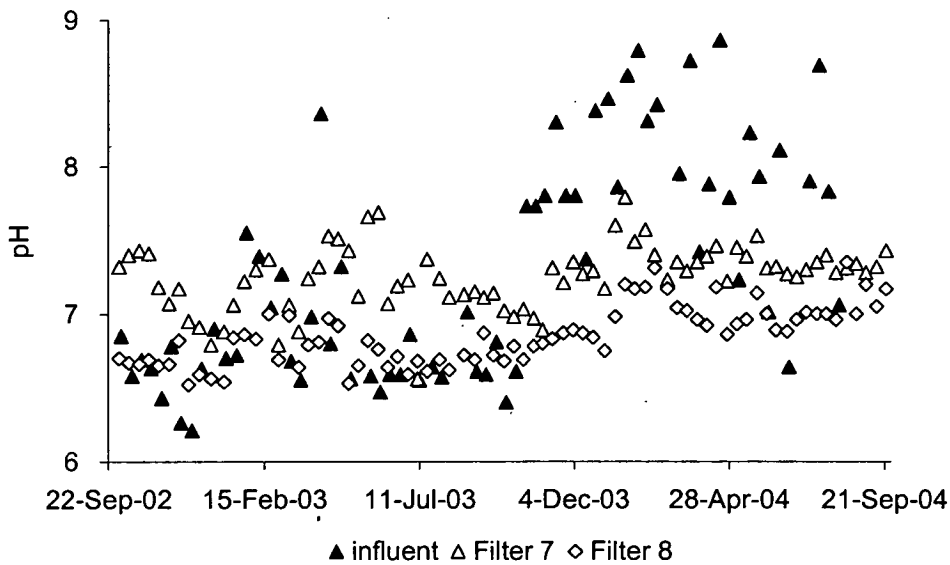
Figure 5-10. Changes of influent and effluent pH in filters 7 and 8

The effluent pH values for the planted filters were recorded slightly lower than those for the unplanted filters. The effluent pH levels decreased, since the pH of the inflow was artificially raised (Figure 5-10).

The conversion of ammonium to nitrite results in the formation of hydrogen ions (Equation 5-5), and subsequently, the hydrogen ions are neutralized by bicarbonate ions during the nitrification process (Equation 5-6). Both a decrease in bicarbonate alkalinity and an increase in the carbon dioxide lower the pH. Theoretically, 7.2 mg of alkalinity (as $CaCO_3$) are required to neutralize the hydrogen ions produced by the oxidation of 1 mg of ammonia-N to nitrite. Thus, low pH can significantly reduce the rate of nitrification. Below a pH of 7.2, the rate falls precipitously, approaching zero at a pH 6 (Tchobanoglous et al., 2003; Rich, 2005).

$$NH_4^+ + 1.5O_2 \rightarrow 2H^+ + H_2O + NO_2^- \qquad \text{5-5}$$

$$H^+ + HCO_3^- \rightarrow CO_2 + H_2O \qquad \text{5-6}$$

105

From this point of view, it can be inferred that addition of sodium hydroxide during the second year functioned as supplemental alkalinity to facilitate the nitrification process in the wetland system. This is supported by the fact that the ammonia-N removal rate constant (= 0.262 m/d) of the second year is higher, compared to those (= 0.120 m/d) of first year in Filter 8 (Table 5-2).

The lower pH level in planted systems is likely due to more active nitrification process compared to unplanted systems (Table 4-2). In addition, plants utilize N and can contribute to lower pH through respiration and litter decomposition processes (Collins *et al.*, 2004). A similar relation between pH change and N removal was observed by Sun *et al.* (2003).

Addition of excessive nitrate. With the addition of copper nitrate in the autumn 2004, 1.95g nitrate was added to Filter 3. Figure 5-11 shows the effluent nitrate-N values of Filters 3, 7 and 8. There is no sign of breakthrough of nitrate in Filter 3, compared to Filters 7 and 8 (Figure 5-11), showing a great nitrate-N removal potential of the present system.
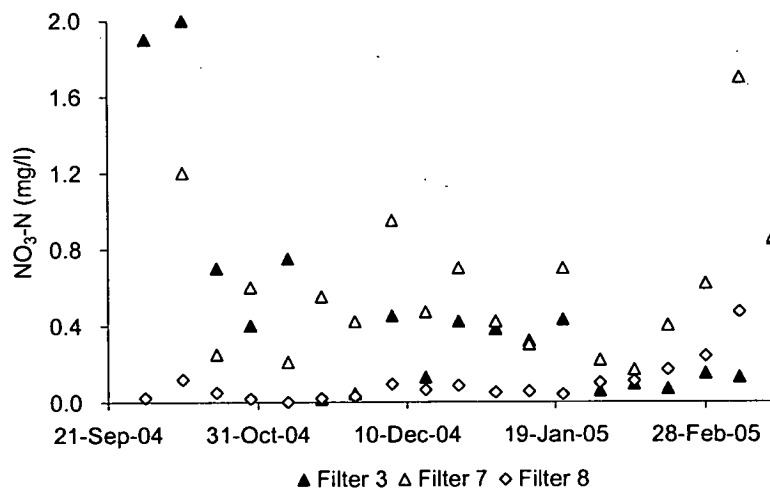
Figure 5-11. Effluent nitrate-N concentrations in Filters 3, 7 and 8

However, the exact mechanism is still unclear. More investigation is needed to determine the longevity of wetlands in terms of nutrient treatment.

5.3. Phosphorus removal

5.3.1. Removal performance

Figure 5-12 and Figure 5-13 present the outflows of phosphate-P in terms of concentration and mass loads, respectively. Effluent P concentrations were satisfactory compared to the P limit (= 1mg/l) of the national pollutant discharge elimination system (NPDES) by US EPA. Phosphate-P concentrations and mass outflows were relatively high during spring, even though mass inflows were randomly distributed throughout the two years.
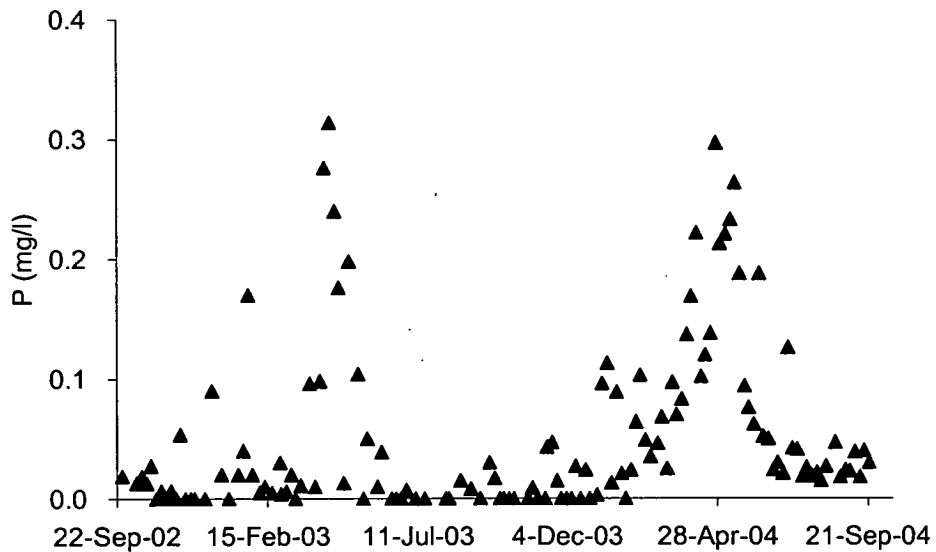
Figure 5-12. Effluent phosphorus concentrations in Filter 12. Outlier (0.530, 22-Oct-03) is not shown.
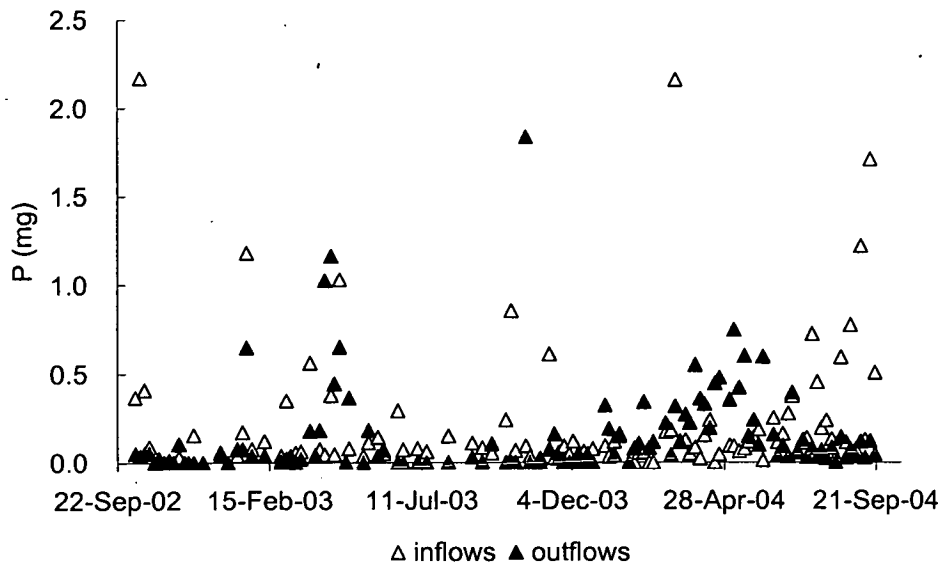
Figure 5-13. Mass inflows and outflows of phosphorus in Filter 12

Figure 5-14 presents the average seasonal mass inflows and outflows of the system in Filter 12. Mass outflows of P increased through filtration process during the spring in both years, implying that nutrient release increased due to the decaying macrophyte debris which was retained in the system during the previous season. Higher outflow of TP during spring compared to other seasons was also reported by Tanner et al. (2005) and Braskerud (2002).

Table 5-8 presents the annual mass loading, mass removal and corresponding reduction rate. Reduction rates for planted filters (Filter 8) were higher than those for comparable unplanted filters (Filter 7), indicating that the contribution of macrophytes to P removal was considerable in the present system. This result is also supported by wilcoxon p value (= 0.00) for effluent P concentrations between Filters 7 and 8, particularly during second year.
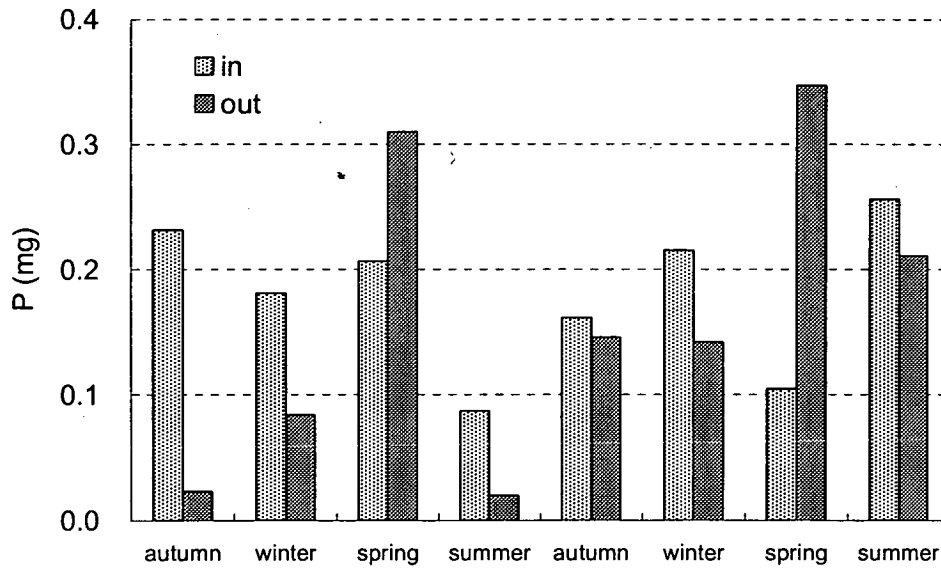
Figure 5-14. Seasonal comparison of phosphorus mass balance in Filter 12

Table 5-8. Mass loading rate and removal rate of phosphorus

Filter Number	First year			Second year		
	Loading $(g/m^2 \cdot d)$	Removal[a] $(g/m^2 \cdot d)$	Reduction rate (%)	Loading $(g/m^2 \cdot d)$	Removal[a] $(g/m^2 \cdot d)$	Reduction rate (%)
7	0.006	0.002	32.9	0.005	-0.002	-29.7
8	0.006	0.003	48.7	0.005	0.003	51.6
12	0.012	0.005	37.5	0.014	0.003	21.9

[a](in – out)/area · retention time, where in = mass inflow, out = mass outflows

The average k_P values of first-order model were calculated to evaluate P removal efficiencies of the systems. The k_P values of Filters 8 and 12 were 0.025 and 0.151, respectively during the two years. As a comparison, Carleton et al., (2001) estimated k values of -0.011 to 0.210 m/d in the US stormwater treatment wetlands and the IWA specialist group (2000) reported the k values of 0.027 m/d for non-forested wetlands.

5.3.2. Role of macrophytes and filter media

Amounts of total P in the aboveground tissues of macrophytes were given in Table 5-9. P amounts of harvested macrophytes in Filter 8 were 7.0 and 6.4 mg during first and second year, respectively. Corresponding annual loads of phosphate-P were 9.1 and 14.2 mg. Considering their P loads, it is evident that harvesting macrophytes is a good source of P removal in this system. Lantzke *et al.* (1999) also found that planted vertical-flow wetlands reduced TP concentrations (> 90 %), storing most of the influent TP in plants (70 %), gravel (20 %) and biofilm (10%).

Table 5-9. Amounts of phosphorus removed by harvest

	P (mg)					
Filter Number	4	6	8	10	11	12
First year	2.8	3.2	7.0	3.4	2.6	14.3
Second year	8.3	7.4	6.4	11.4	8.3	8.7

The Wilcoxon signed-rank analysis p values between different filter media are presented in Table 5-10, to assess the role of filter media in the P removal. There have been several researches which reported high P adsorption capacity of Filtralite (Mæhlum and Stlnacke, 1999; Johanssen, 2006). Particularly, Zhu *et al.* (1997) showed that Norwegian Filtralite has P adsorption capacity of 1390 mg P/kg.

Table 5-10. Comparison of effluent phosphorus concentrations for different filter media

Filter Number	Wilcoxon p value
3 and 5	0.25
4 and 6	1.00
7 and 9	0.84
8 and 10	0.94

Data collected from 21-Sep-02 to 27-Feb-03 were used.

However, all p values of each pair of filters are higher than 0.05, indicating that

there is little difference in P removal performance between sand-gravel based filters and Filteralite based filters. Considering the influence of macrophytes on the P removal (see above), macrophytes are a more crucial factor than filter media to control P removal in this experimental system.

5.3.3. Factors affecting phosphorus removal

The relationships between effluent P concentrations and other influent water quality variables are illustrated in the SOM map created with performance data from Filter 12 (Figure 5-15).
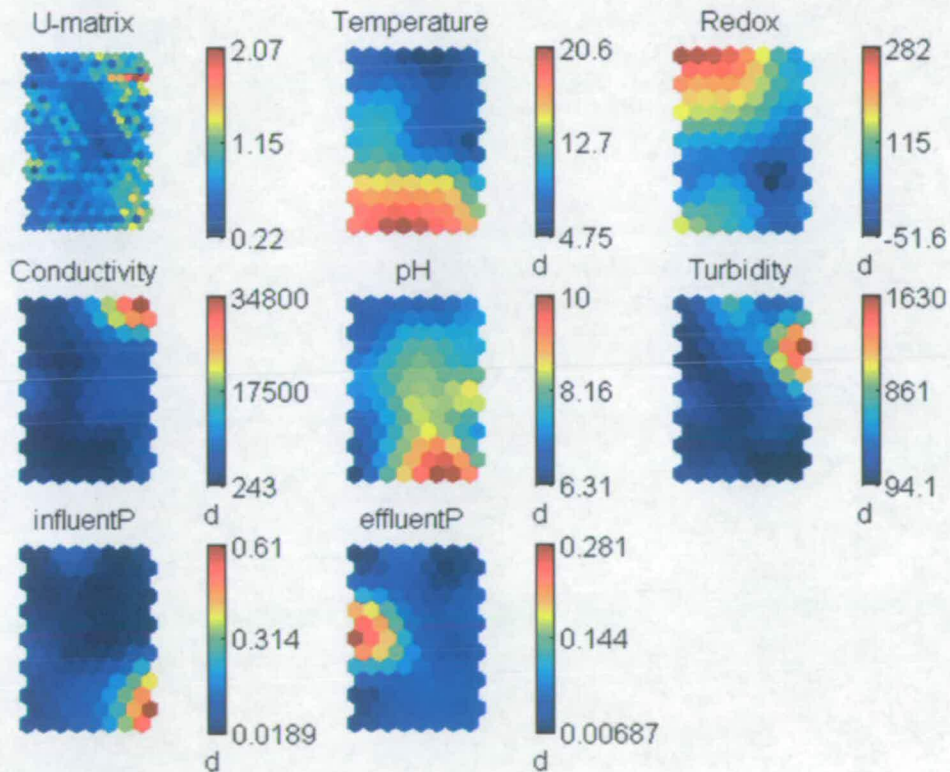
Figure 5-15. Visualization of relationship between influent water quality indicators and effluent phosphorus concentrations in Filter 12.

High effluent P concentrations are not shown to link to other variables such as conductivity, pH and temperature, indicating that P removal performance was not significantly controlled by the temperature and conductivity, unlike the case of the

ammonia-N removal.

It is known that high salt concentrations are likely to inhibit the activity of microorganisms. Abu-ghararah and Sherrard (1993) also observed a decreased P removal percentage in the treatment of high salinity wastewater. Therefore, little impact of high salt concentrations on the P removal performance implies that the role of microorganisms in the P removal processes was not considerable in the present system. This is consistent with fact that the macrophytes significantly contributed to P removal processes rather than biofilm (see above).

5.4. Summary

This chapter has demonstrated that temporarily flooded vertical-flow wetlands outperformed other types of wetland systems in terms of nutrient removal. Temporarily flooded systems were highly efficient for oxygen supply into system, and consequently nitrification (> 46 % of removed ammonia-N) was found to be the predominant removal mechanism of ammonia-N in the present system.

The N removal performance of planted systems was relatively stable throughout the seasons particularly after the systems were matured, whereas the performance of unplanted systems was significantly affected by the variations of conductivity and temperature. This is attributed to the adverse effect of salt and positive effect of temperature on the activity of nitrifying bacteria. The macrophytes were found to contribute significantly to N removal processes as plant uptake and oxygen transfer through root systems improved greatly the N removal efficiency. Furthermore, substantial amount (17.5 %) of N was removed by harvesting macrophytes in the present system.

The effluent pH levels decreased consistently, since the pH of the inflow was artificially raised, indicating that wetland filters had a great buffer capacity for pH. The elevated pH contributed significantly to improve the ammonia-N removal performance of wetland filters.

P removal performance was not improved by special filter media such as Filtralite, suggesting that adsorption to media is not a main source of P removal in the present system. Instead, macrophytes were proven to be a more crucial factor than filter media to control P removal. Harvest was also a good source of P removal.

Chapter 6   Heavy metal removal performance

6.1. Introduction

This chapter assesses heavy metal removal performance of the temporarily flooded system and investigates the mechanisms of the removal process. Metal removal efficiencies and removal potentials of the wetland filters are evaluated. The impact of water quality on the metal removal performance is assessed by applying multiple linear regression analysis and the SOM model. In particular, the effect of salt and pH on the metal removal was considered in detail.

The role of macrophytes and filter media is also examined by comparing the performance of each filter, as demonstrated in Chapter 4 and Chapter 5. In addition, ochre pellet is tested to investigate its metal removal potential. Excessively loaded filters with Cu (= 1g) are monitored to determine retention potential for Cu and investigate the fate of Cu in the long-term.

6.2. Removal performance

Figure 6-1 and Table 6-1 show the effluent Ni and Cu concentrations during two years. The breakthrough of Ni was apparent during the first winter, whereas Cu concentrations were consistently low throughout the two years. However, the Cu concentrations in the second year were slightly higher than those in the first year. In comparison to the discharge limit (Ni: 0.0071 mg/l, Cu: 0.0049 mg/l) in secondary effluent of the US EPA, both metal concentrations were over their thresholds

114

(Tchobanoglous *et al.*, 2003).

Table 6-1. Effluent heavy metal concentrations

Filter Number	First year	Second year
Ni (mg/)		
7	0.126	0.079
8	0.205	0.108
12	0.215	0.149
Cu (mg/l)		
7	0.035	0.045
8	0.029	0.043
12	0.032	0.089
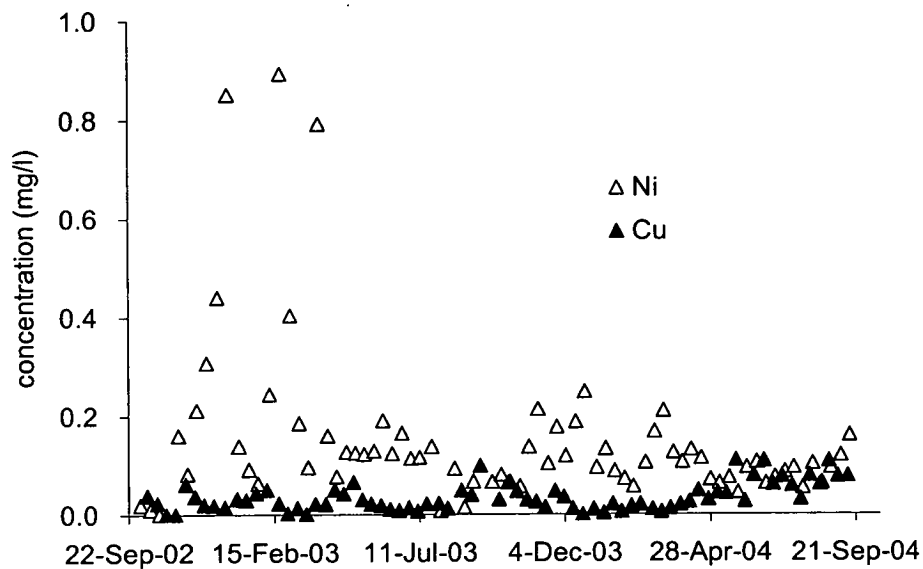
Figure 6-1. Effluent nickel and copper concentrations in Filter 8

In terms of mass variation of both metals, mass inflows of Ni and Cu were stable and decreased consistently due to decreasing volume of the filters (section 4.4) as illustrated in Figure 6-2 and Figure 6-3. Two trend lines for mass inflows reflect hydraulic cycles (50% and 100% filling) of the present system. In particular, mass outflows of Ni peaked in the first winter, but peaks were not recorded during the second year as shown in variation of Ni concentrations (Figure 6-1 and Figure 6-2)

115
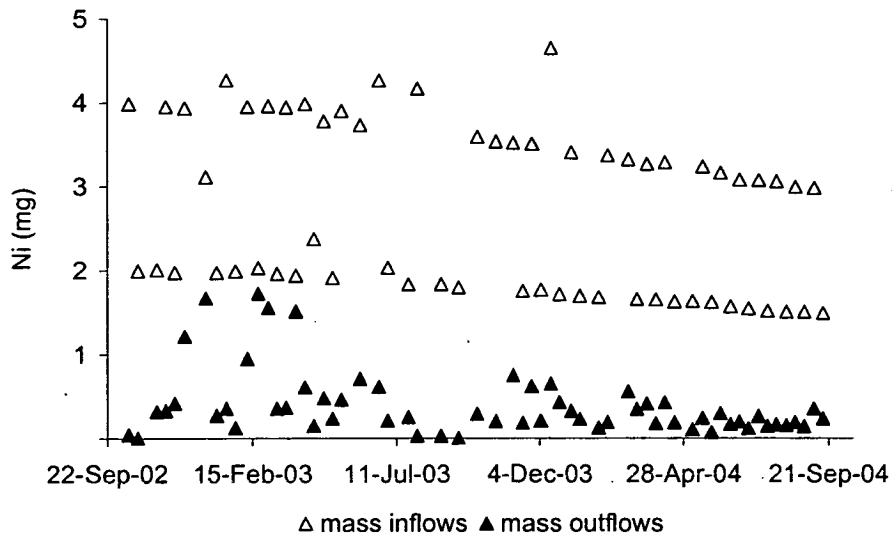
Figure 6-2. Mass inflows and outflows of nickel in Filter 8

On the other hand, mass outflows of Cu were low and stable throughout the two years (Figure 6-3). This is in contrast to a previous study that showed distinct seasonal variation in removal performance with a higher efficiency during the summer (Faulkner and Skousen, 1994).
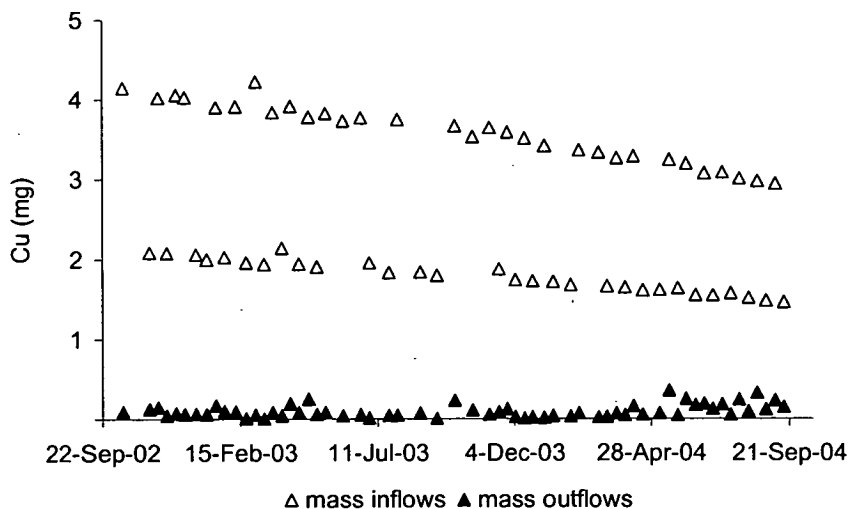
Figure 6-3. Mass inflows and outflows of copper in Filter 8

Average loading and removal rates for Ni and Cu are presented in Table 6-2. Reduction rates of Cu were high (>92 %) regardless of plant regime during the two

116

years. In contrast, Ni reduction rates of the unplanted filter (Filter 7) were higher than those of the planted filter (Filter 8).

The Cu reduction rates in the second year were lower, compared to those in the first year, whereas the Ni reduction rates increased over time (Table 6-2). Nevertheless, Ni and Cu removal rates were significantly higher, compared to Ni and Cu removal rates of 0.009 and 0.065 $g/m^2 \cdot d$, respectively, estimated in SSF wetlands (Sinicrope et al., 1992).

Table 6-2. Mass loading and removal[a] rates of heavy metal

Filter Number	First year			Second year		
	Loading ($g/m^2 \cdot d$)	Removal ($g/m^2 \cdot d$)	Reduction rate (%)	Loading ($g/m^2 \cdot d$)	Removal ($g/m^2 \cdot d$)	Reduction rate (%)
Ni						
7	0.080	0.071	89.4	0.068	0.062	92.1
8	0.076	0.062	81.5	0.064	0.057	89.0
12	0.192	0.161	83.9	0.161	0.139	86.0
Cu						
7	0.077	0.074	96.2	0.067	0.064	95.4
8	0.074	0.072	97.3	0.063	0.061	95.5
12	0.180	0.175	97.4	0.162	0.149	91.8

[a](in – out)/area · retention time, where in = mass inflows, out = mass outflows

As shown in Figure 6-4 and Figure 6-5, there are linear relationships between the loading and removal rates of Ni and Cu. The reduced gradient (= 0.85) of regression line of Ni compared to that (= 0.96) of Cu in Filter 8, indicates that removal rates of Ni were lower than those of Cu. Furthermore, removal performance for Cu was more stable in comparison to those for Ni. With respect to Ni removal, gradients of regression lines obtained from Filters 7 (= 0.91) and 8 (= 0.85) indicate that the unplanted (Filter 7) system shows higher removal capacity for Ni than the planted (Filter 8) system (Figure 6-4). The role of macrophytes in metal removal is discussed

in detail in section 6.3.3.
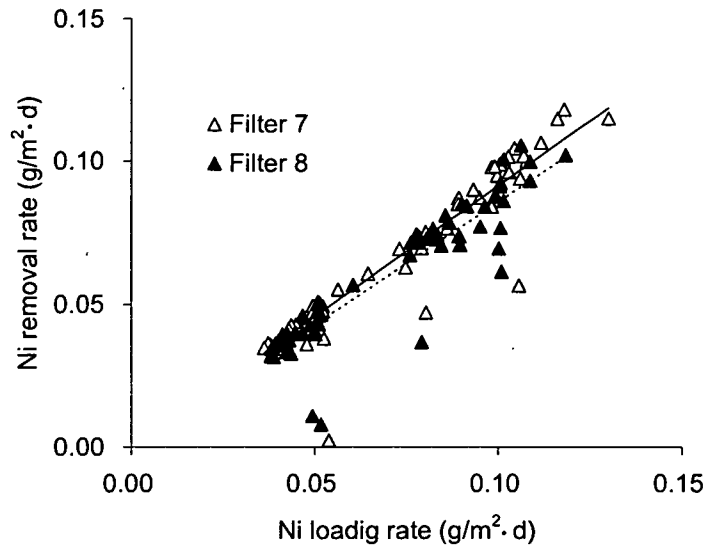
Figure 6-4. Mass loading and retention rates of nickel in Filters 7 and 8

As illustrated in Figure 6-5, the Cu removal rate of Filter 12 did not decrease significantly at a given higher loading rate, indicating that filters did not reach the maximum removal capacity of metal. Longevity of filters in terms of metal retention is further investigated in section 6.4.
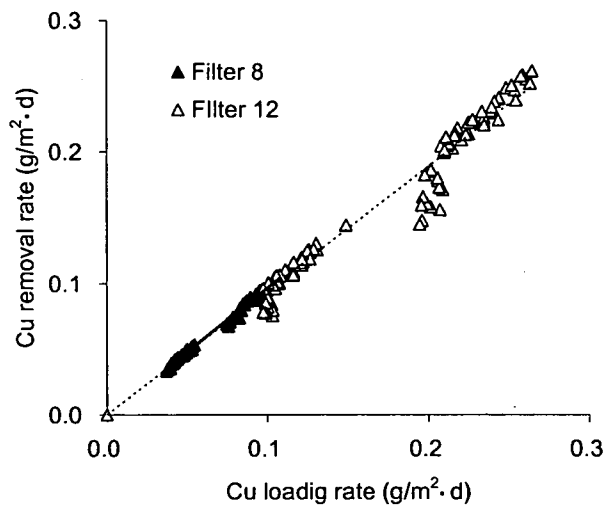
Figure 6-5. Mass loading and removal rates of copper in Filters 8 and 12

First-order removal models were applied to compare metal removal potential with other systems (see section 4.5.2 and 4.6.2). Removal rate constants (= k) were presented (Table 6-3). Average k values (0.471 - 0.660 m/d) of Cu in Filter 12 were much higher than k values (0.068 - 0.329 m/d) obtained in SF wetlands (Srinivasan and Kadlec, 1995). Sinicrope *et al.* (1992) reported k values of Cu (0.049 - 0.129 m/d) and of Ni (0.041 - 0.049 m/d) in SSF wetlands. This suggests that the temporarily flooded vertical-flow system was highly efficient for heavy metal removal, compared to other flow types of wetlands.

Table 6-3. Removal rate constants of heavy metal

Filter Number	k (m/d)	
	First year	Second year
Ni		
7	0.244	0.184
8	0.168	0.144
12	0.415	0.324
Cu		
7	0.269	0.229
8	0.282	0.224
12	0.660	0.471

The average k values of both Ni and Cu in second year were lower, compared to those in the first year. This is most likely due to the decreased loads during the second year (Figure 6-2 and Figure 6-3).

The k values of Ni in Filter 7 (unplanted filters) were higher in comparison to those in Filter 8 (planted system), implying that macrophytes provided an undesirable condition for Ni removal. Such a result is further discussed in section 6.3.3. However, the k values of planted and unplanted systems for Cu removal were similar.

6.3. Mechanism of metal removal

6.3.1. Factors affecting nickel removal

In contrast to previous findings (Schutes *et al.*, 2001), Ni instead of Cu broke through the filter. While others (Schutes *et al.*, 2001; Revitt *et al.*, 2004) speculate that the decomposing of aquatic plants and consequently the release of metals resulted in the breakthrough of predominantly Cu, it is assumed that the breakthrough of Ni is linked to road grit containing salt (NaCl).

Multiple linear regression analysis was carried out to identify the effect of environmental variables (temperature, redox, conductivity, pH, SS and BOD) on the Ni removal performance. This analysis demonstrates that conductivity and SS could explain 30 – 59 % of the variations of the effluent Ni concentrations (Table 6-4).

Table 6-4. Statistical models for nickel removal

Filter Number	Regression Equation[a]	R^2
7	$C_e = 1.59 * 10^{-5} CON + 0.047$	0.59
8	$C_e = 1.35 * 10^{-5} CON + 0.108$	0.33
12	$C_e = 1.02 * 10^{-5} CON - 3.6 * 10^{-5} SS + 0.161$	0.30

[a] C_e = effluent Ni concentration, CON = influent conductivity, SS = influent suspended solids concentration.

As expected, conductivity was selected statistically as optimal regressor and shown to have a negative effect on the Ni removal. With respect to annual change of Ni reduction rate (Table 6-2), it was shown that Ni reduction rates were negatively correlated with average annual conductivity. The average conductivity (= 2272.2 μS) in the second year was lower than that (= 5139.1 μS) in the first year (Table 4-1).

As illustrated in Figure 6-6, high levels of conductivity representing salts were recorded in the inflow and outflows due to road gritting (including salt) after 13 December 2002 and 10 December 2003. Salt reduction in the filters was low and its reduction rates were negative in winter. Furthermore, most nickel salts except nickel phosphate ($Ni_3(PO_4)_2$), nickel hydroxide ($Ni(OH)_2$) and nickel sulfide (NiS) are more soluble than most of the other cationic heavy metals (APHA, 1995; Bäckström *et al.*,2004; Norrström and Jacks, 1998). This in combination with a relatively low pH should have resulted in the breakthrough of Ni during the first winter (Figure 6-6).
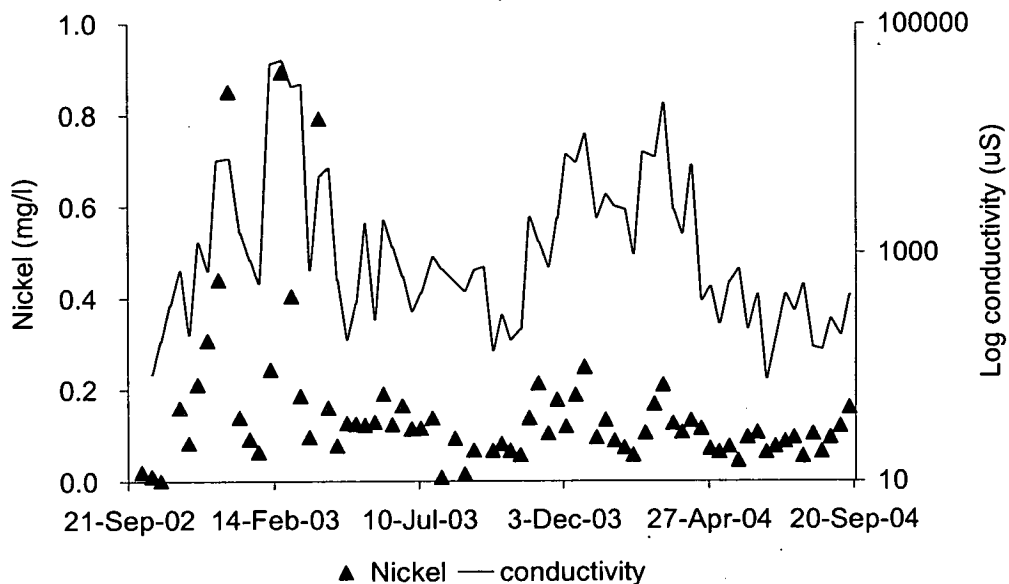
Figure 6-6. Relation between conductivity and nickel concentration in Filter 8

Influent pH appeared not to be significant statistically (Table 6-4). However, effluent pH was selected as significant regressor for effluent Ni concentrations (regression equations are not shown). Ni is highly mobile in acid soils and other acid environments, so that a pH increase would help to demobilize Ni compounds (EA, 2002).

Figure 6-7 shows the relation between Ni concentration and pH variation. It is

121

clearly shown that Ni breakthrough did not take place after influent pH was raised, despite high conductivity during the second winter.
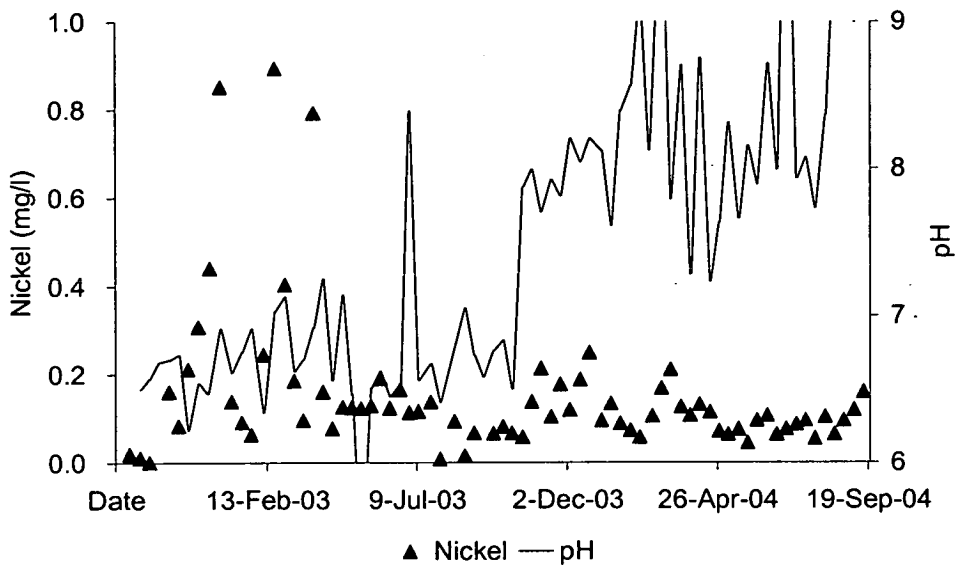
Figure 6-7. Relation between pH and nickel concentration in Filter 8

There is the potential for Ni ions to come out of solution if the environmental conditions are optimal for leaching (Tchobanoglous *et al.*, 2003; Lim *et al.*, 2003). Nickel hydroxide ($Ni(OH)_2$) may precipitate at pH 6.9 and pH 9.1 if the corresponding metal concentrations are 1 mg/l each, similar to the inflow concentration (Figure 2-7). Thus, it can be inferred that the precipitation of Ni as hydroxides was facilitated under condition of high influent pH ranging from 8 and 9 during the second year. This is supported by previous research that found increasing reduction of Mn with NaOH addition (Ye *et al.*, 2001a).

SS appeared to decrease the effluent Ni concentrations as shown in the regression equation of Filter 12 (Table 6-4), suggesting that a sorption on SS is one of the main mechanism of metal removal (Obarska-Pempkowiak and Klimkowska, 1999). Furthermore, this is supported by the fact that average SS concentration (= 853.9

mg/l) of the second year was higher than that (= 335.7 mg/l) of the first year (Table 4-1).

Redox is also regarded as important factor, even though it is not statistically selected in multiple linear regression analysis (Table 6-4). At low redox (anoxic conditions), metals form stable insoluble metal sulfides. If the sediment turns aerobic, sulfide is oxidized and bound metals are released. However, iron hydroxide is a sink for metal as well and adsorbs metals under aerobic conditions. Thus, metals are adsorbed and released in both oxidizing and reducing sediments. Generally, the constantly changing oxygen content of sediments leads to net release of metals (Deng *et al.*, 2004; Wood and Shelley, 1999; Obarska-Pempkowiak and Klimkowska, 1999; Gladden *et al.*, 2002).

Redox in the sediments was not monitored in the present study. Instead, redox of effluents was used to carry out the correlation analysis. Effluent Ni concentrations were shown to have a weak negative correlation (-0.11) with redox of effluents, suggesting that Ni removal was improved in aerobic conditions, but its impact was not considerable.

It can be therefore summarized that Ni removal was largely influenced by conductivity, and partly by SS and pH in combination with other environmental variables such as redox. Goulet *et al.* (2001) showed that environmental variables such as pH, alkalinity and temperature could predict as much as 40 % of the seasonal variation in the ratio of dissolved to total Mn at the outlet.

Figure 6-8 presents the comprehensive relationship between effluent Ni concentrations and other water variables. High effluent Ni concentrations (> 0.325
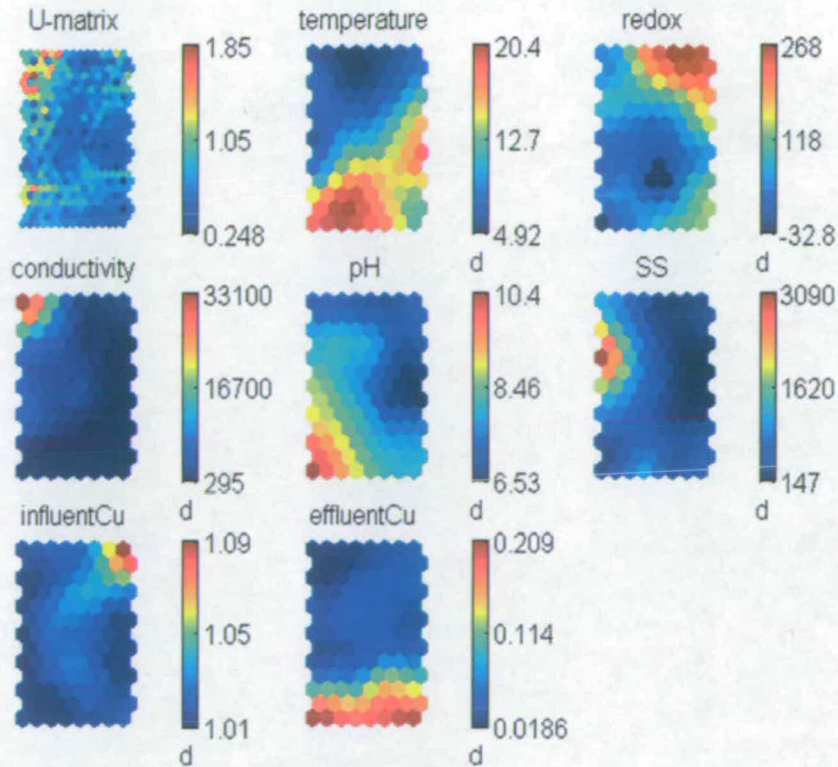
Figure 6-9. Visualization of relationship between influent water quality indicators and effluent copper concentrations in Filter 12.

Concerning the impact of redox on Cu removal, the map shows that high Cu concentrations are linked to relatively low redox. According to the Cu-C-S-O-H model (Figure 2-6), copper sulfides would be the main species in the wetland hydrosoil under redox of -100 (Gladden *et al.*, 2002). Ferrous iron is oxidized to its metal adsorbing form, ferric iron, at +120 mV. Thus between these transformation levels, Cu is least likely to be retained (Sinicrope *et al.*, 1992). As shown in SOM map, effluent Cu concentrations were relatively high under redox of 120 mV.

High temperature is clearly associated with high Cu concentrations, indicating that high temperature has a negative influence on Cu removal in the present filters. A similar finding that a higher temperature increased the metal dissolution rate in stormwater runoff treatment was reported by Rangsivek and Jekel (2005).

Unlike the case of the Ni removal, influent water variables such as SS concentrations, pH and Conductivity were not shown to have clear relationships with effluent Cu concentrations. This suggests that the mobility of Cu was not significantly affected by salt increase during the winter. Bäckström et al. (2004) also reported that 60 – 80% of dissolved Cu was associated to organic matter and only a few percent of Cu was found as chloride complexes in the roadside environment when a deicing agent was used during the winter.

6.3.3. Role of macrophytes and filter media

Total loads and exports of heavy metal are given in Table 6-5. Amounts of heavy metal accumulated in the macrophytes (leaf and stem) are also presented. Amounts of metals removed by harvesting were negligible, compared to those retained in the system. For example, 1.8 and 0.08% of Cu loads were accumulated in the aboveground tissues of macrophytes during first and second year, respectively. It can therefore be concluded that most of the loads of heavy metal were accumulated in sediment rather than in the macrophytes in the present systems. Little difference in the total removal amount of metal between Filter 7 (unplanted) and 8 (planted) confirms this result.

Table 6-5. Mass balance of heavy metal for Filters 7, 8 and 12.

Filter Number	First year			Second year		
	Total loads	Total retention	Removal by harvest	Total loads	Total retention	Removal by harvest
			Ni (mg)			
7	166.6	146.9	na	135.0	124.6	na
8	158.3	127.9	nd	127.0	113.6	0.3
12	305.4	243.8	nd	259.4	221.4	0.4
			Cu (mg)			
7	161.1	155.7	na	135.0	129.0	na
8	153.0	148.7	1.8	127.0	121.7	0.1
12	295.3	286.1	0.7	259.3	236.8	0.1

na = not applicable, nd = not detectable. Detection limit for Ni is 0.05 mg/l.

Table 6-6 presents the amounts of heavy metal accumulated in aboveground tissues of macrophytes during two years. Cu concentrations of leaf and stem of macrophytes (Filter 8) harvested in December 2003 were 68 and 58 mg/kg, respectively.

In comparison, Deng et $al.$ (2004) estimated averaging 67 mg/kg in the aboveground tissues and 871 mg/kg in the underground tissues in the wetland near Cu mine area, suggesting harvesting plants is not an effective source of metal removal in a wetland system. Similar results were reported in previous researches (Mungur et $al.$, 1997; Mantovi et $al.$, 2003; Peltier et $al.$, 2003; Ye et al, 2001a). In contrast, Cheng et $al.$, (2002) found that more than 30% of Cu and Mn loads were accumulated in $C.$ $alternifolius$, especially the root of plant, suggesting that this species has a great potential for heavy metal removal in vertical-flow constructed wetlands.

Table 6-6. Amounts of heavy metal accumulated in stem and leaf of macrophytes.

Filter	Heavy metal (mg)				
Number	Cu	Ni	Fe	Mn	Zn
First year					
4	0.81	nd	1.61	1.81	0.40
6	0.94	nd	0.63	1.28	0.42
8	1.81	nd	1.45	1.04	0.47
10	0.47	nd	1.37	0.63	0.19
11	0.95	nd	0.42	0.48	0.15
12	0.70	nd	1.08	0.37	0.46
Second year					
4	1.63	0.72	1.95	2.51	0.87
6	0.27	0.19	3.04	2.17	1.69
8	0.13	0.27	1.97	2.41	0.69
10	0.25	0.53	4.49	1.94	2.21
11	0.15	0.40	2.12	1.42	0.65
12	0.13	0.37	2.54	1.06	0.49

nd = not detectable. Detection limit for Ni is 0.05 mg/l.

In general, elemental uptake by wetland plants varies among species and is related to rooting depth and plant life form. Allocation of elements within plants can vary with the uptake pathway and the physiological function of the element in the plant tissues. However, most trace elements show higher concentrations in roots than shoots (Collins et al., 2004). Therefore, metal content of the underground organs of macrophytes (i.e. root) also need to be analyzed to estimate the contribution of macrophytes to heavy metal retention.

Annual amounts of heavy metal taken up by macrophytes in the second year were greater than those in the first year, except the case of Cu in some filters. Although many environmental factors are known to alter the bioavailability of metals, the pH environment is regarded as a most important factor in controlling plant uptake of

metals. The pH influence on the plant uptake could be interpreted in terms of the chemical speciation of the metals and competition between metal ions and protons at the plant-soil-water interface (Deng *et al.*, 2004). Sediment pH was found to have positive effect on heavy metal uptake by plants, and their effect increased significantly under more alkaline conditions (Batty *et al.*, 2000; Deng *et al.*, 2004).

Most metals (Ni, Fe, Mn and Zn) in the present study confirm previous findings. Metals appeared to be more accumulated in macrophytes under high pH (= 8.1) conditions during the second year than relatively low pH (= 6.7) conditions during the first year.

Another important element is redox. Jackson *et al.*, (1993) suggested that the oxidizing conditions led to the observed pattern of high metal concentrations in the sediments, but relatively low concentration in the plants by Al co-precipitation or adsorption to Fe and Mn oxides in the plants rooting zone. Deng *et al.* (2004) also found similar trends. Such a trend is consistent with result that metal concentrations in macrophytes were higher with the lower redox in the second year, compared to those in the first year (Table 4-1).

Also, salinity affects the availability of metals as high salinity causes the formation of metal chlolide complexes which are hard for plants to take up (Prasad *et al.*, 2001). Thus, it can be inferred that relatively low conductivity contributed to increase plant uptake of metals during the second year (Table 4-1).

Concerning the relationship between external metal concentration and the uptake of metal by macrophytes, significant differences in the metal amounts were not shown between contaminated filters (Filters of 8, 10, 11 and 12) and uncontaminated

filters (Filters 4 and 6). Most previous studies have also shown poor correlations between the two variables (Keller *et al.*, 1998; Greger. 1999).

Despite the ability of macrophytes to take up metals, effluent Ni concentrations of a planted (Filter 8) systems was higher than those of an unplanted (Filter 7) system, as indicated by Wilcoxon p values (Table 6-7). This confirms results that removal rates and constants of planted systems are lower, compared to those of unplanted systems (Table 6-2 and Table 6-3).

Higher effluent Ni concentrations of the planted system is most likely attributed to the lower effluent pH (6.72 – 6.93), compared to that (7.19 – 7.31) of the unplanted system as shown in section 5.2.3. Macrophytes are likely to provide undesirable conditions for precipitation of Ni by lowering pH in the process. Collins *et al.* (2004) reported similar results, that water in planted wetlands had lower pH, and higher Fe and Mn than water in unplanted systems.

In contrast, p value for Cu concentrations between Filters 7 and 8 show little differences for Cu removal between planted and unplanted systems (Table 6-7), suggesting that the degree of Cu removal was not significantly affected by the change of pH. This could be due to the much lower solubility of Cu in comparison to that of Ni at the given pH range. Scholz *et al.* (2002) reported similar results, that differences of Cu removal rate between planted and unplanted system were not considerable even though higher pH was produced in unplanted system.

Table 6-7. Comparison of effluent nickel and copper concentrations

Filter Number	Wilcoxon p values	
	First year	Second year
Ni		
7 and 8	0.00	0.00
8 and 12	0.90	0.03
Cu		
7 and 8	0.25	0.63
8 and 12	0.43	0.00

When comparing the performance of Filters 8 and 12, Ni and Cu concentrations of Filter 12 were not different statistically during the first year, but higher than those of Filter 8 during the second year. This suggests that high loading effect on metal removal apparently increased over time. The long term trend of metal retention is discussed in detail in section 6.4.

In addition, Wilcoxon p values were presented to compare the removal performance of Filtralite-Barley straw based filters with sand-gravel based filters (Table 6-8). Agricultural wastes, as alternative cost-effective material, have been employed by several researchers. Kumar *et al.* (2000) reported that straw showed significant Cr^{3+} removal efficiency (> 80 %). Shukla *et al.* (2006) also found that lignocellulosic fibre had a high adsorption capacity for Ni, Zn and Fe.

However, in the present study, the presence of Filtralite and barley straw (adsorption filter media) in selected filters as a replacement for aggregates did not result in an obvious reduction of metal in effluent waters (Table 6-8). This suggests that adsorption materials within each filter are not likely to be responsible for the reduction of metals in the present system.

Table 6-8. Comparisons of effluent nickel concentrations for different filter media

Filter Number	Wilcoxon p values
3 and 5	0.46
4 and 6	0.93
7 and 9	0.63
8 and 10	0.54

Data collected from 21-Sep-02 to 10-Mar-03 were used.

6.4. Long-term performance in copper retention

After two year's operation, some of filters were loaded with excessive Cu to investigate whether the wetlands could retain the heavy metal in the long-term, and determine the fate of Cu in the system. Considering the annual amount of Cu loaded in the filters (Table 6-2), 1 g of Cu loaded in Filters 3 and 4 is amount which could be loaded approximately for 7 years in the present system. Cu breakthroughs were observed in Filters 3 and 4 since the filters were highly loaded with Cu (Figure 6-10).
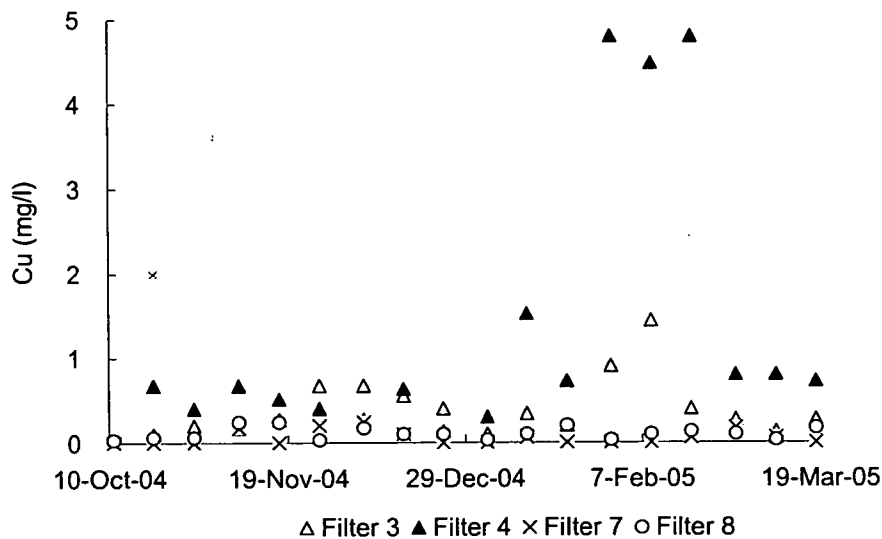
Figure 6-10. Effluent copper concentrations

132

Higher peaks of Cu of Filter 4 (planted system) were recorded compared to Filter 3 (unplanted system). High Cu concentrations of the planted system were caused by the relatively low pH values (data not shown) in the planted system. Planted filters produced relatively low pH values due to the active nitrification, as discussed in section 5.2.3.

As illustrated in Figure 6-11, relatively low redox appeared to be related to the peaks of Cu concentrations in Filter 3. This is most likely attributed to adsorbing metal form (i.e. ferric iron), which was formed around at +120 mV as discussed in section 6.3.2. The correlation coefficients were -0.31 between Cu concentrations and redox of outflows.
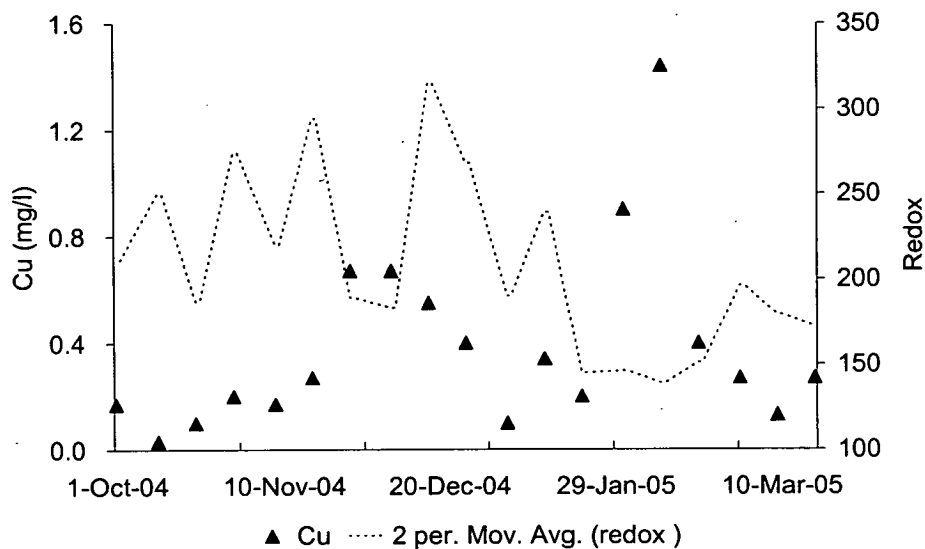
Figure 6-11. Effluent copper concentrations and redox potential in Filter 3

Therefore, it can be summarized that metal retention in the wetlands is more susceptible to change of environmental condition such as pH and redox in the long-term. Furthermore, macrophytes have great impact on metal retention by lowering pH in the aged wetland system.

In March 2005, Ni and Cu contents in the upper layer of sediment (1 - 5cm) of all filters were determined (Table 6-9). The metal concentrations in the sediments were comparable to those of other treatment wetlands (Yet *et al.*, 2001b). This result apparently indicates that sediment is the primary sink for metals in this system, which is consistent with previous researches (Ye *et al.*, 2001a, b; Mitsch and Wise, 1998).

Table 6-9. Nickel and copper concentration in sediments

Filter Number	Ni (mg/kg)	Cu (mg/kg)
1	64.4	4806.0
2	726.0	1660.4
3	62.0	7180.0
4	74.8	2024.0
5	71.8	4950.0
6	79.2	1534.0
7	726.0	1332.0
8	680.0	1106.0
9	718.6	1360.0
10	684.8	1084.8
11	1279	1166.0
12	925.4	1949.0

Ni concentrations were much lower than Cu concentrations, indicating that Ni has relatively greater mobility in the sediment. High Cu concentrations imply that filters have great potential for immobilizing Cu in sediments in the long-term. Ye *et al.* (2001a) demonstrated that constructed wetlands sustained high efficiency of trace element removal in 10 years after their construction. However, further estimations for speciation and distribution of metal in the sediments are needed to identify the longevity and capacity of system for metal retention

6.5. Performance of ochre filter

6.5.1. Adsorption capacity of ochre

The adsorption of Cu and Ni to ochre can be characterized by the adsorption isotherm. Table 6-10 shows the adsorption isotherm parameters for both metals. Langmuir and Freundlich equations were fitted to adsorption data obtained form batch isotherm experiments (Heal *et al.*, 2004). The forms of isotherm equations are as follows:

Langmuir equation; $\dfrac{C_e}{x/m} = \dfrac{1}{ab} + \dfrac{C_e}{b}$ 6-1

Where :

C_e =   the concentration of the metal in solution at equilibrium (mg/l);

x/m   =   the amount adsorbed at equilibrium (mg/g);

a   =   a constant related to the binding strength; and

b   =   the maximum adsorption capacity of the material (mg/g)

Freundlich equation; $x/m = KC_e^{1/n}$ 6-2

Where :

C_e =   the concentration of the metal in solution at equilibrium (mg/l);

x/m   =   the amount adsorbed at equilibrium (mg/g); and

K and n   =   constants related to the strength of affinity.

As presented in Table 6-10, ochre pellets have higher values of a and b for Cu in comparison to Ni, suggesting that ochre binds Cu more strongly and has higher adsorption capacity for Cu. K and n values obtained from Freundlich equation also support that ochre has a higher removal potential for Cu than Ni.

Table 6-10. Estimated isotherm parameters for copper and nickel.

Equation	Parameter	Ni	Cu
	K	0.18	0.57
Freundlich	n	1.61	1.30
	R^2	0.95	0.97
	a	0.12	0.14
Langmuir	b	1.38	4.84
	R^2	0.98	0.92

However, these values for both Ni and Cu were lower in comparison to P removal capacity of ochre reported by Heal *et al.* (2004), showing higher b values (21.5) and K value (7.5) for P removal by the ochre. This suggests that ochre is more effective at removing P than heavy metal.

The maximum adsorption capacities for Ni and Cu estimated from the Langmuir equation are 1.38 and 4.84, respectively (Table 6-10). Table 6-11 presents the adsorption capacities of various adsorbents evaluated in previous adsorption studies to compare with retention capacity of ochre pellet. Among various adsorbents, biosorbents such as Chitosan and Pear moss have outstanding potentials for metal retention. Adsorption capacity of ochre is comparable to that of fly ash and zeolite.

Table 6-11. Adsorption capacity of various adsorbents (Babel and Kurniawan, 2003, Recou *et al.*, 1999)

Adsorbent	Adsorption capacity (mg/g)	
	Ni	Cu
Ochre	1.38	4.84
Chitosan	2.40	16.80
Zeolite	0.48	1.64
Fly ash	2.6	2.2
Peat moss	11.15	12.07
Activated carbon	2	9

Concerning the similar adsorbents to ochre, the maximum Cr^{6+} adsorption capacity of iron hydroxide waste from fertilizer industries was found to be 0.47 mg /g (Babel and Kurniawan, 2003). Lai and Chen (2001) reported that maximum capacity of iron-oxide coated sand for Cu and Pb were 0.259 and 1.211 mg/g, respectively.

6.5.2. Removal performance of ochre

Figure 6-12 and Figure 6-13 present the variation of influent and effluent concentration for Cu and Ni, respectively, obtained in the ochre column experiment. The effluents of constructed rigs were filtered through the ochre cylinder (Figure 3-5). Thus, the effluent metal concentrations of constructed rigs represent the influent metal concentrations of ochre filters. High Cu concentrations were apparently reduced through the filtration by ochre, but metal reductions for relatively low metal influents were not clear in both Cu and Ni (Figure 6-12 and Figure 6-13).
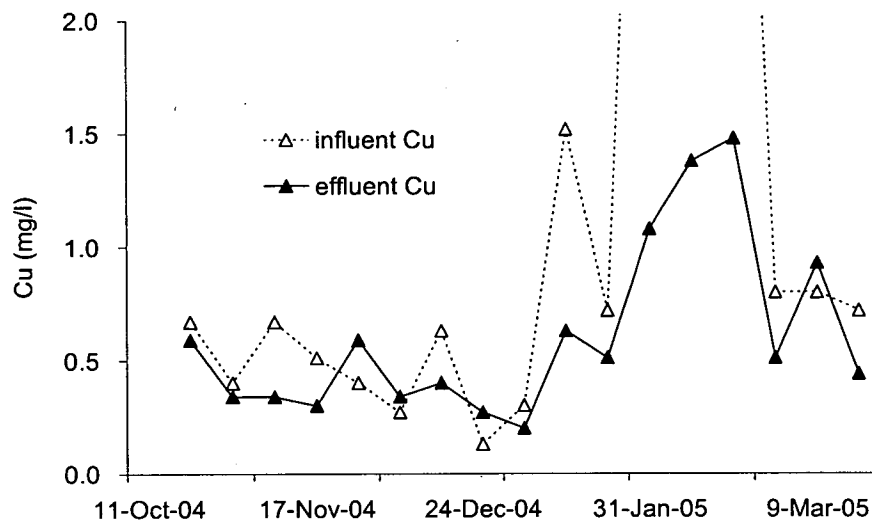
Figure 6-12. Influent and effluent copper concentrations in Filter 4. Three outliers (4.80, 31-Jan-05; 4.48, 9-Feb-05; 4.80, 18-Feb-05) are not shown.
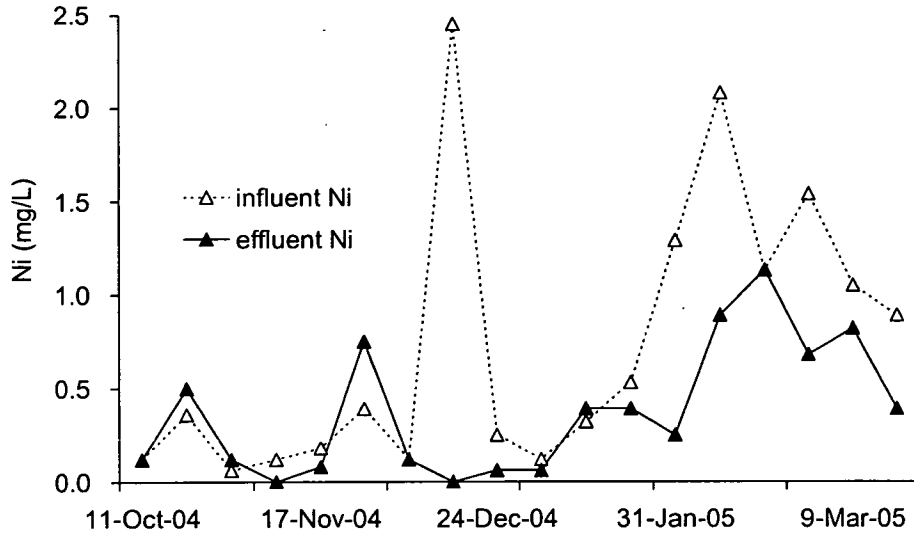
Figure 6-13. Influent and effluent nickel concentrations in Filter 8

Average loading and removal rates for Ni and Cu are presented in Table 6-12. Metal removal rates of the ochre filters were considerably high compared to those of constructed wetland filters (Table 6-12). Removal rates of Cu were higher than those of Ni. This confirms results from the isotherm analysis above.

However, reduction percentages of metal were low for both Ni and Cu. This is likely due to relatively short infiltration time (15 – 20 sec) as 99 % of Ni and Cu were reduced within 5 minutes of contact time with ochre in the batch experiment. Möller et al. (2002) also reported that 91 – 94 % of Cu was removed by iron-oxide coated sand (IOCS) within a contact time of 6 minutes in the column experiment for stormwater runoff treatment.

138

Table 6-12. Mass loading and removal rates of heavy metal

Metal	Numbers of data sets	Loading (g/m²·h)	Removal[a] (g/m²·h)	Reduction (%)
Cu	70	17.9	8.2	46.2
Ni	35	22.8	7.7	33.6

[a](in – out)/area · retention time, where in = mass inflow, out = mass outflows

As demonstrated in Figure 6-14, removal rates for both metals increased with increasing loading rate. The gradients of these trend lines show that removal potential for Cu is not greater than that of Ni. However, the higher R^2 value (= 0.92) of regression line of Cu removal indicates that Cu removal performance is more stable in comparison to Ni (R^2= 0.80). The degree of Ni removal appeared to be influenced by change of environmental factors such as pH and conductivity. Like ochre filters, Ni removal performance of constructed wetlands were also susceptible to change of environmental conditions as discussed in section 6.3.1.
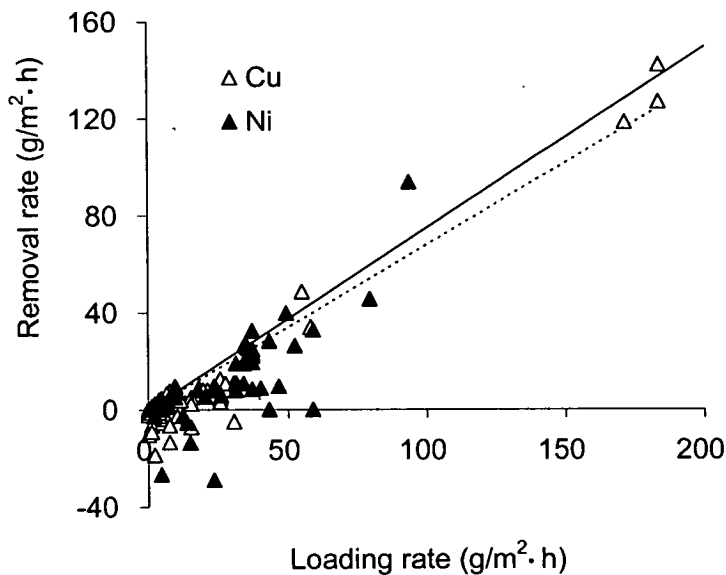
Figure 6-14. Mass loading and removal rates of copper and nickel.

Figure 6-15 and Figure 6-16 present the monthly changes of influent and effluent Ni concentrations with changing conductivity and pH. Effluent Ni concentrations were relatively high under high conductivity conditions. The correlation coefficient between effluent Ni concentration and conductivity was 0.79 in Filter 8. This is attributed to formation of soluble nickel salts, as discussed in section 6.3.1.

With respect to pH influence on the Ni retention, low pH in combination with high conductivity appeared to be associated with high Ni concentrations, showing the correlation coefficient of – 0.64 between two variables in Filter 7. This suggests that Ni removal rates increased under high pH condition, as discussed in section 6.3.1.
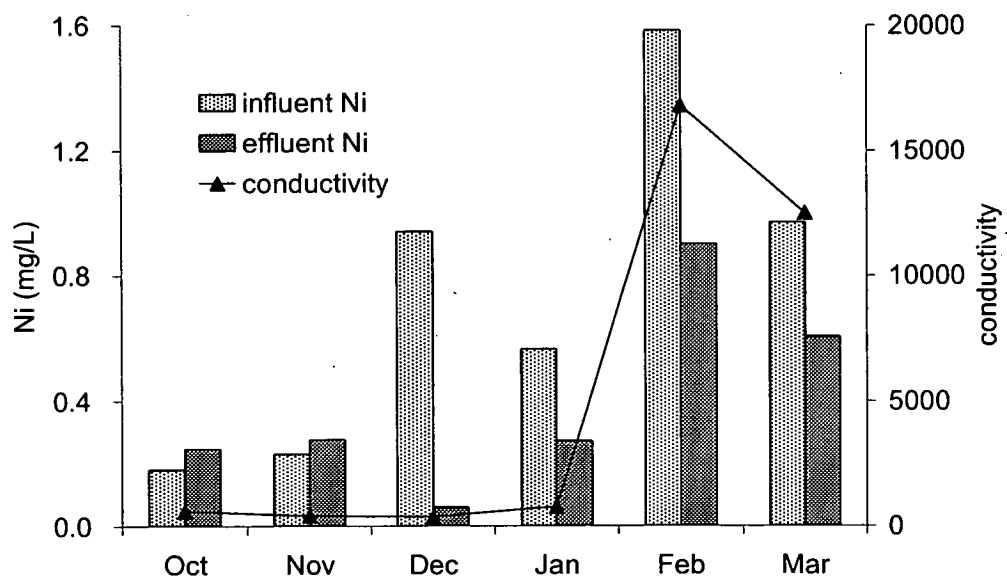
Figure 6-15. Monthly nickel concentration and conductivity in Filter 8.
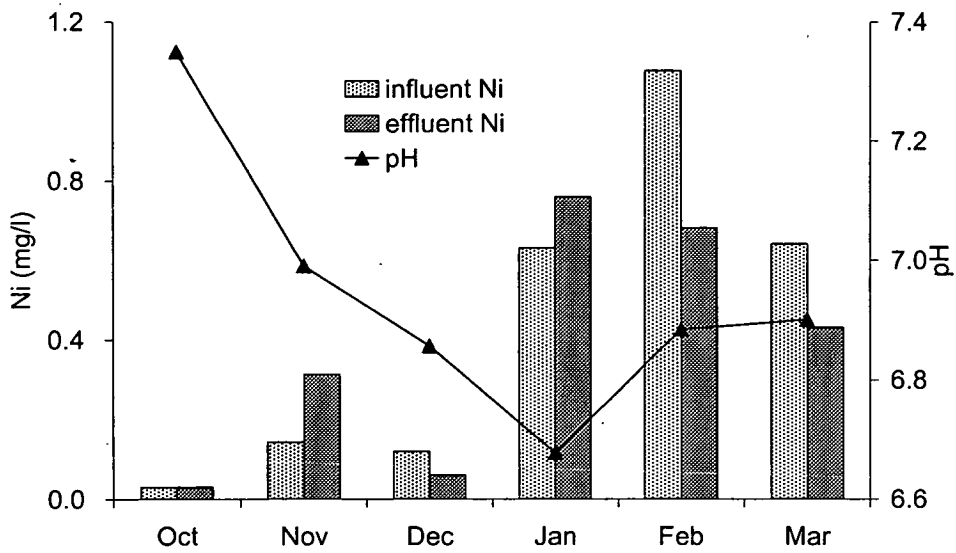
Figure 6-16. Monthly nickel concentration and pH in Filter 7

The ochre pellets made of fine ochre from the Silkstone mine wastewater treatment scheme (Yorkshire, UK) were used in the present study. Chemical compositions of ochre in each column before and after infiltration treatment for six month were presented in Table 6-13. Increased Cu and Ni concentrations in ochre pellets after filtration treatment were not remarkable compared to other metal concentrations, suggesting that ochre is more efficient for adsorption of P, Fe, Al and Mn.

Table 6-13. Chemical compositions of ochre pellets before and after infiltration

	Filter	Concentration (mg/kg)									
	Number	P	N	K	Cu	Ni	Fe	Al	Mg	Ca	Mn
Before		400	1199	1127	44	20	23127	12325	5713	82992	474
After	3	572	1174	2637	46	24	25030	14104	5760	122550	562
	4	472	778	2547	72	23	25222	14155	5753	120253	535
	7	419	1025	2469	40	23	24182	13773	5571	116552	498
	8	452	987	2003	42	26	24657	27307	5682	118384	507

141

6.6. Summary

The findings indicate that a large part of Ni in constructed wetland filters is likely to leach when exposed to a high sodium chloride concentration in winter, and possibly also to reducing conditions and a low pH. A breakthrough of dissolved Ni correlated well with high conductivity values (as a result of road salting).

After creating an artificially high inflow pH of approximately eight after one year of operation, Ni was successfully treated. Moreover, the elevated pH had no apparent negative effect on the macrophytes. These results indicate that conventional pH adjustment can be successfully applied to constructed wetland systems for urban runoff treatment.

With respect to Cu removal, its performance was constantly sustained throughout the two years and the effluent Cu concentrations were considerably lower than Ni concentrations. This suggests that Cu removal performance is more stable under variable environmental condition in comparison to the case of Ni.

Amounts of metals removed by harvest were negligible, compared to those retained in the system. Furthermore, higher effluent Ni concentrations were recorded in the planted system, despite their ability to take up the heavy metal. This suggests that macrophytes are likely to provide undesirable conditions for precipitation of Ni by lowering pH in the process.

A Wilcoxon signed-rank analysis indicated that all constructed wetland filters were virtually similar in terms of their metal removal performance despite their different set-ups. It follows that high investment costs for more complex filters are not justified by their relatively low performance. Moreover, microbiological activity

within each filter is likely to be responsible for the reduction of Ni and Cu, rather than aggregates and macrophytes.

Concerning the long-term trend of Cu retention in the constructed wetlands, the performance of metal removal is more susceptible to variation of environmental condition such as pH and redox. Furthermore, adverse impact of macrophytes on metal retention is likely to increase in the aged wetland system.

Adsorption capacity of ochre was shown to be comparable to that of other filter media (i. e. fly ash and zeolite). Cu retention potential of ochre was greater in comparison to Ni, resulting in more stable performance for Cu removal. The Ni removal performance of ochre filters appeared to be significantly influenced by variation of environmental factors such as pH and conductivity.

Chapter 7   Application of machine learning techniques to support constructed wetland management

7.1. Introduction

This chapter introduces machine learning for the indirect prediction of water quality indicators of experimental constructed wetland. The KNN, SVM and SOM models were applied to predict effluent BOD, SS, nutrients and heavy metals of constructed wetland systems with other effluent variables such as redox potential and conductivity, which can be monitored cost-effectively.

This chapter is structured as follows: Section 7.2 introduces the recent machine learning tools applied for wastewater treatment systems. Section 7.3 gives descriptions of three machine learning models and their theoretical backgrounds. Sections 7.4, 7.5 and 7.6 show the tuning methods of input variables and the prediction results for BOD, SS, nutrients and heavy metals. The prediction performance of three models is compared and input resources for prediction are also assessed in these sections.

7.2. Machine learning applied to wastewater treatment processes

Machine learning techniques are part of the research area of artificial intelligence. Computer programs are created by the analysis of data sets. Machine learning

144

overlaps with statistics, but is predominantly concerned with the algorithmic complexity of computational implementations. There is a wide range of applications including web search engines, medical and biological research, economics, linguistics, sport, robotics and control systems for complex environmental engineering processes.

Constructed treatment wetlands are often seen as complex 'black box' systems, and the processes within an experimental wetland are difficult to model due to the complexity of the relationships between most water quality variables (Gernaey *et al.*, 2004). However, it is necessary to monitor, control and predict the treatment processes to meet environmental and sustainability policies, and regulatory requirements such as secondary wastewater treatment standards (Scholz, 2004).

The measurement of BOD and SS concentrations is widely applied for wastewater before and after treatment, as they give a general indication of the water quality status. However, taking BOD measurements can both be expensive (measurements are labor intensive and capital costs of modern on-line equipment are relatively high; approximately £15,000) and only of historical value (results are not available until five days after the sample has been taken). Furthermore, it takes at least two, possibly even three hours of costly manual labor to obtain SS concentrations. Therefore, an indirect method of prediction of BOD and SS, if it could be made reliable enough, would be advantageous.

A variety of machine learning methods such as KNN and ANN have been widely used in a broad range of domains including wastewater treatment engineering. The KNN model is a simple methodology and a memory-based model defined by a set of examples for which the outcomes are known. Moreover, the KNN model estimates

the outcome by finding k examples that are closest in distance to the target point. The prediction value can be obtained by averaging values of the k nearest neighbors.

The KNN model has been compared with advanced neural networks, and tested for a wide range of areas such as medical diagnosis, chemical analysis and remote sensing (Carpenter and Markuzon, 1998; Dong *et al.*, 2005a; Ruiz-Jimenez *et al.*, 2004). In the case of the application of KNN models in the wastewater treatment industry, Belanche *et al.* (2000) employed a KNN model for reference purposes in predicting sludge bulking.

Neural networks are relatively effective in simulating and predicting water treatment processes. The advantages of ANN are as follows: ease of use, rapid prototyping, high performance, minor assumptions, reduced expert knowledge required, non-linearity, multi-dimensionality and easy interpretation (Werner and Obach, 2001).

ANNs such as feed-forward neural networks were developed to predict the effluent concentrations including BOD, COD and SS for wastewater treatment plants (Grieu *et al.*, 2005; Hamed *et al.*, 2004; Onkal-Engin *et al.*, 2005), and to control water treatment processes automatically by modeling the alum dose (Maier *et al.*, 2004). These studies have shown that ANN could be applied to establish a mathematical relationship between variables describing a process state and different measured quantities.

Although ANN methods are cost-effective and highly reliable in analyzing processes, the traditional neural networks have suffered from their inherent drawbacks; i.e. over-training, local minima, poor generalization and difficulties in

their practical application (Lu and Wang, 2005). The SVM, a supervised machine learning technique, developed by Vapnik (1995), can provide a novel approach to improve the generalization performance of neural networks.

The SVM technique uses a linear model to implement nonlinear class boundaries through mapping input vectors into a high-dimensional feature space. The SVM seeks this linear model (i.e. the maximum margin hyperplane), which gives the maximum separation between decision classes. The 'support vector' is selected from the training data set, and its data are located closest to the maximum margin hyperplane (Vapnik, 1995).

Originally, SVM models have been applied for pattern recognition problems. However, along with the introduction of Vapnik's ε insensitive loss function, SVM also have been extended to solve non-linear regression estimation problems (Pai and Hong, 2005; Vapnik, 1995). It classifies the data based on the similarity between the examples measured by the similarity function or kernel function. This function can be chosen according to the problem at hand, and thus making the algorithm flexible in handling a wide variety of problems (Dubey *et al.*, 2005). Moreover, previous studies demonstrated that the SVM is superior to the conventional neural network in predicting chemical and biological variables (Liu *et al.*, 2004; Lu and Wang, 2005). However, this novel method has not yet been applied in the field of wastewater treatment including constructed treatment wetlands.

The SOM, which is based on an unsupervised learning algorithm, uses powerful pattern analysis and clustering methods, and at the same time provides excellent visualization capabilities (Garcia and Gonzalez, 2004). The term 'self organizing' refers to the ability to learn and organize information without being given the

corresponding dependent output values for the input pattern (Mukherjee, 1997).

The SOM is able to map a structured, highly dimensional data set onto a much lower dimensional network in an 'orderly' fashion, and organizes itself by adjusting the weights according to the input patterns (Lu and Lo, 2002). It offers the distinctive ability to gather knowledge by detecting the patterns and relationships from a given data set, learning from relationships and adapting to change. The SOM potentially outperforms current methods of analysis, because it can successfully deal with the non-linearity of a system, handle 'noisy' or irregular data and be easily updated (Hong *et al.*, 2002).

Interesting approaches of SOM have been reported in water quality assessment. The SOM models were developed to evaluate the state of water quality of a reservoir, and to predict the trophic status of coastal waters, showing a strong ability to identify the diversity between data (Aguilera *et al.*, 2001; Gervrey *et al.*, 2004).

Moreover, Verdenius and Broeze (1999) used this model as an indexing mechanism in case-based reasoning algorithms to control wastewater treatment processes, and it was employed to diagnose the diverse states of a wastewater treatment plant (Garcia and Gonzalez, 2004; Hong *et al.*, 2002). These studies demonstrated that the SOM can assist a process engineer by analyzing multi-dimensional data and simplifying them into visual information that can be easily applied to control plant performance. However, applications of SOM in water treatment process control are relatively new and were not implemented as much as traditional neural networks such as free forward neural networks (Grieu *et al.*, 2005; Hamed *et al.*, 2004).

It follows that comparative studies of traditional KNN models with novel neural networks (e.g. SVM and SOM) applied to predict indirectly water quality indicators of constructed wetlands are required to advance operation process control. Moreover, ANN should be used to find out if these models can be effectively applied to predict water quality variables such as BOD and SS effluent concentrations in constructed treatment wetlands using their potential for data classification and clustering.

7.3. Methodology and software

7.3.1. Experimental data and variables

Experimental data were collected by monitoring the effluent concentrations of the filters including BOD and SS for two years (22/09/02 to 21/09/04). The amount of data points used was comparable and even greater than those used in other prediction models (Aguilera *et al.*, 2001; Liu *et al.*, 2004). These data were stored in a data base together with up to six input variables; turbidity (NTU), conductivity (μS), redox (mV), outflow water temperature ($^{\circ}$C), DO (mg/l) and pH (-). The corresponding output variables were BOD (mg/l), SS (mg/l), nutrients (mg/l) and heavy metals (mg/l). The input variables were selected according to their goodness of correlation with both BOD, SS, nutrients and heavy metals (Scholz, 2003b), because they are both more cost-effective and easier to measure in comparison to the output variables.

The performance of sustainable urban drainage systems including constructed treatment wetlands is known to change significantly over time. A high level of treatment performance a few weeks after commissioning is followed by a rapid decline a few months later, before equilibrium is reached after about a year (Scholz, 2003b). However, it can be argued that most engineered wetland systems in the urban

water area never reach an equilibrium that is comparable to natural systems because they are frequently being disturbed by high fluctuations of inflow water quality (e.g., gritting and salting in the winter) and operational changes to the system (e.g., temporary flooding of the wetlands) as described elsewhere (Gernaey *et al.*, 2004; Lee *et al.*, 2005). The machine learning models used for this research take data fluctuations within the first year of operation into account, because two years of data are used for a very broad range of input variables.

7.3.2. Training and testing of data sets

The overall data set was divided into training and testing data sub-sets. Each model was tested for each data sub-set associated with one wetland filter (Filters 3 to 12). The training of the corresponding model was performed with the data belonging to the remaining nine filters.

For example, when predicting the water quality variables of Filter 3, the remaining nine data sub-sets (Filters 4 to 12) were used as training data. The validation process was therefore undertaken with independent data sub-sets that were partly significantly different to the testing data sub-set (see above). It follows that the models can be used for an entirely different set of stormwater runoff treatment data in the future.

7.3.3. K-nearest neighbours

A KNN model used to predict the effluent BOD and SS concentrations of the system was created using MATLAB 7.0. The KNN model is based on averaging of the outcomes of the k-nearest neighbors. KNN searches its database for those whose characteristics are most similar to the characteristics of the new problem case to be

classified. Similarity can be estimated by comparing attribute values between two cases.

A prediction for a new problem case is made by examining the target values of the k most similar cases in the training data sets and averaging them. Thus, the determination of the optimal value for k is essential in building the KNN model because it should be the maximum number of neighbors with the minimum possible error (Ruiz-Jimenez *et al.*, 2004), as demonstrated in Figure 7-1.
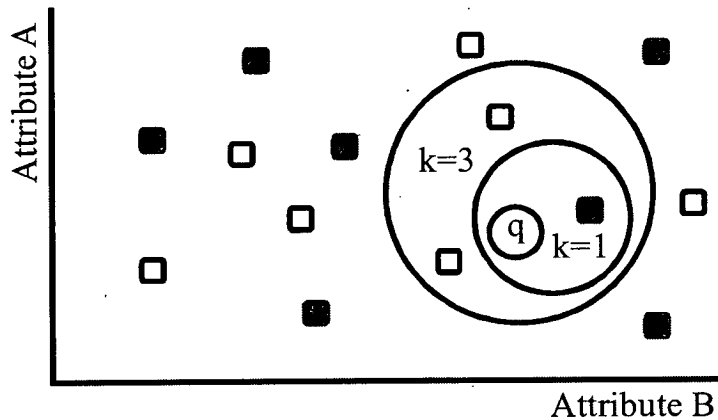
Figure 7-1. KNN used to select cases

If the KNN model is presented with a new problem case (i.e. measurements at a particular day), the similarity of each past case with the problem case will be calculated. The most similar cases will subsequently be selected, and used to calculate the predicted output of the new problem case.

The similarity of each past case with the problem case is calculated by comparing one input variable at a time. In Equation 7-1, a variable i for the past case and problem case is normalized over the range of the past.

$$V_{norm,i} = (V_i - MV_i)/SDV_i \qquad\qquad 7\text{-}1$$

Where :

$V_{norm, i}$ = the normalized value of variable i for the case;

V_i = the value of variable i for the case;

MV_i = the mean of variable i found in the case; and

SDV_i = the standard deviation of the values of the case.

The differences between each past case and the problem case are then calculated with respect to each variable. The function f in Equation 7-2, converts the local difference to the local similarity.

$$local\,sim_i = f(V_{norm,ip} - V_{norm,ic}) \qquad\qquad 7\text{-}2$$

Where :

$localsim_i$ = the local similarity of variable i for past case c and problem case p;

$V_{norm,\,ip}$ = the normalized value of variable i for the problem case;

$V_{norm,\,ic}$ = the normalized value of variable i for the past case;

$V_{norm,ip} - V_{norm,ic}$ = the local difference; and

f = function, which maps the local difference onto the local similarity.

The local similarity (the similarity of a past case and the problem case with respect to only one variable) is found via a mathematical function of the difference between the each past case and a problem case for one variable.

The Gaussian function (bell-shaped curve) is used to map the local difference onto the local similarity is defined in Equation 7-3 that applies fuzzy theory (Dubois and Prade, 1998). This function has a tuning parameter α, which is used to determine the flatness of the smoothing function.

$$f(x) = e^{\left(-0.5\left(\frac{x}{\alpha \times SDV_i}\right)^2\right)} \qquad\qquad 7\text{-}3$$

Where :

f   =   the function, which converts the local difference into the local similarity;

x   =   the local difference between each past case and a problem case;

α =   the tuning parameter; and

SDV_i =   the standard deviation of the local differences of variable i.

The global similarity (i.e. the similarity between the past case and the problem case considering all variables) can be found from the local similarity of each variable. Each local similarity is first multiplied by a weighting factor that corresponds to the importance of that variable in predicting the output. Equation 7-4 defines how the local similarities of each variable are combined to calculate the global similarity of the past case and problem case.

$$Glob\,sim = \sum_{i=1}^{n}\left(local\,sim_i \times w_i\right) / \sum_{i=1}^{n} w_i \qquad\qquad 7\text{-}4$$

Where :

i   = $1, 2, \ldots , n$;

n   =   the number of variables used to represent a case;

w_i =   the weighting associated with variable i; and

$local\,sim_i$ =   the local similarity of the past case and problem case for variable i.

An algorithm proposed by Duch and Grundzinski (1999) was used to identify feature weightings. For the initial ranking of features, all weighting factors are set to one, and evaluation with a single feature turned off (i.e. zero) is made for all features. Thus, ranking is done in the same way as the feature dropping selection method (Duch and Grudzinski, 1999). The important feature has a fixed weighting factor of one and the optimal weighting value for the second factor in the ranking is determined by the search procedure. The remaining factors are all fixed to one. The search is implemented by means of the leave-one-out (LOO) cross validation process

153

(Kohavi, 1995).

When the global similarity of each past case with the problem case is found, the past cases can be ranked in order of their corresponding sum to decide which of the past cases would be deemed similar enough to be selected for adaptation and the past cases can be selected by the first k closest cases. The three to five past cases with the highest similarity rankings were chosen in this study. Tests undertaken on different sets of data show that between two and six cases are usually sufficient to achieve the best performance. The tuning parameter α of the Gaussian function and the k value were determined by LOO cross validation in the training phase (Duch and Grudzinski, 1999).

7.3.4. Support Vector Machine

In SVM, the basic idea is to map original data into a feature space, which has a large number of dimensions via a non-linear mapping function $\phi_i(x)$, which is usually unknown, and then carry out linear regression in the feature space (Vapnik, 1995). Hence, the regression addresses a problem of estimating a function based on a given data set (Equation 7-5).

$$G = \left\{ \left(x_i, y_i \right) \right\}_i^l \qquad\qquad 7\text{-}5$$

Where :

G = data set;

x_i = input vector; and

y_i = desired values, which are produced from $\phi_i(x)$, a non-linear mapping function.

The SVM approximates the optimum decision function using Equation 7-6:

$$f(x) = \sum_{i=1}^{l} \omega_i \phi_i(x) + b \qquad\qquad 7\text{-}6$$

Where :

f(x)   =   decision function;

$\phi_i(x)$ =   non-linear mapping function representing the features of inputs; and

ω and b   =   coefficients, which are estimated by minimizing the regularized risk function R(C).

The regularized risk function R(C) is shown in Equation 7-7.

$$R(C) = C\frac{1}{1}\sum_{i=1}^{l} L_\varepsilon \left(y_i, f(x_i)\right) + \frac{1}{2}\|\omega\|^2 \qquad\qquad 7\text{-}7$$

Where :

R(C)   =   regularized risk function;

C   =   regularized constant determining the trade-off between the training error and the model flatness;

$\frac{1}{1}\sum_{i=1}^{l} L_\varepsilon \left(y_i, f(x_i)\right)$ =   empirical error measured by the ε-insensitive loss function (Equation 7-8);

y_i =   desired values;

$f(x_i)$ =   decision function; and

$\frac{1}{2}\|\omega\|^2$ =   measurement of function flatness.

The ε-insensitive loss function is defined in Equation 7-8

$$L_\varepsilon \left(y_i, f(x_i)\right) = \begin{cases} |y_i - f(x_i)| - \varepsilon, & |y_i - f(x_i)| \ge \varepsilon \\ 0 \end{cases} \qquad\qquad 7\text{-}8$$

Where :

L_ε = ε-insensitive loss function;

y_i =   desired values;

$f(x_i)$ =   decision function; and

ϵ = prescribed parameter.

Equation 7-8 defines a ϵ tube, so that, if the predicted value is within the tube, the loss is zero, while, if the predicted value is outside the tube, the loss is magnitude of the difference between the predicted value and the radius ϵ of the tube (Figure 7-2).
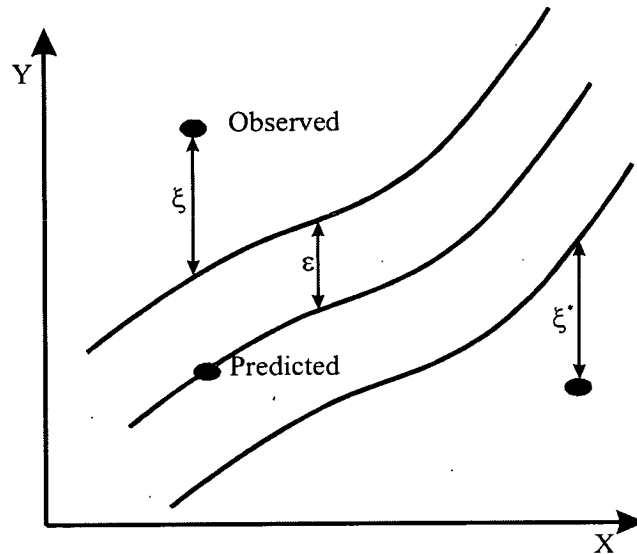
Figure 7-2. The parameter for support vector regression (after Vapnik, 1995)

To get the estimation of ω and b, Equation 7-7 is transformed to the primal objective function (Equation 7-9) by introducing the positive slack variables ξ and ξ^*, which represent the distance from the actual values to the corresponding boundary values of ϵ -tube (Vapnik, 1995).

$$R(\omega,\xi,\xi^*) = \frac{1}{2}\|\omega\|^2 + C\frac{1}{1}\sum_{i=1}^{1}\left(\xi+\xi^*\right) \qquad 7\text{-}9$$

Finally, introducing Lagrangian multipliers and maximizing the dual function of Equation 7-9 changes Equation 7-10 to the following form:

$$R(\alpha_i-\alpha_i^*) = \sum_{i=1}^{1}y_i\left(\alpha_i-\alpha_i^*\right) - \epsilon\sum_{i=1}^{1}y_i\left(\alpha_i+\alpha_i^*\right) - \frac{1}{2}\sum_{i=1}^{1}\sum_{j=1}^{1}(\alpha_i-\alpha_i^*)\left(\alpha_j-\alpha_j^*\right)\left(\phi(x_i)\cdot\phi(x_j)\right) \qquad 7\text{-}10$$

In Equation 7-10, the Lagrangian multipliers α_i and α_i^* are calculated and an

156

optimal desired weighting vector of the regression hyperplane is

$$\omega = \sum_{i=1}^{l}\left(\alpha_i - \alpha_i^*\right)\phi\left(x_i\right) \qquad\qquad 7\text{-}11$$

Hence, the regression function is Equation 7-12.

$$f(x) = \sum_{i=1}^{l}\left(\alpha_i - \alpha_i^*\right)\phi\left(x_i\right)\cdot\phi\left(x\right) + b \qquad\qquad 7\text{-}12$$

By introducing the kernel function, Equation 7-12 can be transformed into the explicit Equation 7-13.

$$f(x) = \sum_{i=1}^{l}\left(\alpha_i - \alpha_i^*\right)K\left(x_i, x_j\right) + b \qquad\qquad 7\text{-}13$$

Where :

$f(x)$ =   decision function;

α, α_i =   Lagrange multipliers; and

$K\left(x_i, x_j\right)$ =   kernel function, obtained by $K\left(x_i, x_j\right) = \phi\left(x_i\right)\times\phi\left(x_j\right)$ in the feature space.

For the kernel function, there are several design choices such as the linear, polynomial and radial basis functions (RBF), and the sigmoid kernel. However, most of the previous research selected the RBF kernel, which non-linearly maps samples into a higher dimensional space, unlike the linear kernel (Dong *et al.*, 2005b). The RBF kernel is shown in Equation 7-14.

$$K\left(x_i, x_j\right) = \exp\left\{-\gamma\left\|x_i - x_j\right\|^2\right\} \qquad\qquad 7\text{-}14$$

Where :

$K\left(x_i, y_i\right)$ =   kernel function ; and

γ =   kernel parameter.

The detailed theoretical background to SVM was described by Vapnik (1995). In this study, the SVM[light] was used due to its fast optimization algorithms and good

potential for regression (Joachims, 1999). Concerning the kernel function, the RBF kernel was selected to analyze the cases, which show non-linear relationships between input and output data sets in the present study. The RBF kernel contains the parameters γ, C and ε (see above). There are no general rules determining these parameters (Lu and Wang, 2005). A five-fold cross validation was conducted to find out appropriate parameters for training steps (Dong *et al.*, 2005b).

7.3.5. Self-organizing map

A SOM consists of neurons, which are connected to adjacent neurons by neighborhood relations. In the training step, one vector x from the input set is chosen and all the weight vectors of the SOM are calculated using some distance measure such as the Euclidian distance (Kohonen, 2001). The neuron, whose weight vector is closest to the input x is called the best-matching unit (BMU), subscripted here by c (Equation 7-15):

$$\|x - m_c\| = \min\{\|x - m_i\|\} \qquad \text{7-15}$$

Where :

x = input vector;

m = weight vector; and

$\| \; \|$ = the distance measure.

After finding the BMU, the weighting vectors of the SOM are updated, so that the BMU is moved closer to the input vector. This adaptation procedure stretches the BMU and its topological neighbors towards the input vector as shown in Figure 7-3.

The SOM update rule for the weight vector of a unit is shown in Equation 7-16. The detailed algorithm of the SOM can be found in Kohonen (2001) for theoretical

considerations:

$$m_i(t+1) = m_i(t) + \alpha(t)h_{ci}(t)[x(t) - m_t(t)]$$ 7-16

Where :

m(t) = weight vector indicating the output unit's location in the data space at time t;

$\alpha(t)$ = the learning rate at time t;

$h_{ci}(t)$ = the neighborhood kernel around the 'winner unit' c; and

$x(t)$ = an input vector drawn from the input data set at time t.
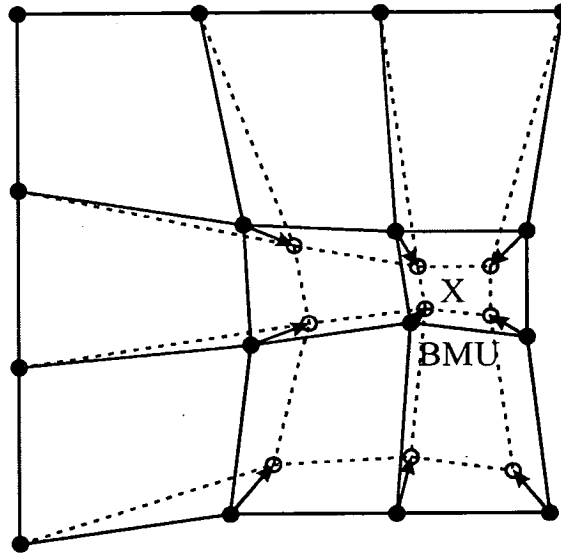
Figure 7-3. Updating the best matching unit (BMU) and its neighbors towards the input vector marked with x. The solids and dashed lines correspond to situations before and after updating (after Vesanto et al., 2000).

After the SOM has been trained, the map needs to be evaluated to find out if it has been optimally trained or if further training is required. The SOM quality is usually measured with two criteria: quantization error (QE) and topographic error (TE). The QE is the average distance between each data point and its BMU, and TE represents

the proportion of all data for which the first and second BMU are not adjacent with respect to the measurement of topology preservation (Kohonen, 2001).

In this study, a SOM toolbox (version 2) for Matlab 5.0 developed by the Laboratory of Information and Computer Science at the Helsinki University of Technology was used (Vesanto *et al.*, 1999). After training the map with different map sizes, the optimum map size was determined on the basis of the minimum QE and minimum TE. The prediction was implemented by finding BMU in the trained map for each test data set.

7.4. BOD and SS prediction

7.4.1. Model performance evaluation

When comparing the performance of different models, the scale-dependent measures based on the absolute error (Equation 7-17) or squared error (Equation 7-18) have been commonly used (Maier *et al.*, 2004; Gevrey *et al.*, 2005).

$$MAE = mean\left(\left|m_i - p_i\right|\right) \qquad\qquad 7\text{-}17$$

$$MSE = mean\left(\left|m_i - p_i\right|^2\right) \qquad\qquad 7\text{-}18$$

$$RMSE = \sqrt{MSE} \qquad\qquad 7\text{-}19$$

Where :

MAE   = mean absolute error;

m_i = measured values;

p_i = predicted values;

MSE   = mean square error; and

RMSE = root mean square error.

Absolute and squared errors are useful when comparing different methods on the same data set, but should not be used, when comparing across data sets that have different scales. The RMSE and MSE have been popular due to their theoretical relevance in statistical modeling. However, they are more sensitive to outliers than MAE (Hyndman and Koehler, 2005).

Percentage errors have the advantage of being scale-independent, and so are frequently used to compare prediction the performance across different data sets. The most commonly used measure is described in Equation 7-20.

$$MAPE = mean\left(\frac{|m_i - p_i|}{m_i} \times 100\right)$$
7-20

Where :

MAPE = mean absolute percentage error;

m_i = measured values; and

p_i = predicted values.

The MAPE has the disadvantage of being infinite, if $m_i = 0$, and having an extremely skewed distribution, when any m_i is close to zero. In the present study, it is impossible to use this measure due to frequent occurrence of zero values for BOD.

Therefore, the MASE method proposed by Hyndman and Koehler (2005), was used to measure the performance of each model. The prediction error is scaled by the in-sample mean absolute error obtained using the naïve predicting method. This new method is clearly independent of the scale of the data, less sensitive to outliers, more easily interpreted and less variable for small samples compared to most of the other methods (see above). If MASE is higher than one, the predictions are worse than in-sample one-step predictions from the naïve method. The MASE is defined in

Equation 7-21.

$$MASE = \frac{MAE}{\frac{1}{n-1}\sum_{i=2}^{n}|m_i - m_{i-1}|} \qquad 7\text{-}21$$

Where :

MASE = mean absolute scaled error;

MAE = $\frac{1}{n}\sum_{i=1}^{n}|m_i - p_i|$

m_i = measured values;

p_i = predicted values; and

n = number of data sets.

7.4.2. Correlation analysis

Table 7-1 summarizes the findings from a correlation analysis comprising input (turbidity, conductivity, redox, outflow water temperature, DO and pH) and target (BOD and SS) variables. Correlations were all weak except between BOD and turbidity, SS and turbidity, and SS and conductivity (at 1% significance level). Therefore, turbidity and conductivity are likely to be the most important input variables to predict BOD and SS concentrations. This information is used to optimize input variables of ANN models.

Table 7-1. Correlation coefficients from a correlation analysis comprising input (column headings) and target (row headings) variables

Variable	Turbidity	Redox	pH	Conductivity	Temperature	DO
BOD[a]	0.413	-0.338	-0.271	0.254	-0.120	-0.074
SS[b]	0.509	-0.308	0.013	0.930	-0.322	-0.127

[a]five-day @ 20 °C N-Allylthiourea biochemical oxygen demand; [b]suspended solids.

7.4.3. Multiple linear regression analysis

Scholz (2003) demonstrated that wetland performance could be predicted by identifying the correlation between water quality variables using simple correlation and regression analysis. Multiple linear regression analysis was carried out to examine whether this simple statistical analysis can be applied for indirect prediction of system performance indicators and to compare with prediction performance of the machine learning technique. Regression analysis was carried out for each data sub-set associated with one wetland filter (Filters 3 to 12). The training was performed with the data belonging to the remaining nine filters, as described in section 7.3.2.

Table 7-2 and Figure 7-4 present BOD prediction results predicted by multiple linear regression analysis for two years (22/09/02 – 21/09/04) of wetland operation. Effluent water temperature, redox, pH and turbidity were selected as optimal regressors for effluent BOD prediction.

Table 7-2. Multiple linear regression analysis applied to predict the five-day @ 20°C N-Allylthiourea biochemical oxygen demand (BOD) (mg/l) concentrations

Filters	a	b	c	d	e	MASE[a]	r^2[b]
3	0.217	-0.044	-12.321	0.163	96.618	1.22	0.092
4	0.227	-0.043	-13.079	0.151	102.037	1.64	0.489
5	0.198	-0.042	-12.316	0.164	96.624	0.93	0.407
6	0.243	-0.045	-12.474	0.151	97.696	1.31	0.191
7	0.205	-0.043	-12.423	0.164	97.426	1.05	0.218
8	0.000	-0.034	-12.678	0.151	100.951	1.64	0.466
9	0.195	-0.040	-12.304	0.178	95.920	1.04	0.249
10	0.172	-0.041	-11.381	0.127	90.449	1.08	0.465
11	0.175	-0.041	-12.219	0.165	96.066	1.16	0.255
12	0.000	-0.024	-12.698	0.286	97.863	1.14	0.137

Multiple regression equation ($BOD_{prediction}$ = a*temperature + b*redox potential+ c*pH + d*turbidity + e) was fitted. [a]mean absolute scaled error; [b]prediction coefficient of determination

As given in Table 7-2, prediction errors (MASE) are higher than one and prediction coefficients of determination (r^2) are considerably low in most cases of filters. Furthermore, multiple regression method showed a weak ability to predict outlying data, as shown in BOD prediction of Filter 8 (Figure 7-4). This suggests that multiple linear regression analysis is not appropriate for BOD prediction.
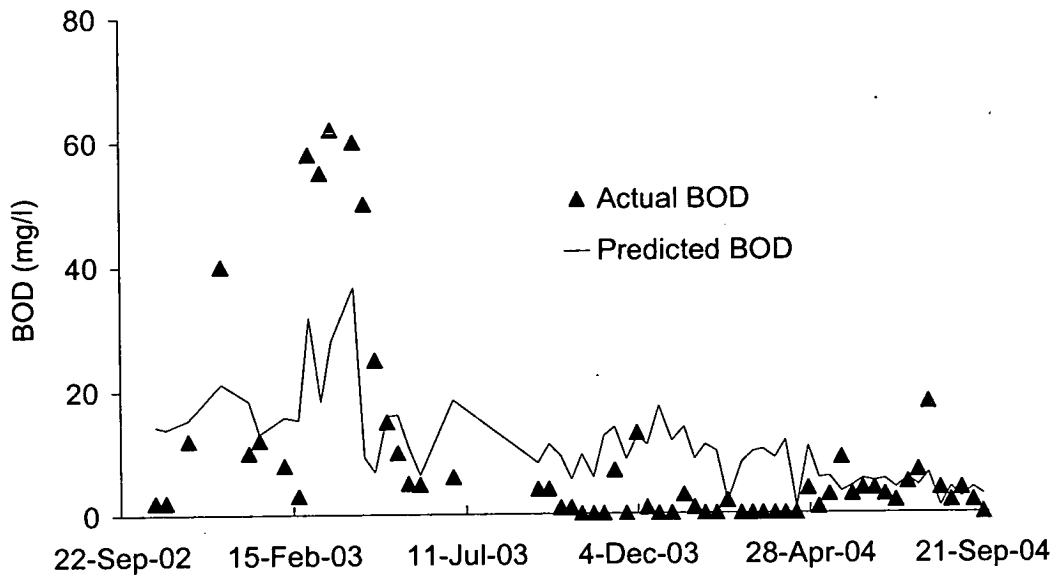
Figure 7-4. Five-day @ 20°C N-Allylthiourea biochemical oxygen demand (BOD) curve predicted by multiple linear regression analysis for Filter 8.

As shown in Table 7-3 and Figure 7-5, application of multiple linear regression analysis for SS prediction was relatively successful, compared to BOD predictions. This is attributed to a high correlation between SS and other variables such as conductivity and turbidity. The selected optimal regressors for SS predictions were effluent water temperature, turbidity and conductivity.

Table 7-3. Multiple linear regression analysis applied to predict the suspended solids (SS) concentrations.

Filters	a	b	c	d	MASE[a]	r^{2} [b]
3	-1.848	0.728	0.020	35.090	0.40	0.960
4	-1.888	0.831	0.019	35.110	0.44	0.93
5	-1.462	0.779	0.020	26.465	0.40	0.957
6	-1.831	0.729	0.020	34.714	0.35	0.932
7	-1.832	0.711	0.020	33.489	0.50	0.857
8	-1.872	0.731	0.020	35.684	0.50	0.927
9	-1.810	0.723	0.019	35.267	0.62	0.884
10	-1.881	0.751	0.019	36.289	0.58	0.919
11	-1.717	0.727	0.019	33.397	0.50	0.823
12	-2.201	0.000	0.020	45.276	0.77	0.743

Multiple regression equation ($SS_{prediction}$ = a*temperature + b*turbidity + c*conductivity + d) was fitted. [a]mean absolute scaled error; [b]prediction coefficient of determination
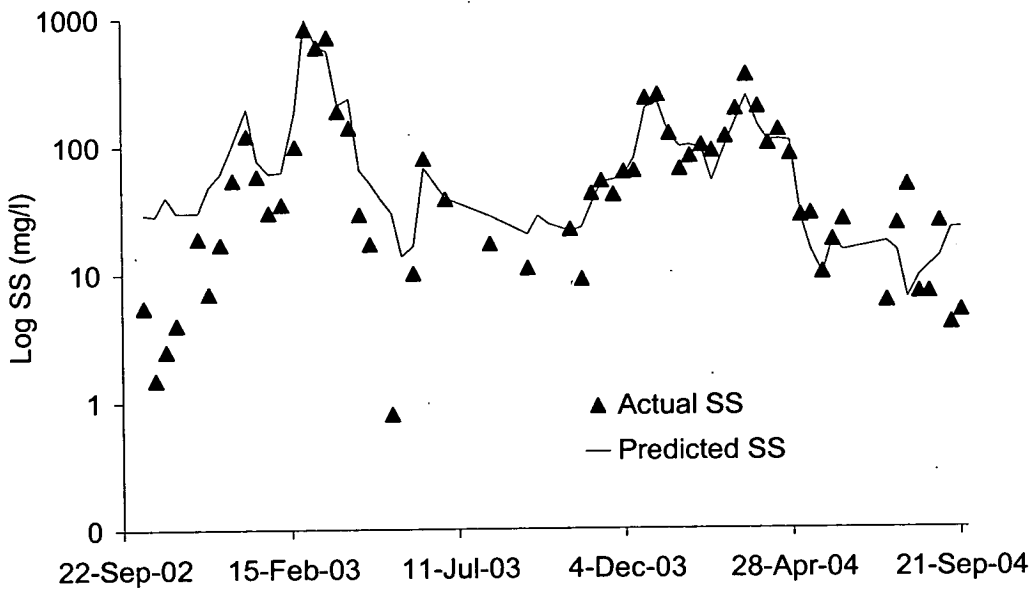
Figure 7-5. Suspended solids (SS) curve predicted by multiple linear regression analysis for Filter 8.

7.4.4. Optimization of input variables

When analyzing the data sets with the KNN model, the optimal k value and weighting factors for all variables were determined by LOO cross validation. The selected k value was between 3 and 5 for most data sets, and weighting factors were different depending on the individual characteristics of the chosen case base.

For example, when predicting the effluent BOD concentration for Filter 8, the k value was fixed at 3 and the weighting factors 1.00, 0.78, 1.00, 0.30 and 0.78 for water temperature (°C), redox (mV), conductivity (μS), pH (-), and turbidity (NTU), respectively of the outflow were assigned.

When conducting the SVM analysis, the parameters C and ε were identified by the five-fold cross-validation approach. Theoretically, a small value of C will under-fit the training data, because the weight placed on the training data is too small, thus resulting in a large error for the test data set. On the contrary, when C is too large, the SVM model will be over-trained (Dong *et al.*, 2005b). The ε is set to be 0.1 when varying C in the one-time search method (Cao and Francis, 2003). There exists an optimum point for C, as shown in Figure 7-6 (a). Thus C was determined to be 10 at the point of the lowest MAE value.

In general, the larger ε, the smaller is the number of support vectors and thus the sparser the representation of the solution. However, if ε is too large, it can deteriorate the accuracy of the training data set (Cao and Francis, 2003). According to Figure 7-6 (b), parameter ε was fixed at 0.1. Furthermore, γ of the RBF kernel was set to 0.2, according to Equation 7-22 (Chang and Lin, 2001; Dong *et al.*, 2005b).

$$\gamma = \frac{1}{n}$$

7-22

Where :

γ = parameter of the kernel function; and

n = number of variables in the input data.
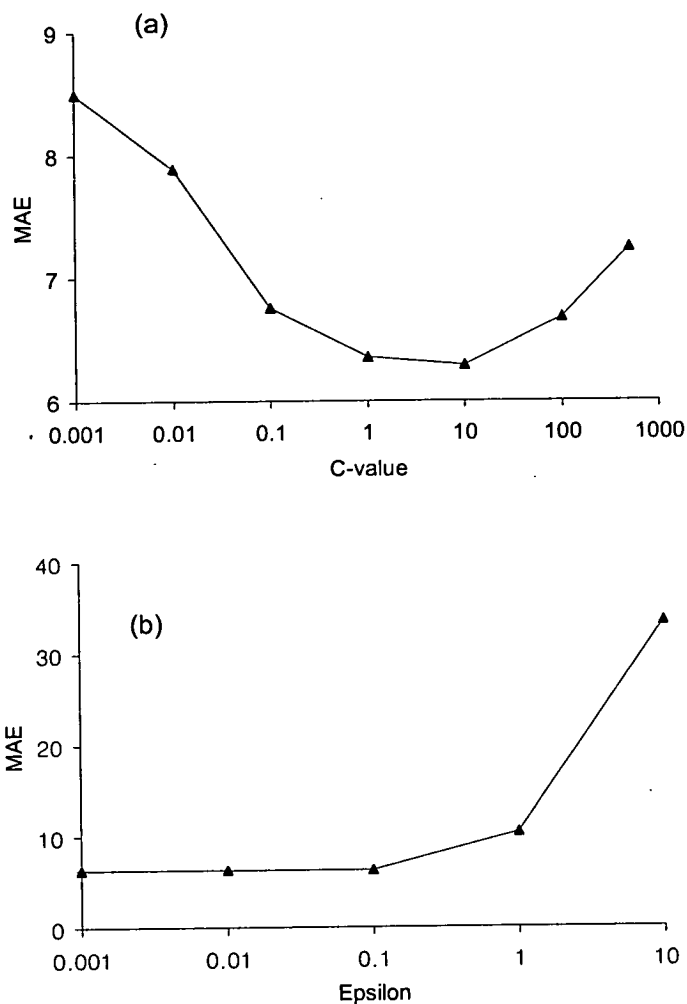
Figure 7-6. (a) C-value (ε=0.1), and (b) epsilon (C=10) versus.

In the SOM model, the map size is the most important factor to detect the differences of data. If the map is too small, it might not explain some important differences. On the contrary, it is possible to 'over-train' the models (Leflaive *et al.*, 2005). After creating maps with several different map sizes, the optimum map size,

which has lower errors for both QE and TE, was chosen. For example, when predicting the BOD and SS of Filter 8, the map size comprised 2304 and 1908 units, respectively, as presented in Table 7-4.

Table 7-4. Quantization error (QE) and topographic error (TE) for different self-organizing map sizes. Optimal map size and corresponding errors are underlined.

	BOD prediction					
Map size	608	1508	2006	2304	2613	2911
QE	0.038	0.017	0.008	0.007	0.005	0.004
TE	0.108	0.091	0.124	0.091	0.148	0.120
	SS prediction					
Map size	600	1001	1504	1908	2300	2500
QE	0.025	0.015	0.008	0.006	0.005	0.004
TE	0.041	0.033	0.020	0.012	0.028	0.030

Table 7-5 summarizes the findings of an input variable combination optimization exercise. The purpose was to identify the optimum combination of input variables by estimating both BOD and SS with as few input variables as possible to reduce the prediction error, sampling costs and effort.

Therefore, the data sets contained the following input variables in order of decreasing priority based on a correlation analysis (Table 7-1): turbidity, redox, pH, conductivity and outflow water temperature in terms of correlation with BOD; conductivity, turbidity, outflow water temperature, redox and DO in terms of correlation with SS.

In the SVM model, best prediction results were obtained with five input variables for both BOD and SS. However, when applying the SOM model, the BOD and SS predictions were most accurate with the single input variable turbidity and conductivity, respectively. The best combination of variables for each model is

highlighted (underlined figures) in Table 7-5. Consequently, input variable combinations for each model were determined on the basis of this information.

Table 7-5. Optimization of input attribute combinations for Filters 8. K-nearest-neighbors (KNN), support vector machine (SVM) and self-organizing map (SOM) applied to predict the five-day @ 20°C N-Allylthiourea biochemical oxygen demand (BOD) (mg/l) and the suspended solids (SS) (mg/l) concentrations. The training and test data sets contained the following input variables: 1 = turbidity (NTU); 2 = redox potential (mV); 3 = pH (-); 4 = conductivity (μS); 5 = outflow water temperature (°C); 6 = dissolved oxygen (mg/l). The figures for the best combinations of variables are underlined.

Input variables	Number of test data sets	KNN		SVM		SOM	
		MASE[a]	r^{2b}	MASE[a]	r^{2b}	MASE[a]	r^{2b}
BOD prediction							
1	60	1.42	0.394	1.35	0.621	0.29	0.998
1+2	60	1.49	0.394	1.27	0.621	0.30	0.988
1+2+3	60	1.51	0.330	1.09	0.639	0.34	0.984
1+2+3+4	60	1.34	0.342	0.95	0.699	0.46	0.955
1+2+3+4+5	60	1.01	0.680	0.94	0.720	0.41	0.947
SS prediction							
4	64	0.55	0.936	0.38	0.959	0.29	0.999
4+1	64	0.44	0.943	0.40	0.950	0.30	0.992
4+1+5	64	0.37	0.948	0.39	0.950	0.31	0.980
4+1+5+2	64	0.39	0.955	0.39	0.954	0.31	0.969
4+1+5+2+6	64	0.39	0.951	0.36	0.949	0.39	0.956

[a]mean absolute scaled error; [b]prediction coefficient of determination.

7.4.5. Comparison of applications

The prediction results of the effluent BOD and SS concentrations using KNN, SVM and SOM models are summarized in Table 7-6. Figure 7-7 and Figure 7-8 visualize the BOD and SS prediction performance of the KNN, SVM and SOM models for Filter 8 (typical UK reed bed according to Scholz (2004)).

Table 7-6. Prediction of water quality vairables of constructed treatment wetlands. K-nearest-neighbors (KNN), support vector machine (SVM) and self-organizing map (SOM) applied to predict the five-day @ 20°C N-Allylthiourea biochemical oxygen demand (BOD) (mg/l) and the suspended solids (SS) (mg/l) concentrations.

Filter number	Number of test data	KNN		SVM		SOM	
		MASE[a]	$r^{2\,b}$	MASE[a]	r^{2b}	MASE[a]	r^{2b}
BOD prediction							
3	55	1.02	0.461	0.98	0.384	0.77	0.997
4	58	1.01	0.681	1.07	0.713	0.17	0.994
5	59	0.58	0.696	0.67	0.666	0.35	0.994
6	61	0.76	0.798	0.83	0.643	0.44	0.997
7	58	0.78	0.609	0.77	0.503	0.85	0.999
8	60	1.01	0.680	0.94	0.720	0.29	0.998
9	57	0.76	0.544	0.90	0.431	0.20	0.998
10	60	0.71	0.744	0.87	0.513	0.41	0.999
11	59	0.79	0.645	0.96	0.451	0.37	0.985
12	115	0.88	0.342	0.87	0.213	0.24	0.997
3-12	642	0.79	0.550	0.84	0.463	0.36	0.888
SS prediction							
3	60	0.49	0.973	0.33	0.966	0.17	0.999
4	61	0.38	0.957	0.28	0.954	0.08	0.998
5	60	0.66	0.938	0.28	0.978	0.20	0.999
6	64	0.57	0.941	0.32	0.940	0.17	0.998
7	57	0.32	0.892	0.38	0.883	0.08	0.995
8	64	0.37	0.948	0.36	0.949	0.29	0.999
9	62	0.53	0.882	0.51	0.883	0.54	0.996
10	65	0.48	0.922	0.51	0.949	0.62	0.998
11	64	0.42	0.839	0.36	0.895	0.48	0.999
12	113	0.83	0.803	0.68	0.770	0.47	0.953
3-12	670	0.54	0.844	0.43	0.883	0.31	0.932

[a]mean absolute scaled error; [b]prediction coefficient of determination.

Figure 7-7. The prediction of five-day @ 20°C N-Allylthiourea biochemical oxygen demand (BOD) concentrations. BOD curve predicted by k-nearest-neighbors (KNN), support vector machine (SVM) and self-organizing map (SOM) for (a) the first year (22/09/02 – 21/09/03), and (b) the second year (22/09/03 – 21/09/04) of wetland operation for Filter 8. The entry (32.6, 3-Dec-03) for the KNN prediction is beyond the displayed range.

171
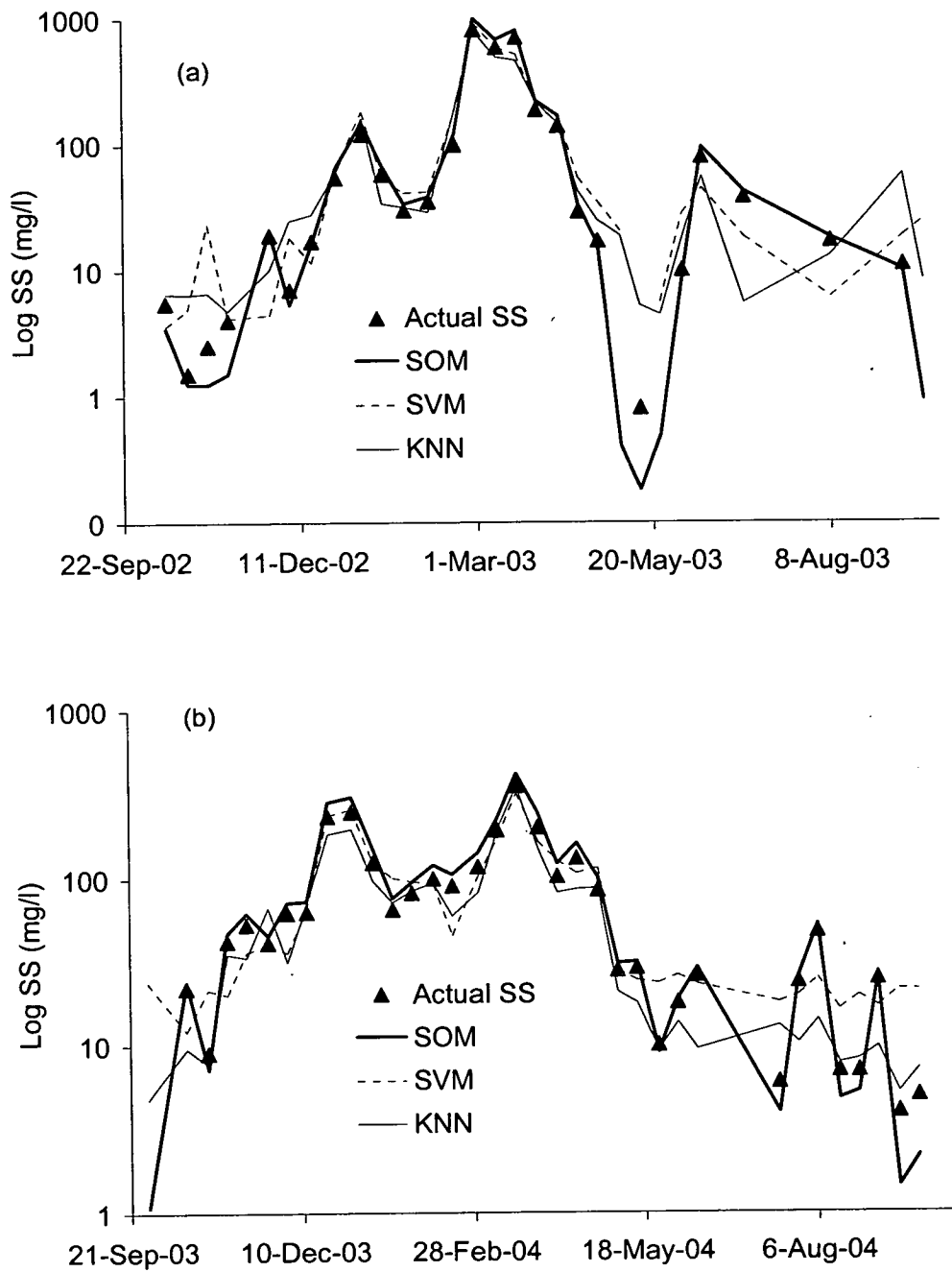
Figure 7-8. The prediction of suspended solids (SS) concentrations. SS curve predicted by k-nearest-neighbors (KNN), support vector machine (SVM) and self-organizing map (SOM) for (a) the first year (22/09/02 – 21/09/03), and (b) the second year (22/09/03 – 21/09/04) of wetland operation for Filter 8.

The results show that the BOD and SS concentrations are reasonably well predicted with given input variables. Despite the greater variability of SS in contrast

to BOD (Scholz, 2004), SS has a smaller MASE value between measured and predicted concentrations in comparison to BOD (Table 7-5 and Table 7-6).

The average MASE from the BOD prediction with SOM, SVM, and KNN are 0.36, 0.84 and 0.79, respectively. While the performance of the SVM model was not superior to that of KNN, the SOM model gave excellent prediction performance values compared to the other models (Table 7-6; Figure 7-7 and Figure 7-8).

To ensure the statistical significance of these findings, the prediction results were compared with each other and analyzed by using an analysis of variance (ANOVA). The ANOVA threshold for statistically significant findings is $p < 0.05$. It follows that pairs of MASE associated with $p \geq 0.05$ can be regarded as similar. The analysis showed that the MASE of the SOM model were statistically different from those of SVM and KNN. However, the MASE of SVM and KNN were similar to each other, showing that corresponding p-values were higher than 0.05.

From the findings, it can be concluded that the SOM model outperformed KNN and the SVM model. In contrast to traditional curve fitting techniques, the neural networks such as SOM are capable of 'picking-up' rapidly fluctuating trends among the different input variables. The SOM is well suited for relatively highly variable water quality data sets such as those from constructed treatment wetlands.

Figure 7-9 shows the regression analysis between measured and predicted BOD, and measured and predicted SS for Filter 8 using the SOM model. The associated data set contained turbidity and conductivity for both BOD and SS predictions. The application of linear trendlines result in very good fits for both target variables; the prediction coefficients of determination are 0.998 for BOD and 0.999 for SS.
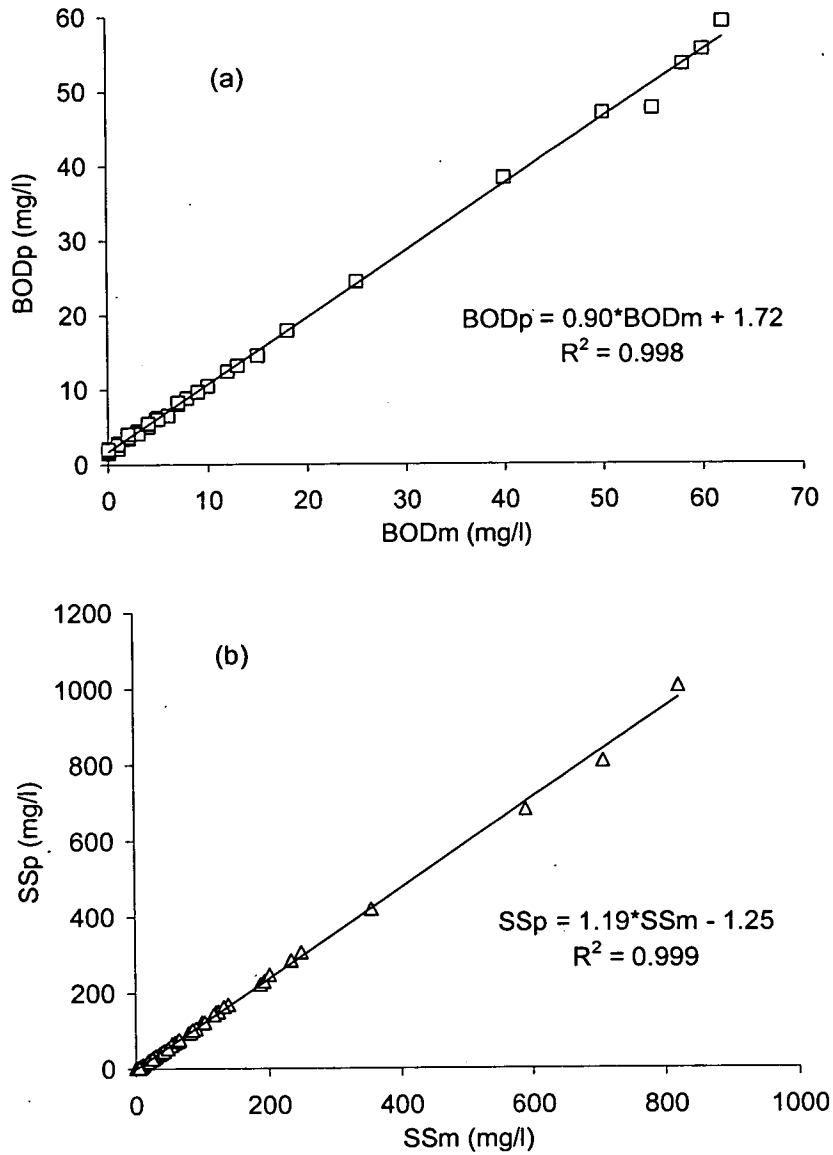
Figure 7-9. Regression analysis between the measured and predicted values. Regression analysis (a) between the measured five-day @ 20°C N-Allylthiourea biochemical oxygen demand (BODm) and the predicted BOD (BODp) applying self-organizing map (SOM), and (b) between the measured suspended solids (SSm) and the predicted SS (SSp) applying the SOM model for Filter 8.

Concerning the supervised and unsupervised methods, a previous study has shown that the prediction accuracy of unsupervised neural networks is lower than the one for supervised networks, as generally expected (Lee *et al.*, 2005). However, this result indicated that the SOM model (an unsupervised method) is superior to the

SVM (a supervised method) model. Moreover, the SOM model provides better prediction results with smaller input variables.

Basically, the outstanding performance of the SOM models is attributed to the potential of clustering and classification of data. Particularly, in comparison with other neural networks, SOM was convenient for detecting the outliers which are displayed in particular parts of the map without affecting the remaining parts, because each outlier takes its place in one unit of the map, and only the weights of that unit and its neighbors are affected (Cereghino *et al.*, 2001; Leflaive *et al.*, 2005).

Additionally, the SOM model showed its high performance in the visualization of relationship for non-linear and complex biochemical data sets. Visualization gives better understanding of the relationships between most variables in biochemical processes. For example, Figure 4-11 displays component planes on the trained map. The U-matrix visualizes distances between neighboring map units, and helps to identify the cluster structures of the map. Each component plane shows values for each variable with its corresponding unit.

The likelihoods of correct predictions, if the effluent concentrations are either below or above the thresholds for secondary wastewater treatment, are also shown in Table 7-7. The BOD and SS concentrations for compliance are 20 and 30 mg/l, respectively (Tchobanoglous *et al.*, 2003). The correct predictions of compliance were all >87%. The probabilities are therefore all at least by 0.37 higher in comparison to 'pure guessing (i.e. probability of 50%)'. This suggests that three models can be used as effective tools to support the constructed treatment management on the daily basis.

Table 7-7. Correct prediction of compliance (%).

models	SOM[a]	SVM[b]	KNN[b]
BOD	97.0	87.9	87.2
SS	96.4	90.0	88.1

[a]self-organizing map; [b]support vector machine; [c]k-nearest neighbors.

7.4.6. Optimization of the size of the input database

Table 7-8 shows an unbiased assessment of data sub-sets to optimize the size of the input database for BOD and SS prediction using SOM. The data base contained turbidity and conductivity as input variables for both BOD and SS predictions, because the combinations of these variables have the lowest MASE (Table 7-5). The data sub-sets were selected systematically (in sequence; x out of y, where $x \leq y$), but statistically at random. The probabilities of all filters to contribute to any calculation were equal. Findings show that the BOD and SS can still be predicted reasonably well with relatively small data sets. The optimum number of data sets can be selected by trial and error.

Figure 7-10 and Figure 7-11 present the BOD and SS curve predicted by small training data base. Each SOM map for BOD and SS prediction was created with 39 and 40 data sets, respectively. In the case of BOD prediction, the SOM model becomes weak in its ability to predict some outlying data when smaller training data sets used, as shown in Figure 7-10. In contrast, SS prediction was highly satisfactory even with extremely small training data sets. This is attributed to high correlation between output data (SS concentrations) and input data (conductivity).

Table 7-8. Unbiased assessment of data sub-sets for Filters 3 to 12. Self-organizing map (SOM) applied to predict the five-day @20 °C N-Allylthiourea biochemical oxygen demand (BOD) and the suspended solids (SS) concentrations with the input variables turbidity (NTU) and conductivity (μS), respectively.

Filter number	Number of training data sets	MASE[a]	Correct prediction of compliance (%)[b]	r^{2} [c]
BOD prediction				
1 out of 15	39	0.67	100	0.801
1 out of 10	59	0.61	100	0.964
1 out of 5	117	0.44	100	0.992
1 out of 4	147	0.39	100	0.975
1 out of 3	195	0.44	98.33	0.862
1 out of 2	292	0.31	100	0.989
2 out of 3	388	0.26	100	0.995
3 out of 4	437	0.20	100	0.995
4 out of 5	466	0.22	100	0.997
1 out of 1	582	0.29	100	0.998
SS prediction				
1 out of 15	40	0.14	95.31	0.995
1 out of 10	61	0.21	98.44	0.981
1 out of 5	125	0.35	95.31	0.996
1 out of 4	152	0.19	95.31	0.998
1 out of 3	202	0.37	93.75	0.998
1 out of 2	304	0.37	98.44	0.996
2 out of 3	404	0.22	98.44	0.999
3 out of 4	454	0.31	95.31	0.999
4 out of 5	481	0.27	96.88	0.997
1 out of 1	606	0.29	95.31	0.999

[a]mean absolute scaled error; [b]likelihoods of correct predictions, if the effluents are either below or above the thresholds for secondary wastewater treatment (The BOD and SS for compliance are 20 and 30 mg/l, respectively); [c]prediction coefficient of determination.
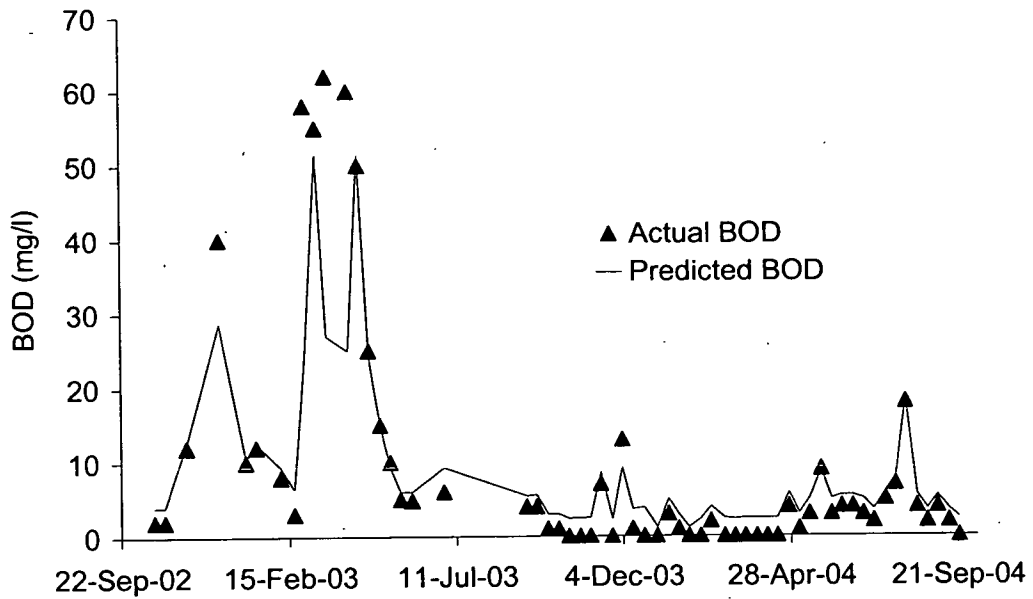
Figure 7-10. the five-day @20 °C N-Allylthiourea biochemical oxygen demand (BOD) curve predicted by self-organizing map (SOM) trained with small data sets (= 39) for Filter 8
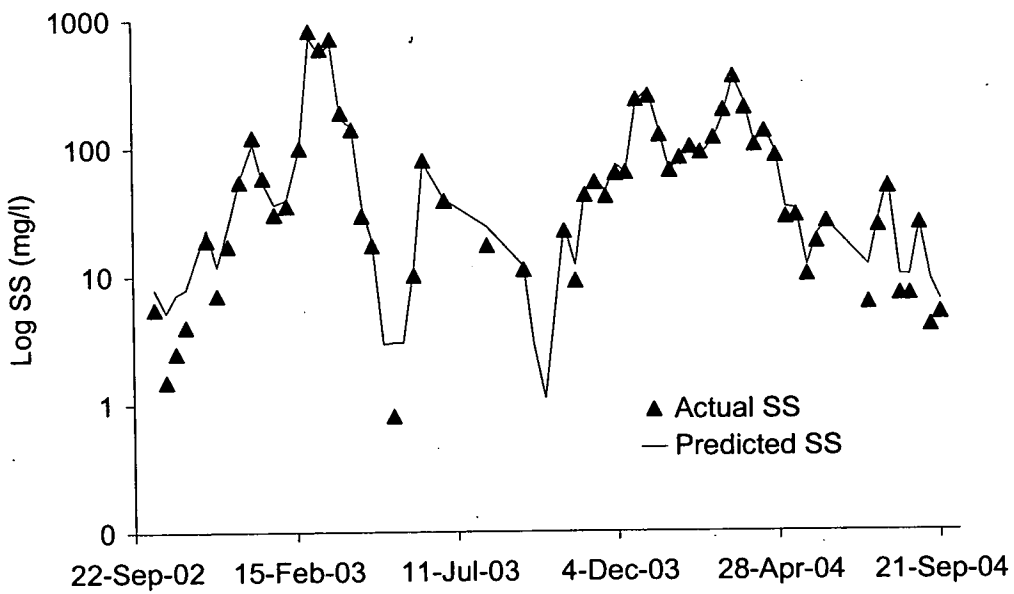
Figure 7-11. Suspended solids (SS) curve predicted by self-organizing map (SOM) trained with small data sets (= 40) for Filter 8.

7.5. Nutrient prediction

Table 7-9 presents a correlation analysis result for ammonia-N, nitrate-N and P. A correlation analysis was carried out to assess the possibility of application of the SOM model and to identify the optimal combination of input variables for estimating nutrients concentrations in constructed wetlands.

As shown in Table 7-9, conductivity was highly correlated with ammonia-N concentrations. However, correlations between input variables and nitrate-N (or P) concentrations were not strong enough to predict reasonably target values (nitrate-N and P). Therefore, the SOM model was applied to estimate only ammonia-N concentration. Conductivity, temperature and redox were selected as input variables, according to the correlation analysis.

Table 7-9. Correlation coefficients from a correlation analysis comprising input (column headings) and target (row headings) variables.

Variable	Conductivity	Temperature	Redox	Turbidity	pH
Ammonia -N	0.617	-0.341	-0.322	0.221	-0.083
Nitrate-N	0.004	-0.245	-0.069	0.162	0.016
P	-0.059	0.032	-0.005	-0.047	0.052

The SOM model was tested for each data sub-set associated with one wetland filter (Filters 7, 8 and 12). The training of the model was performed with the data belonging to the remaining two filters. For example, when estimating the performance of Filter 7, the data sub-sets of Filter 8 and 12 were used as training data.

Table 7-10 and Figure 7-12 show the prediction results of the effluent ammonia-N concentrations. The ammonia-N concentrations of Filter 8 were well estimated by using the data sub-set of Filter 7 and 12 as presented in Figure 7-12.

Table 7-10. Self-organizing map (SOM) applied to predict ammonia-nitrogen (mg/l) concentrations

Filter number	Number of test data sets	MASE[a]	r^{2} [b]
7	63	0.28	0.974
8	65	0.46	0.832
12	119	0.32	0.940

[a]mean absolute scaled error; [b]prediction coefficient of determination
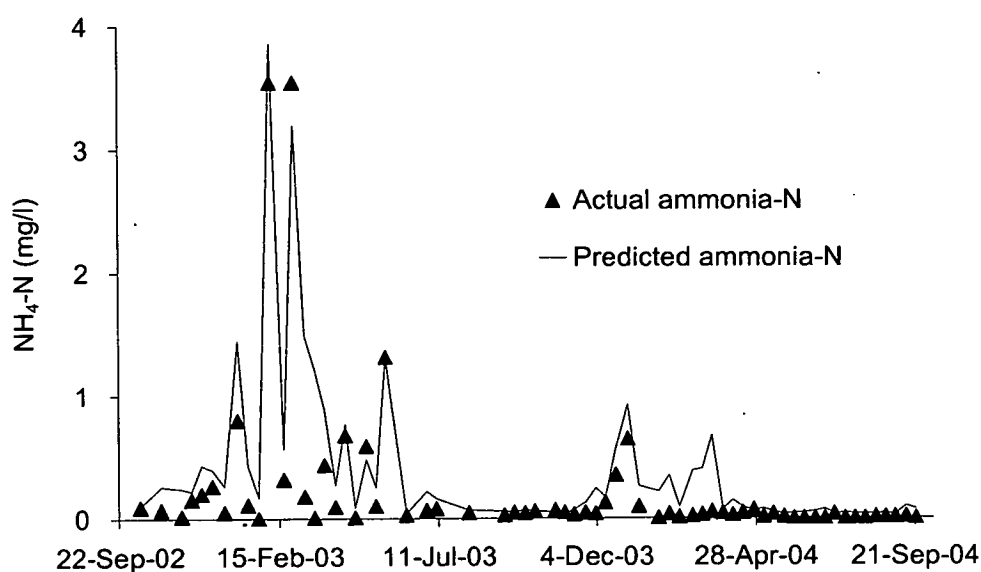
Figure 7-12. Ammonia-nitrogen curve predicted by self-organizing map (SOM) for two years (22/09/02 – 21/09/04) of wetland operation for Filter 8.

The nitrogen concentrations of planted filter (Filter 8) were well predicted using the measured variables of unplanted filter (Filter 7), suggesting that the SOM model is highly efficient at prediction of water quality variables of different filters.

7.6. Heavy metal prediction

As demonstrated in sections 7.4.2 and 7.5, a correlation analysis was carried out to identify the optimal combination of input variables for estimating Ni and Cu

concentrations. Conductivity and redox were highly correlated with Ni and Cu concentrations, respectively (Table 7-11). Conductivity and pH were selected as input variables to estimate Ni concentrations, based on the correlation analysis. In the case of Cu prediction, the redox and temperature were chosen. The training and testing data sub-set was divided as shown in section 7.5.

Table 7-11. Correlation coefficients from a correlation analysis comprising input (column headings) and target (row headings) variables.

Variable	Conductivity	pH	Turbidity	Temperature	Redox
Ni	0.676	-0.309	0.234	-0.204	-0.116
Cu	-0.245	0.121	-0.097	0.466	0.498

The results of SOM model performance for the effluent Ni and Cu concentrations prediction are shown in Table 7-12. Figure 7-13 illustrates the Ni and Cu prediction results for Filter 8. Ni has a smaller MASE value between measured and predicted concentrations in comparison to Cu, even though the Ni concentrations are more variable compared to Cu throughout the operation periods.

The low Ni prediction errors are due to the high correlation coefficient between conductivity and Ni. Nevertheless, Cu concentrations are reasonably well predicted with given input variables as well (Table 7-12).
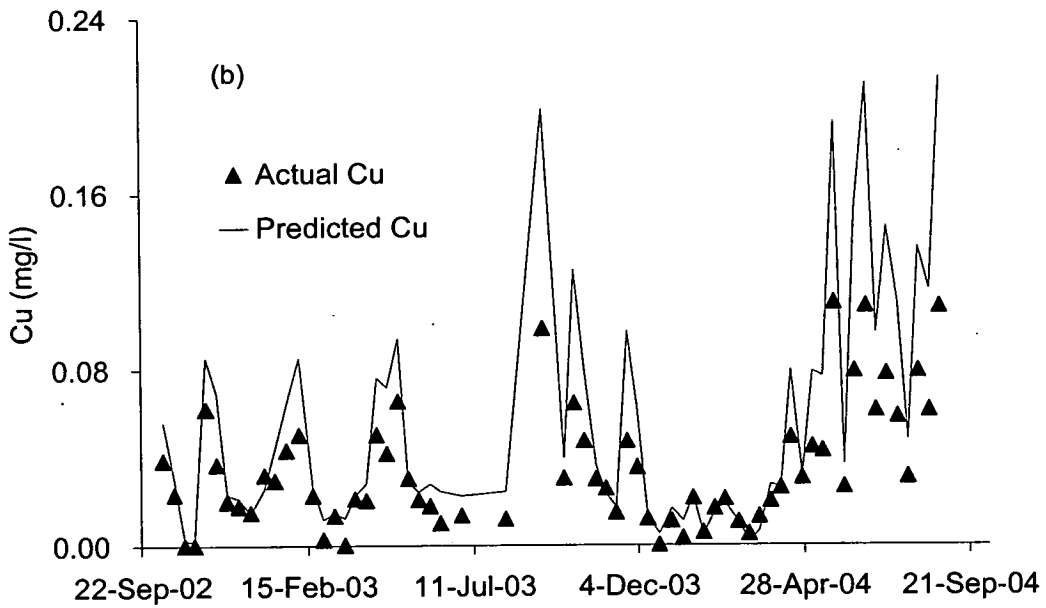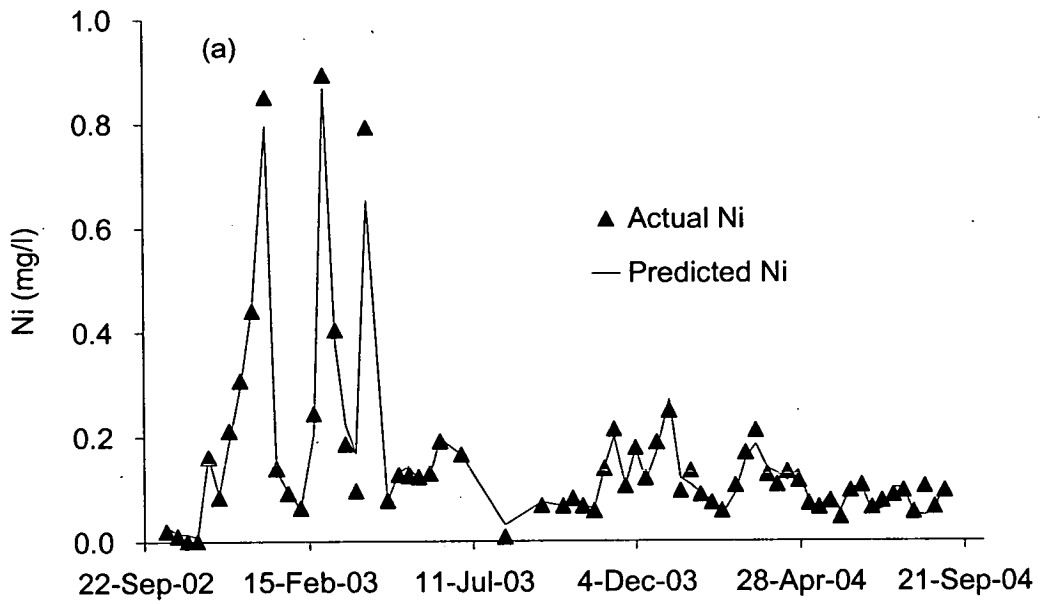
Figure 7-13. (a) nickel and (b) copper curve predicted by self-organizing map (SOM) for two years (22/09/02 – 21/09/04) operation of wetland for Filter 8.

Table 7-12. Self-organizing map (SOM) applied to predict nickel (mg/l) and copper (mg/l) concentrations.

Filter number	Number of test data sets	MASE[a]	r^{2} [b]
Ni prediction			
7	65	0.71	0.967
8	67	0.14	0.985
12	112	0.57	0.965
Cu prediction			
7	66	0.50	0.889
8	68	1.18	0.952
12	114	1.00	0.970

[a]mean absolute scaled error; [b]prediction coefficient of determination

7.7. Summary

The KNN, SVM and SOM models were successfully applied to predict water quality variables of constructed treatment wetlands. The BOD and SS which are expensive to estimate, can be cost-effectively monitored by applying machine learning tools with input variables such as turbidity and conductivity. Furthermore, the SOM model was successfully applied for the prediction of nutrients and heavy metals. Their performance is encouraging and the use of these models as management tools for the day-to-day process control is therefore recommended. Moreover, little domain knowledge is required to build a model and the input variables can be optimized by trial and error.

In terms of accuracy of prediction, the SOM model provided better performance using smaller input variables in comparison to both KNN and SVM models. Particularly, the SOM model demonstrated its potential to analyze the relationship between complex biochemical variables.

However, establishing the SOM model required more time due to the long searching process of the optimal map (i.e. computer run time of 4-5 hours), compared to the KNN and SVM models. Thus, in addition to the accuracy of model predictions, the resource that is required to build and test the model should be considered when selecting the optimal model. This chapter demonstrates the successful application of KNN, SVM and SOM to typical 'black box' systems such as constructed treatment wetlands governed by biochemical processes.

Chapter 8   Conclusions

8.1. Overall conclusion

Laboratory-scale column experiments to investigate constructed wetlands treating concentrated urban runoff and studies on application of machine learning methods to support constructed wetland management were undertaken. The following conclusions show that the novel temporarily flooded filters are highly efficient for the treatment of urban runoff characterized by high seasonal water quality variation and machine learning methods were successfully applied to predict water quality variables of constructed treatment wetlands.

The most vital conclusions of this study are summarized in the following four sub-sections:

1. Temporarily flooded vertical-flow wetlands showed high treatment performance with respect to BOD, SS, nutrient and heavy metal. The following conclusions were drawn:

- Despite of highly variable loading, the BOD removal performance in the wetland filters was satisfactory and stable throughout the seasons in cold climate. This suggests that the temporarily flooded vertical-flow wetland system could be well adapted to the highly variable environmental conditions.

- The SS treatment performance improved considerably over time, however, slightly reduced particularly in the late autumn and winter. This indicates that

the SS removal performance was deteriorated with increasing salt and grit content in their flow.

- The temporarily flooded wetland systems outperformed other types of wetland systems in terms of nutrient removal. Oxygen supply into the systems was significantly enhanced by temporarily flooding, and consequently nitrification (> 46 % of removed ammonia-N) was found to be the predominant mechanism in ammonia-N removal processes.

- Cu removal was satisfactory in comparison to Ni, and high degree of Cu removal was constantly sustained, suggesting that Cu removal performance is stable under highly variable environmental conditions.

- The performance of metal retention became susceptible to seasonal change in environmental factors such as pH and redox potential in the aged wetland system. Furthermore, adverse impact of macrophytes on metal retention is likely to increase over time.

2. Optimal design and operation guidelines were proposed by assessing the role of macrophytes and filter media in the treatment processes of the systems.

2.1. The following design guidelines were obtained:

- The maximum possible removal rates of the systems for BOD and SS were estimated as 37 $g/m^2 \cdot d$ and 500 $g/m^2 \cdot d$, respectively. This is a useful parameter to compare the removal potential of system with others. However, further experiment should be implemented to obtain appropriate design criteria for temporarily flooded vertical-flow wetlands.

- BOD and SS removal performance was not significantly affected by filter compositions. With respect to the effect of macrophytes, macrophytes had a negative impact on the BOD removal processes, whereas macrophytes provided good filtration conditions by preventing the filters from clogging.

- The N removal performance of planted systems was more efficient and stable throughout the season particularly after the system were matured, compared to that of unplanted systems. The macrophytes were found to contribute significantly to the N removal process as plant uptake and oxygen transfer through the root system facilitated greatly the N removal.

- The P removal performance was not improved by special filter media such as Filtralite, suggesting that adsorption to media is not a main source of P removal in the present system. Compared to filter media, macrophytes were proven to be more crucial factor to control P removal.

- Higher effluent Ni concentrations were recorded in the planted systems, despite their ability to take up the heavy metals. Macrophytes provided undesirable conditions for precipitation of Ni by lowering pH in the processes.

- The metal removal performance of constructed wetland filters was virtually similar regardless of their filter media composition. Nevertheless, the cost-effective material such as ochre can be added as post treatment system of constructed wetlands.

- High investment costs for more complex filters are not justified by their low contribution to removal performance of pollutants. The sand-gravel based reed beds are recommended as optimal type of wetlands for urban runoff treatment.

187

However, impact of macrophytes on the target heavy metal needs to be examined to avoid adverse effect of macrophytes on the metal removal performance.

2.2. Operational guidelines were obtained as follows:

- System performance with respect to BOD, SS, heavy metal and nutrients removal were mainly controlled by operational conditions such as retention time rather than filter compositions. The performance of most filters becomes degraded at higher loading rates. However, the applied loading rates in the present study did not reach the maximum. Further investigations under the condition of higher loading rate are needed to obtain the optimal operational guideline.

- A large part of Ni in constructed wetland filters is likely to leach when exposed to a high salt concentration in winter, and possibly also to reducing conditions and a low pH. Therefore, road runoff such as gully pot effluent contaminated with heavy metals and road salts should not be treated with constructed wetlands during winter. Conventional pH adjustment can also be considered to prevent Ni leaching.

- Harvesting macrophyte was a good source of nutrients removal. Substantial amount (17.5 %) of N was removed by harvesting macrophytes. However, amounts of metals removed by harvest were negligible (< 1 % on average), if compared to those retained in the system.

- Artificial aeration improved the BOD removal efficiency in the new filter systems, whereas the effect of aeration on BOD removal was not apparent in the matured systems. In addition, aeration was shown to assist nitrification.

3. The feasibility of conventional pH adjustment to improve the performance of wetlands was investigated. The following conclusions with respect to the impact of pH on the treatment process were drawn:

- The effluent pH levels decreased consistently, since the pH of the inflow was artificially raised up to approximately eight, indicating that wetland filters had a great pH buffer capacity.

- After creating an artificially high inflow pH, the BOD removal efficiency did not decrease, indicating high pH had no apparent influence on microorganism in the present system.

- The elevated pH contributed significantly to prevent Ni breakthrough during winter and enhance the ammonia-N removal potential of wetland filters.

- The high pH had no apparent negative effect on the growth of macrophytes.

- These results indicate that conventional pH adjustment can be successfully applied to constructed wetland systems for urban runoff treatment.

4. Machine learning models such as KNN, SVM and SOM were successfully applied to predict water quality variables of constructed treatment wetlands.

- The BOD and SS, which are expensive to estimate, can be cost-effectively monitored by applying machine learning tools with input variables such as turbidity and conductivity.

- The SOM model was also successfully applied for the prediction of nutrients and heavy metals. Moreover, little domain knowledge is required to build a model and the input variables can be optimized by trial and error.

- The SOM model provided better performance using smaller input variables in comparison to both KNN and SVM models. However, establishing the SOM model required more time due to the long training process. Thus, in addition to the accuracy of model predictions, the resource that is required to build and test the model should be considered when selecting the optimal model.

- The performance of machine learning models is encouraging and the use of these models as management tools for the day-to-day process control is therefore recommended.

8.2. Recommendations for future work

The findings have significant implications on the future design, operation, monitoring and management of constructed treatment wetlands for urban runoff treatment since a proposed temporarily flooded system was highly efficient and its performance was stable in a cold climate. Furthermore, costs can be saved on filter material, aquatic plants and water sampling.

The physical and chemical pollutant removal mechanisms in constructed wetlands were identified in this study. The contribution of macrophyte and filter media to the wetlands performance was also assessed. However, the comprehensive removal mechanism in the present system is still unclear.

Further analysis for N species (i. e. total N or total Kjeldahl N) is required to quantify the mass transformation of N and to identify the exact mechanisms of N removal in the constructed wetlands. The investigations for speciation and distribution of metal in the sediments may also enhance the understanding of the mobility and retention mechanism of metals in constructed wetland, and subsequently, metal retention capacity of the system can be estimated.

In the present column experiment, macrophytes did not contribute significantly to pollutant removal except the case of N. Moreover, macrophytes have negative effects on BOD and heavy metal removal.

Generally, the most important function of macrophytes in constructed wetlands is known as their physical effect: stabilizing the surface bed, providing good conditions for physical filtration, insulating the surface against frost during the winter, and supplying a surface area for attached microbial growth (Brix, 1997). However, the column-scale systems have a limitation to assess such a physical role of macrophytes. Thus, further research into the impact of macrophytes in a full-scale system is required to evaluate a comprehensive contribution of macrophytes to the treatment processes.

Previous research showed that microorganisms can be bioindicators to determine the water quality and identify microbiological processes in constructed wetlands (Scholz *et al.*, 2002). Moreover, microbiological activity within each filter is likely to be also responsible for the reduction of Ni and Cu. For example, extended storage (Filters 1 and 2) showed a considerable reduction in most water quality variables such as BOD and SS. However, the microbiological feature in the pollutant removal process was not investigated in this study.

Therefore, research on microorganisms in the wetland system may contribute to deeper and broader understanding of underlying mechanisms in pollutant removal processes. Microbial community changes due to salt and heavy metals should also be undertaken. The aim should be to quantify the microbiological potential in comparison to physical and chemical processes.

The proposed design guideline (i.e. the sand-gravel based reed beds with temporarily flooding) can be applied to the field-scale system. The optimal design outline for the urban runoff (i.e. gully pot effluent) treatment would be a combination of a pond and vertical-flow system. It is more practical to design the constructed wetland to treat only the first flush of stormwater, rather than all stormwater. Therefore, research should be focused on the performance of system particularly during the first flush after a storm event.

The integration of a compact vertical-flow wetland into sustainable urban drainage systems (SUDS) can also be implemented. Integrated systems include a combination of silt trap, infiltration trap and pond, which are located prior to the constructed wetlands. Diversion of flow can also be designed according to the nature of the pollutants (Revitt et al., 2003). For example, a heavily salt-laden stormwater could be diverted to a holding area (i.e. pond) to avoid to adverse effect of salt on the pollutant removal performance of constructed wetland (see section 4.6.3 and 6.3.1) and then diluted with the following higher flow of stormwater. This work will give further details to establish the specific design criteria for sustainable constructed wetlands in an urban area.

The application of machine learning methodologies into full-scale constructed wetlands should be examined. Further studies on the possibility of their application

for other types of each SUDS device (i. e. pond and swale) as well as SUDS

integrated with constructed wetlands are also needed. This approach will provide

useful tools to monitor and control the urban runoff quality through SUDS on a daily

basis.

Reference

Abu-ghararah, Z.H. and Sherrard, J.H. (1993), Biological nurient removal in high salinity wastewater. *J. Envion. Sci. Health.* 28, 599-613.

Aguilera, P. A., Frenich, A. G., Torres, J. A., Castro, H., Vidal J. L. M. and Canton, M. (2001), Application of the Kohonen Neural Network in Coastal Water Management: Methodological Development for the Assessment and Prediction of Water Quality. *Water Res.* 35, 4053-4062.

Allen, S.E. (1974), *Chemical Analysis of Ecological Materials.* Blackwell: Oxford, UK.

American Public Health Association (APHA). (1995), Standard Methods for the Examination of Water and Wastewater; 19th edition, APHA-AWWWA-WEF: Washington DC, USA.

Babel, S. and Kurniawan, T.A. (2003), Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *J. Hazar. Mater.* B97, 219-243.

Balizon, M.E., Dolmus, R., Quintana, J., Navarro, Y. and Donze, M. (2002), Comparison of conventional and macrophyte-based systems for the treatment of domestic wastewater. *Water Sci. Technol.* 45, 111-116.

Batty, L.C. (2003), Wetland plants–more than just a pretty face? *Land Contamination & Reclamation* 112 (2).

Batty, L.C., Baker, A.J.M., Wheeler, B.D. and Curtis, C.D. (2000), The effect of pH and Plaque of Cu and Mn in Phragmites australis (Cav.) Trin ex. Steudel. *Ann. Bot-Londony.* 86. 647-653.

Bavor, H.J. and Schulz, T.J. (1993), Sustainable suspended solids and nutrient removal in large-scale, solid matrix, constructed wetland systems. Constructed Wetlands for Water Quality Improvement (Moshiri, G.A.).

Bäckström, M., Karlsson, S., Bäckman, L., Folkeson, L. and Lind, B. (2004), Mobilization of heavy metals by deicing salts in a roadside environment. *Water Res.* 38, 720-732.

Belanche, L., Valdes, J. J., Comas, J., Roda, I. R. and Poch, M. (2000), Prediction of

the Bulking Phenomenon in Wastewater Treatment Plants, *Artif. Intell. Eng.* 14, 307-317.

Bezbaruah, A.N. and Zhang, T.C. (2003), Performance of a constructed wetland with a sulfur/limestone denitrification section for wastewater nitrogen removal. *Environ. Sci. Technol.* 37, 1690-7.

Braskerud, B.C. (2002), Factors affecting N retention in small constructed wetlands treating agricultural non-point source pollution, *Ecol. Eng.*, 18, 351-370.

Brix, H. (1994), Constructed wetlands for municipal wastewater treatment in Europe. In: Mitsch, W.J. (Ed.), Global Wetlands: Old World and New. Elsevier, Amsterdam, The Netherlands, 325-333.

Brix, H. (1997), Do macrophytes play a role in constructed treatment wetlands? *Water Sci. Technol.*, 35(5), 11-17

Brix, H. (1998), In: Constructed Wetlands for Wastewater Treatment in Europe, Vymazal, J., Brix, H., Cooper, P.F., Green, M.B., and Haberl, R. (eds). Backhuys Publisher, Leiden, The Netherlands, 123-152.

Brix, H., Arias, C.A., del Bubba, M. (2001), Media selection for sustainable phosphorus removal in subsurface flow constructed wetlands. *Water Sci. Technol.* 44, 47-54.

Butler, D. and Davies, J.W. (2004), *Urban Drainage.* 2nd Edition. Spon Press, London and New York.

Butler, D., Xiao, Y., Karunaratne, S.H.P.G, and Thedchananamoorthy, S. (1995), The gully pot as a physical, chemical and biological reactor. *Water Sci. Technol.* 31, 219-228.

Campbell, C.S. and Ogden, M. (1999), *Constructed wetlands in the sustainable landscape.* John Wiley & Sons, Inc.

Cao, L. J. and Francis, E.H.Tay. (2003), Support Vector Machine with Adaptive Parameters in Financial Time Series Forecasting, *IEEE Transactions on Neural Networks,* 14, 6.

Carleton, J.N., Grizzard, T.J., Godrej, A.N. and Post, H.E. (2001), Factors affecting the performance of stormwater treatment wetlands. *Water Res.* 35, 1552-

1562.Carpenter, G. A. and Markuzon, N. (1998), ARTMAP-IC and Medical Diagnosis: Instance Counting and Inconsistent Cases, *Neural Networks* 11, 323-336.

Cereghino, R., Giraudel, J. L. and Compin, A. (2001), Spatial Analysis of Stream Invertebrates Distribution in the Adour-Garonne Drainage Dasin (France) Using Kohonen Self-organizing Maps. *Ecol. Model.* 146, 167-180.

Chang, C.-C. and Lin, C.-J. (2001), LIBSVM: a Library for Support Vector Machines. Software available at http://www.csie.ntu.edu.tw/~cjlin/libsvm.

Cheng, S., Grosse, W., Karrenbrock, F. and Thoennessen, M. (2002), Efficiency of constructed wetlands in decontamination of water polluted by heavy metal. *Ecol. Eng.* 18, 317-325.

CIRIA (2000), *Sustainable Urban Drainage Systems: Design Manual for Scotland and Northern Ireland.* Construction Industry Research and Information Association (CIRIA) Report C521, Cromwell Press., UK.

Clark, S. and Pitt, R. (1999), Stormwater treatment at critical area, evaluation of filtration media. US Environmental Protection Agency, EPA/600/R-00/010.

Collins, B., McArthur, J.V. and Sharitz, R.R. (2004), Plant effects on microbial assemblages and remediation of acidic coal pile runoff in mesocosm treatment wetlands. *Ecol. Eng.* 23, 107 – 115.

Collins, M.R., Eighmy, T.T., Fenstermacher, J.M. and Spanos, S.K. (1992), Removal of natural organic matter by conventional slow sand filtration. *J. Am. Wat.* 84, 80-90.

Cooper, P.F., Job, G.D., Green, M.B., Shutes, R.B.E. (1996), Reed beds and Constructed Wetlands for Wastewater Treatment. WRc plc.: Swindon, UK.

Deng, H., Ye, Z.H. and Wong, M.H. (2004), Accumulation of lead, zinc, copper and cadmium by 12 wetland plant species thriving in metal-contaminated sites in China. *Environmental Pollut.* 132. 29-40.

Dong, B., Cao, C. and Lee, S. E. (2005a), Applying Support Vector Machines to Predict Building Energy Consumption in Tropical Region, *Energ. Build.* 37, 545-553.

Dong, N., Lu W. C., Chen N. Y., Zhu Y. C. and Chen K. X. (2005b), Using Support

Vector Classification for SAR of Fentanyl Derivatives, *Acta Pharmacol. Sin.* 26, 107-112.

Drever, J.I. (1988), *The Geochemistry of Natural Waters*. 2nd ed. Englewood Cliffs, N.J.: Prentice-Hall, 347.

Drizo, A., Frost, C.A., Smith, K. A. and Grace, J. (1997), Phosphate and ammonium removal by constructed wetlands with horizontal subsurface flow, using shale as a substrate. *Water Sci. Technol.* 35, 95-102.

Dubey, A., Realff, M. J., Lee, J. H. and Bommarius, A. S. (2005), Support Vector Machines for Learning to Identify the Critical Position of a Protein, *J. Theor. Biol.* 234, 351-361.

Dubois, D. and Prade, H. (1998), An Introduction to Fuzzy Systems, *Clin. Chim. Acta* 270, 3-29.

Duch, W. and Grudzinski, K. (1999), Weighting and Selection of Features, *Proceedings of Intelligent Information Systems VIII Workshop*, Ustron, Poland. June 1999, pp. 32-36.

Ellis, J.B., Shutes, R.B.E. and Revitt, D.M. (2003), Guidance Manual for Constructed Wetlands, Urban Pollution Research Centre, Middlesex University, London.

Environment Agency (EA). (2002), Contaminants in Soil: Collation of Toxicological Data and Intake Values for Humans. Nickel; Department for Environment, Food and Rural Affairs and the Environment Agency, Bristol, England, UK.

Environment Agency (EA). (2003), Constructed wetlands and links with sustainable drainage systems. R&D Technical Report, P2-159/TR1, Bristol, England, UK.

Färm, C. (2002), Metal sorption to natural filter substrates for storm water treatment-column study. *Sci. total Environ.*, 298, 17-24.

Faulkner, B. and Skousen, J. (1994), Treatment of acid mine drainage by passive treatment systems. P. 250 – 257. *In Proceedings, Int. Land Reclamation and Mine drainage Conference*. 24 – 29 Apr. 1994. Vol. 2. Bureau of Mines SP 063 – 94. U.S. Dep. Of Interior, Pittsburgh, PA.

Garcia, H. L. and Gonzalez, I. M. (2004), Self-organizing Map and Clustering for Wastewater Treatment Monitoring, *Appl. Artif. Intel.* 17, 215-225.

Gernaey, K. V., Van Loosdrecht M. C. M., Henze, M., Lind, M. and Jørgensen, S. B. (2004), Activated Sludge Wastewater Treatment Plant Modeling and Simulation: State of the Art. *Environ. Modell. Softw.* 19, 763-783.

Gevrey, M., Rimet, F., Park, Y. S., Giraudel, J. L., Ector, L. and Lek, S. (2004), Water Quality Assessment Using Diatom Assemblages and Advanced Modelling Techniques, *Freshwater boil.* 49, 208-220.

Gladden, J.B.; Specht, W.L. and Nelson, E.A. 2002. Comparison of Constructed Wetland Mesocoms Designed for Treatment of Copper-Contaminated Wastewater. Westinghouse savannah River Company.

Goulet, R.R. and Pick, F.R. (2001), Changes in dissolved and total Fe and Mn in a young constructed wetland: Implications for retention performance. *Ecol. Eng.* 17. 373-384.

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

Green, M., Friedler, E. and Safrai, I. (1998), Enhancing nitrification in vertical flow constructed wetland utilizing a passive air pump. *Water Res.* 32, 3513-3520.

Greger, M. (1999), *Metal availability and bioconcentration* in plants. In: Prasad, M.N.V., Hagemeyer, J. (Eds.), Heavy Metal Stress in Plants-From Molecules to Ecosystems. Springer Press, Berlin, pp. 1-27.

Grieu, S., Traore, A., Polit, M. and Colprim, J. (2005), Prediction of Parameters Characterizing the State of a Pollution Removal Biologic Process, *Eng. Appl. Artif. Intel.* 18, 559-573.

Gosselink, J.G. and Turner, R.E. (1978) "The role of hydrology in freshwater wetland ecosystems". In *Freshwater wetlands: ecological processes and management potential* (ed. R.E. Good, D.F. Whigam and R.L. Simpson), pp. 63-78. New York, USA: Academic Press

Halverson, N.V. (2004), Review of constructed subsurface flow vs. surface flow wetlands. available at http://www.osti.gov/bridge.

Hamed, M. M., Khalafallah, M. G. and Hassanien, E. A. (2004), Prediction of Wastewater Treatment Plant Performance Using Artificial Neural Networks. *Environ. Model. Softw.* 19, 919-928.

Hampton, R.E. (1994), *Introductory Biological Statistics*, Wm. C. Brown Publishers, Oxford, England.

Harbel, R., Perfler, R. and Mayer, H. (1995), Constructed wetland in Europe. *Water Sci. Technol.* 32, 305-315.

Haung, J., Reneau JR. R.B. and Hagedorn, C. (2000), Nitrogen removal in constructed wetlands employed to treat domestic wastewater. *Water Res.* 34, 2582-2588.

Heal, K.V., Younger, P.L., Smith, K.A., McHaffie, H. and Batty, L.C. (2004), Removing P from sewage effluent and agricultural runoff using ochre recovered from mine water treatment. In: Valsami-Jones, E. (ed) *P in environmental technology: removal, recovery and applications.* IWA Publishing, London, 320-334

Hong, Y-S. T., Rosen, M. R. and Bhamidimarri, R. (2003), Analysis of a Municipal Wastewater Treatment Plant Using a Neural Network – Based Pattern Analysis, *Water Res.* 37, 1608-1618.

Hyndman, R. J. and Koehler, A. B. (2005), Another Look at Measures of Forecast Accuracy, Monash Econometrics and Business Statistics Working Papers, 13/05.

IWA Specialist Group on Use of Macrophytes in Water Pollution Control. (2000), *Constructed Wetlands for Pollution Control.* Scientific and Technical Report n°8. IWA Publishing.

Jackson, L.J., Kalff, J. and Rasmussen, J.B. (1993), Sediment pH and redox potential affect the bioavailability of Al, Cu, Fe, Mn and Zn to rooted aquatic macrophyte. *Can. J. Fish. Aquat. Sci.* 50, 143 – 148.

Jefferies, C., Aitken, A., Mclean, N., MacDonald, K. and McKissock, G. (1999), Assessing the performance of urban BMPs in Scotland. *Water Sci. Technol.* 39, 123-131.

Joachims, T. (1999), Making Large-scale SVM Learning Practical. Advances in Kernel Methods – Support Vector Learning in B. Scholkopf, C. Burges and A. Smola (eds.), MIT-Press. Software available at http://svmlight.joachims.org.

Johansson, L. (2006), Substrate of P removal-potential benefits for on-site wastewater treatment? *Water Res.* 40, 23-36.

Kadlec, R.H. (1999), Chemical, physical and biological cycles in treatment wetlands. *Water Sci. Technol.* 40, 37-44

Kadlec, R.H. (2000), The inadequacy of first-order treatment wetland models. *Ecol. Eng.* 15, 105-119.

Kadlec, R. H. (2002), *Effects of Pollutant Speciation in Treatment Wetlands Design*; Wetland Management Services, Chelsea, Michigan, USA.

Kadlec, R. H. and Knight, R. L. (1996), *Treatment Wetlands*; CRC Press: Boca Raton, Florida, USA.

Karathanasis, A.D., Potter, C.L. and Coyne, M.S. (2003), Vegetation effects on fecal bacteria, BOD, and suspended solid removal in constructed wetlands treating domestic wastewater. *Ecol. Eng.* 20, 157-169.

Karathanasis, A.D. and Thomson, Y.L. (1995), Mineralogy of iron precipitates in a constructed acid mine drainage wetland. *Soil Sci. Am. J.* 59, 1773-81.

Keller, B.E.M., Lajtha, K. and Crisofor, S. (1998), Trace metal concentrations in the sediments and plants of the Danube Delta, Romania. *Wetlands.* 18, 42-50.

Kietliñska, A. and Renman, G. (2005), An evalustion of reactive filter media for treating landfill leachate. *Chemosphere.* 61. 933-940.

Klomjek, P. and Nitisoravut, S. (2005), Constructed treatment wetland: a study of eight plant species under saline conditions. *Chemosphere.* 58, 585-593.

Knight, R.L., Kedlec, R.H. and Ohlendorf, H.M. (1999), The use of treatment wetland for petroleum industry effluents. *Environ. Sci. Tech.*, 33(7).

Knight, R.L., Payne, V.W.E., Borer, R.E., Clarke, R.A. and Pries, J.H. (2000), Constructed wetlands for livestock wastewater management. *Ecol. Eng.* 15, 41-55.

Kohavi, R. (1995), A Study of Cross-validation and Bootstrap for Accuracy Estimation and Model Selection, *Proceedings of the 14th International Joint Conference on Artificial Intelligence*, 1137-1143.

Kohonen, T. (2001), *Self-organizing Maps*, 3rd edition. Springer: Berlin, Germany.

Korkusuz, E.A., Berklioglu, M. and Demirer, G.N. (2005), Comparison of the treatment performances of blast furnace slag-based and gravel-based vertical flow

wetlands operated identically for domestic wastewater treatment in Turkey. *Ecol. Eng.* 24, 187-200.

Kowalik, P. and Obarska-Pempkowiak, H. (1998). In: Constructed Wetlands for Wastewater Treatment in Europe, Vymazal, J., Brix, H., Cooper, P.F., Green, M.B., and Haberl, R. (eds). Backhuys Publisher, Leiden, The Netherlands, 217-225

Kumar, A., Rao, N.N. and Kaul, S.N. (2000), Alkali-treated straw and insoluble straw xanthate as low cost adsorbents for heavy metal removal – preparation, characterization and application. *Bioresource Technol.* 71. 133-142.

Kuschk, P., Kappelmeyer, E., Kastner, M. and Stottmeister, U. (2003), Annual cycle of nitrogen removal by a pilot-scale subsurface horizontal flow in a constructed wetland under moderate climate. *Water Res.* 37, 4236-4242.

Lai, C.H. and Chen, C.Y. (2001), Removal of metal ions and humic acid from water by iron-coated filter media. *Chemoshere.* 44, 1177-1184.

Lantzke, I.R., Mitchell, D.S., Heritage, A.D. and Sharma, K.P. (1999), A model of factors controlling orthophosphate removal in planted vertical flow wetlands. *Ecol. Eng.* 12, 93 – 105.

Lee B.-H., Scholz M. and Horn A. (2005), Constructed Wetlands for the Treatment of Concentrated Stormwater Runoff (Part A). *Environ. Eng. Sci.* 23, 191-202.

Lee, C.Y., Lee C.C., Lee, F.Y., Tseng, S.K. and Liao, C.J. (2004), Performance of subsurface flow constructed wetland taking pretreated swine effluent under heavy loads. *Bioresource technol.* 92, 173-179.

Lee, K., Booth D. and Alam P. (2005), A Comparison of Supervised and Unsupervised Neural Networks in Predicting Bankruptcy of Korean Firms, *Expert Syst. Appl.* 29, 1-16.

Leflaive, J., Cereghino, R., Danger, M., Lacroix, G. and Ten-Hage, L. (2005), Assessment of Self-organizing Maps to Analyze Sole-carbon Source Utilization Profiles, *J. Microbiol. Meth.* 62, 89-102.

Leonard, K.M. (2000), Analysis of residential subsurface flow constructed wetlands performance in Northern Alabama. *Small Flows Quart.* 2, 34–39.

Lim, P.E., Tay, M.G., Mak, K.Y. and Mohamed, N. (2003), The effect of heavy metals on N and oxygen demand removal in constructed wetlands. *Sci. total Environ.*, 301, 13-21.

Lim, P.E., Wong, T.F. and Lim, D.V. (2001), Oxygen demand, N and copper removal by free-water-surface and subsurface-flow constructed wetlands under tropical conditions. *Environ. Int.* 26, 425-431.

Lin, Y.F., Jing, S.-R., Lee, D.-Y., Chang, Y-F., Chen, Y.-M. and Shih, K-C. (2005), Performance of a constructed wetland treating intensive shrimp aquaculture wastewater under high hydraulic loading rate. *Environ. Pollut.* 134, 411-421.

Liu, H.-X., Zhang, R.-S., Yao, X.-J., Liu, M.-C., Hu, Z.-D. and Fan, B.-T. (2004), Prediction of Electrophoretic Mobility of Substituted Aromatic Acids in Different Aqueous-alcoholic Solvents by Capillary Zone Electrophoresis Based on Support Vector Machine. *Anal. Chim. Acta* 525, 31-41.

Lu, W.-Z. and Wang, W.-J. (2005), Potential Assessment of the Support Vector Machine Method in Forecasting Ambient Air Pollutant Trends. *Chemosphere* 59, 693-701.

Lu, R.-S. and Lo, S.-L. (2002), Diagnosing Reservoir Water Quality Using Self-organizing Maps and Fuzzy Theory. *Water Res.* 36, 2265-2274.

Luederits, V., Eckert, E., Lange-Weber, M. and Lange A. (2001), Nutrient removal efficiency and resource economics of vertical flow and horizontal flow constructed wetlands. *Ecol. Eng.* 18, 157 – 171.

Maier, H. R., Morgan, N. and Chow, C. W. K. (2004), Use of Artificial Neural Networks for Predicting Optimal Alum Doses and Treated Water Quality Parameters. *Environ. Model. Softw.* 19, 485-494.

Magmedov, V.G, Zakharchenko, M.A., Yakovleva, L.I. and Ince, M.E. (1996), The use of constructed wetlands for the treatment of run-off and drainage waters: The UK and Ukraine experience. *Water Sci. Technol.* 33, 315-323.

Mantovi, P., Marmiroli, M., Maestri, E., Tagliavini, S., Piccinini, S. and Marmiroli, N. (2003), Application of a horizontal subsurface flow constructed wetland on treatment of dariy parlor wastewater. *Bioresource Technol.* 88, 85-94.

Mashauri, D.A., Mulungu, D. M. M. and Abdulhussein, B. S. (1999), Constructed wetland at the University of Dar es Salaam. *Water Res.* 34, 1135-1144.

Mays, P.A. and Edwards, G.S. (2001), Comparison of heavy metal accumulation in a natural wetland and constructed wetlands receiving acid mine drainage. *Ecol. Eng.* 16, 487-500.

Mæhlum, T. and Stlnacke, P. (1999), Removal efficiency of three cold-climate constructed wetlands treating domestic wastewater: Effect of temperature, seasons, loading rates and input concentrations. *Water Sci. Technol.* 40, 273-281.

McCabe, O.M., Daldwin, J.L. and Otte, M.L. (2001), Metal tolerance in wetland plants?. *Minerva Biotechnol.* 13, 141 – 149.

Memon, F. A.; Butler, D. (2002), Assessment of gully pot management strategies for runoff quality control using a dynamic model. *Sci. Total Environ.* 295, 115-129.

Mitchell, C. and McNevin, D. (2001), Alternative analysis of BOD removal in subsurface flow constructed wetlands employing monod kinetics. *Water Res.*, 35, 1295-1303.

Mitsch, W.J. and Wise, K.M. (1997), Water quality, fate of metals, and predictive model validation of a constructed wetland treating acid mine drainage. *Water Res.* 32, 1888-1900.

Möller,J., Ledin,A. and Mikkelsen,P.S. (2002), Removal of dissolved heavy metals from pre-settled stormwater runoff by iron-oxide coated sand (IOCS). In: Strecker, E. W. & Huber, W. C. (eds.): Global solutions for urban drainage. 9ICUD, Portland, Oregon, 8-13 September 2002. CD-ROM, ASCE Publications, Reston, VA.

Monod, J. (1949), The growth of bacterial cultures. *Annu. Rev. of Micorbiol.* 3, 371-394.

Morrison, G.M., Revitt, D.M. and Ellis, J.B. (1995), The gully pot as a biochemical reactor. *Water Sci. Technol.* 31, 229-236.

Moshiri, G.A. (2000), *Constructed Wetland for Water Quality Improvement*, CRC Press, Florida, USA

Mukherjee, A. (1997), Self-organizing Neural Network for Identification of Natural Models. *J. Comput. Civil. Eng.* 11, 74-77.

Munger, A.S., Shutes, R.B.E., Revitt, D.M. and House, M.A. (1995), An assessment of metal removal form highway runoff by a natural wetland. *Water Sci. Technol.*

32, 169-175.

Mungur, A.S., Shutes, R.B.E., Revitt, D.M. and House, M.A. (1997), An assessment of metal removal by laboratory scale wetland. *Water Sci. Technol.* 35, 125-133.

Neralla, S., Weaver, R.W., Leikar, B.J. and Rersys, R.A. (2000), Improvement of domestic wastewater quality by subsurface flow constructed wetlands. *Bioresource Technol.* 75, 19-25.

Newman, J.M., Clausen, J.C. and Neafsey, J.A. (2000), Seasonal performance of a wetland constructed to process dairy milkhouse wastewater in Connecticut. *Ecol. Eng.* 14, 181-198.

Nguyen, L.M. (2000), Organic matter composition, microbial biomass and microbial activity in gravel-bed constructed wetlands treating farm dairy wastewaters. *Ecol. Eng.* 16, 199-221

Norrström, A.C. and Jacks, G. (1998), Concentration and fractionation of heavy metals in roadside soils receiving de-icing salts. *Sci. Total Environ.* 218, 161-174.

Novontny, V. and Olem, V. (1994), *Water Quality: Prevention, Identification and Management of Diffuse Pollution.* Van Nostrand Reinhold, New York, USA

Obarska-Pempkowiak, H. and Klimkowska, K. (1999), Distribution of nutrients and heavy metals in a constructed wetland system. *Chemoshere,* 39, 303-312.

Onkal-Engin, G., Demir, I. and Engin, S. N. (2005), Determination of the Relationship between Sewage Odor and BOD by Neural Networks, *Environ. Model. Softw.* 20, 843-850.

Osborne, M., Butler, D., Clarke, P. and Memon, F. (1998), Management of gully pots for improved runoff quality. Construction Industry Research and Information Association (CIRIA). Report 183.

Pai, P.-F. and Hong, W.-C. (2005), Support Vector Machines with Simulated Annealing Algorithms in Electricity Load Forecasting, *Energ. Convers. Manage* 46, 2669-2688.

Peltier, E.F., Webb, S.M. and Gaillard, J-F. (2003), Zinc and lead sequestration in an impacted wetland system. *Adv. Environ. Res.* 8. 103-112.

Pinney, M.L., Westerhoff, P.K. and Baker, L. (2000), Transformations in dissolved organic carbon through constructed wetlands. *Water Res.* 34, 1897-1911.

Pitcher, S.K., Slade, R.C.T. and Ward, N.I. (2004), Heavy metal removal from motorway stormwater using zeolites. *Sci. Total Environ.* 334-335, 161-166.

Pontier, H., Williams, J.B. and May, E. (2001), Metals in combined conventional and vegetated road run-off control systems. *Water Sci. Technol.* 44, 607-614.

Pontier, H., Williams, J.B. and May, E. (2004), Progressive changes in water and sediment quality in a wetland system for control of highway runoff. *Sci. Total Environ.* 319, 215-224.

Prasad, M.N.V, (2001), *Metals in the Environment, Analysis by Biodiversity.* marcel Dekker, Inc.

Rangsivek, R. and Jekel, M.R. (2005), Removal of dissolved metals by zero-valent iron (ZVI): Kinetics, equilibria, processes and implications for stormwater runoff treatment. *Water Res.* 39, 4153-4163.

Reed S.C. and Brown D. (1995), Subsurface flow wetlands-performance evaluation. *Water Environ. Res.* 67, 244-8.

Reddy, K.R., Patrick, W.H. and Lindau, C.W. (1989), Nitrification-denitrification at the plant root-sediment interface in wetlands. *Limnol. Oceanogr.* 34.

Revitt, D.M., Ellis, J.B., Shutes, R.B.E. and Scholes, L. (2003), Review of the use of stormwater BMPs in Europe. Project under EU RTD 5th framework program, Contract No EVK1-CT-2002-00111.

Revitt, D.M., Shutes, R.B.E., Jones, R.H., Forshaw, M. and Winter, B. (2004), The performances of vegetative treatment systems for highway runoff during dry and wet conditions. *Sci. Total Environ.* 334-335, 261-270.

Rich, L.G. (2005), Nitrification in aerated lagoons and with intermittent sand filters. *Technical Note 6.* available at *http://www.ces.clemson.edu/ees/rich/technotes.*

Ruiz-Jimenez, J., Priego-Capote, F., Garcia-Olmo, J. and Luque de Castro, M. D. (2004), Use of Chemometrics and Mid Infrared Spectroscopy for the Selection of Extraction Alternatives to Reference Analytical Methods for Total Fat Isolation. *Anal. Chim. Acta* 525, 159-169.

Sansalone, J. J. (1999), Adsorptive infiltration of metals in urban draiange – media characteristics. *Sci. Total Environ.* 235, 179-188.

Scholes, L. Shustes, R.B.E., Revitt, D.M., Forshaw, M. and Purchase, D. (1998),

The treatment of metals in urban runoff by constructed wetlands. *Sci. total Environ.* 214, 211-219.

Scholz, M. (2003a), Case study: Design, Operation, Maintenance and Water Quality Management of Sustainable Storm Water Ponds for Roof Runoff. *Bioresource Technol.* 95, 269-279.

Scholz, M. (2003b), Performance Predictions of Mature Experimental Constructed Wetlands which Treat Urban Water Receiving High Loads of Lead and Copper, *Water Res.* 37, 1270-1277.

Scholz M. (2004), Treatment of Gully Pot Effluent Containing Nickel and Copper with Constructed Wetlands in a Cold Climate, *J. Chem. Technol. Biot.* 79, 153-162.

Scholz. M, Anderson, P. and Forman, B. I. (2005), Treatment of gully pot liquor containing heavy metals with constructed wetlands in Scotland. *Water Sci. Technol.* 51, 251-8.

Scholz, M., Hohn, P. and Minall, R. (2002), Mature Experimental Constructed Wetlands Treating Urban Water Receiving High Metal Lloads. *Biotechnol. Prog.* 18, 1257-1264.

Scholz, M. and Lee, B.-H. (2005), Constructed Wetlands: A Review. *Int. J. Environ. Stud.* 62, 421-447.

Scholz, M. and Martin, R.J. (1998), Control of bio-regenerated granular activated carbon by spreadsheet modelling. *J. Chem. Tech. Biotechnol.* 71, 253-261.

Scholz, M. and Xu, Jing. (2002), Comparison of constructed reed beds with different filter media and macrophytes treating urban stream water contaminated with lead and copper. *Ecol. Eng.* 18, 385-390.

Selim, M.I. and Wang, J. (1994), Fate of atrazine in biologically active granular activated carbon. *Environ. Toxicol. Chem.* 13, 3-8.

Shutes, R.B.E., Revitt, D.M., Lagerberg, I.M. and Barraud, V.C.E. (1999), The design of vegetative constructed wetlands for the treatment of highway runoff. *Sci. total Environ.* 235, 1189-197.

Shutes, R.B.E., Revitt, D.M., Scholes, L.N.L., Forshaw, M. and Winter, B. (2001), An experimental constructed wetland system for the treatment of highway runoff in the UK. *Water Sci. Technol.* 44, 571-578.

Shukla, S.R., Pai, R.S. and Shendarkar, A.D. (2006), Adsorption of Ni, Zn and Fe on modified coir fibres. *Sep. Purif. Technol.* 47, 141-147.

Sinicrope, T.L., Langis, R, Gersberg, R.M., Busanardo, M.J. and Zedler, J.B. (1992), Metal removal by wetland mesocosms subjected to different hydroperiods. *Ecol. Eng.* 1, 309-322.

Sobolewski, A. (1996), Metal species indicate the potential of constructed wetlands for long-term treatment of metal mine drainage. *Ecol. Eng.* 6, 259-271.

Srinivasan, K.R. and Kadlec, R.H. (1995), Wetland Treatment of Oil and Gas Well Wastewaters. Report to U.S. Department of Energy.

Stottmeister, U., Wiesner, A., Kuschk, P., Kappelmeyer, M. and Kaster, M. (2003), Effects of plants and microorganisms in constructed wetlands for wastewater treatment. *Biotech. Advan.* 22, 93-117

Su, J.L. and Ouyang, C.F. (1996), Nutrient removal using a combined process with activated sludge and fixed biofilm. *Water Sci. Technol.* 34, 477-486.

Sun, G, Gray, K.R., Biddlestone, A.J., Allen, S.J. and Cooper, D.J. (2003), Effect of effluent recirculation on the performance of a reed bed system treating agricultural wastewater. *Process Biochem.* 39, 351-357.

Sun, G, Zhao, Y. and Allen, S. (2005), Enhanced removal of organic matter and ammoniacal-N in a column experiment of tidal flow constructed wetland system. *J. Biotechnol.* 115, 189-197.

Sundaravadivel, M. and Vigneswaran, S. (2001), Constructed wetlands for wastewater treatment. *Crit. Rev. Env. Sci. Tech.* 31(4), 351-409

Tanner, C.C., Clayton, J.S. and Upsdell, M.P. (1995), Effect of loading rate and planting on treatment of dairy farm wastewaters in constructed wetlands: removal of oxygen demand, suspended solids and fecal coliforms. *Water Res.*, 29, 17-26.

Tanner, C.C., Nguyen, M. L. and Sukias, J. P. S. (2005), Nutrient removal by a constructed wetland treating subsurface drainage from grazed dairy pasture. *Agr. Ecosyst. Environ.* 105, 145-162.

Thomas, P.R., Glover, P. and Kalaroopan, T. (1995), An evaluation of pollutant removal from secondary treated sewage effluent using a constructed wetland system. *Water Sci. Technol.* 32, 87-93.

Tchobanoglous, G.; Burton, F.L.; Stensel, H.D. (2003), *Wastewater Engineering: Treatment and Reuse*; 4th edition (revised), Metcalf & Eddy Inc., McGraw Hill Companies Inc: New York, USA.

Tseng, K.-F. and Wu, K.-L. (2004), The ammonia removal cycle for a submerged biofilter used in a recirculating eel culture system. *Acuacult. Eng.* 31, 17-30.

US Environmental Protection Agency. (1988), Design manual: Constructed wetlands and aquatic plant systems for municipal wastewater treatment. EPA 625-1-88-022.

US Environmental Protection Agency. (1994), North American Wetlands for Water Quality Treatment Database, Vol. 1.0. Washington D.C.

Uygur, A. and Kargi, F. (2004), Salt inhibition on biological nutrient removal from saline wastewater in a sequencing batch reactor. *Enz. Mic. Tech.* 34, 313-318.

Vapnik, V. (1995), *The Nature of Statistics Learning Theory.* Springer-Verlag: New York, USA.

Verdenius, F. and Broeze, J. (1999), Generalized and Instance-specific Modeling for Biological Systems. *Environ. Model. Softw.* 14, 339-348.

Verhoeven, J.T.A. and Mæleman, A.F.M. 1999. Wetlands for wastewater treatment: Opportunities and limitations. *Ecol. Eng.* 12, 5-12.

Vesanto, J., Himberg, J., Alhoniemi, E. and Parhankangas, J. (1999), Self-organizing Map in Matlab: the SOM Toolbox, *Proceedings of the Matlab DSP Conference*, Espoo, Finland, Nov. pp. 35-40. Software available at http://www.cis.hut.fi/projects/somtoolbox/.

Viklander, M., Marsalek, J., Malmquist, P.A. and Watt, W.E. (2003), Urban drainage and highway runoff in cold climates: conference overview. *Water Sci. Technol.* 48, 1-10.

Vymazal, J. (1999), Removal of BOD in constructed wetland with horizontal sub-surface flow: Czech experience. *Water Sci. Technol.* 40, 133-138

Wallace, S., Parkin, G. and Cross, C. (2000), Cold climate wetlands: Design and performance. *International Water Association 7th International Conference* on Wetland Systems for Water Pollution Control, Nov. 11-16.

Warren, L.A. and Zimmerman, A.P. (1994), The influence of temperature and NaCl on cadmium, copper, and zinc partitioning among suspended particulate and

dissolved phases in an urban river. *Water Res.* 28, 1921-1931.

Werker, A.G., Dougherty, J.M., McHenry, J.L. and Van Loon, W.A. (2002), Treatment variability for wetland wastewater treatment design in cold climates. *Ecol. Eng.*, 19, 1-11.

Werner, H. and Obach, M. (2001), New Neural Network Types Estimating the Accuracy of Response for Ecological Modeling. *Ecol. Model.* 146. 289-298.

Wood, T.S. and Shelley, M.L. (1999), A dynamic model of bioavailability of metals in constructed wetland sediments. *Ecol. Eng.* 12, 231-252.

Ye, Z.H., Baker, A.J.M., Wong, M.H. and Willis, A.J. (2003), Copper tolerance, uptake and accumulation by Phragmites australis. *Chemosphere.* 50, 795 – 800.

Ye, Z.H., Whiting, S.N., Qian, J.H., Lytle, C.M., Lin, Z.Q., and Terry, N. (2001a), Trace element removal from coal ash leachate by a 10-year-old constructed wetland. *J. Environ.Qual.* 30, 1710-9.

Ye, Z.H., Whiting, S.N., Lin, Z.Q., Lytle, C.M., Qian, J.H. and Terry, N. (2001b), Removal and Distribution of Iron, Manganese, Cobalt, and Nickel within a Pennsylvania constructed wetland treating coal combustion by-product leachate. *J. Environ.Qual.*, 30, 1464-73.

Younger, P.L., Banwart, S.A. and Hedin, R.S. (2002), *Mine Water: Hydrology, Pollution, Remediation,* Kluwer Academic Publ., London.

Zhu, T., Jenessen, P.D., Mæhlum, T. and Krogstad, T. (1997), P sorption adn chemical characteristics of light-weight aggregate (LWA)-potential filter media in treatment wetlands. *Water Sci. Tchnol.* 35, 103-108.

Appendix

1. Publications

Scholz M. and **Lee B.-H**. (2005), Constructed Wetlands: A Review, *The International Journal of Environmental Studies*, Vol. 62, No. 4, pp. 421-447.

Lee B.-H., Scholz M. and **Horn A**. (2005), Constructed Wetlands for the Treatment of Concentrated Stormwater Runoff (Part A), *Environmental Engineering Science*, Vol. 23, No. 2, 191-202.

Lee B.-H., Scholz M., Horn A. and **Furber A. M**. (2005), Prediction of Constructed Treatment Wetland Performance with Case-based Reasoning (Part B), *Environmental Engineering Science*, Vol. 23, No. 2, 203-211.

Lee B.-H. and **Scholz M.** (2006), A Comparative Study: Prediction of Constructed Treatment Wetland Performance with K-nearest Neighbors and Neural Networks, *Water, Air and Soil Pollution,* accepted for publication.

2. Experimental data for BOD, SS, metals and nutrients (confidential)*

* This can be obtained via m.scholz@ed.ac.uk

R Routledge

Constructed wetlands: a review

MIKLAS SCHOLZ* AND BYOUNG-HWA LEE

Institute for Infrastructure and Environment, The University of Edinburgh, The King's Buildings,
Mayfield Road, Edinburgh, UK

The first aim of this invited literature review is critically to review and evaluate hydrological, physical and biochemical processes within natural and constructed wetlands. The second aim is to contribute the thoughts of the authors to the discussion with the help of a case study focusing on gully pot liquor treatment. The performances of constructed treatment wetlands with and without macrophytes, and aggregates of different adsorption capacities will be assessed, principle findings highlighted and conclusions, also relevant to the literature review, will be drawn. The relationships between aggregates, microbial and plant communities as well as the reduction of predominantly biochemical oxygen demand, suspended solids and heavy metals are investigated. After maturation of the biomass, which dominates the litter zone, organic and inorganic contaminants are usually reduced similarly for all wetland types. There appears to be no additional benefit in using macrophytes and expensive adsorption media in constructed wetlands.

Keywords: Constructed treatment wetlands; Aggregates; Macrophytes; Micro-organisms; Water quality; Heavy metals

1. Critical literature review

1.1. Introduction

Wetlands have been recognized to be a natural resource throughout human history. Their importance is appreciated in their natural state by such people as the Marsh Arabs around the confluence of the rivers Tigris and Euphrates in southern Iraq, as well as in managed forms, for example rice paddies, particularly in South East Asia [1]. The water purification capability of wetlands is now being recognized as an attractive option in wastewater treatment. For example, the Environment Agency has recently spent more than £1m on a reed bed scheme in South Wales. This system is designed to clean up mine water from the colliery on which the constructed wetland and associated community park is being built.

Reed beds provide a useful complement to traditional sewage treatment systems. They are often a cheap alternative to expensive wastewater treatment technologies such as trickling filters and activated sludge processes [2–7]. Vertical-flow and horizontal-flow wetlands based on soil, sand and/or gravel are used to treat domestic and industrial wastewater [4,8–12]. They

*Corresponding author. Email: m.scholz@ed.ac.uk

are also applied as passive treatment of diffuse pollution including mine wastewater drainage [2,3,13,14] as well as urban and motorway water runoff [3,11,15,16]. Furthermore, wetlands serve as a wildlife conservation resource and can be seen as natural recreational areas for the local community [17]. The functions of macrophytes within constructed wetlands have been reviewed previously. *Phragmites* sp., *Typha* sp. and other swamp plants are widely used in Europe and Northern America [3,18].

A considerable amount of work on constructed wetlands has already been carried out in the UK by universities, the water authorities and the Natural History Museum. WRc Swindon, Severn Trent Water and Middlesex University, in particular, have made an important text-book contribution to constructed wetland research [4].

1.2. Definitions

Defining wetlands has long been a problematic task, partly due to the diversity of environments that are permanently or seasonally influenced by water but also due to the specific requirements of the diverse groups of people involved with the study and management of these habitats.

The Ramsar Convention, which brought wetlands to the attention of the international community, proposed the following [19]: 'Wetlands are areas of marsh, fen, peatland or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish or salt, including areas of marine water the depth of which at low tide does not exceed six metres.'

Another, more succinct, definition is as follows [20]: 'Wetlands are a half-way world between terrestrial and aquatic ecosystems and exhibit some of the characteristics of each.'

This complements the Ramsar description, since wetlands are the interface between water and land. This concept is particularly important in areas where wetlands may only be 'wet' for relatively short periods of time in a year, such as in areas of the tropics with marked wet and dry seasons.

These definitions put an emphasis on the ecological importance of wetlands. However, the natural water purification processes occurring within these systems have become increasingly relevant to those people involved with the practical use of wetlands for waste water treatment. There is no single accepted ecological definition of wetlands. Wetlands are characterised by the following [21]:

(1).The presence of water.
(2) Unique soils that differ from upland soils.
(3) The presence of vegetation adapted to saturated conditions.

Whichever definition is adopted, it can be seen that wetlands encompass a wide range of hydrological and ecological types, from high altitude river sources, to shallow coastal regions, in each case being affected by prevailing climatic conditions. For the purpose of this review, however, the main emphasis will be upon constructed treatment wetlands in a temperate climate.

1.3. Hydrology of wetlands

1.3.1. Background. The biotic status of a wetland is intrinsically linked to the hydrological factors by which it is affected. These affect the nutrient availability as well as physicochemical

parameters such as soil and water pH and anaerobiosis within soils. In turn, biotic processes will have an impact upon the hydrological conditions of a wetland.

Water being the hallmark of wetlands, it is not surprising that the input and output of water (the water budget) of these systems determines the biochemical processes occurring within them. The net result of the water budget, the hydroperiod, may show great seasonal variations but ultimately delineates wetlands from terrestrial and fully aquatic ecosystems.

From an ecological standpoint, as well as an engineering one, the importance of hydrology cannot be overstated; it defines the species diversity, productivity and nutrient cycling of specific wetlands. That is to say, hydrological conditions must be considered if one is interested in the richness of flora and fauna or utilizing wetlands for pollution control.

1.3.2. Hydroperiod and water budget. The stability of particular wetlands is directly related to their hydroperiod – that is the seasonal shift in surface and sub-surface water levels. The terms flood duration and flood frequency refer to wetlands that are not permanently flooded and give some indication of the time period involved in which the effects of inundation and soil saturation will be most pronounced.

Of particular relevance to riparian wetlands is the concept of flooding pulses as described elsewhere [22]. These pulses cause the greatest difference in high and low water levels and benefit wetlands by the input of nutrients and washing out of waste matter that these sudden high volumes of water provide on a periodic or seasonal basis. It is particularly important to appreciate this natural fluctuation and its effects, since wetland management often attempts to control the level by which waters rise and fall. Such manipulation might be due to the overemphasis placed on water and its role in the lifecycles of wetland flora and fauna, without considering the fact that such species have evolved in such an unstable environment [23].

The balance between the input and output of water within a wetland is termed its water budget (see above). This is summarized by equation (1).

$$\Delta V \,/\, \Delta t = P_n + S_i + G_i - ET - S_o - G_o \pm T \tag{1}$$

ΔV = volume of water storage in a wetland; $\Delta V/\Delta t$ = change in volume of water storage in wetland per unit time, t; P_n = net precipitation; S_i = surface inflows including flooded streams; G_i = groundwater inflows; ET = evapotranspiration; S_o = surface outflows; G_o = groundwater outflows; and T = tidal inflow (+) or outflow (−).

1.3.3. Precipitation, interception, through fall and stem flow. In general terms, wetlands are most widespread in those parts of the world where precipitation exceeds water loss through evapotranspiration and surface runoff. The contribution of precipitation to the hydrology of a wetland is influenced by a number of factors. Precipitation often passes through a canopy of vegetation before it becomes part of the wetland. The volume of water retained by this canopy is termed interception. Factors such as precipitation intensity and vegetation type will affect interception, for which median values of several studies have been calculated as 13% for deciduous forests and 28% for coniferous woodland [24].

The precipitation that continues to reach the wetland is termed the through fall. This is added to the stem flow, which is the water running down vegetation stems and trunks, generally considered a minor component of a wetland water budget, such as 3% of through fall in the cypress dome wetlands in Florida [25]. Thus through fall and stem flow form equation (2); the most commonly used precipitation equation for wetlands:

$$P_n = TF_- + SF \tag{2}$$

where P_n = net precipitation; TF = throughfall; and SF = stem flow.

1.4. Wetland chemistry

1.4.1. Oxygen. Because wetlands are associated with waterlogged soils, the concentration of oxygen within sediments and the overlying water is of critical importance. The rate of oxygen diffusion into water and sediment is slow and this coupled with microbial and animal respiration leads to near anaerobic sediments within many wetlands [26]. These conditions favour rapid peat build up, since decomposition rates and inorganic content of soils are low. Furthermore, the lack of oxygen in such conditions affects the aerobic respiration of plant roots and influences plant nutrient availability. Wetland plants have consequently evolved to be able to exist in anaerobic soils.

While deeper sediments are generally anoxic, a thin layer of oxidised soil usually exists at the soil–water interface. The oxidized layer is important, since it permits oxidized forms of prevailing ions to exist. This is in contrast to the reduced forms occurring at deeper levels of soil. The state of reduction or oxidation of iron, manganese, nitrogen and phosphorus ions determines their role in nutrient availability and also toxicity. The presence of oxidized ferric iron (Fe^{3+}) gives the overlying wetland soil a brown coloration, whilst reduced sediments have undergone gleying, a process by which ferrous iron (Fe^{2+}) gives the sediment a blue-grey tint.

The level of reduction of wetland soils is, therefore, important in understanding the chemical processes that are most likely to occur in the sediment and influence the above water column. The most practical way to determine the reduction state is by measuring the redox potential, also called the oxidation-reduction potential, of the saturated soil or water. The redox potential quantitatively determines whether a soil or water sample is associated with a reducing or oxidizing environment. Reduction is the release of oxygen and gain of an electron (or hydrogen), while oxidation is the reverse; i.e. the gain of oxygen and loss of an electron. This is shown by equation (3) [1]:

$$E_H = E^0 + 2.3\,[RT/nF]\log\,[\{ox\}/\{red\}] \tag{3}$$

where E_H = redox potential on hydrogen scale; E^0 = potential of reference (mV); R = gas constant = 81.987 cal/deg/mol; T = temperature; n = number of moles of electrons transferred; and F = Faraday constant = 23,061 cal/mole-volt.

Oxidation (and therefore decomposition) of organic matter (a very reduced material) occurs in the presence of any electron acceptor, particularly O_2, although NO^{3-}, Mn^{2+}, Fe^{3+} and SO_4^{2-} are also commonly involved in oxidation, but the rate will be slower in comparison with O_2. A redox potential range between +400m V and +700 mV is typical for environmental conditions associated with free dissolved oxygen. Below +400 mV, the oxygen concentration will begin to diminish and wetland conditions might become increasingly more reduced (>−400 mV). It should be noted that redox potentials are affected by pH and temperature, which influences the range at which particular reactions occur. The following thresholds are therefore not definitive:

● Once wetland soils become anaerobic, the primary reaction at approximately +250 mV is the reduction of nitrate (NO_3^-) to nitrite (NO_2^-) and finally to nitrous oxide (N_2O) or free nitrogen gas (N_2).

- At about +225 mV, manganese is reduced to manganous compounds. Under further reduced conditions, ferric iron becomes ferrous iron between approximately +100 and −100 mV and sulphates become sulphides between approximately −100 and −200 mV.
- Under the most reduced conditions (<−200 mV) the organic matter itself or carbon dioxide will become the terminal electron acceptor. This results in the formation of low molecular weight organic compounds and methane gas ($CH_4\uparrow$).

1.4.2. Carbon. Organic matter within wetlands is usually degraded by aerobic respiration or anaerobic processes (e.g. fermentation and methanogenesis). Anaerobic degradation of organic matter is less efficient than decomposition occurring under aerobic conditions.

Fermentation is the result of organic matter acting as the terminal electron acceptor (instead of oxygen as in aerobic respiration). This process forms low molecular weight acids (e.g. lactic acid), alcohols (e.g. ethanol) and carbon dioxide. Therefore, fermentation is often central in providing further biodegradable substrates for other anaerobic organisms in waterlogged sediments.

The sulphur cycle is linked with the oxidation of organic carbon in some wetlands, particularly in sulphur-rich coastal systems. Low-molecular weight organic compounds that result from fermentation (e.g. ethanol) are utilised as organic substrates by sulphur-reducing bacteria in the conversion of sulphate to sulphide [1].

Previous work suggests that methanogenesis is the principal carbon pathway in freshwater. Between 30 and 50% of the total benthic carbon flux has been attributed to methanogenesis [27].

1.4.3. Nitrogen. The prevalence of anoxic conditions in most wetlands has lead to them playing a particularly important role in the release of gaseous nitrogen from the lithosphere and hydrosphere to the atmosphere through denitrification [1]. However, the various oxidation states of nitrogen within wetlands are also important to the biogeochemistry of these environments.

Nitrates are important terminal electron acceptors after oxygen, making them relevant in the process of oxidation of organic matter. The transformation of nitrogen within wetlands is strongly associated with bacterial action. The activity of particular bacterial groups is dependent on whether the corresponding zone within a wetland is aerobic or anaerobic.

Within flooded wetland soils, mineralized nitrogen occurs primarily as ammonium (NH_4^+). Ammonium is formed through ammonification, the process by which organically bound nitrogen is converted to ammonium nitrogen under aerobic or anaerobic conditions. Soil-bound ammonium can be absorbed through plant root systems and be reconverted to organic matter, a process that can also be performed by anaerobic micro-organisms.

The oxidized top layer, present in many wetland sediments, is crucial in preventing the excessive build up of ammonium. A concentration gradient will be established between the high concentration of ammonium in the lower reduced sediments and the low concentration in the oxidized top layer. This may cause a passive flow of ammonium from the anaerobic to the aerobic layer, where microbiological processes convert the ion into further forms of nitrogen.

Within the aerobic sediment layer, nitrification of ammonium, firstly to nitrite (NO_2^-) and subsequently to nitrate (NO_3^-), is shown in the equations (4) and (5), preceded by the genus of bacteria involved in each process step. Nitrification may also take place in the oxidized rhizosphere of wetland plants.

$$\textit{Nitrosomonas:} \quad 2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ + \text{energy} \qquad (4)$$

$$\textit{Nitrobacter:} \quad 2NO_2^- + O_2 \rightarrow 2NO_3^- + \text{energy} \qquad (5)$$

A study in southern California indicates that denitrification was the most likely pathway for nitrate loss from experimental macrocosms and larger constructed wetlands [28]. Very high rates of nitrate nitrogen removal were reported (2800 mg $\times$ N $\times$ m^2/d). Furthermore, nitrate removal from inflow (waste)water is generally lower in constructed wetlands compared to natural systems [29]. There is considerable interest in enhancing bacterial denitrification in constructed wetlands in order to reduce the level of eutrophication in receiving water courses such as rivers and lakes [28].

An investigation into the seasonal variation of nitrate removal showed maximum efficiency to occur during summer [29]. This study also indicated a seasonal relationship in the pattern of nitrate retention, in which nitrate assimilation and denitrification are temperature dependent.

Further evidence supporting the importance of denitrification is presented elsewhere [30]. The proportion of nitrogen removed by denitrification from a wetland in southern California was estimated by analysing the increase in the proportion of the nitrogen isotope ^{15}N found in the outflow water. This method is based on the tendency of the lighter isotope ^{14}N to be favoured by the biochemical thermodynamics of denitrification, thus reducing its proportion in water flowing out of wetlands in which denitrification is prevalent. Denitrification seems to be the favoured pathway of nitrate loss from a treatment wetland, as this permanently removes nitrogen from the system, compared to sequestration within algal and macrophyte biomass.

In some wetlands, nitrogen may be derived through nitrogen fixation. In the presence of the enzyme nitrogenase, nitrogen gas is converted to organic nitrogen by organisms such as aerobic or anaerobic bacteria and cyanobacteria (blue-green algae). Wetland nitrogen fixation can occur in the anaerobic or aerobic soil layer, overlying water, rhizosphere of plant roots and on leaf or stem surfaces. Cyanobacteria may contribute significantly to nitrogen fixation. In northern bogs, which are often too acidic for large bacterial populations, nitrogen fixation by cyanobacteria is particularly important [31]. However, it should be noted that while cyanobacteria are adaptable organisms, they are affected by environmental stresses. For example, cyanobacteria are particularly susceptible to ultraviolet radiation, whereby their nitrogen metabolism (along with other functions) becomes impaired [32].

1.4.4. Phosphorus. In wetland soils, phosphorus occurs as soluble or insoluble, organic or inorganic complexes. Its cycle is sedimentary rather than gaseous (as with nitrogen) and predominantly forms complexes within organic matter in peatlands or inorganic sediments in mineral soil wetlands. Over 90% of the phosphorus load in streams and rivers may be present in particulate inorganic form [33].

Soluble reactive phosphorus is the analytical term given to biologically available orthophosphate, which is the primary inorganic form. The availability of phosphorus to plants and microconsumers is limited due to the following main effects:

● Under aerobic conditions, insoluble phosphates are precipitated with ferric iron, calcium and aluminium.
● Phosphates are adsorbed onto clay particles, organic peat and ferric/aluminium hydroxides and oxides.
● Phosphorus is bound up in organic matter through incorporation in bacteria, algae and vascular macrophytes.

There are three general conclusions about the tendency of phosphorus to precipitate with selected ions [34]:

(1) In acid soils, phosphorus is fixed as aluminium and iron phosphates.
(2) In alkaline soils, phosphorus is bound by calcium and magnesium.
(3) The bioavailability of phosphorus is greatest at neutral to slightly acid pH.

Under anaerobic wetland soil conditions, phosphorus availability is altered. The reducing conditions that are typical of flooded soils do not directly affect phosphorus. However, the association of phosphorus with other elements that undergo reduction has an indirect effect upon phosphorus in the environment. For example, as ferric iron is reduced to the more soluble ferrous form, phosphorus as ferric phosphate (reductant-soluble phosphorus) is released into solution [35,36]. Phosphorus may also be released into solution by a pH change brought about by organic, nitric or sulphuric acids produced by chemosynthetic bacteria. Phosphorus sorption to clay particles is greatest under strongly acidic to slightly acidic conditions [37].

Great temporal variability in phosphorus concentrations of wetland influent in Ohio has been reported [38]. However, no seasonal pattern in phosphorus concentration was observed. This was explained by precipitation events and river flow conditions. Dissolved reactive phosphorus levels peaked during floods and on isolated occasions in late autumn. Furthermore, sedimentation of suspended solids appears to be important in phosphorus retention within wetlands [39].

The physical, chemical and biological characteristics of a wetland system affect the solubility and reactivity of different forms of phosphorus. Phosphate solubility has been shown to be regulated by temperature [40], pH [41], redox potential [42], interstitial soluble phosphorus level [43] and microbial activity [44,45].

Where agricultural land has been converted to wetlands, there can be a tendency in solubilization of residual fertiliser phosphorus, which results in a rise of the soluble phosphorus concentration in floodwater. This effect can be reduced by physicochemical amendment, applying chemicals such as alum ($FeCl_3$) and calcium carbonate ($CaCO_3$) to stabilize the phosphorus in the sediment of these new wetlands [46,47].

The redox potential has a significant effect on dissolved reactive phosphorus of chemically amended soils [46,47]. The redox potential can alter with fluctuating water-table levels and hydraulic loading rates. Dissolved phosphorus concentrations are relatively high under reduced conditions, and decrease with increasing redox potential. Iron compounds (e.g. $FeCl_3$) are particularly sensitive to the redox potential, resulting in the chemical amendment of wetland soils. Furthermore, alum and calcium carbonate are suitable to bind phosphorus even during fluctuating redox potentials.

Macrophytes assimilate phosphorus predominantly from deep sediments, thereby acting as nutrient pumps [1,48,49]. The most important phosphorus retention pathway in wetlands is via physical sedimentation [50].

Model simulations on constructed wetlands in north-eastern Illinois, USA, showed an increase in total phosphorus in the water column in the presence of macrophytes mainly during the non-growing period, with little effect during the growing season. Most phosphorus taken from sediments by macrophytes is reincorporated into the sediment as dead plant material and therefore remains in the wetland indefinitely. Macrophytes can be harvested as a means to enhance phosphorus removal in wetlands. Through the harvesting of macrophytes at the end of the growing season, phosphorus can be removed from the internal nutrient cycle within wetlands. Moreover, the model showed a phosphorus removal potential of three-quarters of that of the phosphorus inflow. Therefore, harvesting would reduce phosphorus levels in upper sediment layers and drive phosphorus movement into deeper layers,

particularly the root zone. In deep layers of sediment, the phosphorus sorption capacity increases along with a lower desorption rate [50].

1.4.5. Sulphur. In wetlands, sulphur is transformed by microbiological processes and occurs in several oxidation stages. Reduction may occur between -100 and -200 mV on the redox potential scale. Sulphides provide the characteristic 'bad egg' odour of some wetland soils.

Assimilatory sulphate reduction is accomplished by obligate anaerobes such as *Desulfovibrio* spp. Bacteria may use sulphates as terminal electron acceptors (equation (6)) in anaerobic respiration at a wide pH range but highest around neutral [1].

$$4H_2 + SO_4^{2-} \rightarrow H_2S \uparrow + 2H_2O + 2OH^- \tag{6}$$
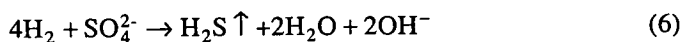
The greatest loss of sulphur from freshwater wetlands to the atmosphere is via hydrogen sulphide ($H_2S\uparrow$). In oceans, however, this is through the production of dimethyl sulphide from decomposing phytoplankton [51].

Oxidation of sulphides to elemental sulphur and sulphates can occur in the aerobic layer of some soils and is carried out by chemoautotrophic (e.g. *Thiobacillus* sp.) and photosynthetic microorganisms. *Thiobacillus* sp. may gain energy from the oxidation of hydrogen sulphide to sulphur and further, by certain other species of the genus, from sulphur to sulphate (equations (7) and (8)):

$$2H_2S + O_2 \rightarrow 2S + 2H_2O + energy \tag{7}$$

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 + energy \tag{8}$$
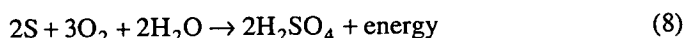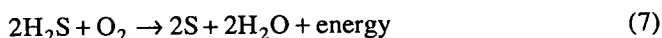
In the presence of light, photosynthetic bacteria, such as purple sulphur bacteria of salt marshes and mud flats, produce organic matter as indicated in equation (9). This is similar to the familiar photosynthesis process, except that hydrogen sulphide is used as the electron donor instead of water.

$$CO_2 + H_2S + light \rightarrow CH_2O + S \tag{9}$$
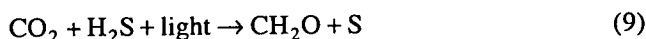
Direct toxicity of free sulphide in contact with plant roots has been noted. There is a reduced toxicity and availability of sulphur for plant growth if it precipitates with trace metals. For example, the immobilisation of zinc and copper by sulphide precipitation is well known.

The input of sulphates to freshwater wetlands, in the form of Aeolian dust or as anthropogenic acid rain, can be significant. Sulphate deposited on wetland soils may undergo dissimilatory sulphate reduction by reaction with organic substrates (equation (10)).

$$2CH_2O + SO_4^{2-} + H^+ \rightarrow 2CO_2 + HS^- + 2H_2O \tag{10}$$
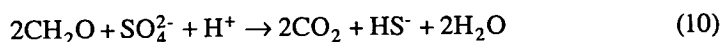
Protons consumed during this reaction generate alkalinity. This is illustrated by the increase in pH with depth in wetland sediments [52]. It has been suggested that this 'alkalinity effect' can act as a buffer in acid rain affected lakes and streams [53,54].

The sulphur cycle can vary greatly within different zones of a particular wetland. The stable isotope $\delta^{34}S$ within peat, the $^{35}SO_4^{2-} : Cl^-$ ratio and the stable isotopes $\delta^{18}O$ and $\delta^{34}S$ of sulphate within different waters were analysed previously. The variability in the sulphur

cycle within the watershed can affect the distribution of reduced sulphur stored in soil. This change in local sulphur availability can have marked effects upon stream water over short distances [55].

The estimation of generated alkalinity may be complicated due to the potential problems associated with the use of the $^{35}SO_4^{2-}$: Cl^- ratio and/or $\delta^{34}S$ value in order to estimate the net sulphur retention. These problems may exist because ester sulphate pools can be a source of sulphate availability for sulphate reduction and a $\delta^{34}S$ sulphate buffer within stream water.

1.5. Wetland ecosystem mass balance

The general mass balance for a wetland, in terms of chemical pathways, uses the following main pathways: inflows, intrasystem cycling and outflows. The inflows are mainly through hydrologic pathways such as precipitation, surface water runoff and groundwater. The photosynthetic fixation of both atmospheric carbon and nitrogen are important biological pathways. Intrasystem cycling is the movement of chemicals in standing stocks within wetlands, such as litter production and remineralization. Translocation of minerals within plants is an example of physical movement of chemicals. Outflows involve hydrologic pathways but also include the loss of chemicals to deeper sediment layers, beyond the influence of internal cycling (although the depth at which this threshold occurs is not certain). Furthermore, the nitrogen cycle plays an important role in outflows, such as nitrogen gas lost as a result of denitrification. However, respiratory loss of carbon is also an important biotic outflow.

There is great variation in the chemical balance from one wetland to another, but the following generalizations may be made:

- Wetlands act as sources, sinks or transformers of chemicals depending on wetland type, hydrological conditions and length of time the wetland has received chemical inputs. As sinks, the long-term sustainability of this function is associated with hydrologic and geomorphic conditions as well as the spatial and temporal distribution of chemicals within wetlands.
- Particularly in temperate climates, seasonal variation in nutrient uptake and release is expected. Chemical retention will be greatest in the growing seasons (spring and summer) due to higher rates of microbial activity and macrophyte productivity.
- The ecosystems connected to wetlands affect and are affected by the adjacent wetland. Upstream ecosystems are sources of chemicals, while those downstream may benefit from the export of certain nutrients or the retention of particular chemicals.
- Nutrient cycling in wetlands differs from that in terrestrial and aquatic systems. More nutrients are associated with wetland sediments than with most terrestrial soils, while benthic aquatic systems have autotrophic activity which relies more on nutrients in the water column than in the sediments.
- The ability of wetlands to remove anthropogenic waste is not limitless.

Equation (11) indicates a general mass balance for a pollutant within a treatment wetland. Within this equation, transformations and accretion are long-term sustainable removal processes, while storage does not serve in long-term average removal but can lessen or accentuate the cyclic activity.

$$In - Out = Transformation + Accretion + Biomass\ Storage + Water\ /\ Soil\ Storage \quad (11)$$

1.6. Macrophytes in wetlands

1.6.1. Background. Wetland plants are often central to wastewater treatment wetlands. The following requirements of plants should be considered for use in such systems [56]:

- Ecological adaptability (no disease or weed risk to the surrounding natural ecosystems).
- Tolerance of local conditions in terms of climate, pests and disease.
- Tolerance of pollutants and hypertrophic waterlogged conditions.
- Ready propagation, rapid establishment, spread and growth.
- High pollutant removal capacity, through direct assimilation or indirect enhancement of nitrification, denitrification and other microbial processes.

Interest in macrophyte systems for sewage treatment by the UK water industry dates back to 1985 [57]. The ability of macrophyte species and their assemblages within systems to most efficiently treat wastewater has been examined previously [58]. The dominant species of macrophyte varies from locality to locality. The number of genera (e.g. *Phragmites* sp., *Typha* sp. and *Scirpus* sp.) common to all temperate locations is great. The improvement of water quality with respect to key parameters including biochemical oxygen demand, chemical oxygen demand, total suspended solids, nitrates and phosphates has been studied [59]. Relatively little work has been conducted on the enteric bacteria removal capability of macrophyte systems [60].

1.6.2. Primary productivity. There have been many studies to determine the primary productivity of wetland macrophytes, although estimates have generally tended to be fairly high [1]. The estimated dry mass production for *Phragmites australis* (Cav.) Trin. ex Steud. (common reed) is 1000–6000 $g/m^2 \times$ a in the Czech Republic [61], 2040–2210 $g/m^2 \times$ a for *Typha latifolia* L. (cattail) in Oregon, USA [62], and 943 $g/m^2 \times$ a for *Scirpus fluviatilis* (Torr.) A. Gray [JPM][H&C] (river bulrush) in Iowa, USA [63].

Little of this plant biomass is consumed as live tissue; it rather enters the pool of particulate organic matter following tissue death. The breakdown of this material is consequently an important process in wetlands and other shallow aquatic habitats [64]. Litter breakdown has been studied along with extensive work on one of the most widespread aquatic macrophyte; *P. australis* [65].

There has been an emphasis on studying the breakdown of aquatic macrophytes in such a way as most closely resembles that of natural plant death and decomposition, principally by not removing plant tissue from macrophyte stands. Many species of freshwater plants exhibit so-called 'standing-dead' decay, which describes the observation of leaves remaining attached to their stems after senescence and death [66]. Different fractions (leaf blades, leaf sheaths and culms) of *P. australis* differ greatly in structure and chemical composition and may exhibit different breakdown rates, patterns and nutrient dynamics [64].

1.6.3. *Phragmites australis*. *Phragmites australis* (Cav.) Trin. ex Steud. (common reed), formerly known as *P. communes* (Norfolk reed), is a member of the large family Poaceae (roughly 8000 species within 785 genera). Common reed occurs throughout Europe to 70° North and is distributed world-wide. It may be found in permanently flooded soils of still or slowly flowing water. This emergent plant is usually firmly rooted in wet sediment but may form lightly anchored rafts of 'hover reed'. It tends to be replaced by other species at drier sites. The density of this macrophyte is reduced by grazing (e.g. by waterfowl) and may then be replaced by other emergent species such as *Phalaris arundinacea* L. (reed canary grass).

P. australis is a perennial with shoots emerging in spring. Hard frost kills these shoots, illustrating the tendency for reduced vigour towards the northern end of its range. The hollow stems of the dead shoots in winter are important in transporting oxygen to the relatively deep located rhizomes [67].

Reproduction in closed stands of this species is mainly by vegetative spread, although seed germination enables the colonisation of open habitats. Detached shoots often survive and regenerate away from the main stand [68].

Common reed or Norfolk Reed is most common in nutrient-rich sites and absent from the most oligotrophic zones. However, the stems of this species may be weakened by nitrogen-rich water and are subsequently more prone to wind and wave damage, leading to an apparent reduction in density of this species in Norfolk (England) and elsewhere in Europe [69,70].

1.6.4. *Typha latifolia*. *Typha latifolia* L. (cattail, reedmace, bulrush) is a species belonging to the small family *Typhaceae*. This species is widespread in temperate parts of the northern hemisphere but extends to South Africa, Madagascar, Central America and the West Indies and is naturalised in Australia [68]. A Typha latifolia is typically found in shallow water or on exposed mud at the edge of lakes, ponds, canals and ditches and less frequently near fast flowing water. This species rarely grows at water depths below 0.3 m, where it is frequently replaced by *P. australis*. Reedmace is a shallow-rooted perennial producing shoots throughout the growing season, which subsequently die in autumn. Colonies of this species expand by rhizomatous growth at rates of 4 m/a, while detached portions of rhizome may float and establish new colonies [2].

In contrast, colony growth by seeds is less likely. Seeds require moisture, light and relatively high temperatures to germinate, although this may occur in anaerobic conditions. Where light intensity is low, germination is stimulated by temperature fluctuation.

1.7. Physical and biochemical variables

The key physicochemical variables relevant for wetlands include the biochemical oxygen demand, turbidity and the redox potential. The biochemical oxygen demand is an empirical test to determine the molecular oxygen used during a specified incubation period (usually five days), for the biochemical degradation of organic matter (carbonaceous demand) and the oxygen used to oxidise inorganic matter (e.g. sulphides and ferrous iron). An extended test (up to 25 days) may also measure the amount of oxygen used to oxidise reduced forms of nitrogen (nitrogenous demand), unless this is prevented by an inhibitor chemical [71]. Inhibiting the nitrogenous oxygen demand is recommended for secondary effluent and pollution samples [72].

The European Union (EU) freshwater fisheries directive sets an upper biochemical oxygen demand limit of 3 mg/l for salmonid rivers and 6 mg/l for coarse fisheries. A river is deemed polluted if the biochemical oxygen demand exceeds 5 mg/l. Municipal wastewater values are usually between approximately 150 and 1000 mg/l [73].

Turbidity is a measure of the cloudiness of water, caused predominantly by suspended material, such as clay, silt, organic and inorganic matter, plankton and other microscopic organisms, scattering and absorbing light. Turbidity in wetlands and lakes is often due to colloidal or fine suspensions, while in fast flowing waters the particles are larger and turbid conditions are prevalent during flood times [73].

The redox potential is another key parameter for monitoring wetlands. The reactivities and mobilities of elements such as Fe, S, N, C and a number of metallic elements depend strongly

on the redox potential conditions. Reactions involving electrons and protons are pH and redox potential dependent. Chemical reactions in aqueous media can often be characterised by pH and redox potential together with the activity of dissolved chemical species. The redox potential is a measure of intensity and does not represent the capacity of the system for oxidation or reduction [72]. The interpretation of redox potential values measured in the field is limited by a number of factors, including irreversible reactions, 'electrode poisoning' and multiple redox couples.

1.8. Natural and constructed wetlands (review examples)

1.8.1. Riparian wetlands. Riparian wetlands are ecosystems under the influence of adjacent streams or rivers [74]. A succinct definition is as follows [75]:

> Riparian zones are the interface between terrestrial and aquatic ecosystems. As ecotones, they encompass sharp gradients of environmental factors, ecological processes and plant communities. Riparian zones are not easily delineated but are composed of mosaics of landforms, communities, and environments within the larger landscape.

There are four main reasons as to why the periodic flooding, which is typical of riparian wetlands, contributes to the observed higher productivity compared to adjacent upland ecosystems:

- There is an adequate water supply for vegetation.
- Nutrients are supplied and coupled with a favourable change in soil chemistry (e.g. nitrification, sulphate reduction and nutrient mineralization).
- In comparison to stagnant water conditions, a more oxygenated root zone follows flooding.
- Waste products (e.g. carbon dioxide and methane) are removed by the periodic 'flushing'.

Nutrient cycles in riparian wetlands can be described as follows:

- Nutrient cycles are 'open' due to the effect of river flooding, runoff from upslope environments or both (depending on season and inflow stream or river type).
- Riparian forests have a great effect on the biotic interactions within intrasystem nutrient cycles. The seasonal pattern of growth and decay often matches available nutrients.
- Water in contact with the forest floor leads to important nutrient transformations. Therefore, riparian wetlands can act as sinks for nutrients that enter the system as runoff and/or groundwater flow.
- Riparian wetlands have often appeared to be nutrient transformers, changing a net input of inorganic nutrients to a net output of their corresponding organic forms.

The nitrogen cycle within a temperate stream-floodplain environment is of particular interest to ecological engineers. During winter, flooding contributes to the accumulation of dissolved and particulate organic nitrogen that is not assimilated by the trees due to their dormancy. This fraction of nitrogen is retained by filamentous algae and through immobilisation by detritivores on the forest floor. As the waters warm in spring, nitrogen is released by decomposition and by shading of the filamentous algae by the developing tree canopy. Nitrate is then assumed to be immobilized in the decaying litter and gradually made available to plants. As vegetation increases, the plants take up more nitrogen and water levels fall due

to evapotranspiration. Ammonification and nitrification rates increase with exposure of the sediments to the atmosphere. Nitrates produced in nitrification are lost when denitrification becomes prevalent as flooding later in the year creates anaerobic conditions.

In terms of reducing the effects of eutrophication of open water by runoff, the use of riparian buffer zones, particularly of *Alnus incana* (grey alder) and *Salix* sp. (willow) in conjunction with perennial grasses has been recommended [76]. Riparian zones are also termed riparian forest buffer systems [77]. Such zones were found to reduce the nutrient flux into streams.

The role of riparian ecosystems in nutrient transformations is specifically important in relation to production of the greenhouse gas nitrous oxide (N_2O). Due to the inflow of excess agricultural nitrogen into wetland systems, the riparian zones, in particular, are likely 'hot spots' for nitrous oxide production [78].

The control of non-point source pollution can be successfully achieved by riparian forest buffers in some agricultural watersheds and most effectively if excess precipitation moves across, in or near the root zone of the riparian forest buffers. For example, between 50 and 90% retention of total nitrate loading in both shallow groundwater and sediment subject to surface runoff within the Chesapeake Bay, USA, watershed was observed. In comparison, phosphorus retention was found to be generally much less [77].

1.8.2. Constructed wetlands. Natural wetlands usually improve the quality of water passing through them, acting as ecosystem filters. Constructed wetlands are artificially created wetlands used to treat water pollution in its variety of forms. Therefore, they fall into the category of treatment wetlands. Treatment wetlands are solar powered ecosystems. Solar radiation varies diurnally, as well as on an annual basis [79].

Constructed wetlands have the purpose to remove bacteria, enteric viruses, suspended solids, biochemical oxygen demand, nitrogen (as ammonia and nitrate), metals and phosphorus [80]. Two general forms of constructed wetlands are used in practice: surface-flow (horizontal-flow) and sub-surface-flow (vertical-flow). Surface-flow constructed wetlands most closely mimic natural environments and are usually more suitable for wetland species because of permanent standing water. In sub-surface-flow wetlands, water passes laterally through a porous medium (usually sand and gravel) with a limited number of macrophyte species. These systems have often no standing water.

Constructed treatment wetlands can be built at, above or below the existing land surface if an external water source is supplied (e.g. wastewater). The grading of a particular wetland in relation to the appropriate elevation is important for the optimal use of the wetland area in terms of water distribution. Soil type and groundwater level must also be considered if long-term water shortage is to be avoided. Liners can prevent excessive desiccation, particularly where soils have a high permeability (e.g. sand and gravel) or where there is limited or periodic flow.

Rooting substrate is also an important consideration for the most vigorous growth of macrophytes. A loamy or sandy topsoil layer of 20–30 cm in depth is ideal for most wetland macrophyte species in a surface-flow wetland. A sub-surface-flow wetland will require coarser material such as gravel and/or coarse sand [3].

The use of flue-gas-desulphurisation by-products from coal fired electric power plants in wetland liner material was investigated previously [81]. These by-products are usually sent to landfill sites. This is now recognized as an increasingly unsuitable, impractical and not sustainable waste disposal method. Although this study was short (two years), no detrimental impact on macrophyte biomass production was reported. Moreover, flue-gas-desulphurisation material may be a good substrate and liner to enhance phosphorus retention in constructed wetlands.

The understanding of chemical transformations in constructed treatment wetlands has recently become a main research focus. Dissolved organic carbon is an important variable in potable water treatment due to its reaction with disinfectants (e.g. chlorine) to form carcinogenic by-products, such as trihalomethanes. The transformations of dissolved organic carbon through a constructed wetland were observed previously. The following conclusions with implications for treatment wetland design were made [80]:

- High levels of dissolved organic carbon may enter water supplies where soil aquifer treatment is used for groundwater recharge, as the influent for this method is likely to come from long hydraulic retention time wetlands. There is consequently a greater potential for the formation of disinfection by-products.
- A shorter hydraulic retention time will result in less dissolved organic carbon leaching from plant material compared to a longer hydraulic retention time in a wetland.
- Dissolved organic carbon leaching is likely to be most significant in wetlands designed for ammonia removal, which requires long hydraulic retention time.

1.8.3. Constructed wetlands for storm water treatment.

Most constructed wetlands in the USA and Europe are soil or gravel based horizontal-flow systems planted with T. latifolia and/or P. australis. They are used to treat storm runoff, domestic and industrial wastewater [3,4,82,83], and have also been applied for passive treatment of mine wastewater drainage [84,85].

Storm runoff from urban areas has been recognized as a major contributor to pollution of the receiving urban watercourses. The principal pollutants in urban runoff are biochemical oxygen demand, suspended solids, heavy metals, de-icing salts, hydrocarbons and faecal coliforms [86,87].

Although various conventional methods have been applied to treat storm water, most technologies are not cost-effective or too complex. Constructed wetlands integrated into a best management practice concept are a sustainable means of treating storm water and prove to be more economical (e.g. construction and maintenance) and energy efficient than traditional centralized treatment systems [83,88]. Furthermore, wetlands enhance biodiversity and are less susceptibility to variations of loading rates [4,74].

Contrary to standard domestic wastewater treatment technologies, storm water (e.g. gully pot liquor and effluent) treatment systems have to be robust to highly variable flow rates and water quality variations. The storm water quality depends on the load of pollutants present on the road, and the corresponding dilution by each storm event [74,82].

In contrast to standard horizontal-flow constructed treatment wetlands, vertical-flow wetlands are flat, intermittently flooded and drained, allowing air to refill the soil pores within the bed [4,89,90]. When the wetland is dry, oxygen (as part of the air) can enter the top layer of debris and sand. The following flow of runoff will absorb the gas and transport it to the anaerobic bottom of the wetland. Furthermore, aquatic plants such as macrophytes transport oxygen to the rhizosphere. However, this natural process of oxygen enrichment is not as effective as the previously explained engineering method [3,91].

While it has been recognized that vertical-flow constructed wetlands have usually higher removal efficiencies with respect to organic pollutants and nutrients in comparison to horizontal-flow wetlands, denitrification is less efficient in vertical-flow systems [92].

Heavy metals within storm water are associated with fuel additives, car body corrosion, and tire and brake wear. Common metal pollutants from cars include copper, nickel, lead,

zinc, chromium and cadmium. Freshwater quality standards are most likely to be exceeded by copper [4,93,94].

Metals occur in soluble, colloidal or particulate forms. Heavy metals are most bioavailable when they are soluble, either in ionic or weakly complexed form [4,95,96].

There have been many studies on the specific filter media within constructed wetlands to treat heavy metals economically, such as limestone, lignite, activated carbon, peat, and barley straw leaves [71, 86]. Metal bioavailability and reduction are controlled by chemical processes including acid volatile sulphide formation and organic carbon binding and sorption in reduced sediments of constructed wetlands [95,97,98]. It follows that metals usually accumulate in the top layer (fine aggregates, sediment and litter) of vertical-flow and near the inlet of horizontal-flow constructed treatment wetlands [96,99,100].

Physical and chemical properties of the wetland soil and aggregates affecting metal mobilization include particle size distribution (texture), redox potential, pH, organic matter, salinity, and the presence of inorganic matter such as sulphides and carbonates [101].

The cation exchange capacity of maturing wetland soils and sediments tend to increase as texture becomes finer because more negatively charged binding sites are available. Organic matter has a relative high proportion of negatively charged binding sites. Salinity and pH can influence the effectiveness of the cation exchange capacity of soils and sediments because the negatively charged binding sites will be occupied by a high number of sodium or hydrogen cations [102].

Sulphides and carbonates may combine with metals to form relatively insoluble compounds. Especially the formation of metal sulphide compounds may provide long-term heavy metal removal, because these sulphides will remain permanently in the wetland sediments as long as they are not re-oxidized [3,4].

2. Evaluation based on a case study

2.1. Summary

The aim is to assess the treatment efficiencies for gully pot liquor of experimental vertical-flow constructed wetland filters containing *P. australis* and filter media of different adsorption capacities. Six out of twelve filters received inflow water spiked with metals. For two years, hydrated nickel and copper nitrate were added to sieved gully pot liquor to simulate contaminated primary treated storm runoff.

For those six constructed wetland filters receiving heavy metals, an obvious breakthrough of dissolved nickel was recorded after road salting during the first winter. However, a breakthrough of nickel was not observed since the inflow pH was raised to eight after the first year of operation. High pH facilitated the formation of particulate metal compounds such as nickel hydroxide.

During the second year, reduction efficiencies of heavy metal, biochemical oxygen demand and suspended solids improved considerably. Concentrations of biochemical oxygen demand were frequently <20 mg/l, an international threshold for secondary wastewater treatment. This is likely due to biomass maturation, and the increase of pH[71].

The case study is based on data and observations from an on-going research project (since September 2002). Only the methodology and preliminary data (less than six months) have been published previously [71]. The following sections focus on the principle observations relevant for this review and not on specific data that may be only of importance for this particular experimental set-up.

—

2.2. Purpose

The major purpose of this case study is to improve the design, operation and management guidelines of constructed treatment wetlands to secure a high wastewater treatment performance during all seasons particularly in cold climates. The main processes that have been discussed as part of the literature review will be looked at from a practical point of view. The objectives are to assess:

(1) The performance of vertical-flow constructed treatment wetland filters.
(2) The compliance with water quality standards in terms of the reduction efficiencies of experimental constructed wetlands treating gully pot liquor receiving high loads of biochemical oxygen demand, suspended solids, nickel, copper, nitrate and turbidity.
(3). The impact of environmental conditions, such as variations of salt concentrations, pH and temperature on the treatment performance of constructed wetlands during all seasons.
(4) Heavy metal leaching at low and high pH levels.
(5) The overall role of adsorption media and *P. australis*.

2.3. Area description, materials and methods

2.3.1. Study site. Twelve wetland filters (figure 1) were located outdoors at The King's Buildings campus (The University of Edinburgh, Scotland) to assess the system performance (09 September 2002 to 21 September 2004). The 12 first days of operation were not analysed because the water quality was not representative. Inflow water, polluted by road runoff, was collected from randomly selected gully pots on the campus, the nearby predominantly housing estates and two major roads. After mixing both the sediment and the water phase within the gully pot, water was collected by manual abstraction with a 2 l beaker.

2.3.2. Filter design and media composition. Round drainage pipes were used to construct the filters. All 12 vertical-flow wetland filters (figure 1) were designed with the following dimensions: height = 83 cm and diameter = 10 cm. In September 2002, the calculated empty filter bed volumes were approximately 6.2, 6.4, 4.0, 4.1, 3.8, 4.1, 3.8, 4.0, 3.8, 4.0, 4.0 and 4.0 l for filters 1–12, respectively. The filter volume capacities were measured by draining the filters entirely.

Different packing order arrangements of filter media and plant roots were used in the wetland filters (tables 1 and 2). The outlet of each constructed wetland comprised a valve at the bottom of each filter.

The inflow waters of filter 2 and filters 7–12 were dosed with hydrated copper nitrate $(Cu(NO_3)_2 \cdot 3H_2O)$ and hydrated nickel nitrate $(Ni(NO_3)_2 \cdot 6H_2O)$. Filters 1 and 2 (controls) are similar to wastewater stabilization ponds or gully pots (extended storage) without a significant amount of filter media (table 2). In comparison, filters 3, 5, 7 and 9 are similar to gravel and slow sand filters, and filters 4, 6, 8 and 10 are typical reed bed filters. The reed bed filters contain gravel and sand substrate and native *P. australis*, all of similar total biomass weight during planting and from the same local source. However, filters 5, 6, 9 and 10 also contain adsorption media. Additional natural adsorption media (Filtralite and Frogmat) were used. Filtralite (containing 3% of calcium oxide [CaO]) with diameters between 1.5 and 2.5 mm is associated with enhanced metal and nutrient reduction [99,103]. Furthermore, Frogmat (natural product based on raw barley straw) has a high adsorption area and is therefore likely to be associated with a high heavy metal reduction potential. The use of other filter media with
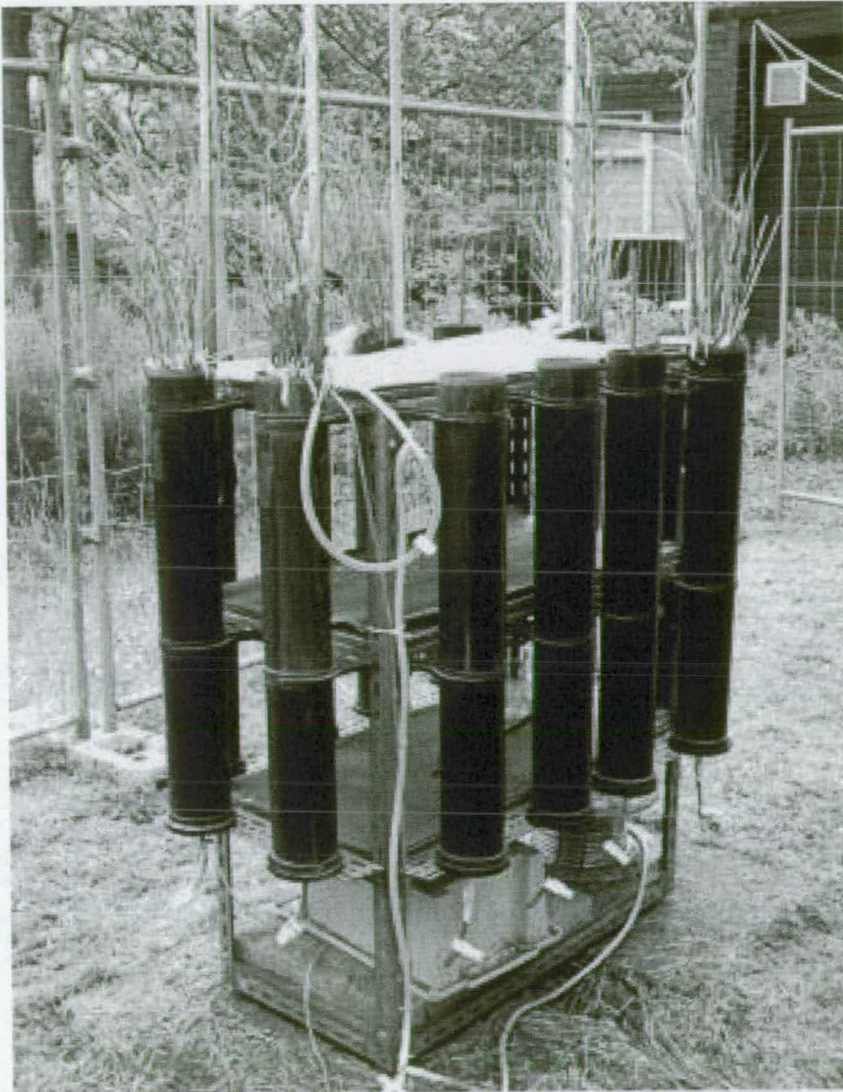
Figure 1.   Constructed treatment wetland rig (The King's Buildings campus; The University of Edinburgh) in May 2004.

high adsorption capacities such as activated carbon [86,93] and oxide-coated sand [104] has been discussed elsewhere.

Filters 11 and 12 are more complex in their design and operation (table 1). The top water layer of both filters is aerated (with air supplied by air pumps) to enhance oxidation (minimizing zones of reducing conditions) and nitrification [89,96,98]. Filter 12 receives about 153% of filter 11's mean annual inflow volume and load (tables 1 and 3).

2.3.3. Environmental conditions, operation and analytical methods. The filtration system was designed to operate in batch flow mode to reduce pumping and computer control costs (table 3). The hydraulic regime of filter 12 differs from that for filters 1–11 to identify the

Table 1. Systematic and stratified experimental set-up of the filter (Figure 1) content and operation.

Filter	Planted	Media type[a]	Plus metals[b]	Aerated	High loading[c]
1	No	1	No	No	No
2	No	1	Yes	No	No
3	No	2	No	No	No
4	Yes	2	No	No	No
5	No	3	No	No	No
6	Yes	3	No	No	No
7	No	2	Yes	No	No
8	Yes	2	Yes	No	No
9	No	3	Yes	No	No
10	Yes	3	Yes	No	No
11	Yes	3	Yes	Yes	No
12	Yes	3	Yes	Yes	Yes

Notes: [a] 1 = no media, 2 = standard, 3 = addition of Filtralite (light expanded clay product) and Frogmat (barley straw); [b] addition of hydrated copper and nickel nitrate; [c] see Table 3.

Table 2. Packing order of vertical-flow wetland filters (Figure 1).

Height (cm)	Filter 1	Filter 2	Filter 3	Filter 4	Filter 5	Filter 6
61–83	W	W	W	W	W	W
56–60	W	W	6	6 + P	7	7 + P
51–55	W	W	6	6 + P	6	6 + P
36–50	W	W	4	4 + P	5	5 + P
31–35	W	W	3	3	5	5
26–30	W	W	3	3	4	4
21–25	W	W	2	2	3	3
16–20	W	W	2	2	2	2
11–15	2	2	2	2	2	2
0–10	1	1	1	1	1	1

Height (cm)	Filter 7	Filter 8	Filter 9	Filter 10	Filter 11	Filter 12
61–83	W	W	W	W	AW	AW
56–60	6	6 + P	7	7 + P	7 + P	7 + P
51–55	6	6 + P	6	6 + P	6 + P	6 + P
36–50	4	4 + P	5	5 + P	5 + P	5 + P
31–35	3	3	5	5	5	5
26–30	3	3	4	4	4	4
21–25	2	2	3	3	3	3
16–20	2	2	2	2	2	2
11–15	2	2	2	2	2	2
0–10	1	1	1	1	1	1

Notes: W = water; P = *Phragmites australis* (Cav.) Trin. ex Steud. (common reed); AW = aerated water; 1 = stones; 2 = large gravel; 3 = medium gravel; 4 = small gravel; 5 = Filtralite (light expanded clay product); 6 = sand (0.6–1.2 mm); 7 = Frogmat (barley straw).

Table 3.   Systematic regime for manually controlled filling and emptying (expressed as a percentage of drainage volume) of the experimental filters.

No.	Date	Day	Filter 1 to 11	Filter 12	No.	Date	Day	Filter 1 to 11	Filter 12
1–16	09-24/09/02	...	...	...	27	05/10/02	Sat	100	100
17	25/09/02	Wed	100	100	28	06/10/02	Sun	100	100
18	26/09/02	Thurs	100	100	29	07/10/02	Mon	100	100→50
19	27/09/02	Fri	100	100→50	30	08/10/02	Tue	100	50
20	28/09/02	Sat	100	50	31	09/10/02	Wed	100	50→100
21	29/09/02	Sun	100	50	32	10/10/02	Thurs	100	100
22	30/09/02	Mon	100	50→100	33	11/10/02	Fri	100→0	100→0
23	01/10/02	Tue	100	100	34	12/10/02	Sat	0	0
24	02/10/02	Wed	100→50	100→0	35	13/10/02	Sun	0	0
25	03/10/02	Thurs	50	0	36	14/10/02	Mon	0→100	0→100
26	04/10/02	Fri	50→100	0→100	37	15/10/02-(...)	...	...	...

Notes: The first periodic cycle for filters 1–11 is the duration from 25 September to 14 October 2002. The first periodic cycle for filter 12 is the duration from 25 September to 04 October 2002. One and two complete cycles for filters 1–11, and filter 12 are shown, respectively.

upper limit of filtration performance. A higher hydraulic load should result in greater stress on *P. australis* and biomass.

According to table 3, all filters were periodically inundated with pre-treated inflow gully pot liquor and partially drained (50%) or fully drained (100%) to encourage air penetration through the aggregates [4,71,90,99]. The theoretical hydraulic residence time (about 2 to 7 days) was variable. It follows that the hydraulic conductivity is also highly variable due to frequent wetting and drying cycles.

Since 22 September 2003, the pH value of the inflow has been artificially raised by addition of sodium hydroxide (NaOH) to the sieved gully pot liquor. It follows that the inflow pH was therefore increased from a mean pH 6.7 to pH 8.1.

The analytical methods have been described previously [71,93]. A detailed account is beyond the scope of this literature review.

2.4. Results and discussion

2.4.1. Inflow water quality.
The pH of the inflow was artificially raised to assess its influence on the treatment performance and particularly on the potential breakthrough of heavy metals during the second winter.

Raw gully pot liquor was sieved (pore size of 2.5 mm) to simulate preliminary treatment [94]. Sieving resulted in a mean annual reduction of the biochemical oxygen demand and suspended solids by approximately 12 and 22%, respectively.

The inflow data set was divided into two sub-sets (winter and summer) to assess the effect of seasonal variations (e.g. temperature) and road management (e.g. road gritting and salting) on the water quality. Most variables including biochemical oxygen demand (except for the first year of operation), suspended solids, total solids, turbidity and conductivity were relatively high in winter compared to summer as indicated in table 4 [71].

2.4.2. Comparison of annual outflow water qualities.
Concerning biochemical oxygen demand removal, the performances of all filters (except for filters 1 and 2; extended storage)

Table 4.   Key water quality variables of primary treated gully pot liquor (inflow) after contamination with hydrated copper nitrate and hydrated nickel nitrate, and corresponding removal (%) per wetland filter of outflow variables.

					Filter 7: removal (%) (winter)	Filter 7: removal (%) (summer)	Filter 8: removal (%) (winter)	Filter 8: removal (%) (summer)
Variable	Unit	No. of samples	Mean inflow (winter)	Mean inflow (summer)				
22 September 20002–21 September 2003								
BOD	mg/l	58	43.8	86.9	53	94	32	92
SS	mg/l	70	743.7	160.7	60	98	62	91
Total solids	mg/l	66	9403.9	376.5	15	25	32	N
Turbidity	NTU	71	690.6	162.1	97	99	95	96
Conductivity	µS	71	15311.6	501.0	N	N	11	N
22 September 2003–21 September 2004 (artificial increase of pH after 21 September 2003)								
BOD[a]	mg/l	73	89.7	66.6	99	95	99	91
SS	mg/l	75	1955.2	366.7	89	99	91	96
Total solids	mg/l	71	5296.4	794.7	42	72	46	50
Turbidity	NTU	78	546.2	143.6	98	99	98	98
Conductivity	µS	78	6191.7	403.6	16	N	17	N

Notes: BOD = five-day at 20°C N-Allylthiourea biochemical oxygen demand; SS = suspended solids; N = negative removal (i.e. more input than output).

improved greatly over time (table 4). The reductions in biochemical oxygen demand were also satisfactory for most filters if compared to minimum American and European standards (<20 mg/l) for the secondary treatment of effluent [71].

Furthermore, the artificial increase of pH after the first year of operation had no apparent influence on the treatment performance of the biochemical oxygen demand. There is no obvious difference in performance between filters 8 and 11, indicating that aeration did not contribute significantly to the removal of the biochemical oxygen demand. This has been confirmed by an analysis of variance.

In contrast to previous researchers who reported the worst seasonal performance for biochemical oxygen demand removal during winter [91], all filters with exception of filters 1 and 2 showed high biochemical oxygen demand removal figures (>94%) in the second winter (table 4). This suggests that soil microbes still have the capacity to decompose organic matter in winter.

Concerning other variables, reduction rates for suspended solids increased also in the second year although outflow concentrations exceeded frequently the threshold of 30 mg/l throughout the year except for summer [71]. Turbidity values of the outflow decreased greatly over time. In contrast, conductivity removal deteriorated (table 4). Despite the artificial increase of pH in the inflow, the pH of the outflow was approximately neutral and comparable to the first year of operation. Moreover, the pH of the outflow was relatively stable in the second year.

2.4.3. Heavy metal removal. Heavy metal removal efficiencies improved during the second year of operation. Figure 2 shows selected inflow and selected outflow concentrations for nickel. However, the reduction in metals was not sufficient to comply with American standards for secondary wastewater treatment. Dissolved nickel and dissolved copper concentrations should not exceed 0.0071, 0.0049 mg/l, respectively [94].

It has been known that the decomposition of aquatic plants after autumn, reducing soil conditions, road gritting and salting during periods of low temperatures and acid rain contribute to
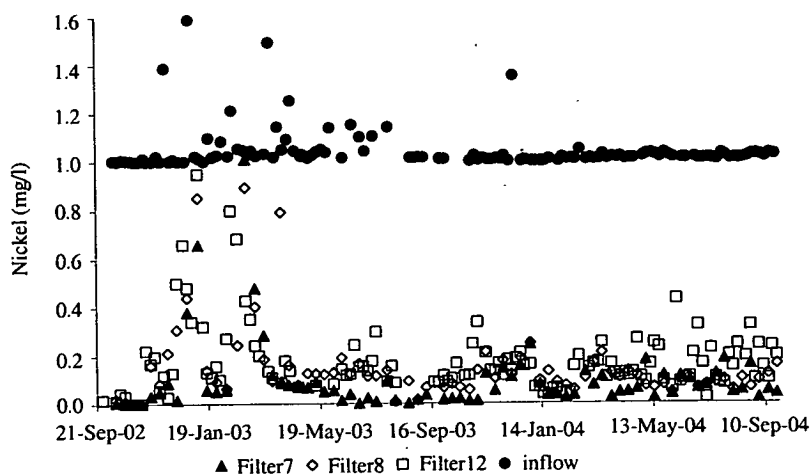
Figure 2. Daily nickel concentrations (mg/l) in the inflow and outflows of filters 7 (unplanted), 8 (planted) and 12 (planted and high loading).

increases of metal concentrations in the outflow [105,106]. For example, high levels of conductivity were recorded in the filter inflow and outflows, and the breakthrough of dissolved nickel was observed during the first winter (figure 2).

Concerning the effect of retention time on the treatment efficiency of metals, the heavy metal outflow concentrations of filter 12 (higher loading rate) were slightly higher than the corresponding concentrations for the other filters (e.g. filters 7 and 8). According to previous studies [3,95], metal removal efficiencies for wetlands are highly correlated with influent concentrations and mass loading rates. Moreover, it was suggested that the formation of metal sulphides was favoured in wetlands with long retention times. This may lead to a more sustainable management of constructed treatment wetlands.

2.4.4. Link between pH and the treatment of metals. After the increase of the inflow pH, mean reduction efficiencies for nickel increased during the second winter compared to the first winter; e.g. 90 and 65%, respectively, for filter 7. Moreover, an obvious breakthrough of nickel was not observed during the second winter despite the presence of high salt concentrations in the inflow (figure 2). This is likely due to the artificial increase of pH. A high pH facilitates nickel precipitation. For example, nickel hydroxide $(Ni(OH)_2)$ may precipitate at pH 9.1 if the corresponding metal concentration is 1 mg/l [94], which is similar to the inflow concentrations of spiked filters (see above). Moreover, dissolved copper did not break through any filters throughout the study.

All filters acted as pH buffers after pH increase, and pH levels were subsequently reduced. It can be assumed that this buffering capacity is greatly enhanced by the presence of active biomass rather than macrophytes [3,105]. However, the outflow pH values for the planted filters recorded were slightly lower than those for the unplanted filters. For example, the overall mean pH value for filter 7 (unplanted filters) is 7.31, and the corresponding value for filter 8 (planted filters) is 6.98 during the second year of operation.

2.4.5. Treatment of nutrients. Nitrogen is used by *P. australis* and micro-organisms for new biomass development. This explains the higher reduction of ammonia and nitrate for

planted in comparison to unplanted filters. Moreover, storage of nutrients in plant-derived debris is another sustainable mechanism removing nitrogen as well as phosphate [3,93].

Ammonification is slower in anaerobic than in aerobic soils because of the reduced efficiency of heterotrophic decomposition in anaerobic environments. Nitrification requires oxygen that was provided during the drawdown periods and/or during artificial aeration (filters 11 and 12). Denitrification is supported by facultative anaerobes. These organisms are capable of breaking down oxygen-containing compounds such as nitrate-nitrogen to obtain oxygen in an anoxic environment that was dominant during the long periods of filter flooding.

Some research indicates that most of the observed variation in ammonia-nitrogen removal could be attributed to fluctuations of the residence time in most wetlands [3]. In comparison, this system showed also a decreased capability to treat ammonia-nitrogen in filters with low retention times. Therefore, it might be a beneficial approach to use planted and intermittently loaded systems with long retention times to obtain high ammonia-nitrogen removal.

As similar to previous findings [3], the reduction rates of ammonia-nitrogen decreased during the winter. Such temperature-dependent processes may result in the ammonia-nitrogen removal target to become the determining design component for constructed treatment wetlands in cold climate. In contrast, ortho-phosphate-phosphorus concentrations were low in winter but high in spring and summer. However, concentrations were always relatively low (<0.35 mg/l).

2.4.6. Macrophyte influence on the performance. Ammonia-nitrogen reduction efficiencies for planted filters were higher than for comparable unplanted filters. Similar findings have been reported elsewhere [3]. It can be inferred that the higher removal rate in the planted filters could be attributed to plant uptake of ammonia-nitrogen, and increase in nitrification near the rhizomes and roots of *P. australis*.

While the ammonia-nitrogen outflow concentrations of the unplanted filters (e.g. filter 7) decreased in summer, nitrate-nitrogen concentrations increased. It can be assumed that ammonia-nitrogen removal is mostly due to the increase of the nitrification rate in summer.

The nitrate-nitrogen concentration in planted filters (e.g. filter 8) was much lower than that of unplanted filters (e.g. filter 7) in summer. The filter with higher loading rates and shorter hydraulic retention time (filter 12) experienced a breakthrough of nitrate-nitrogen during low temperature periods. It can be concluded that the transfer of ammonia to nitrate and plant uptake attributed greatly to the overall nitrogen removal during periods of high temperature.

The ortho-phosphate-phosphorus reduction efficiencies for unplanted filters were slightly higher than for comparable planted filters. However, phosphorus concentrations were relatively low indicating that most wetlands are phosphorus and not nitrogen limited.

The contribution of macrophytes to the overall treatment performance is assumed to vary to a large extent depending on the wetland design and operation practices. Previous work indicates that macrophytes are likely to affect considerably the removal of pollutants in horizontal sub-surface constructed treatment wetland, while their role is minor in pollutant removal for periodically loaded vertical-flow wetlands [107]. Nevertheless, the secondary role of macrophytes concerning oxygen transport, clogging prevention and provision of an energy source for micro-organism can influence positively the treatment performance of wetlands [4].

3. Conclusion and recommendations

The critical review sections highlighted the importance of hydrological and biochemical processes in natural and constructed wetlands. The latter are either dominated by *Typha*

latifolia in the USA or *Phragmites australis* in Europe. Most research work has been performed in the USA and northern countries of West Europe. There is a gap of knowledge and understanding relating to natural and constructed wetlands in the tropics and arid areas of South America, Africa and Asia.

The importance of biochemical oxygen demand, suspended solids, nitrogen and phosphorus as performance indicator variables for engineering applications was stressed. The main quantitative and qualitative relationships between these variables have been summarized. This includes mass balance equations and nutrient transformation processes. Moreover, a high variability of particularly the heavy metal removal efficiencies in constructed wetlands has been reported.

The review was subsequently evaluated with the help of a case study in the area of urban water. Despite the highly variable water quality of road runoff, the wetland filters showed great treatment performances particularly with respect to the biochemical oxygen demand reduction in a cold climate. Removal efficiencies for suspended solids and nitrogen improved considerably over time and dissolved copper ·was removed satisfactorily in comparison to values obtained from the literature.

A breakthrough of dissolved nickel during the first winter of the first year of operation was observed. After creating an artificially high inflow pH of approximately eight after one year of operation, nickel was successfully treated despite vulnerability to leaching when exposed to a high salt concentration during the second winter.

A high pH was apparently also linked to high suspended solids and ammonia-nitrogen removal efficiencies. The elevated pH had no apparent negative effect on the biomass including macrophytes. Moreover, filters showed a great pH buffering capacity. Findings indicate that conventional pH adjustment can be successfully applied to constructed wetland systems for storm water treatment.

The presence of Filtralite (adsorption filter media) and *P. australis* did not result in an obvious reduction of metal concentrations in outflow waters. Operational conditions such as inflow pH and retention time were more important for the heavy metal treatment.

This literature review has shown the great popularity of natural and constructed wetland research. The general governing processes within natural wetlands have been covered adequately by the scientific literature. However, information on detailed processes within constructed wetlands contributing to the treatment performance of specific wastewater streams is lacking.

For example, the literature review has shown that a diverse micro-organism community dominated by bacteria, fungi, algae and protozoa is present in the aerobic and anaerobic zones of wetlands. The diverse microbial ecology and plant community structure within complex wetland ecosystems has not yet been fully reported. The author recommends further research into the dynamics of wetland microbial ecology in order to perform sound temporal and spatial modelling of microbial pollution and treatment performance indicators.

References

[1] Mitsch, W.J. and Gosselink, J.G., 2000, *Wetlands*, 3rd edn (New York: John Wiley & Sons).
[2] Hammer, D.A., 1989, *Constructed Wetlands for Wastewater Treatment – Municipal, Industrial and Agricultural* (Chelsea, MI: Lewis Publishers).
[3] Kadlec, R.H. and Knight, R.L., 1996, *Treatment Wetlands* (Boca Raton, FL: CRC Press).
[4] Cooper, P.F., Job, G.D., Green, M.B. and Shutes, R.B.E., 1996, *Reed Beds and Constructed Wetlands for Wastewater Treatment* (Swindon, UK: WRc). .
[5] Bannister, A.F., 1997, Lagoon and reed-bed treatment of colliery shale tip water at Dodworth, South Yorkshire. In: P.L. Younger (Ed.) *Mine Water Treatment Using Wetlands*. Proceedings of the CIWEM National Conference (CIWEM, Newcastle, UK), pp. 105–131.
[6] Mulamoottil G., McBean E. A. and Rovers, F. (Eds), 1999, *Constructed Wetlands for the Treatment of Landfill Leachates* (Boca Raton, FL: Lewis Publishers).
[7] Scholz, M. and Xu, J., 2001, Comparison of vertical-flow constructed wetland treatment of wastewater containing lead and copper. *J. Ch. Inst. Wat. & Envir. Mangt.*, **15**(4), 287–293.
[8] Rivera, F., Warren, A., Ramirez, E., Decamp, O., Bonilla, P., Gallegos, Alderón, A. and Sánchez, J.T., 1995, Removal of pathogens from wastewater by the root zone method (RZM). *Wat. Sci. Tech.*, **32**(3), 211–218.
[9] Decamp, O. and Warren, A., 1998, Bacterivory in ciliates isolated from constructed wetlands (reed beds) used for wastewater treatment. *Wat. Res. Tech.*, **32**(7), 1989–1996.
[10] Decamp, O., Warren, A. and Sanchez, R, 1999, The role of ciliated protozoa in subsurface flow wetlands and their potential as bioindicators. *Wat. Sci. Tech.*, **40**(3), 91–98.
[11] Green, M.B., Martin, J.R. and Griffin, P., 1999, Treatment of combined sewer overflow at small wastewater treatment works by constructed reed beds. *Wat. Sci. Tech.*, **40**(3), 357–364.
[12] Sun, G., Gray, K.R., Biddlestone, A.R. and Cooper, D.J., 1999, Treatment of agricultural wastewater in a combined tidal flow-downflow reed bed system. *Wat. Sci. Tech.*, **40**(3), 139–146.
[13] Mungur, S., Shutes, R.B.E., Revitt, D.M. and House, M.A., 1995, An assessment of metal removal from highway runoff by a natural wetland. *Wat. Sci. Tech.*, **32**(3), 169–175.
[14] Mungur, S., Shutes, R.B.E., Revitt, D.M. and House, M.A., 1997, An assessment of metal removal by laboratory scale wetland. Wat. Sci. Tech., **35**(5), 125–133.
[15] McNeill, A. and Olley, S., 1998, The effects of motorway runoff on watercourses in south-west Scotland. *J. Ch. Inst. Wat. & Envir. Mangt.*, **12**(6) 433–439.
[16] Scholes, L.N.L., Shutes, R.B.E., Revitt, D.M., Purchase, D. and Forshaw, M., 1999, The removal of urban pollutants by constructed wetlands during wet weather. *Wat. Sci. Tech.*, **40**(3), 333–340.
[17] Hawke, C.J. and José, P.V., 1996, *Reed bed Management for Commercial and Wildlife Interests* (Sandy, UK:. RSPB).
[18] Brix, H., 1999, Functions of macrophytes in constructed wetlands. *Wat. Sci. Tech.*, **29**(4), 71–78.
[19] Convention on Wetlands of International Importance Especially as Waterfowl Habitat, 1997, Ramsar, Iran.
[20] Smith, R.L., 1980, *Ecology and Field Biology*, 3rd edn (New York: Harper and Row).
[21] United States Army Corps of Engineers, 2000, *Wetlands Engineering Handbook – ERDC/EL TR-WRP-RE-21* (Washington, DC: United States Army Engineer Research and Development Center Cataloging-in-Publication Data).
[22] Junk, W.J., Bayley, P.B. and Sparks, R.E., 1989, The flood pulse concept in river-floodplain systems. In: D.P. Dodge (Ed.) *Proceedings of the International Large River Symposium, J. Can. Fish. Aqu. Sci.*, **106**(special issue), 11–127.
[23] Fredrickson, L.H. and Reid, F.A., 1990, Impacts of hydrologic alteration on management of freshwater wetlands. In: J.M. Sweeney (Ed.) *Management of Dynamic Ecosystems* (West Lafayette, IN: North Central Section, Wildlife Society), pp. 71–90.
[24] Dunne, T. and Leopold, L.B., 1978, *Water in Environmental Planning* (New York: W. H. Freeman and Company).
[25] Heimburg, K., 1984, Hydrology of north-central Florida cypress domes. In: K.C. Ewel and H.T. Odum (Eds) *Cypress Swamps* (Gainesville, FL: University Presses of Florida), pp. 72–82.
[26] Moss, B., *Ecology of Fresh Waters*, 3rd edn (Oxford, UK: Blackwell).
[27] Boon, P.I. and Mitchell, A., 1995, Methanogenesis in the sediments of an Australian freshwater wetland: comparison with aerobic decay and factors controlling methanogenesis. *FEMS Microbiol. Ecol.*, **18**(3), 174–190.
[28] Bachand, P.A.M. and Horne, A.J., 1999, Denitrification in constructed free-water surface wetlands: I. Very high nitrate removal rates in a macrocosm study. *Ecol. Eng.*, **14**(1–2), 9–15.
[29] Spieles, D.J. and Mitsch, W.J., 2000, The effects of season and hydrologic and chemical loading on nitrate retention in constructed wetlands: a comparison of low- and high-nutrient riverine systems. *Ecol. Eng.*, **14**(1–2), 77–91.
[30] Lund, L.J., Horne, A.J. and Williams, A.E., 2000, Estimating denitrification in a large constructed wetland using stable nitrogen isotope ratios. *Ecol. Eng.*, **14**(1–2), 67–76.

[31] Etherington, J.R., 1983, *Wetland Ecology* (London, UK: Edward Arnold).

[32] Donkor, V.A. and Häder, D.-P., 1996, Effects of ultraviolet radiation on photosynthetic pigments in some filamentous cyanobacteria. *Aquat. Microb. Ecol.*, 11(2), 143–149.

[33] Overbeck, J., 1988, Qualitative and quantitative assessment of the problem. In: S.E. Jørgensen and R.A. Vollenweider (Eds) *Guidelines for Lake Management: Principles of Lake Management, Vol. 1* (Geneva: International Lake Environment Committee, United Nations Environment Programme), pp. 19–36.

[34] Reddy, K.R., Kadlec, R.H., Flaig, E. and Gale, P.M., 1999, Phosphorus retention in streams and wetlands: a review. *Crit. Rev. Env. Sci. Tech.*, 29(1), 83–146.

[35] Gambrell, R.P. and Patrick Jr., W.H., 1978, Chemical and microbiological properties of anaerobic soils and sediments. In: D.D. Hook and R.M.M. Crawford (Eds) *Plant Life in Anaerobic Environments* (Ann Arbor, MI: Ann Arbor Science), pp. 375–423.

[36] Faulkner, S.P. and Richardson, C.J., 1989, Physical and chemical characteristics of freshwater wetland soils. In: D.A. Hammer (Ed.) *Constructed Wetlands for Wastewater Treatment* (Chelsea, MI: Lewis Publishers), pp. 41–72.

[37] Stumm, W. and Morgan, J.J., 1996, *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd edn (New York, NY: John Wiley and Sons).

[38] Nairn, R.W. and Mitsch, W.J., 2000, Phosphorus removal in created wetland ponds receiving river overflow. *Ecol. Eng.*, 14(1–2), 107–126.

[39] Fennessy, M.S., Brueske, C.C. and Mitsch, W.J., 1994, Sediment deposition patterns in restored freshwater wetlands using sediment traps. *Ecol. Eng.*, 3(4), 409–428.

[40] Holdren, G.C. and Armstrong, D.E., 1980, Factors affecting phosphorus release from intact lake sediment cores. *Env. Sci. Tech.*, 14(1), 79–87.

[41] Mayer, T. and Kramer, J.R., 1986, Effect of lake acidification on the adsorption of phosphorus by sediments. *Wat. Air Soil Pol.*, 31(3–4), 949–958.

[42] Moore, P.A. and Reddy, K.R., 1994, Role of E_h and pH on phosphorus geochemistry in sediments of Lake Okeechobee, Florida. *J. Environ. Qual.*, 23(5), 955–964.

[43] Kamp-Nielson, L., 1974, Mud-water exchange of phosphate and other ions in undisturbed sediment cores and factors affecting exchange rates. *Arch. Hydrobiol.*, 73(2), 218–237.

[44] Gächter, R., Meyer, J.S. and Mares, A., 1998, Contribution of bacteria to release and fixation of phosphorus in lake sediments. *Limnol. Oceanogr.*, 33(6), part 2, 1542–1558.

[45] Gächter, R. and Meyer, J.S., 1993, The role of micro-organisms in mobilization and fixation of phosphorus in sediments. *Hydrobiol.*, 253(6), 103–121.

[46] Ann, Y., Reddy, K.R. and Delfino, J.J., 1999, Influence of chemical amendments on phosphorus immobilization in soils from a constructed wetland. *Ecol. Eng.*, 14(1–2), 157–167.

[47] Ann, Y., Reddy, K.R. and Delfino, J.J., 1999, Influence of redox potential on phosphorus solubility in chemically amended wetland organic soils. *Ecol. Eng.*, 14(1–2), 169–180.

[48] Carignan, R. and Kaill, J., 1980, Phosphorus sources for aquatic weeds: water or sediments? *Sci.*, 207(4434), 987–989.

[49] Smith, C.S. and Adams, M.S., 1986, Phosphorus transfer from sediments to *Myriophyllum spicatum*. *Limnol. Oceanogr.*, 31(6), 1312–1321.

[50] Wang, N. and Mitsch, W.J., 2000, A detailed ecosystem model of phosphorus dynamics in created riparian wetlands. *Ecol. Model.*, 126(2–3), 101–130.

[51] Schlesinger, W.H., 1991, *Biogeochemistry: An Analysis of Global Change* (San Diego, CA: Academic Press).

[52] Morgan, M.D. and Mandernack, K.W., 1996, Biogeochemistry of sulfur in wetland peat following 3.5 Y of artificial acidification (HUMEX). *Environ. Intern.*, 22(5), 605–610.

[53] Rudd, J.W.M., Kelly, C.A., St. Louis, V., Hesslein, R.H., Furutani, A. and Holoka, M.H., 1986, The role of sulfate reduction in long term accumulation of organic and inorganic sulfur in lake sediments. *Limnol. Oceanogr.*, 31(6), 1281–1291.

[54] Spratt, H.G. and Morgan, M.D., 1990, Sulfur cycling in a cedar dominated, freshwater wetland. *Limnol. Oceanogr.*, 35(7), 1586–1593.

[55] Mandernack, K.W., Lynch, L., Krouse, H.R. and Morgan, M.D., 2000, Sulfur cycling in wetland peat of the New Jersey Pinelands and its effect on stream water chemistry. *Geochimica et Cosmochimica Acta*, 22(5), 3949–3964.

[56] Tanner, C.C., 1996, Plants for constructed wetland treatment systems – a comparison of the growth and nutrient uptake of eight emergent species. *Ecol. Eng.*, 7(1) 59–83.

[57] Parr, T.W., 1990, Factors affecting reed (*Phragmites australis*) growth in UK reed bed treatment systems. In: P.F. Cooper and B.C. Findlater (Eds) *Constructed Wetlands in Water Pollution Control* (Oxford, UK: Pergamon Press), pp. 67–76.

[58] Kuehn, E. and Moore, J.A., 1995, Variability of treatment performance in constructed wetlands. *Wat. Sci. Tech.*, 32(3), 241–250.

[59] Turner, M.K., 1995, Engineered reed-bed systems for wastewater treatment. *Trends in Biotech.*, 13(7), 248–252.

[60] Perkins, J. and Hunter, C., 2000, Removal of enteric bacteria in a surface flow constructed wetland in York-shire, England. *Wat. Res.*, **34**(6), 1941–1947.

[61] Kvet, J. and Husak, S., 1978, Primary data on biomass and production estimates in typical stands of fishpond littoral plant communities. In: D. Dykyjová and J. Kvet (Eds) *Pond Littoral Ecosystems* (Berlin, Germany: Springer Verlag), pp. 211–216.

[62] McNaughton, S.J., 1966, Ecotype function in the *Typha* community-type. *Ecol. Monogr.*, **36**(4), 297–325.

[63] van der Valk, A.G. and Davis, C.B., 1978, Primary production of prairie glacial marshes. In: R.E. Good, D.F. Whigham and R.L. Simpson (Eds) *Freshwater Wetlands: Ecological Processes and Management Potential* (New York, NY: Academic Press), pp. 21–37.

[64] Gessner, M.O., 2000, Breakdown and nutrient dynamics of submerged *Phragmites* shoots in the littoral zone of a temperate hardwater lake. *Aquat. Bot.*, **66**(1), 9–20.

[65] Wrubleski, D.A., Murkin, H.R., van der Valk, A.G. and Nelson, J.W., 1997, Decomposition of emergent macrophyte roots and rhizomes in a northern prairie marsh. *Aquat. Bot.*, **58**(2), 121–134.

[66] Kuehn, K.A., Gessner, M.O., Wetzel, R.G. and Suberkropp, K., 1999, Standing litter decomposition of the emergent macrophyte *Erianthus giganteus*. *Microb. Ecol.*, **38**(1), 50–57.

[67] Brix, H., 1989, Gas exchange through dead culms of reed, *Phragmites australis* (Cav.) Trin. ex Steud. *Aquat. Bot.*, **35**(1), 81–98.

[68] Preston, C.D. and Croft, J.M., 1997, *Aquatic Plants in Britain and Ireland,* (Colchester: Harley Books).

[69] Boar, R.R., Crook, C.E. and Moss, B., 1989, Regression of *Phragmites australis* reedswamps and recent changes of water chemistry in the Norfolk Broadland, England. *Aquat. Bot.*, **35**(1), 41–55.

[70] Ostendorp, W., 1989, 'Die-back' of reeds in Europe – a critical review of literature. *Aquat. Bot.*, **35**(1), 5–26.

[71] Scholz, M., 2004, Treatment of gully pot effluent containing nickel and copper with constructed wetlands in a cold climate. *J. Chem. Tech. Biotech.*, **79**(2), 153–162.

[72] American Public Health Association, 1995, *Standard Methods for the Examination of Water and Wastewater,* 20th edn (Washington, DC: American Public Health Association, American Water Works Association and Water Environmental Federation).

[73] Kiely, G., 1997, *Environmental Engineering* (Maidenhead: McGraw-Hill International (UK) Limited).

[74] Scholz, M. and Trepel, M., 2004, Water quality characteristics of vegetated groundwater-fed ditches in a riparian peatland. *Sci. Total Environ.*, **332**(1–3), 109–122.

[75] Gregory, S.V., Swanson, F.J., McKee, W.A. and Cummins, K.W., 1991, An ecosystem perspective of riparian zones. *Biosci.*, **41**(8) 540–551.

[76] Mander, U., Kuusemets, V. and Ivask, M., 1995, Nutrient dynamics of riparian ecotones: a case study from the Porijõgi River catchment, Estonia. *Landsc. Urb. Plan.*, **31**(1–3), 333–348.

[77] Lowrance, R., Altier, L.S., Newbold, J.D., Schnabel, R.R., Groffman, P.M., Denver, J.M., Correll, D.L., Gilliam, J.W., Robinson, J.L., Brinsfield, R.B., Staver, K.W., Lucas, W. and Todd, A.H., 1979, Water quality functions of riparian forest buffers in Chesapeake Bay watersheds. *Env. Managem.*, **21**(5), 687–712.

[78] Groffman, P.M., Gold, A.J. and Addy, K., 2000, Nitrous oxide production in riparian zones and its importance to national emission inventories. *Chemosph.: Glob. Change Sci.*, **2**(3–4), 291–299.

[79] Kadlec, R.H., 1999, Chemical, physical and biological cycles in treatment wetlands. *Wat. Sci. Tech.*, **40**(2), 37–44.

[80] Pinney, M.L., Westerhoff, P.K. and Baker, L., 2000, Transformations in dissolved organic carbon through constructed wetlands. *Wat. Res.*, **34**(6), 1897–1911.

[81] Ahn, C., Mitsch, W.J. and Wolfe, W.E., 2001, Effects of recycled FGD liner material on water quality and macrophytes of constructed wetlands: a mesocosm experiment. *Wat. Res.*, **35**(3), 633–642.

[82] Scholz, M., 2003, Case study: design, operation, maintenance and water quality management of sustainable storm water ponds for roof runoff. *Bioresource Technol.*, **95**(3), 269–279.

[83] Scholz, M., Morgan, R. and Picher, A., 2005, Stormwater resources development and management in Glasgow: two case studies. *Intern. J. Environ. Studies*, **62**(3), 263–282.

[84] Mungur, A.S., Shutes, R.B.E., Revitt, D.M. and House, M.A., 1997, An assessment of metal removal by laboratory scale wetland. *Wat. Sci. Tech.*, **35**(5), 125–133.

[85] Mays, P.A. and Edwards, G.S., 2001, Comparison of heavy metal accumulation in a natural wetland and constructed wetlands receiving acid mine drainage. *Ecol. Eng.*, **16**(4), 487–500.

[86] Scholz, M. and Martin, R.J., 1998, Control of bio-regenerated granular activated carbon by spreadsheet modelling. *J. Chem. Tech. Biotechnol.*, **71**(3), 253–261.

[87] Scholz, M., 2004, Stormwater quality associated with a silt trap (empty and full) discharging into an urban watercourse in Scotland. *Intern. J. Environ. Studies*, **61**(4), 471–483.

[88] Kadlec, R., Knight, R.L., Vymazal, J, Brix, H., Cooper, P.F. and Haberl, R., 2000, *Constructed Wetlands for Pollution Control.* International Water Association (IWA) Specialist Group 'Use of Macrophytes for Water Pollution Control', Scientific and Technical Report Number 8 (London, UK: IWA Publishing).

[89] Green, M., Friedler, E. and Safrai, I., 1998, Enhancing nitrification in vertical-flow constructed wetlands utilizing a passive air pump. *Wat. Res.*, **32**(12), 3513–3520.

[90] Gervin, L. and Brix, H., 2001, Reduction of nutrients from combined sewer overflows and lake water in a vertical-flow constructed wetland system. *Wat. Sci. Tech.*, **44**(11–12), 171–176.

[91] Karathanasis, A.D., Potter, C.L. and Coyne, M.S., 2003, Vegetation effects on fecal bacteria, biochemical oxygen demand and suspended solids removal in constructed wetland treating domestic wastewater. *Ecol. Eng.*, **20**(2), 157–169.

[92] Luederits, V., Eckert, E., Lange-Weber, M. and Lange, A., 2001, Nutrient removal efficiency and resource economics of vertical flow and horizontal flow constructed wetlands. *Ecol. Eng.*, **18**(2), 157–171.

[93] Scholz, M., Höhn, P. and Minall, R., 2002, Mature experimental constructed wetlands treating urban water receiving high metal loads. *Biotechnol. Prog.*, **18**(6), 1257–1264.

[94] Tchobanoglous, G., Burton, F.L. and Stensel, H.D., 2003, *Wastewater Engineering: Treatment and Reuse*, 4th edn, rev. (New York, NY: Metcalf & Eddy Inc., McGraw Hill Companies Inc).

[95] Wood, T.S. and Shelley, M.L., 1999, A dynamic model of bioavailability of metals in constructed wetland sediments. *Ecol. Eng.*, **12**(3–4), 231–252.

[96] Cheng, S.P., Grosse, W., Karrenbrock, F. and Thoennessen, M., 2002, Efficiency of constructed wetlands in decontamination of water polluted by heavy metals. *Ecol. Eng.*, **18**(3), 317–325.

[97] Kadlec, R.H., 2002, *Effects of Pollutant Speciation in Treatment Wetlands Design* (Chelsea, MI: Wetland Management Services).

[98] Obarska-Pempkowiak, H. and Klimkowska, K., 1999, Distribution of nutrients and heavy metals in a constructed wetland system. *Chemoshere*, **39**(2), 303–312.

[99] Scholz, M. and Xu, J., 2002, Performance comparison of experimental constructed wetlands with different filter media and macrophytes treating industrial wastewater contaminated with lead and copper. *Bioresource Technol.*, **83**(2), 71–79.

[100] Vymazal, J. and Krasa, P., 2003, Distribution of Mn, Al, Cu and Zn in a constructed wetland receiving municipal sewage. *Wat. Sci. Tech.*, **48**(5), 299–305.

[101] Backstrom, M., Karlsson, S., Backman, L., Folkeson, L. and Lind, B., 2004, Mobilisation of heavy metal by deicing salts in a roadside environment. *Water Res.*, **38**(3), 720–732.

[102] Knight, R.L., Kadlec, R.H. and Ohlendorf, H.M., 1999, The use of treatment wetland for petroleum industry effluents. *Environ. Sci. Technol.*, **33**(7), 973–980.

[103] Brix, H., Arias, C.A. and del Bubba, M., 2001, Media selection for sustainable phosphorus reduction in subsurface flow constructed wetlands. *Wat. Sci. Tech.*, **44**(11–12), 47–54.

[104] Sansalone, J.J., 1999, Adsorptive infiltration of metals in urban drainage: media characteristics. *Sci. Total Environ*, **235**(1–3), 179–188.

[105] Sasaki, K., Ogino, T., Endo, Y. and Kurosawa, K., 2003, Field studies on heavy metal accumulation in a natural wetland receiving acid mine drainage. *Mater. Trans.*, **44**(9), 1877–1884.

[106] Norrstrom, A.C. and Jacks, G., 1998, Concentration and fractionation of heavy metals in roadside soils receiving de-icing salts. *Sci. Total Environ.*, **218**(2–3), 161–174.

[107] Brix, H., 1997, Do macrophytes play a role in constructed treatment wetlands? *Wat. Sci. Tech.*, **35**(5), 11–17.

Constructed Wetlands: Treatment of Concentrated Storm Water Runoff (Part A)

Byoung-Hwa Lee, Miklas Scholz,* and Antje Horn

Institute for Infrastructure and Environment
School of Engineering and Electronics
The University of Edinburgh
Edinburgh EH9 3JL, Scotland
United Kingdom

ABSTRACT

The aim of this research was to assess the treatment efficiencies for gully pot liquor of experimental vertical-flow constructed wetland filters containing *Phragmites australis* (Cav.) Trin. ex Steud. (common reed) and filter media of different adsorption capacities. Six out of 12 filters received inflow water spiked with metals. For 2 years, hydrated nickel and copper nitrate were added to sieved gully pot liquor to simulate contaminated primary treated storm runoff. For those six constructed wetland filters receiving heavy metals, an obvious breakthrough of dissolved nickel was recorded after road salting during the first winter. However, a breakthrough of nickel was not observed, since the inflow pH was raised to eight after the first year of operation. High pH facilitated the formation of particulate metal compounds such as nickel hydroxide. During the second year, reduction efficiencies of heavy metal, 5-days at 20°C N-Allylthiourea biochemical oxygen demand (BOD) and suspended solids (SS) improved considerably. Concentrations of BOD were frequently <20 mg/L. However, concentrations for SS were frequently >30 mg/L. These are the two international thresholds for secondary wastewater treatment. The BOD removal increased over time due to biomass maturation, and the increase of pH. An analysis of the findings with case-based reasoning can be found in the corresponding follow-up paper (Part B).

Key words: storm runoff; gullies; constructed wetlands, biochemical oxygen demand; suspended solids; conductivity

INTRODUCTION

CONSTRUCTED WETLANDS in the United States and Europe are usually soil or gravel based horizontal-flow systems planted with *Typha latifolia* L. (cattail) and/or *Phagmites australis* (Cav.) Trin. ex Steud. (common reed). They are used to treat storm runoff, domestic and industrial wastewater (Cooper *et al.*, 1996; Kadlec and Knight, 1996; Scholz, 2003), and have also been applied for passive treatment of mine wastewater drainage (Mungur *et al.*, 1997; Mays and Edwards, 2001).

---

*Corresponding author: School of Engineering & Electronics, College of Science & Engineering, The University of Edinburgh, Faraday Building, The King's Bu, Edinburgh, EH9 3JL, Scotland. *Phone*: 44(0) 131 650 6780; *Fax*: 44 (0) 131 650 6554; *E-mail*: m.scholz@ed.ac.uk

Storm runoff from urban areas has been recognized as a major contributor to pollution of the receiving urban watercourses (Park and Yoon, 2003). The principal pollutants in urban runoff are 5-day at 20°C N-Allylthiourea [biochemical oxygen demand (BOD)], suspended solids (SS), heavy metals, deicing salts, hydrocarbons, and fecal coliforms (Scholz and Martin, 1998; Scholz and Zettel, 2004).

Although various conventional methods have been applied to treat storm water (Cooper *et al.*, 1996; Park and Yoon, 2003), most technologies are not cost-effective or too complex. Constructed wetlands integrated into a best management practice concept are a sustainable means of treating storm water and proved to be more economical (e.g., construction and maintenance) and energy efficient than traditional centralized treatment systems (Kadlec *et al.*, 2000). Furthermore, wetlands enhance biodiversity and are less susceptibile to variations of loading rates (Cooper *et al.*, 1996; Scholz and Trepel, 2004).

Contrary to standard domestic wastewater treatment technologies, storm water (gully pot liquor and effluent) treatment systems have to be robust to highly variable flow rates and water quality variations. The storm water quality depends on the load of pollutants present on the road, and the corresponding dilution by each storm event (Park and Yoon, 2003; Scholz, 2003).

In contrast to standard horizontal-flow constructed treatment wetlands, vertical-flow wetlands are flat, intermittently flooded, and drained, allowing air to refill the soil pores within the bed (Cooper *et al.*, 1996; Green *et al.*, 1998; Gervin and Brix, 2001). When the wetland is dry, oxygen (as part of the air) can enter the top layer of debris and sand. The following flow of wastewater will absorb the gas and transport it to the anaerobic bottom of the wetland. Furthermore, aquatic plants such as macrophytes transport oxygen to the rhizosphere. However, this natural process of oxygen enrichment is not as effective as the previous engineering method (Kadlec and Knight, 1996; Karathanasis *et al.*, 2003).

While it has been recognized that vertical-flow constructed wetlands usually have higher removal efficiencies with respect to organic pollutants and nutrients in comparison to horizontal-flow wetlands, denitrification is usually less efficient in vertical-flow systems (Luederits *et al.*, 2001).

Heavy metal removal

Heavy metals within storm water are associated with fuel additives, car body corrosion, and tire and brake wear. Common metal pollutants from cars include copper, nickel, lead, zinc, chromium, and cadmium. Freshwater quality standards are most likely to be exceeded by copper (Cooper *et al.*, 1996; Kadlec and Knight, 1996; Scholz *et al.*, 2002; Tchobanoglous *et al.*, 2003).

Metals occur in soluble, colloidal, or particulate forms. Heavy metals are most bioavailable when they are soluble, either in ionic or weakly complexed form (Cooper *et al.*, 1996; Wood and Shelley, 1999; Cheng *et al.*, 2002).

There have been many studies on the specific filter media within constructed wetlands to treat heavy metals economically, such as limestone, lignite, activated carbon, peat, and leaves (Scholz and Martin, 1998; Scholz *et al.*, 2002). Metal bioavailability and reduction are controlled by chemical processes including acid volatile sulfide formation and organic carbon binding and sorption in reduced sediments of constructed wetlands (Obarska-Pemkowiak and Klimkowska, 1999; Wood and Shelley, 1999; Kadlec, 2002). It follows that metals usually accumulate in the top layer (fine aggregates, sediment, and litter) of vertical-flow and near the inlet of horizontal-flow constructed treatment wetlands (Cheng *et al.*, 2002; Scholz and Xu, 2002; Vymazal and Krasa, 2003).

Physical and chemical properties of the wetland soil and aggregates affecting metal mobilization include particle size distribution (texture), redox potential, pH, organic matter, salinity, and the presence of inorganic matter such as sulfides and carbonates (Backstrom *et al.*, 2004).

The cation exchange capacity of maturing wetland soils and sediments tend to increase as texture becomes finer because more negatively charged binding sites are available. Organic matter has a relatively high proportion of negatively charged binding sites. Salinity and pH can influence the effectiveness of the cation exchange capacity of soils and sediments because the negatively charged binding sites will be occupied by a high number of sodium or hydrogen cations (Knight *et al.*, 1999).

Sulfides and carbonates may combine with metals to form relatively insoluble compounds. Especially the formation of metal sulfide compounds may provide long-term heavy metal removal, because these sulfides will remain permanently in the wetland sediments as long as they are not reoxidized (Cooper *et al.*, 1996; Kadlec and Knight, 1996).

Project purpose

The major purpose of this study is to improve the design, operation, and management of vertical-flow constructed treatment wetlands to secure a high wastewater treatment performance during all seasons. The objectives are to assess

1. the performance of vertical-flow constructed treatment wetland filters, combined with a treatment pond (above the litter zone) for gully pot liquor treatment;

Figure 1. Constructed treatment wetland rig (The King's Buildings campus; The University of Edinburgh) in May 2004.

2. the compliance with water quality standards in terms of the reduction efficiencies of BOD, SS, nickel, copper, and nitrate;
3. the impact of environmental conditions, such as variations of salt concentrations, pH, and the temperature on the treatment performance of constructed wetlands during all seasons;
4. the feasibility of conventional chemical pH adjustment to prevent heavy metal leaching during winter; and
5. the overall role of adsorption media and *P. australis*.

EXPERIMENTAL PROTOCOLS

Study site

Twelve wetland filters (Fig. 1) were located outdoors at The King's Buildings campus (The University of Edinburgh, Scotland) to assess the system performance in a cold climate (09/09/02 to 21/09/04). The 12 first days of operation were not analyzed because the water quality was not representative. Inflow water, polluted by road runoff, was collected from randomly selected gully pots on the campus, the nearby predominantly housing estates

and two major roads. After mixing both the sediment and the water phase within the gully pot, water was collected by manual abstraction with a 2-L beaker.

Filter design, media composition, and limitations

Round drainage pipes were used to construct the aboveground filters. All 12 vertical-flow wetland filters (Fig. 1) were designed with the following dimensions: height = 83 cm and diameter = 10 cm. The relatively small size of these wetlands makes them vulnerable to environmental changes. However, a literature search has revealed that the use of small wetlands for experimental purposes is common to simulate industrial-scale systems, and that data variation is similar between small and large systems (Karathanasis *et al.*, 2003; Scholz et al., 2002; Wießner *et al.*, 2004; Zhao *et al.*, 2004).

Aboveground filters experience higher temperatures and associated data variations than below-ground filters in summer. It follows that performance data might be "overly optimistic" for this season. However, aboveground filters are exposed to severe conditions such as relatively low temperatures in winter in comparison to below-ground systems that are insulated by the (frozen) soil, debris, litter, and potentially snow (Picard *et al.*, 2004; Scholz and Xu, 2002). Moreover, the macrophytes and most of the microbial biomass are usually inactive during winter. Therefore, freezing and thawing events have little impact on the filtration performance (Cooper *et al.*, 1996; Kadlec and Knight, 1996).

Different packing order arrangements of filter media and plant roots were used in the wetland filters (Tables

Table 1. Systematic and stratified experimental setup of filter content and operation.

Filter	Planted	Media[a]	Metals[b]	Aerated	Highloading[c]
1	No	1	No	No	No
2	No	1	Yes	No	No
3	No	2	No	No	No
4	Yes	2	No	No	No
5	No	3	No	No	No
6	Yes	3	No	No	No
7	No	2	Yes	No	No
8	Yes	2	Yes	No	No
9	No	3	Yes	No	No
10	Yes	3	Yes	No	No
11	Yes	3	Yes	Yes	No
12	Yes	3	Yes	Yes	Yes

[a]1 = no media, 2 = standard, 3 = addition of Filtralite (light expanded clay) and Frogmat (barley straw), see also Table 2; [b]addition of hydrated copper and nickel nitrate; [c]Filter 12 received approximately 153% additional inflow in comparison to Filter 11 (Table 3), for example.

F1

T1
T2

1 and 2). The outlet of each constructed wetland comprised a valve at the bottom of each filter. In September 2002, the calculated empty filter bed volumes were approximately 6.2, 6.4, 4.0, 4.1, 3.8, 4.1, 3.8, 4.0, 3.8, 4.0, 4.0, and 4.0 L for Filters 1 to 12, respectively. The filter volume capacities were measured by draining the filters entirely.

The inflow waters of Filter 2 and Filters 7 to 12 were dosed with hydrated copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) and hydrated nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$). Filters 1 and 2 (controls) are similar to wastewater stabilization ponds or gully pots (extended storage) without a significant amount of filter media (Table 2). In comparison, Filters 3, 5, 7, and 9 are similar to gravel and slow sand filters, and Filters 4, 6, 8, and 10 are typical reed bed filters. The reed bed filters contain gravel and sand substrate and native *Phragmites australis* (Cav.) Trin. ex Steud. (common reed), all of similar total biomass weight during planting and from the same local source. However, Filters 5, 6, 9, and 10 also contain adsorption media. Additional natural adsorption media (Filtralite and Frogmat) were used. Filtralite [containing 3% of calcium oxide (CaO)] with diameters between 1.5 and 2.5 mm is associated with enhanced metal and nutrient reduction (Brix *et al.*, 2001; Scholz and Xu, 2002). Furthermore, Frogmat (natural product based on raw barley straw) has a high adsorption area, and is therefore likely to be associated with a high heavy metal reduction potential. The use of other filter media with high adsorption capacities such as activated carbon (Scholz and Martin, 1998; Scholz *et al.*, 2002) and oxide-coated sand (Sansalone, 1999) has been discussed elsewhere.

Filters 11 and 12 are more complex in their design and operation (Table 1). The top water layer of both filters is aerated (with air supplied by air pumps) to enhance oxidation (minimizing zones of reducing conditions) and nitrification (Green *et al.*, 1998; Obarska-Pempkowiak and Klimkowska, 1999; Cheng *et al.*, 2002). Filter 12 receives about 153% of Filter 11's mean annual inflow volume and load (Table 1). The hydraulic regime of Filter 12 differs from that of Filters 1 to 11 to identify the best filtration performance. A higher hydraulic load should result in greater stress on *P. australis* and biomass.

Table 2. Packing order of vertical-flow wetland filters (F).

Height (cm)	F1	F2	F3	F4	F5	F6
61–83	W	W	W	W	W	W
56–60	W	W	6	6+P	7	7+P
51–55	W	W	6	6+P	6	6+P
36–50	W	W	4	4+P	5	5+P
31–35	W	W	3	3	5	5
26–30	W	W	3	3	4	4
21–25	W	W	2	2	3	3
16–20	W	W	2	2	2	2
11–15	2	2	2	2	2	2
0–10	1	1	1	1	1	1

Height (cm)	F7	F8	F9	F10	F11	F12
61–83	W	W	W	W	AW	AW
56–60	6	6+P	7	7+P	7+P	7+P
51–55	6	6+P	6	6+P	6+P	6+P
36–50	4	4+P	5	5+P	5+P	5+P
31–35	3	3	5	5	5	5
26–30	3	3	4	4	4	4
21–25	2	2	3	3	3	3
16–20	2	2	2	2	2	2
11–15	2	2	2	2	2	2
0–10	1	1	1	1	1	1

Abbreviations: W, water; P, *Phragmites australis* (Cav.) Trin. ex Steud;. (common reed); AW, aerated water; 1, stones; 2, large gravel; 3, medium gravel; 4, small gravel; 5, Filtralite (light expanded clay product); 6, sand (0.6–1.2 mm); 7, Frogmat (barley straw).

Environmental conditions and operation

The filtration system was designed to operate in batch flow mode to reduce pumping and computer control costs. All filters were periodically inundated with pretreated inflow gully pot liquor and drained to encourage air penetration through the aggregates (Cooper et al., 1996; Gervin and Brix, 2001; Scholz and Xu, 2002).

Since 22 September 2003, the pH value of the inflow has been artificially raised by addition of sodium hydroxide (NaOH) to the sieved gully pot liquor to prevent a breakthrough of metals (see below and Tchobanoglous et al., 2003). It follows that the inflow pH was therefore increased from a mean pH 6.7 to pH 8.1 (Table 3).

Metal nitrates

Copper and nickel were selected as additional heavy metals for investigation because they are commonly occurring contaminants from road vehicles and are not easily bioavailable (Cooper et al., 1996; Kadlec and Knight, 1996; Scholz and Xu, 2002). It follows that these metals are likely to accumulate within the sediment and debris of constructed wetlands. As the buildup continues, metal toxicity increases as does the risk of severe pollution due to leaching (Scholz et al., 2002).

Some heavy metals do accumulate easily in constructed wetlands but may be released if environmental conditions change; for example, road gritting (containing

Table 3. Primary treated gully pot effluent: water quality variables after contamination with hydrated copper nitrate and hydrated nickel nitrate.

Variable	Unit	Number of samples	Mean	SD[a]	Mean (winter)	Mean (summer)
			22/09/02–21/09/03			
Nickel (dissolved)	mg/L	57	1.06	0.143	1.08	1.09
Copper (dissolved)	mg/L	58	1.03	0.036	1.04	1.02
BOD[b]	mg/L	58	61.1	49.29	43.8	86.9
Nitrate-nitrogen	mg/L	63	1.45	1.008	1.43	1.12
Ammonia-nitrogen	mg/L	63	1.65	2.058	1.72	2.11
Ortho-phosphate-phosphorus	mg/L	62	0.06	0.149	0.05	0.03
Suspended solilds	mg/L	70	335.7	377.75	743.7	160.7
Total solids	mg/L	66	2,995.5	6,793.27	9,403.9	376.5
Turbidity	NTU	71	311.7	479.65	690.6	162.1
Dissolved oxygen	mg/L	68	4.70	2.493	5.70	3.16
pH	—	71	6.69	0.411	6.89	6.72
Redox potential	mV	62	142.5	112.72	165.5	2.7
Conductivity	μS	71	5,139.1	11,182.22	15,311.6	501.0
Temperature (air)	°C	70	12.3	5.96	7.2	17.9
Temperature (gully pot)	°C	69	10.7	5.78	4.8	18.0

Variable	Unit	Number of samples	Mean	SD[a]	Mean (winter)	Mean (summer)
		22/09/03–21/09/04 (artificial increase of pH after 21/09/03)				
Nickel (dissolved)	mg/L	68	1.02	0.042	1.01	1.02
Copper (dissolved)	mg/L	66	1.02	0.018	1.01	1.02
BOD[b]	mg/L	73	89.2	55.5	89.7	66.6
Nitrate-nitrogen	mg/L	72	1.38	1.220	1.19	1.14
Ammonia-nitrogen	mg/L	72	1.45	1.934	1.89	1.35
Ortho-phosphate-phosphorus	mg/L	72	0.10	0.136	0.07	0.16
Suspended solids	mg/L	75	853.9	1,420.85	1,955.2	366.7
Total solids	mg/L	71	2,141.8	3,219.84	5,296.4	794.7
Turbidity	NTU	78	274.5	358.57	546.2	143.6
Dissolved oxygen	mg/L	78	3.07	1.49	3.41	3.22
pH	—	78	8.07	1.082	8.25	8.73
Redox potential	mV	78	44.4	93.44	31.8	64.1
Conductivity	μS	78	2,227.2	4,620.82	6,191.7	403.6
Temperature (air)	°C	155	13.7	6.46	7.1	20.6
Temperature (gully pot)	°C	75	12.0	5.65	6.0	18.9

[a]Standard deviation; [b]5-day at 20°C N-Allylthiourea biochemical oxygen demand. Abbreviation: na, not available.

Table 4. Mean and standard deviation of outflow water quality variables.

		Mean (22/09/02–21/09/03)					
Variable	Unit	Filter 1	Filter 2	Filter 3	Filter 4	Filter 5	Filter 6
BOD[a]	mg/L	37.2	43.4	16.4	30.7	23.3	33.5
Suspended solids	mg/L	174.6	189.0	120.8	130.4	132.4	127.3
Total solids	mg/L	2,772.8	3,602.5	2938.7	3.266.2	2,949.1	3,990.4
Turbidity	NTU	79.8	89.0	15.0	39.0	35.4	25.6
Conductivity	μS	5,148.5	6,827.7	5,920.8	5,392.6	5,809.9	5,797.7
Variable	Unit	Filter 7	Filter 8	Filter 9	Filter 10	Filter 11	Filter 12
BOD[a]	mg/L	12.7	22.0	21.8	37.6	20.1	19.8
Suspended solids	mg/L	96.7	92.5	85.8	79.1	73.2	163.5
Total solids	mg/L	2,375.6	2,118.4	1,717.1	1,808.8	1,779.0	2,941.7
Turbidity	NTU	11.2	20.6	27.3	34.3	17.5	43.5
Conductivity	μS	4,912.2	4,346.8	3,808.8	3,667.8	3,528.5	5,941.4

		Mean (22/09/03–21/09/0404; artificial increase of pH after 21/09/03)					
Variable	Unit	Filter 1	Filter 2	Filter 3	Filter 4	Filter 5	Filter 6
BOD[a]	mg/L	30.2	30.4	3.1	2.3	4.4	4.4
Suspended solids	mg/L	434.6	9.07.5	76.6	65.8	130.4	82.7
Total solids	mg/L	1,690.3	1,931.8	1,379.6	1,398.9	1,372.9	1,430.7
Turbidity	NTU	118.6	117.8	6.0	4.8	8.6	6.0
Conductivity	μS	2,268.2	2,356.0	2,339.9	2,260.3	2,220.0	2,507.6
Variable	Unit	Filter 7	Filter 8	Filter 9	Filter 10	Filter 11	Filter 12
BOD[a]	mg/L	2.3	2.7	2.8	3.5	3.6	7.6
Suspended solids	mg/L	147.3	78.1	83.4	71.7	89.9	102.8
Total solids	mg/L	1,390.3	1,497.3	1,509.4	1,804.7	1,578.5	1,647.4
Turbidity	NTU	9.6	6.9	10.2	4.9	7.4	20.1
Conductivity	μS	2,199.2	2,484.2	2,450.6	2,459.6	2,534.5	2,495.3

		Standard deviation (22/09/02–21/09/03)					
Variable	Unit	Filter 1	Filter 2	Filter 3	Filter 4	Filter 5	Filter 6
BOD[a]	mg/L	39.89	41.95	13.09	31.24	22.74	30.33
Suspended solids	mg/L	365.53	440.59	265.83	252.75	249.34	273.44
Total solids	mg/L	7,273.37	10,821.20	6,886.58	6,585.16	6,216.36	8,318.42
Turbidity	NTU	96.15	73.83	24.21	61.19	46.64	28.45
Conductivity	μS	13,473.42	19,920.19	13,442.84	11,789.78	12,286.69	12,860.16
Variable	Unit	Filter 7	Filter 8	Filter 9	Filter 10	Filter 11	Filter 12
BOD[a]	mg/L	13.88	25.03	20.08	35.76	14.04	17.63
Suspended solids	mg/L	225.06	197.81	168.08	166.03	144.40	307.73
Total solids	mg/L	5,948.07	4,720.47	3,580.56	3,648.16	3,659.61	6,450.13
Turbidity	NTU	18.95	30.18	42.51	54.91	18.07	86.23
Conductivity	μS	11,672.86	9.431.98	6,319.37	6,683.83	7,077.11	11,479.77

(continued)

Table 4. Mean and standard deviation of outflow water quality variables. (Continued)

Standard deviation (22/09/03–21/09/0404; artificial increase of pH after 21/09/03) (Continued)

Variable	Unit	Filter 1	Filter 2	Filter 3	Filter 4	Filter 5	Filter 6
BOD[a]	mg/L	21.24	37.06	7.23	3.11	8.11	6.66
Suspended solids	mg/L	449.80	3,580.34	96.29	79.97	263.65	107.28
Total solids	mg/L	1,507.80	2,417.22	1,722.92	1,601.87	1,445.83	1,714.86
Turbidity	NTU	90.33	258.22	6.89	4.44	8.38	4.48
Conductivity	μS	2,945.92	3,000.52	2,839.88	2,565.04	2,476.56	2,857.82

Variable	Unit	Filter 7	Filter 8	Filter 9	Filter 10	Filter 11	Filter 12
BOD[a]	mg/L	3.86	3.83	4.00	4.49	4.24	7.83
Suspended solids	mg/L	228.84	82.75	96.24	86.77	133.64	138.81
Total solids	mg/L	1,623.29	1,538.09	1,716.03	2,553.49	1,905.64	2,426.29
Turbidity	NTU	18.79	7.76	19.59	4.24	10.94	37.18
Conductivity	μS	2,611.49	2,572.43	2,840.91	2,741.12	3,069.47	3,638.43

[a]Five-days at 20°C N-Allylthiourea biochemical oxygen demand.

salt) in winter. Such transformation processes are not well understood (Norrstrom and Jacks, 1998).

Copper nitrate and nickel nitrate were added to the inflow water of Filter 2 and Filters 7 to 12 to give total concentrations of dissolved copper and nickel of approximately 1 mg/L for each metal, comparable to figures reported for urban water heavily contaminated with heavy metals and mine wastewater (Cooper et al., 1996; Kadlec and Knight, 1996; Mungur et al., 1997; Scholz and Xu, 2002).

Concerning the dosed inflow water, the background concentration for nitrate-nitrogen (including nitrite-nitrogen) was only approximately 0.497 mg/L. Therefore, introduced nitrate-nitrogen contributed to 65% (or approximately 0.917 mg/L) of the overall nitrate-nitrogen (including nitrite-nitrogen) load.

The filter volumes available for influent water differ among the filters due to different filter media compositions (Table 2) and hydraulic regimes (Table 1). The mean annual total loading rates for the contaminated filters were therefore between 96 and 187 mg for each metal.

Metal determinations

Metal concentrations were determined in the raw gully pot liquor, sieved (pore size of 0.25 mm) gully pot liquor (partially used as actual inflow water for some filters), contaminated (added metal nitrates) sieved gully pot liquor (partially used as actual inflow water for some filters) and the outflow waters from the experimental rig (Table 1). Raw gully pot liquor was sieved to simulate preliminary and primary treated storm water. This procedure is in line with common practice in the wastewater industry (Cooper et al., 1996; Tchobanoglous et al., 2003).

A Varian Spectr AA 400 Atomic Absorption Spectrometer with a GTA-96 graphite furnace tube atomizer was used for the standard analysis of nickel and copper. Notched GTA partition tubes (coated) were applied, and the carrier gas was argon.

BOD, nutrient, and other determinations

The BOD was determined in all water samples with the OxiTop IS 12–6 system, a manometric measurement device, supplied by the Wissenschaftlich-Technische Werkstätten (WTW), Weilheim, Germany. Nitrification was suppressed by adding 0.05 mL of 5 g/L N-Allylthiourea (WTW Chemical Solution No. NTH 600) solution per 50 mL of sample water.

Nitrate was reduced to nitrite by cadmium and determined as an azo dye at 540 nm (using a Perstorp Analytical EnviroFlow 3000 flow injection analyzer) following diazotization with sulfanilamide and subsequent coupling with N-1-naphthylethylendiamine dihydrocloride (Allen, 1974).

Ammonia-nitrate and ortho-phosphate-phosphorus were determined by automated colorimetry in all water samples from reaction with hypochlorite and salicylate ions in solution in the presence of sodium nitrosopentacyanoferrate (nitroprusside), and reaction with acidic molybdate to form a phosphomolybdenum blue complex, respectively (Allen, 1974). The colored complexes formed were measured spectrometrically at 655 and 882 nm, respectively, using a Bran and Luebbe autoanalyzer (Model AAIII).

Composite water samples were analyzed on Mondays, Wednesdays, and Fridays. All other analytical procedures were performed according to the American standard methods (1995).

EXPERIMENTAL RESULTS
AND DISCUSSION

Inflow water quality

Table 3 summarizes the water quality of the inflow to those filters artificially contaminated with heavy metals after the first and second year of operation. The pH of the inflow was artificially raised to assess its influence on the treatment performance and particularly on the potential breakthrough of heavy metals during the second winter (Table 3).

Raw gully pot liquor was sieved (pore size of 2.5 mm) to simulate preliminary treatment (Tchobanoglous *et al.*, 2003). Sieving resulted in a mean annual reduction of BOD and SS by approximately 12 and 22%, respectively.

The inflow data set was divided into two subsets (winter and summer) to assess the effect of seasonal variations (e.g., temperature) and road management (e.g., road gritting and salting) on the water quality. Most variables including BOD (except for the first year of operation), SS, total solids (TS), turbidity, and conductivity are high in winter compared to summer (Table 3).

Comparison of annual outflow water qualities

The overall filtration performance figures are summarized in Tables 4 and 5. Figure 2 shows selected inflow and selected outflow concentrations for nickel and copper. Concerning BOD removal, the performances of all filters (except for Filters 1 and 2; extended storage) improved greatly over time. The reductions in BOD were also satisfactory for most filters if compared to minimum American and European standards (<20 mg/L) for the secondary treatment of effluent (Tables 3 to 5).

Furthermore, the artificial increase of pH after the first year of operation had no apparent influence on the treatment performance of BOD. There is no obvious difference in performance between Filters 8 and 11, indicating that aeration did not contribute significantly to the removal of BOD (Tables 3 and 4).

Negative reduction rates for TS and conductivity were predominantly caused by road salting in late autumn and winter. Any conventional filter system including constructed wetlands is unable to retain salts in high concentrations. Therefore, salts cannot be retained after a certain loading threshold that is associated with a lag period is exceeded. The lag period is predominantly a function of the buffering capacity of the biomass and the batch-flow operational mode (see above). It follows that after an initial positive removal period, the removal efficiencies are becoming negative (Norrstrom and Jacks, 1998). Furthermore, the dissolved solids fraction increases as microbial biomass mineralizes the organic contaminants.

Conductivity correlates well with dissolved solids that contribute to a large proportion of the TS mass (Cooper *et al.*, 1996; Scholz *et al.*, 2002).

In contrast to previous researchers who reported the worst seasonal performance for BOD removal during winter (Karathanasis *et al.*, 2003), all filters with the exception of Filters 1 and 2 showed high BOD removal figures (>94%) in the second winter. This suggests that soil microbes still have the capacity to decompose organic matter in winter.

Concerning other variables, reduction rates for SS increased also in the second year although outflow concentrations frequently exceeded the threshold of 30 mg/L throughout the year except for summer. Turbidity values of the outflow decreased greatly over time. Despite the artificial increase of pH in the inflow, the pH of the outflow was approximately neutral and comparable to the first year of operation. Moreover, the pH of the outflow was relatively stable in the second year (standard deviation of approximately 0.18).

Heavy metal treatment

Heavy metal removal efficiencies improved during the second year of operation (Fig. 2). However, the reduction in metals was not sufficient to comply with American standards for secondary wastewater treatment. Dissolved nickel and dissolved copper concentrations should not exceed 0.0071, 0.0049 mg/L, respectively (Tchobanoglous *et al.*, 2003).

The decomposition of aquatic plants after fall, reducing soil conditions, road gritting, and salting during periods of low temperatures and acid rain contribute to increases of metal concentrations in the outflow (Norrstrom and Jacks, 1998; Sasaki *et al.*, 2003). For example, high levels of conductivity were recorded in the filter inflow and outflows (Tables 3 to 5), and the breakthrough of dissolved nickel was observed during the first winter (Fig. 2a).

Concerning the effect of retention time on the treatment efficiency of metals, the heavy metal outflow concentrations of Filter 12 (higher loading rate) were slightly higher than the corresponding concentrations for the other filters. According to previous studies (Kadlec and Knight, 1996; Wood and Shelley, 1999), metal removal efficiencies for wetlands are highly correlated with influent concentrations and mass loading rates. Moreover, it was suggested that the formation of metal sulfides was favored in wetlands with long retention times. This may lead to a more sustainable management of constructed treatment wetlands.

Link between pH and treatment of metals

After the increase of the inflow pH, mean reduction efficiencies for nickel increased during the second win-

Table 5. Removal (%) per wetland filter[a] of outflow variables.

22/09/02-21/09/03

Variable	Filter 1 A^b	B^c	C^d	Filter 2 A^b	B^c	C^d	Filter 3 A^b	B^c	C^d	Filter 4 A^b	B^c	C^d	Filter 5 A^b	B^c	C^d	Filter 6 A^b	B^c	C^d
BOD[e]	43	13	82	32	3	80	76	59	85	51	40	84	65	49	88	49	44	86
SS[f]	52	40	81	44	25	78	67	53	92	65	54	86	64	54	92	66	52	88
TS[g]	9	N	N	N	N	21	4	N	6	N	1	N	3	N	N	N	N	N
Turb[h]	78	86	65	71	86	51	96	98	95	90	94	94	90	96	91	93	95	93
Cond[i]	2	N	N	N	N	2	N	N	N	N	N	N	N	N	N	N	N	N

Variable	Filter 7 A^b	B^c	C^d	Filter 8 A^b	B^c	C^d	Filter 9 A^b	B^c	C^d	Filter 10 A^b	B^c	C^d	Filter 11 A^b	B^c	C^d	Filter 12 A^b	B^c	C^d
BOD[e]	79	53	94	66	32	92	67	51	93	43	2	89	69	68	89	69	65	84
SS[f]	72	60	98	73	62	91	75	71	95	77	70	92	78	71	88	51	35	86
TS[g]	20	15	25	29	32	N	42	48	19	39	45	2	40	43	N	2	N	28
Turb[h]	96	97	99	93	95	96	91	94	98	89	90	93	94	96	94	86	85	92
Cond[i]	4	N	N	15	11	N	26	36	N	28	32	N	31	29	N	N	N	N

22/09/03-21/09/0404 (artificial increase of pH after 21/09/03)

Variable	Filter 1 A^b	B^c	C^d	Filter 2 A^b	B^c	C^d	Filter 3 A^b	B^c	C^d	Filter 4 A^b	B^c	C^d	Filter 5 A^b	B^c	C^d	Filter 6 A^b	B^c	C^d
BOD[e]	66	69	76	63	44	71	97	100	96	97	99	94	95	99	96	95	99	93
SS[f]	49	74	52	15	N	76	38	40	65	38	42	58	39	50	64	36	38	49
TS[g]	25	36	37	15	23	62	98	99	95	98	99	98	97	97	96	98	99	98
Turb[h]	57	77	48	61	68	62	N	12	N	N	18	N	0	22	N	N	9	N
Cond[i]	N	7	18	N	8	N	N	12	N	N	N	N	N	N	N	N	N	N

Variable	Filter 7 A^b	B^c	C^d	Filter 8 A^b	B^c	C^d	Filter 9 A^b	B^c	C^d	Filter 10 A^b	B^c	C^d	Filter 11 A^b	B^c	C^d	Filter 12 A^b	B^c	C^d
BOD[e]	97	99	95	97	99	91	97	99	96	96	99	90	96	98	90	91	94	88
SS[f]	81	89	99	90	91	96	91	90	99	91	91	98	89	87	97	28	24	34
TS[g]	39	42	72	34	46	50	34	43	71	21	22	53	31	36	56	93	93	97
Turb[h]	97	98	99	98	98	98	97	99	98	98	99	99	98	97	99	93	93	97
Cond[i]	3	16	N	N	17	N	N	16	N	N	15	N	N	9	N	N	2	N

[a]Change (%) = $\dfrac{(in - out) \times 100\ (\%)}{in}$, where in = inflow and out = outflow; [b]overall mean; [c]mean of the winter; [d]mean of the summer; [e]5-days at 20°C N-Allylthiourea biochemical oxygen demand (mg/L); [f] suspended solids (mg/L); [g]total solids (mg/L); [h]turbidity (NTU); [i]conductivity (μS); in italics: BOD > 20 mg/L and SS > 30 mg/L (outflow values). Abbreviation: N, negative removal (i.e., more output than input).
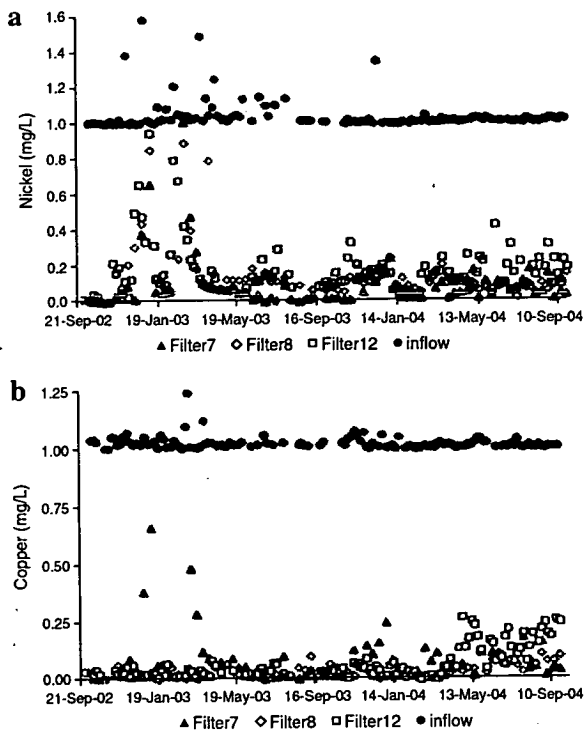
Figure 2. Daily (a) nickel and (b) copper concentrations (mg/L) in the inflow and outflows of Filters 7 (unplanted), 8 (planted), and 12 (planted and high loading).

Analysis of variance and case-based reasoning

An analysis of variance has shown that all filters containing aggregates are relatively similar to each other with respect to most of their outflow variables. It follows that some filters could be considered as replicates (e.g., Filter 7 is a replicate of Filter 3) despite the differences in filter setup (Tables 1 and 2). The p-values of the pairs for Filter 3 and 7 are 0.20, 0.95, and 0.98 for BOD, SS, and turbidity, respectively. Pairs of data associated with $p \geq 0.05$ can be regarded as statistically similar.

The absence of filter replicates is not a serious issue considering that the filter performances are similar (see above), and that the standard deviations (Table 4) of most outflow variables are comparable with large-scale systems (Cooper *et al.*, 1996; Kadlec and Knight, 1996; Vymazal, 2002; Karathanasis *et al.*, 2003). Moreover, a more detailed experimental study with three replicate filters, for example, would not be justified in terms of costs and potential scientific benefit.

Furthermore, case-based reasoning of the experimental data set has been applied by Lee *et al.* (2005). The purpose of this follow-up paper is to show how case-based reasoning can be applied for water quality control purposes.

CONCLUSIONS

Despite the highly variable water quality of road runoff, the novel filters showed great treatment performances particularly with respect to the 5-day at 20°C N-Allylthiourea biochemical oxygen demand (BOD) reduction in a cold climate. Removal efficiencies for SS in particular improved over time and dissolved copper was removed satisfactorily in comparison to values obtained from the literature. However, a breakthrough of dissolved nickel during the first winter of the first year of operation was observed. After creating an artificially high inflow pH of approximately 8 after 1 year of operation, nickel was successfully treated despite vulnerability to leaching when exposed to a high salt concentration during the second winter.

A high pH was apparently also linked to high removal efficiencies. The elevated pH had no apparent negative effect on the biomass including macrophytes. Moreover, filters showed a great pH buffering capacity. Findings indicate that conventional pH adjustment can be successfully applied to constructed wetland systems for storm water treatment.

The presence of Filtralite (adsorption filter media) and *Phragmites australis* (Cav.) Trin. ex Steud., common reed (macrophyte), did not result in an obvious reduction of metal concentrations in outflow waters. Operational conditions such as inflow pH and retention time were more important for the heavy metal treatment.

ter compared to the first winter; for example, 90 and 65%, respectively, for Filter 7 (Fig. 2a). Moreover, an obvious breakthrough of nickel was not observed during the second winter despite the presence of high salt concentrations in the inflow. This is likely to be due to the artificial increase of pH. A high pH facilitates nickel precipitation. For example, nickel hydroxide $(Ni(OH)_2)$ may precipitate at pH 9.1 if the corresponding metal concentration is 1 mg/L (Tchobanoglous *et al.*, 2003), which is similar to the inflow concentrations of spiked filters. Moreover, dissolved copper did not break through any constructed wetland filters throughout the study (Fig. 2b).

All filters acted as pH buffers after pH increase, and pH levels were subsequently reduced. It can be assumed that this buffering capacity is greatly enhanced by the presence of active biomass rather than macrophytes (Kadlec and Knight, 1996; Sasaki *et al.*, 2003). However, the outflow pH values for the planted filters recorded were slightly lower than those for the unplanted filters. For example, the overall mean pH value for Filter 7 (unplanted filters) is 7.31, and the corresponding value for Filter 8 (planted filters) is 6.98 during the second year of operation.

ACKNOWLEDGMENTS

REFERENCES

ALLEN, S.E. (1974). *Chemical Analysis of Ecological Materials.* Oxford, UK: Blackwell.

AMERICAN PUBLIC HEALTH ASSOCIATION (APHA). (1995). *Standard Methods for the Examination of Water and Wastewater,* 19th ed. Washington, DC: Author.

BACKSTROM, M., KARLSSON, S., BACKMAN, L., FOLKESON, L., and LIND, B. (2004). Mobilisation of heavy metal by de-icing salts in a roadside environment. *Water Res.* 38, 720–732

BRIX, H., ARIAS, C.A., and DEL BUBBA, M. (2001). Media selection for sustainable phosphorus reduction in subsurface flow constructed wetlands. *Water Sci. Technol.* 44, 47–54.

CHENG, S.P., GROSSE, W., KARRENBROCK, F., and THOENNESSEN, M. (2002). Efficiency of constructed wetlands in decontamination of water polluted by heavy metals. *Ecol. Eng.* 18, 317–325.

COOPER, P.F., JOB, G.D., GREEN, M.B., and SHUTES, R.B. E. (1996). *Reed Beds and Constructed Wetlands for Wastewater Treatment.* Swindon, UK: WRc plc.

GERVIN, L., and BRIX, H. (2001). Reduction of nutrients from combined sewer overflows and lake water in a vertical-flow constructed wetland system. *Water Sci. Technol.* 44, 171–176.

GREEN, M., FRIEDLER, E., and SAFRAI, I. (1998). Enhancing nitrification in vertical-flow constructed wetlands utilizing a passive air pump. *Water Res.* 32, 3513–3520.

KADLEC, R.H. (2002). *Effects of Pollutant Speciation in Treatment Wetlands Design.* Chelsea, MI: Wetland Management Services.

KADLEC, R.H., and KNIGHT, R.L. (1996). *Treatment Wetlands.* Boca Raton, FL: CRC Press.

KADLEC, R., KNIGHT, R.L., VYMAZAL, J., BRIX, H., COOPER, P.F., and HABERL, R. (2000). *Constructed Wetlands for Pollution Control.* Scientific and Technical Report Number 8. International Water Association (IWA) Specialist Group "Use of Macrophytes for Water Pollution Control." London, UK: IWA Publishing.

KARATHANASIS, A.D., POTTER, C.L., and COYNE, M.S. (2003). Vegetation effects on fecal bacteria, BOD and suspended solids removal in constructed wetlands treating domestic wastewater. *Ecol. Eng.* 20, 157–169.

KNIGHT, R.L., KADLEC, R.H., and OHLENDORF, H.M. (1999). The use of treatment wetlands for petroleum industry effluents. *Environ. Sci. Technol.* 33, 973–980.

LEE, B.-H., SCHOLZ, M., HORN, A., and FURBER, A. 2005. Constructed wetlands: prediction of performance with case-based reasoning (Part B). *Environ. Eng. Sci.*

LUEDERITS, V., ECKERT, E., LANGE-WEBER, M., and LANGE A. (2001). Nutrient removal efficiency and resource economics of vertical flow and horizontal flow constructed wetlands. *Ecol. Eng.* 18, 157–171.

MAYS, P.A., and EDWARDS, G.S. (2001). Comparison of heavy metal accumulation in a natural wetland and constructed wetland receiving acid mine drainage. *Ecol. Eng.* 16, 487–500.

MUNGUR, A.S., SHUTES, R.B.E., REVITT, D.M., and HOUSE, M.A. (1997). An assessment of metal reduction by laboratory-scale wetland. *Water Sci. Technol.* 35, 125–133.

NORRSTROM, A.C., and JACKS, G. (1998). Concentration and fractionation of heavy metals in roadside soils receiving de-icing salts. *Sci. Total Environ.* 218, 161–174.

OBARSKA-PEMPKOWIAK, H., and KLIMKOWSKA, K. (1999). Distribution of nutrients and heavy metals in a constructed wetland system. *Chemoshere* 39, 303–312.

PARK, S.J., and YOON, T.I. (2003). Weighted coagulation with glass and diatomite for storm water treatment and sludge disposal. *Environ. Eng. Sci.* 20, 307–317.

PICARD, C.R., FRASER, L.H., and STEER, D. (2004). The interacting effects of temperature and plant community type on nutrient removal in wetland microcosms. *Bioresource Technol.* 96, 1039–1047.

SANSALONE, J.J. (1999). Adsorptive infiltration of metals in urban drainage—Media characteristics. *Sci. Total Environ.* 235, 179–188.

SASAKI, K., OGINO, T., ENDO, Y., and KUROSAWA, K. (2003). Field studies on heavy metal accumulation in a natural wetland receiving acid mine drainage. *Mater. Trans.* 44, 1877–1884.

SCHOLZ, M. (2003). Case study: Design, operation, maintenance and water quality management of sustainable storm water ponds for roof runoff. *Bioresource Technol.* 95, 269–279.

SCHOLZ, M., and MARTIN, R.J. (1998). Control of bio-regenerated granular activated carbon by spreadsheet modeling. *J. Chem. Tech. Biotechnol.* 71, 253–261.

SCHOLZ, M., and TREPEL, M. (2004). Water quality characteristics of vegetated groundwater-fed ditches in a riparian peatland. *Sci. Total Environ.* 332, 109–122.

SCHOLZ, M., and XU, J. (2002). Performance comparison of experimental constructed wetlands with different filter media and macrophytes treating industrial wastewater contaminated with lead and copper. *Bioresource Technol.* 83, 71–79.

SCHOLZ, M., and ZETTEL, S. (2004). Storm water quality associated with a full silt trap discharging into urban watercourses. *J. Ch. Inst. Water Environ. Manage.* **18,** 226–229.

SCHOLZ, M., HÖHN, P., and MINALL, R. (2002). Mature experimental constructed wetlands treating urban water receiving high metal loads. *Biotechnol. Prog.* **18,** 1257–1264.

TCHOBANOGLOUS, G., BURTON, F.L., and STENSEL, H.D. (2003). *Wastewater Engineering: Treatment and Reuse,* 4th ed., revised. New York: Metcalf & Eddy Inc. and McGraw Hill.

VYMAZAL, J. (2002). The use of sub-surface constructed wetlands for wastewater treatment in the Czech Republic: 10 years experience. *Ecol. Eng.* **18,** 633–646.

VYMAZAL, J., and KRASA, P. (2003). Distribution of Mn, Al, Cu and Zn in a constructed wetland receiving municipal sewage. *Water Sci. Technol.* **48,** 299–305.

WIESSNER, A., KAPPELMEYER, U., KUSCHK, P., and KASTNER, M. (2004). Influence of the redox condition dynamics on the removal efficiency of a laboratory-scale constructed wetland. *Water Res.* **39,** 248–256.

WOOD, T.S., and SHELLEY, M.L. 1999. A dynamic model of bioavailability of metals in constructed wetland sediments. *Ecol. Eng.* **12,** 231–252.

ZHAO, Y.Q., SUN, G., and ALLEN S.J. (2004). Purification capacity of a highly loaded laboratory scale tidal flow reed bed system with effluent recirculation. *Sci. Total Environ.* **330,** 1–18.

Constructed Wetlands: Prediction of Performance with Case-Based Reasoning (Part B)

Byoung-Hwa Lee, Miklas Scholz,* Antje Horn, and Alison M. Furber

Institute for Infrastructure and Environment
School of Engineering and Electronics
The University of Edinburgh
Edinburgh EH9 3JL, Scotland
United Kingdom

ABSTRACT

The aim of this research was to assess the treatment efficiencies for gully pot liquor of experimental vertical-flow constructed wetland filters containing *Phragmites australis* (Cav.) Trin. ex Steud. (common reed) and filter media of different adsorption capacities. Six out of 12 filters received inflow water spiked with metals. For 2 years, hydrated nickel and copper nitrate were added to sieved gully pot liquor to simulate contaminated primary treated storm runoff. The findings were analyzed and discussed in a previous paper (Part A). Case-based reasoning (CBR) methods were applied to predict 5 days at 20°C N-Allylthiourea biochemical oxygen demand (BOD) and suspended solids (SS), and to demonstrate an alternative method of analyzing water quality performance indicators. The CBR method was successful in predicting if outflow concentrations were either above or below the thresholds set for water-quality variables. Relatively small case bases of approximately 60 entries are sufficient to yield relatively high predictions of compliance of at least 90% for BOD. Biochemical oxygen demand and SS are expensive to estimate, and can be cost-effectively controlled by applying CBR with the input variables turbidity and conductivity.

Key words: storm runoff; gullies; constructed wetlands; case-based reasoning; sampling scheme optimization; effluent standards

INTRODUCTION

CASE-BASED REASONING (CBR) is a method of problem solving, which has arisen out of the field of artificial intelligence, and aims to recreate the robust problem solving technique often used by humans within the constraints of a computer program (Aamodt and Plaza, 1994; Arditi and Tokdemir, 1999). When a human encounters a problem he or she tends to remember similar situations that they have come across in the past, and the methodology in which solutions were found. By recalling these events, it becomes possible to reuse the previous solution(s) to solve the current problem, perhaps adjusting the methodology and outcome slightly to meet the

---

*Corresponding author: Institute for Infrastructure and Environment, School of Engineering and Electronics, The University of Edinburgh, Faraday Building, The King's Buildings, Mayfield Road, Edinburgh EH9 3JL, Scotland, United Kingdom. *Phone:* +44 131 6 506780; *Fax:* +44 131 6 506554; *E-mail:* M.Scholz@ed.ac.uk

specific requirements of the new task (Aamodt and Plaza, 1994).

Case-based reasoning works very similarly to the human logic of data handling. A data base of past experiences that may be useful to solve a particular type of query is kept. The difficulty in CBR is the design of a system that is capable of recalling past experiences, which would provide useful information when a new problem is introduced to the system. In CBR terminology, the event in which a solution to a former problem was found is referred to as a "case," and is stored in the system's "case base." For the purpose of CBR, each case should be recorded within the case base systematically and the useful information must be stored consistently through the entire case base, the chosen structure used being referred to as the "case representation" (Ardity and Tokdemir, 1999).

When a new problem is introduced to the CBR system, it should be represented in the same format as the stored cases, and then the process of deciding which of the past cases may be of use in finding a solution to this problem can begin. The main assumption underlying a CBR methodology is that similar problems will have similar solutions. It follows that the most useful cases in the case base will be those that are most similar to the problem case.

The concept of similarity is fundamental in CBR theory, making inexact matching possible, which is required when previously unseen problems arise. A mechanism is implemented within the system that is capable of recalling past cases that are most closely matched to the problem presented in terms of the variable(s) used to describe the cases. Therefore, the variables used should be carefully chosen such that the solutions recalled will also be relevant to the problem case. Once the most similar cases have been selected, the predicted solution is found using an adaptation or learning process (Aamodt and Plaza, 1994).

CBR applied to biochemical data

Concerning general data sets, CBR systems are often seen as simple, convenient, and effective methods of artificial intelligence for multicomponent analysis (Arditi and Tokdemir, 1999). The methodology is based on assuming regularity, typicality, and consistency. Moreover, it can be characterized by the four "re" steps: retrieve, reuse, revise, and retain. The output or target variable is determined from input variables that are associated with weightings. Various methods of their determination exist: uniform (i.e., no weightings), correlated, and calibrated weightings, as well as exact and fuzzy matched meta weightings (Watson, 1997).

Case-based reasoning has been successfully applied to the development and implementation of a knowledge-based hybrid supervisory system to support the operation of a real wastewater treatment plant (Rodriguez-Roda et al., 2002). The CBR system can be structured into three separated levels: data gathering, diagnosis, and decision support. The different tasks of the system can be performed in a seven-step cycle: data gathering and update, diagnosis, supervision, prediction, communication, actuation, and evaluation (Rodriguez-Roda et al., 2002).

With respect to biochemical data sets, hybrid CBR systems for monitoring water quality based on chemical variables and algae populations have been applied previously (Policastro et al., 2004). A CBR system was also successfully developed to supervise complex biochemical processes such as the activated sludge process (Roda et al., 2001). The suitability of CBR has also been shown in aqueous solutions containing mixtures of ions of different nature and concentration. For example, CBR has been successfully applied to the rapid recognition and evaluation of mineral water samples (Colilla et al., 2002).

Constructed treatment wetlands are often seen as complex "black box" systems, and have therefore not been used previously for a detailed CBR analysis. The processes within an experimental constructed treatment wetland are difficult to model due to the complexity of the relationships between most water quality variables (Gernaey et al., 2003; Nunez et al., 2004). However, it is necessary to monitor, control, and predict the treatment processes to meet environmental and sustainability policies, and regulatory requirements such as secondary wastewater treatment standards (Lee et al., 2005). CBR methodologies (Aamodt and Plaza, 1994) could be used to make water quality predictions and to optimize the operation of treatment wetlands. Consideration should also be given to CBR as a learning tool.

The measurement of biochemical oxygen demand (BOD) and suspended solids (SS) concentrations is widely applied for wastewater before and after treatment, as they give a general indication of the water quality status. BOD is a measurement of the oxygen consumed in 5 days by organisms within the water sample stored within an incubator at 20°C. N-Allylthiourea is usually added to inhibit nitrification [American Public Health Association (APHA), 1995]. A regulator such as the Scottish Environmental Protection Agency imposes thresholds for water quality variables. The corresponding secondary wastewater treatment thresholds for BOD and SS are 20 and 30 mg/L, respectively (Scholz et al., 2002; Lee et al., 2005).

Methods of measuring or reliably predicting BOD and SS are useful for the day-to-day operation of constructed treatment wetlands. Unfortunately, taking BOD measurements is both expensive (measurements are labor intensive and capital costs of modern on-line equipment are

relatively high; approximately £15,000) and only of historical value (results are not available until 5 days after the sample has been taken). Furthermore, the procedures to estimate BOD and SS concentrations are time-consuming and labor-intensive. Therefore, some method of prediction, if it could be made reliable enough, would be advantageous (Lee *et al.*, 2005).

CBR could be a methodology well suited to the analysis of biochemical data. Verdenius and Broeze (1999) discussed the difficulties that arise in modeling environmental systems, highlighting particularly the complexity of the relationships between the different variables, and how these relationships change over time. The creation of any model, using traditional techniques, requires expertise of the environmental system, mathematical technique, and software packages used. Once compiled, the model will then require continual updating as the system evolves over time. In many circumstances, mathematical models have proved insufficient, and environmental experts have had to be called in to find solutions based on empirical observations. Experts do recall their experience of similar past problems to come up with a new solution (Nunez *et al.*, 2004). As CBR also uses this technique to find solutions, it is thought that CBR may be beneficially applied to environmental problems. Moreover, CBR has been shown to function well with highly complex "black box" system problems, and as a CBR system can be designed to "learn" solutions to the new problems it comes across, the system is dynamic and will update itself without much intervention from the system designer (Sanchez-Marre *et al.*, 1999).

The application of CBR to predict variables as part of complex biochemical data sets should be considered. The predictions of BOD and SS serve as examples of one possible application of CBR to biochemical data. Successful predictions could help to optimize the operation and maintenance of constructed treatment wetlands.

Project purpose

The major purpose of this part of the study is to improve water quality monitoring and interpretation guidelines of vertical-flow constructed treatment wetlands with case-based reasoning, and to use a case study (Lee *et al.*, 2005) as an educational tool. The objectives are to assess

1. the potential of CBR for analyzing biochemical data, interpretation of wetland data, and predicting BOD and SS;
2. the most appropriate method of selecting input variables,
3. the optimum size of the case base;
4. the goodness of prediction with a CBR analysis; and
5. the potential of CBR as a teaching tool to enhance understanding of "black box" systems.

METHODOLOGY AND SOFTWARE APPLIED TO UNDERTAKE CBR

The experimental data set applied for this study has been described in detail by Lee *et al.* (2005). The CBR system used to predict the BOD and SS concentrations of treated gully pot liquor samples was created using simple mathematical functions in Microsoft Excel. Past cases were sorted in the case base represented by up to six input variables: turbidity (NTU), conductivity (μS), redox potential (mV), outflow water temperature (°C), dissolved oxygen, DO (mg/L) and pH (−). Total dissolved solids were not selected because of very high correlations (usually >0.9 for most filters and seasons) with conductivity (Lee *et al.*, 2005). Calibrated weights were assigned to each input variable. Biochemical oxygen demand (mg/L) or SS (mg/L) were the corresponding output variables. The input variables were selected due to their potential predictive relationships (based on correlation and regression analysis) with the BOD and SS (Scholz, 2003), and the fact that they are both more cost-effective and easier to measure in comparison to BOD and SS.

If the CBR system is presented with a new problem case (measurements at a particular day), the similarity of each past case with the problem case will be calculated. The most similar cases will subsequently be selected, and used to calculate the predicted output of the new problem case. The similarity of each past case with the problem case is calculated one case at a time and by comparing one input variable at a time. The local similarity (the similarity of a past case and the problem case with respect to only one variable) is found via a mathematical function of the difference between the two cases for one variable. In Equation (1), a variable i for the past case and problem case is normalized over the range of the past cases by dividing each case by the mean of the past cases. The differences between each past case and the problem case are then calculated with respect to each variable. The function f in Equation (1) converts the local difference to the local similarity.

$$\text{local\_sim}_i = f(|(V_{ip}/MV_i) - (V_{ic}/MV_i)|) \qquad (1)$$

where: local_sim_i is the local similarity of variable i for past case c and problem case p; V_{ip} is the value of variable i for the problem case; MV_i is the mean of variable i found in the case base; V_{ic} is the value of variable i for the past case; $|(V_{ip}/MV_i) - (V_{ic}/MV_i)|$ is the local difference; and f is the function, which maps the local difference onto the local similarity.

The function used to map the local difference onto the local similarity is defined in Equation (2) that applies fuzzy theory such that a difference of zero scores a similarity of one and a difference of more than two standard

Table 1. Correlation coefficients from a correlation analysis comprising input (column headings) and target (row headings) variables used for a subsequent case-based reasoning analysis.

Variable	Turbidity (NTU)	Conductivity (μS)	Redox potential (mV)	Temperature (°C)	Dissolved oxygen (mg/L)	pH (−)
BOD[a] (mg/L)	0.535	0.244	−0.374	−0.121	−0.074	−0.242
SS[b] (mg/L)	0.531	0.833	−0.338	−0.323	−0.135	0.035

[a]Five-days at 20°C N-Allylthiourea biochemical oxygen demand; [b]suspended solids; Note: 5% significance level: 0.078; 1% significance level: 0.102.

deviations scores a similarity of zero. The global similarity (similarity of the past case to the problem case considering all variables) of a past case can be found from the local similarity of each variable. Each local similarity is first multiplied by a weighting factor that corresponds to the importance of that variable in predicting the output. These should be found by calibrating the system using an independent data set. As the calibration data set is introduced to the system the weighting of each factor should be adjusted one at a time until the best possible output is achieved. Equation (3) defines how the local similarities of each variable are combined to calculate the global similarity of the past case and problem case.

$$f(x) = \exp(-0.5(x/SDV_i)^2) \qquad (2)$$

Table 2. Constructed treatment wetlands: Case-based reasoning (CBR) applied to predict the 5-day at 20°C N-Allylthiourea biochemical oxygen demand (BOD) and the suspended solids (SS) concentrations with the input variables turbidity (NTU), conductivity (μS), redox potential (mV), and the outflow water temperature (°C).

Filter no.	No. of cases	Mean concentration_measured	Mean concentration_predicted	Error (%)	Correct prediction of compliance (%)[a]	a[b]	b[b]	r[2b]
			CBR for BOD (mg/L)					
3	56	7.55	10.86	30.5	89.29	−0.035	2.038	0.258
4	55	12.69	9.92	27.9	87.27	−0.005	0.991	0.614
5	59	11.41	13.35	14.4	91.53	−0.013	1.703	0.731
6	60	16.20	9.85	64.5	81.67	−0.008	0.911	0.230
7	58	6.70	9.88	32.2	89.66	−0.040	2.386	0.546
8	60	11.05	11.05	0.0	95.00	−0.013	1.509	0.751
9	58	9.83	13.44	26.9	87.93	−0.017	1.826	0.513
10	62	18.75	11.11	68.8	87.10	−0.003	0.655	0.629
11	60	10.08	12.23	17.6	81.67	0.000	1.077	0.529
12	112	11.31	13.27	14.8	83.04	0.000	0.999	0.303
3–12	640	11.60	11.65	0.4	87.03	−0.007	1.125	0.396
			CBR for SS (mg/L)					
3	60	106.67	111.72	4.5	85.00	−0.001	1.231	0.863
4	42	58.20	94.43	38.4	78.57	0.000	0.554	0.349
5	58	146.86	121.50	20.9	84.48	−0.001	1.500	0.791
6	62	114.76	114.19	0.0	85.48	−0.001	1.297	0.792
7	57	127.61	111.87	14.1	84.21	0.000	1.124	0.688
8	62	91.76	86.18	6.5	87.10	0.000	0.970	0.960
9	60	91.72	97.86	6.3	88.33	0.000	1.000	0.614
10	64	81.05	94.04	13.8	89.06	0.000	1.138	0.924
11	62	82.43	81.72	0.0	88.71	−0.001	1.246	0.851
12	110	134.86	108.84	23.9	77.27	0.000	0.884	0.808
3–12	637	111.50	100.52	10.9	84.46	−0.001	1.140	0.732

[a]The likelihoods of correct predictions, if the effluent concentrations are either below or above the thresholds for secondary wastewater treatment. The BOD and SS concentrations for compliance are 20 and 30 mg/L, respectively; [b]concentration_predicted = $a \times$ concentration_measured^2 + $b \times$ concentration_measured + c, where $c = 0$ and r^2 = coefficient of determination.
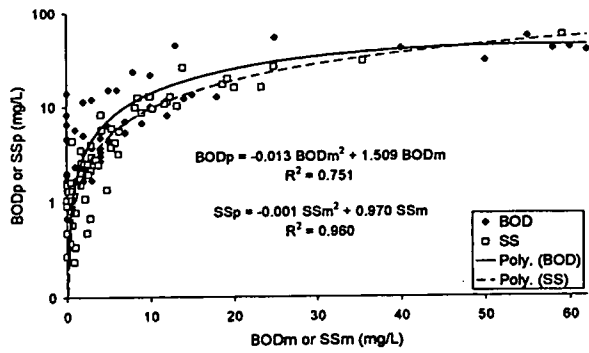
Figure 1. Regression analysis between the measured 5-day at 20°C N-Allylthiourea biochemical oxygen demand BOD$_{mea-sured}$ (BODm) and BOD$_{predicted}$ (BODp), and between the measured suspended solids SS$_{measured}$ (SSm) and SS$_{predicted}$ (SSp) for Filter 8. The case base contained the input variables turbidity, conductivity, redox potential, and the outflow water temperature. The following SS entries are beyond the displayed range: (3.8, 0.023), (70.8, 55.234), and (82.1, 73.32).

where x is the local difference; f is the function, which converts the local difference into the local similarity; and SDV$_i$ is the standard deviation of the differences of variable i found in the case base of past cases.

$$\text{Glob\_sim} = \Sigma[(\text{local\_sim}_i * w_i)/\Sigma w_i \times 100] \quad (3)$$

where: i is $1, 2, \ldots, n$; n is the number of variables used to represent a case; w_i is the weighting associated with variable i; and Local_sim$_i$ is the local similarity of the past case and problem case for variable i.

When the global similarity of each past case with the problem case is found, the past cases can be ranked in order of their corresponding sum to decide which of the past cases would be deemed similar enough to be selected for adaptation. The three to five past cases with the highest similarity rankings were chosen in this study. Tests undertaken on different sets of data show that between two and six cases are usually sufficient to achieve the best performance. The CBR usually requires a relatively large data set for optimization exercises.

Equations (4) and (5) show how a prediction is made for the target variables of the problem case by combining the numerical value of the target variable for the three to five selected cases.

$$\text{Proportion } P_j = \text{Glob\_sim}_j/\text{Glob\_sim}_T \quad (4)$$

where: j is 1, 2, 3, 4, or 5; P_j is the proportion of the prediction that is obtained from the past case j; and Glob_sim$_T$ is the sum of the global similarities of the three to five selected cases.

$$\text{Prediction } P = \Sigma(P_j \times \text{TV}_j) \quad (5)$$

where P_j is the proportion of the prediction that is obtained from the past case j; and TV$_j$ is target variable of past case j.

CBR RESULTS AND DISCUSSION

Correlation analysis

Table 1 summarizes the findings from a correlation analysis comprising input (turbidity, conductivity, redox potential, outflow water temperature, dissolved oxygen, and pH) and target (BOD and SS) variables. These findings are used for a subsequent CBR analysis. Correlations were strong between BOD and turbidity, SS and turbidity, and SS and conductivity (at the 1% significance level). Therefore, turbidity and conductivity are likely to be the most important input variables.

Comparison of different filters

Table 2 shows the application of a CBR system for the prediction of the outflow BOD and SS. Figure 1 visualizes the regression analysis between measured and predicted BOD and measured and predicted SS for Filter 8 (typical UK reed bed; Lee *et al.* 2005). The associated case base contained the following input variables: turbidity, conductivity, redox potential, and outflow water temperature. The application of second-order polynomial trendlines results in very good fits for both target variables.

The likelihoods of correct predictions if the effluent concentrations are either below or above the thresholds for secondary wastewater treatment are also shown in

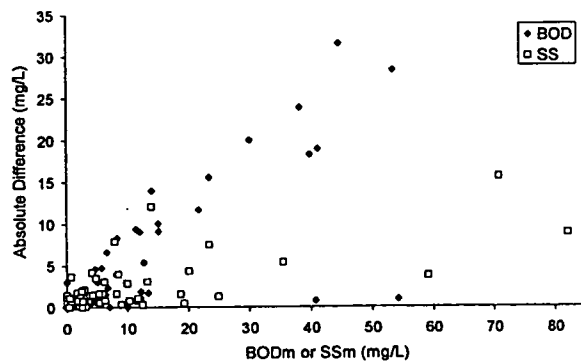**Figure 2.** Distribution of absolute differences between measured and predicted concentrations for 5-day at 20°C N-Allylthiourea biochemical oxygen demand (BODm) and measured and predicted suspended solids (SSm) for Filter 8. The case base contained the input variables turbidity, conductivity, redox potential, and the outflow water temperature. The BOD entry (24.88, 75.12) is beyond the displayed range.

Table 3. Comparison between extended storage (Filters 1 and 2) and Constructed treatment wetlands (Filters 3 to 11) for a similar retention time: case-based reasoning (CBR) applied to predict the 5-day at 20°C N-Allylthiourea biochemical oxygen demand (BOD) and the suspended solids (SS) concentrations with the input variables turbidity (NTU), conductivity (μS), redox potential (mV) and the outflow water temperature (°C).

Filter no.	No. of cases	Mean concentration_measured	Mean concentration_predicted	Error (%)	Correct prediction of compliance (%)[a]	a[b]	b[b]	r[2b]
			CBR for BOD (mg/L)					
1–2	109	35.52	35.16	1.0	68.81	−0.005	1.282	0.249
3–11	528	11.66	11.31	3.1	87.88	−0.001	1.083	0.423
			CBR for SS (mg/L)					
1–2	132	304.60	243.40	25.1	84.85	0.000	0.968	0.510
3–11	527	106.60	98.80	7.9	85.96	−0.001	1.202	0.724

[a]The likelihoods of correct predictions, if the effluent concentrations are either below or above the thresholds for secondary wastewater treatment. The BOD and SS concentrations for compliance are 20 and 30 mg/L, respectively. [b]concentration_predicted = $a \times$ concentration_measured^2 + $b \times$ concentration_measured + c, where $c = 0$ and r^2 = coefficient of determination.

Table 2. The BOD and SS concentrations for compliance are 20 and 30 mg/L, respectively. The correct predictions of compliance were all >77%. The probabilities are therefore all at least by 0.27 higher in comparison to pure guessing. The predictions are encouraging and support the potential for future use of CBR as a management tool for the day-to-day process control.

Figure 2 shows the distribution of prediction errors for a selected CBR result (Filter 8; typical UK reed bed; Cooper et al. (1996)) visualized in Fig. 1. Where the distribution is clustered, the errors are least. This is promis-

ing, as it appears that if the density of the case base can be increased, then the error can be reduced further (see below). More cases are likely to lead to a better CBR performance.

Moreover, research has shown that new case-based methods that utilize the cluster information of data sets are likely to be superior to conventional CBR systems (Verdenius and Broeze, 1999; Roh et al., 2003; Yang et al., 2004). Despite the greater variability of SS in contrast to BOD (Lee et al., 2005), SS has smaller absolute differences between measured and predicted concentra-

Table 4. Optimization of input variable combinations for Filters 3 to 12: Case-based reasoning (CBR) applied to predict the 5-day at 20°C N-Allylthiourea biochemical oxygen demand (BOD) and the suspended solids (SS) concentrations.

Input variables	No. of cases	Mean concentration_measured	Mean concentration_predicted	Error (%)	Correct prediction of compliance (%)[a]	a[b]	b[b]	r[2b]
			CBR for BOD (mg/L)					
1	640	11.60	11.48	1.0	82.66	−0.005	0.874	0.092
1+2	640	11.60	14.33	19.1	80.94	0.000	0.543	−0.015
1+2+3	640	11.60	11.24	3.2	84.84	−0.006	0.997	0.236
1+2+3+4	640	11.60	11.65	0.4	87.03	−0.007	1.125	0.396
1+2+3+4+5	640	11.60	11.39	1.8	85.47	−0.006	1.059	0.413
			CBR for SS (mg/L)					
1	637	111.50	124.71	10.6	54.47	−0.001	0.964	−0.092
1+2	637	111.50	102.76	8.5	85.56	−0.001	1.174	0.685
1+2+3	637	111.50	97.15	14.8	85.71	−0.001	1.160	0.714
1+2+3+4	637	111.50	100.52	10.9	84.46	−0.001	1.140	0.732
1+2+3+4+5	637	111.50	98.80	16.9	82.52	−0.001	1.149	0.706

The case base contained the following input variables: 1 = turbidity (NTU); 2 = conductivity (μS); 3 = redox potential (mV); 4 = outflow water temperature (°C); 5 = dissolved oxygen (mg/L); [a]the likelihoods of correct predictions, if the effluent concentrations are either below or above the thresholds for secondary wastewater treatment. The BOD and SS concentrations for compliance are 20 and 30 mg/L, respectively; [b]concentration_predicted = $a \times$ concentration_measured^2 + $b \times$ concentration_measured + c, where $c = 0$ and r^2 = coefficient of determination.

tions (Fig. 2) than BOD. It follows that relatively high raw data variability is not necessarily an indication for an underperforming CBR analysis as can be intuitively expected.

The system typically achieved an 85% success rate for predicting whether or not the water samples met regulatory requirements (Table 2). The theoretical probability of the system predicting a correct answer is 0.5 (right or wrong), based on the number of cases below or above the threshold in the case base and the actual concentration of the target variable of the test cases used. In comparison, prediction errors of up to 54% were recorded for an unrelated project previously, compared to 17% corresponding to pure guessing (Wendler and Bach, 2004).

Table 2 suggests that the system is fit for purpose considering relatively high coefficients of determination r^2, particularly for measured and predicted SS. However, the system requires optimization to further increase the accuracy. Optimization measures would be certain to in-

clude the selection of cases with greater process control and data availability. The aim would be to reduce the number of unknown variables.

Extended storage vs. constructed wetlands

Table 3 shows a CBR comparison between extended ◀ (T3) storage (Filters 1 and 2) and constructed treatment wetlands (Filters 3 to 11) characterized by similar retention times. CBR was applied to predict the BOD and SS concentrations. The case base contained turbidity, conductivity, redox potential, and outflow water temperature as input variables. Concerning the prediction of BOD, relatively high likelihoods of correct predictions were achieved for the wetlands but not for extended storage. This is surprising, considering that extended storage is a much simpler process with a reduced number of unknown variables. However, the buffering capacity of the system is low, and data variability is subsequently higher than for the wetlands.

Table 5. Unbiased assessment of data subsets for Filters 3 to 12: Case-based reasoning (CBR) applied to predict the 5-day at 20°C N-Allylthiourea biochemical oxygen demand (BOD) and the suspended solids (SS) concentrations with the input variables turbidity (NTU), conductivity (μS), redox potential (mV), and the outflow water temperature (°C).

Selection	No. of cases	Mean concentration_measured	Mean concentration_predicted	Error (%)	Correct prediction of compliance (%)[a]	a[b]	b[b]	r[2b]
CBR for BOD (mg/L)								
1 out of 15	40	11.05	13.52	18.3	83.33	−0.008	1.106	0.052
1 out of 10	58	11.05	11.15	0.9	95.00	−0.005	0.976	0.476
1 out of 6	90	11.05	10.46	1.7	90.00	−0.011	1.216	0.363
1 out of 5	116	11.05	10.87	1.7	91.67	−0.010	1.157	0.231
1 out of 4	144	11.05	10.45	5.7	93.33	−0.003	0.826	0.552
1 out of 3	194	11.05	12.30	10.2	93.33	−0.010	1.399	0.658
1 out of 2	290	11.05	10.48	5.4	90.00	−0.007	1.060	0.585
2 out of 3	385	11.05	9.28	19.1	90.00	0.011	1.208	0.564
3 out of 4	435	11.05	10.15	8.9	93.33	−0.012	1.369	0.655
4 out of 5	464	11.05	10.99	0.5	95.00	−0.010	1.359	0.805
1 out of 1	580	11.05	11.05	0.0	95.00	−0.013	1.509	0.751
CBR for SS (mg/L)								
1 out of 15	39	91.76	85.76	7.0	69.4	−0.001	0.952	0.092
1 out of 10	57	91.76	68.84	33.3	75.8	0.000	0.628	0.400
1 out of 6	97	91.76	84.07	9.1	79.0	0.000	0.885	0.761
1 out of 5	115	91.76	86.99	5.5	77.4	0.000	0.869	0.686
1 out of 4	144	91.76	79.28	15.7	85.5	−0.001	1.061	0.810
1 out of 3	192	91.76	101.97	10.0	85.5	0.000	0.956	0.872
1 out of 2	288	91.76	85.59	7.2	90.3	0.000	0.990	0.923
2 out of 3	383	91.76	86.83	5.7	87.1	0.000	0.973	0.925
3 out of 4	433	91.76	89.10	3.0	83.9	0.000	1.022	0.936
4 out of 5	461	91.76	81.18	13.0	88.7	0.000	1.041	0.939
1 out of 1	575	91.76	86.18	6.5	87.1	0.000	0.970	0.960

[a]The likelihoods of correct predictions, if the effluent concentrations are either below or above the thresholds for secondary wastewater treatment. The BOD and SS concentrations for compliance are 20 and 30 mg/L, respectively; [b]concentration_predicted = $a \times$ concentration$_{measured}^2$ + $b \times$ concentration$_{measured}$ + c, where $c = 0$ and r^2 = coefficient of determination.

Optimization of the numbers and type of input variables

T4 ⟩➤   Table 4 summarizes the findings of an input variable combination optimization exercise. The purpose was to estimate both BOD and SS with as few input variables as possible to reduce costs and effort. The case base therefore contained the following input variables in order of priority (Table 1): turbidity, conductivity, redox potential, outflow water temperature and dissolved oxygen. All predictions of compliance were high except for the prediction of SS with turbidity alone despite a relatively high corresponding correlation coefficient of 0.531 (Table 1). It follows that the first two variables (turbidity and conductivity) that are inexpensive to obtain are sufficient to predict the most important, expensive, and time-consuming to obtain target variables BOD and SS.

Optimization of the size of the input database

T5 ⟩➤   The data set of this case study has been described in detail by Lee *et al.* (2005). Table 5 shows an unbiased assessment of data subsets to optimize the size of the input database. The case base contained turbidity, conductivity, redox potential, and outflow water temperature as input variables, because the combination of these variables has the highest mean prediction compliance percentage (Table 4). The data subsets were selected systematically (in sequence; x out of y, where x ≤ y), but technically at random. The probabilities of all filters and input variables to contribute to any calculation were statistically the same; 0.1 and 0.25, respectively.

In contrast to traditional curve fitting techniques, the CBR system is capable of picking up rapidly fluctuating trends among the different input variables (Lee *et al.*, 2005), because the distribution of cases is relatively dense (Table 5). Only neighboring cases will be picked up for relatively small case bases. In comparison, a large case base is likely to be beneficial, if data are sparse and not erratic. This may be the case for most data sets in physics and mechanical engineering but not environmental engineering and science. It follows that the distribution and density of cases, and the relationships between the variables (gradual or erratic trends) should be considered when selecting the optimum number of cases.

CBR is well suited for relatively highly variable water quality data sets such as those from constructed treatment wetlands. Little domain knowledge is required, and the optimum number of cases can be selected by trial and error (Table 5). Findings show that the case study data set could be reduced by 75%, and that BOD and SS can still be predicted reasonably well with four inexpensive variables measured only every 2 weeks. Nevertheless, the

CBR should be calibrated with cases of known output to minimize the error.

CONCLUSIONS

CBR was successfully applied to predict BOD and SS, but there is room for improvement by applying optimization techniques to control the variances of the input variables. This would lead to a relatively accurate data set that should be used to calibrate the system. BOD and SS are expensive to estimate, and can be cost-effectively controlled by applying CBR with the input variables turbidity and conductivity and possibly also redox potential.

The CBR system showed better performance for constructed wetlands ("buffers" due to biomass between aggregates) in comparison to extended storage (no "buffer" capacity). Small data sets based on 2-week sampling were sufficient to monitor the water quality.

This paper demonstrates to the reader the successful application of CBR to typical "black box" systems such as constructed wetlands governed by biochemical processes. This paper may also find use as a learning aid for water and environmental engineers and managers.

ACKNOWLEDGMENTS

REFERENCES

AAMODT, A., and PLAZA, E. (1994). Case-based reasoning: foundational issues, methodological variations, and system approaches. *AI Communications* **7**, 39–59.

AMERICAN PUBLIC HEALTH ASSOCIATION (APHA). (1995). *Standard Methods for the Examination of Water and Wastewater*, 19th ed. Washington, DC: author.

ARDITI, D., and TOKDEMIR, O.B. (1999). Comparison of case-based reasoning and artificial neural networks. *J. Comp. Civ. Eng.* **13**, 162–168.

COLILLA, M., FERNANDEZ, C.J., and RUIZ-HITZKY, E. (2002). Case-based reasoning (CBR) for multicomponent analysis using sensor arrays: Application to water quality evaluation. *Analyst* **127**, 1580–1582.

COOPER, P.F., JOB, G.D., GREEN, M.B., and SHUTES, R.B.E. (1996). *Reed Beds and Constructed Wetlands for Wastewater Treatment*. Swindon, UK: WRc plc.

GERNAEY, K.V., VAN LOOSDRECHT M.C.M., HENZE, M., LIND, M., and JØRGENSEN, S.B. (2004). Activated

sludge wastewater treatment plant modeling and simulation: state of the art. *Environ. Model. Software* **19**, 763–783.

LEE, B.-H., SCHOLZ, M., and HORN, A. (2005). Constructed wetlands: Treatment of concentrated storm water runoff (Part A). *Environ. Eng. Sci.*

NUNEZ, H., SANCHEZ-MARRE, M., CORTES, U., COMAS, J., MARTINEZ, M., RODRIGUEZ-RODA, I., and POCH, M. (2004). A comparative study on the use of similarity measures in case-based reasoning to improve the classification of environmental system situations. *Environ. Model. Software* **19**, 809–819.

POLICASTRO, C.A., CARVALHO, A.C.P.L.F., and DELBEM, A.C.B. (2004). A hybrid case-based reasoning approach for monitoring water quality. *Lect. Notes Comput. Sci.* **3029**, 492–501.

RODA, I.R., SANCHEZ-MARRE, M., COMAS, J., CORTES, U., and POCH, M. (2001). Development of a case-based system for the supervision of an activated sludge process. *Environ. Technol.* **22**, 477–486.

RODRIGUEZ-RODA, I., SANCHEZ-MARRE, M., COMAS, J., BAEZA, J., COLPRIM, J., LAFUENTE, J., CORTES, U., and POCH, M. (2002). A hybrid supervisory system to support WWTP operation: implementation and validation. *Water Sci. Technol.* **45**, 289–297.

ROH, T.H., OH, K.J., and HAN, I. (2003). The collaborative filtering recommendation based on SOM cluster-indexing CBR. *Expert System Appl.* **25**, 413–423.

SANCHEZ-MARRE, M., CORRES, U., RODA, I.R., and POCH, M. (1999). Sustainable case learning for continuous domains. *Environ. Model. Software* **14**, 349–357.

SCHOLZ, M. (2003). Case study: Design, operation, maintenance and water quality management of sustainable storm water ponds for roof runoff. *Bioresource Technol.* **95**, 269–279.

SCHOLZ, M., HÖHN, P., and MINALL, R. (2002). Mature experimental constructed wetlands treating urban water receiving high metal loads. *Biotechnol. Prog.* **18**, 1257–1264.

VERDENIUS, F., and BROEZE, J. (1999). Generalized and instant-specific modeling for biological systems. *Environ. Model. Software.* **14**, 339–348.

WATSON, I. (1997). *Applying Case-based Reasoning Techniques for Enterprise Systems.* San Francisco, CA: Morgan Kauhmann.

WENDLER, J., and BACH, J. (2004). Recognizing and predicting agent behavior with case-based reasoning. *Lect. Notes Comput. Sci.* **3020**, 729–738.

YANG, B.S., HAN, T., and KIM, Y.S. (2004). Integration of ART-Kohonen neural network and case-based reasoning for intelligent fault diagnosis. *Expert Syst. Appl.* **26**, 387–395.

A COMPARATIVE STUDY: PREDICTION OF CONSTRUCTED TREATMENT WETLAND PERFORMANCE WITH K-NEAREST NEIGHBORS AND NEURAL NETWORKS

BYOUNG-HWA LEE[1] and MIKLAS SCHOLZ[1,*]

[1]*Institute for Infrastructure and Environment, School of Engineering and Electronics,*
The University of Edinburgh, The King's Buildings, Edinburgh EH9 3JL, Scotland, United Kingdom
(*Corresponding author: Phone: +44 131 6 506780; Fax: +44 131 6 506554; E-mail: M.Scholz@ed.ac.uk)

Abstract. K-nearest neighbours (KNN), support vector machine (SVM) and self-organizing map (SOM) were applied to predict five-day @ 20 C N-Allylthiourea biochemical oxygen demand (BOD) and suspended solids (SS), and to assess novel alternative methods of analyzing water quality performance indicators for constructed treatment wetlands. Concerning the accuracy of prediction, SOM showed a better performance compared to both KNN and SVM. Moreover, SOM had the potential to visualize the relationship between complex biochemical variables. However, optimizing the SOM requires more time in comparison to KNN and SVM because of its trial and error process in searching for the optimal map. The results suggest that BOD and SS can be efficiently estimated by applying machine learning tools with input variables such as redox potential and conductivity, which can be monitored in real time. Their performances are encouraging and support the potential for future use of these models as management tools for the day-to-day process control.

Keywords: constructed treatment wetland; effluent standards; black box system; k-nearest-neighbors; neural network; self-organizing map; support vector machine; cross-validation; biochemical oxygen demand; suspended solids.

1. Introduction

1.1. PROJECT PURPOSE

The purpose of this research project was to examine the goodness of applying K-nearest neighbours (KNN), support vector machine (SVM) and self-organizing map (SOM) to predict the outflow water quality of experimental constructed treatment wetlands by comparing the accuracy of these models. Additionally, this study describes how machine learning can be used for water treatment monitoring and assessment. The objectives are to assess
1. the most appropriate method for assessing the performance of constructed treatment wetlands, considering both the accuracy of estimations and input costs;

2. the potential of KNN, SVM and SOM for analyzing biochemical performance data;
3. the optimization of input variables associated with predictive models; and
4. the potential use of KNN, SVM and SOM as teaching tools to enhance the understanding of 'black box' systems.

1.2. MACHINE LEARNING APPLIED TO WASTEWATER TREATMENT PROCESSES

Machine learning techniques are part of the research area of artificial intelligence. Computer programs are created by the analysis of data sets. Machine learning overlaps with statistics, but is predominantly concerned with the algorithmic complexity of computational implementations. There are a wide range of applications including web search engines, medical and biological research, economics, linguistics, sport, robotics and control systems for complex environmental engineering processes.

Constructed treatment wetlands are often seen as complex 'black box' systems, and the processes within an experimental wetland are difficult to model due to the complexity of the relationships between most water quality variables (Gernaey *et al.*, 2004). However, it is necessary to monitor, control and predict the treatment processes to meet environmental and sustainability policies, and regulatory requirements such as secondary wastewater treatment standards (Scholz, 2004).

The measurement of five-day @ 20 C N-Allylthiourea biochemical oxygen demand (BOD) and suspended solids (SS) concentrations is widely applied for wastewater before and after treatment, as they give a general indication of the water quality status. However, taking BOD measurements can both be expensive

1

(measurements are labor intensive and capital costs of modern on-line equipment are relatively high; approximately £15,000) and only of historical value (results are not available until five days after the sample has been taken). Furthermore, it takes at least two, possibly even three hours of costly manual labor to obtain SS concentrations, which unfortunately only correlate insignificantly with turbidity (see below and Scholz, 2003b). A certain SS value may represent virtually millions of fine clay particle (i.e. high turbidity) or only a few large sand grains (i.e. low turbidity). Therefore, an indirect method of prediction of BOD and SS, if it could be made reliable enough, would be advantageous.

A variety of machine learning methods such as k-nearest-neighbors (KNN) and artificial neural networks (ANN) have been widely used in a broad range of domains including wastewater treatment engineering. The memory-based KNN model is a simple methodology defined by a set of examples for which the outcomes are known (Hand et al., 2001; Alpaydin, 2004). Moreover, the KNN model estimates the outcome by finding k examples that are closest in distance to the target point. The prediction value can be obtained by averaging values of the k nearest neighbors. The determination of the optimal value for k is essential in building the KNN model, because it should be the maximum number of neighbors with the minimum possible error (Ruiz-Jimenez et al., 2004).

The KNN model has been compared with advanced neural networks, and tested for a wide range of areas such as medical diagnosis, chemical analysis and remote sensing (Carpenter and Markuzon, 1998; Dong et al., 2005; Ruiz-Jimenez et al., 2004). In the case of the application of KNN models in the wastewater treatment industry, Belanche et al. (2000) employed a KNN model for reference purposes in predicting sludge bulking.

Neural networks are relatively effective in simulating and predicting water treatment processes. The advantages of ANN are as follows: ease of use, rapid prototyping, high performance, minor assumptions, reduced expert knowledge required, non-linearity, multi-dimensionality and easy interpretation (Iovine, 1998; Werner and Obach, 2001).

Artificial neural networks such as feed-forward neural networks were developed to predict the effluent concentrations including BOD, chemical oxygen demand (COD), and SS for wastewater treatment plants (Grieu et al., 2005; Hamed et al., 2004; Onkal-Engin et al., 2005), and to control water treatment processes automatically by modeling, for example, the alum dose (Maier et al., 2004). These studies have shown that ANN could be applied to establish a mathematical relationship between variables describing a process state and different measured quantities.

Although ANN methods are cost-effective and highly reliable in analyzing processes, traditional neural networks have suffered from their inherent drawbacks; i.e. over-training, local minima, poor generalization and difficulties in their practical application (Lu and Wang, 2005). The SVM, a supervised machine learning technique, developed by Vapnik (1995), can provide a novel approach to improve the generalization performance of neural networks. The SVM technique uses a linear model to implement nonlinear class boundaries through mapping input vectors into a high-dimensional feature space. The SVM seeks this linear model (i.e. the maximum margin hyperplane), which gives the maximum separation between decision classes. The 'support vector' is selected from the training data set, and its data are located closest to the maximum margin hyperplane (Vapnik, 1995).

Originally, SVM models have been applied for pattern recognition problems. However, along with the introduction of Vapnik's ε insensitive loss function, SVM also have been extended to solve non-linear regression estimation problems (Pai and Hong, 2005; Vapnik, 1995). It classifies the data based on the similarity between the examples measured by the similarity function or kernel function. This function can be chosen according to the problem at hand, and thus

2

making the algorithm flexible in handling a wide variety of problems (Dubey et al., 2005). Moreover, previous studies demonstrated that the SVM is superior to the conventional neural networks in predicting chemical and biological variables (Liu et al., 2004; Lu and Wang, 2005). However, this novel method has not yet been applied in the field of wastewater treatment including constructed treatment wetlands.

The SOM (Kohonen, 2001), which is based on an unsupervised learning algorithm, uses powerful pattern analysis and clustering methods, and at the same time provides excellent visualization capabilities (Garcia and Gonzalez, 2004). The term 'self organizing' refers to the ability to learn and organize information without being given the corresponding dependent output values for the input pattern (Mukherjee, 1997). The SOM is able to map a structured, highly dimensional data set onto a much lower dimensional network in an 'orderly' fashion, and organizes itself by adjusting the weights according to the input patterns (Lu and Lo, 2002). It offers the distinctive ability to gather knowledge by detecting the patterns and relationships from a given data set, learning from relationships and adapting to change. The SOM potentially outperforms current methods of analysis, because it can successfully deal with the non-linearity of a system, handle 'noisy' or irregular data and be easily updated (Hong et al., 2002).

Interesting approaches of SOM have been reported in the research area of water quality assessment. The SOM models were developed to evaluate the state of water quality of a reservoir, and to predict the trophic status of coastal waters, showing a strong ability to identify the diversity between data (Aguilera et al., 2001; Gervrey et al., 2004).

Moreover, Verdenius and Broeze (1999) used this model as an indexing mechanism in case-based reasoning algorithms to control wastewater treatment processes, and it was employed to diagnose the diverse states of a wastewater treatment plant (Garcia and Gonzalez, 2004; Hong et al.,

2002). These studies demonstrated that the SOM can assist a process engineer by analyzing multi-dimensional data and simplifying them into visual information that can be easily applied to control plant performance. However, applications of SOM in water treatment process control are relatively new and were not implemented as much as traditional neural networks such as free forward neural networks (Grieu et al., 2005; Hamed et al., 2004; Mohanty et al., 2002).

It follow that comparative studies of traditional KNN models with novel neural networks (e.g., SVM and SOM) applied to predict wastewater treatment performances are required to advance operation process control. Moreover, ANN should be used to find out if these models can be effectively applied to predict water quality variable such as BOD and SS effluent concentrations in wastewater treatment systems using their potential for data classification and clustering.

2. Methodology and Software

2.1. EXPERIMENTAL DATA AND VARIABLES
Twelve wetland filters (Figure 1) were operated to assess the system performance to treat gully pot liquor in a cold climate.
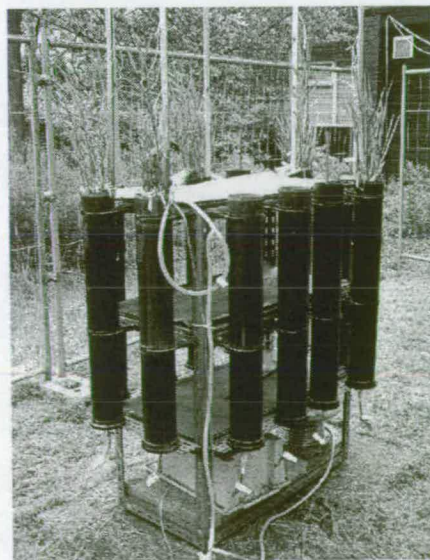

Figure 1. Constructed treatment wetland rig (The King's Buildings campus; The University of Edinburgh) in May 2004.

3

Gully pot liquor is concentrated surface runoff that is detained in the wet gully pot until it overflows into the sewer due to incoming surface runoff from new rainfall events. Design, operation and monitoring methods of the system were explained previously (Scholz, 2004). Different packing order arrangements of filter media and plant roots were used in the wetland filters (Tables 1). In comparison, Filters 3, 5, 7 and 9 are similar to gravel and slow sand filters, and Filters 4, 6, 8 and 10 are typical reed bed filters. Filters 11 and 12 are more complex in their design and operation (Table 1).

TABLE 1
Systematic and stratified experimental set-up of filter content and operation.

Filter number	Plan- ted	Me- dia[a]	Me- tals[b]	Aera- ted	High loading[c]
1	No	1	No	No	No
2	No	1	Yes	No	No
3	No	2	No	No	No
4	Yes	2	No	No	No
5	No	3	No	No	No
6	Yes	3	No	No	No
7	No	2	Yes	No	No
8	Yes	2	Yes	No	No
9	No	3	Yes	No	No
10	Yes	3	Yes	No	No
11	Yes	3	Yes	Yes	No
12	Yes	3	Yes	Yes	Yes

[a]1=no media, 2=standard, 3=addition of Filtralite (light expanded clay) and Frogmat (barley straw); [b]addition of hydrated copper and nickel nitrate; [c]Filter 12 received approximately 153% additional inflow in comparison to Filter 11, for example.

Experimental data were collected by monitoring the effluent concentrations of the filters including BOD and SS for more than two years (09/09/02 to 21/09/04). The amount of data points used was comparable and even greater than those used in other prediction models (Aguilera et al., 2001; Liu et al., 2004). These data were stored in the data base together with up to six input variables; turbidity (NTU), conductivity (S), redox potential (mV), outflow water temperature (°C), dissolved oxygen, DO (mg L^{-1}) and pH (-). The corresponding output variables were BOD (mg L^{-1}) or SS (mg L^{-1}). The input variables were selected according to their goodness of correlation with both BOD and SS (Scholz, 2003a), because they are both more cost-effective and easier to measure in comparison to the output variables.

2.2. K-NEAREST NEIGHBORS

A KNN model used to predict the effluent BOD and SS concentrations of the system was created using MATLAB 7.0. The KNN model is based on averaging of the outcomes of the k-nearest neighbors. The local similarity (i.e. the similarity of a past case and the problem case with respect to only one variable) is found via a mathematical function of the difference between each past case and a problem case. The Gaussian function (bell-shaped curve) used to map the local difference onto the local similarity is defined in Equation 1, which applies fuzzy theory (Dubois and Prade, 1998). This function has a tuning parameter α, which is used to determine the flatness of the smoothing function.

$$f(x) = e^{\left(-0.5\left(\frac{x}{\alpha \times SDV_i}\right)^2\right)} \quad (1)$$

where:
f = the function, which converts the local difference into the local similarity;
x = the local difference between each past case and a problem case;
α = the tuning parameter; and
SDV_i = the standard deviation of the local differences of variable i.

The global similarity (i.e. the similarity between the past case and the problem case considering all variables) can be found from the local similarity of each variable. Each local similarity is first multiplied by a weighting factor that corresponds to the importance of that variable in predicting the output.

An algorithm proposed by Duch and Grundzinski (1999) was used to identify feature weightings. For the initial ranking of features, all weighting factors are set to one, and evaluation with a single feature turned off (i.e. zero) is made for all features. Thus, ranking is done in the same way as the feature dropping selection method (Duch and Grudzinski, 1999). The important feature has a fixed weighting factor of one and the optimal weighting value for the second factor in the ranking is determined by the search procedure. The remaining factors are all fixed to one. The search is

4

implemented by means of the leave-one-out (LOO) cross validation process (Kohavi, 1995).

When the global similarity of each past case with the problem case is found, the past cases can be selected by the first k closest cases. The tuning parameter α of the Gaussian function and the k value were determined by LOO cross validation in the training phase (Duch and Grudzinski, 1999).

2.3. SUPPORT VECTOR MACHINE

In SVM, the basic idea is to map original data into a feature space, which has a large number of dimensions via a non-linear mapping function $\phi_i(x)$, which is usually unknown, and then carry out linear regression in the feature space (Vapnik, 1995). Hence, the regression addresses a problem of estimating a function based on a given data set (Equation 2).

$$G = \left\{ (x_i, y_i) \right\}_i^l \quad (2)$$

where:

G = data set;

x_i = input vector; and

y_i = desired values, which are produced from $\phi_i(x)$, a non-linear mapping function.

The SVM approximates the optimum decision function using Equation 3:

$$f(x) = \sum_{i=1}^{l} w_i \phi_i(x) + b \quad (3)$$

where:

$f(x)$ = decision function;

$\phi_i(x)$ = non-linear mapping function representing the features of inputs; and

w and b = coefficients, which are estimated by minimizing the regularized risk function (Equation 4).

The regularized risk function R(C) is shown in Equation 4.

$$R(C) = C \frac{1}{l} \sum_{i=1}^{l} L_\varepsilon (y_i, f(x_i)) + \frac{1}{2} \|w\|^2 \quad (4)$$

where:

$R(C)$ = regularized risk function;

C = regularized constant determining the trade-off between the training error and the model flatness;

$\frac{1}{l} \sum_{i=1}^{l} L_\varepsilon (y_i, f(x_i))$ = empirical error measured by the ε-insensitive loss function (Equation 5);

y_i = desired values;

$f(x_i)$ = decision function; and

$\frac{1}{2} \|w\|^2$ = measurement of function flatness.

The ε-insensitive loss function is defined in Equation 5

$$L_\varepsilon (y_i, f(x_i)) = \begin{cases} |y_i - f(x_i)| - \varepsilon, & |y_i - f(x_i)| \ge \varepsilon \\ 0 \end{cases} \quad (5)$$

where:

L_ε = ε-insensitive loss function;

y_i = desired values;

$f(x_i)$ = decision function; and

ε = prescribed parameter.

By introducing the kernel function, Equation 3 can be transformed into the explicit Equation 6.

$$f(x) = \sum_{i=1}^{l} (\alpha_i - \alpha_i^*) K(x_i, x_j) + b \quad (6)$$

where:

$f(x)$ = decision function;

α, α_i = Lagrange multipliers; and

$K(x_i, x_j) = \phi(x_i) \times \phi(x_j)$ = kernel function in the feature space.

For the kernel function, there are several design choices such as the linear, polynomial and radial basis functions (RBF), and the sigmoid kernel. However, most of the previous research selected the RBF kernel, which non-linearly maps samples into a higher dimensional space, unlike the linear kernel (Dong et al., 2005). The RBF kernel is shown in Equation 7.

$$K(x_i, x_j) = \exp\left\{ -\gamma \|x_i - x_j\|^2 \right\} \quad (7)$$

where:

$K(x_i, y_i)$ = kernel function; and

γ = kernel parameter.

The detailed theoretical background to SVM was described by Vapnik (1995). In this study, the SVM^{light} was used due to its fast optimization algorithms and good potential for regression (Joachims, 1999).

Concerning the kernel function, RBF kernel was selected to analyze the cases, which show non-linear relationships between input and output data sets in this study. The RBF kernel contains the parameters γ, C and ε (see above). There are no general rules determining these parameters (Lu and Wang, 2005). A five-fold cross validation was conducted to find out appropriate parameters for training steps (Dong et al., 2005).

2.4. SELF-ORGANIZING MAP

A SOM consists of neurons, which are connected to adjacent neurons by neighborhood relations. In the training step, one vector x from the input set is chosen and all the weight vectors of the SOM are calculated using some distance measure such as the Euclidian distance (Kohonen, 2001). The neuron, whose weight vector is closest to the input x is called the best-matching unit (BMU), subscripted here by c (Equation 8):

$$\|x - m_c\| = \min\left\{\|x - m_i\|\right\} \quad (8)$$

where:

x = input vector;

m = weight vector; and

$\|\ \|$ = the distance measure.

After finding the BMU, the weighting vectors of the SOM are updated so that the BMU is moved closer to the input vector. The SOM update rule for the weight vector is shown in Equation 9. The detailed algorithm of the SOM can be found in Kohonen (2001) for theoretical considerations.

$$m_i(t+1) = m_i(t) + \alpha(t) h_{ci}(t)\left[x(t) - m_i(t)\right] \quad (9)$$

where:

$m(t)$ = weight vector indicating the output unit's location in the data space at time t;

$\alpha(t)$ = the learning rate at time t;

$h_{ci}(t)$ = the neighborhood kernel around the 'winner unit' c; and

$x(t)$ = an input vector drawn from the input data set at time t.

After the SOM has been trained, the map needs to be evaluated to find out if it has been optimally trained, or if further training is required. The SOM quality is usually measured with two criteria: quantization error (QE) and topographic error (TE). The QE is the average distance between each data point and its BMU, and TE represents the proportion of all data for which the first and second BMU are not adjacent with respect to the measurement of topology preservation (Kohonen, 2001).

In this study, a SOM toolbox (version 2) for Matlab 5.0 developed by the Laboratory of Information and Computer Science at the Helsinki University of Technology was used (Vesanto et al., 1999). After training the map with different map sizes, the optimum map size was determined on the basis of the minimum QE and minimum TE. The prediction was implemented by finding the BMU in the map for each test data set.

2.5. TRAINING AND TESTING OF DATA SETS

The overall data set (see above) was divided into training and testing data sub-sets. Each model was tested for each data sub-set associated with one wetland filter (Filters 3 to 12). The training of the corresponding model was performed with the data belonging to the remaining nine filters.

For example, when predicting the performance of Filter 3, the remaining nine data sub-sets (Filters 4 to 12) were used as training data. The validation process was therefore undertaken with independent data sub-sets that were partly significantly different to the testing data sub-set (see above). It follows that the models can be used for an entirely different set of gully pot treatment data in the future.

3. Results and Discussion

3.1. PERFORMANCE EVALUATION

When comparing the performances of different models, the scale-dependent measures based on the absolute error or squared error have been commonly used (Maier et al., 2004; Gevrey et al., 2004). In this study, the performances of each

6

model were measured by the mean absolute scaled error (MASE) method proposed by Hyndman and Koehler (2005), because it is independent of the scale of the data, less sensitive to outliers, easier to interpret and less variable for small samples compared to most of the other methods (see above). The MASE is defined in Equation 10.

$$MASE = \frac{MAE}{\dfrac{1}{n-1}\sum_{i=2}^{n}|m_i - m_{i-1}|}$$ (10)

where:

$MASE$ = mean absolute scaled error;

$$MAE = \frac{1}{n}\sum_{i=1}^{n}|m_i - p_i|;$$

M_i = measured values;

p_i = predicted values; and

n = number of data sets.

3.2. CORRELATION ANALYSIS

Table 2 summarizes the findings from a correlation analysis comprising input (turbidity, conductivity, redox potential, outflow water temperature, DO and pH) and target (BOD and SS) variables.

Correlations were all weak except between BOD and turbidity, SS and turbidity, and SS and conductivity (at 1% significance level). Therefore, turbidity and conductivity are likely to be the most important input variables.

3.3. OPTIMIZATION OF INPUT VARIABLES

When analyzing the data set with the KNN model, the optimal k value and weighting factors for all variables were determined by LOO cross validation. The selected k value was between 3 and 5 for most data sets, and weighting factors were different depending on the individual characteristics of the chosen case base.

For example, when predicting the outflow BOD concentration for Filter 8, the k value was fixed at 3, and the weighting factors 1.00, 0.78, 1.00, 0.30 and 0.78 were assigned for water temperature (°C), redox potential (mV), conductivity (μS), pH (-) and turbidity (NTU), respectively, of the outflow.

When conducting the SVM analysis, the parameters C and ε were identified by the five-fold cross-validation approach (see above). Theoretically, a small value of C will under-fit the training data, because the weight placed on the training data is too small, thus resulting in a large error for the test data set. On the contrary, when C is too large, the SVM model will be over-trained (Dong et al., 2005). The ε is set to be 0.1, when varying C in the one-time search method (Cao et al., 2003). There exists an optimum point for C, as shown in Figure 2(a). Thus C was determined to be 10 at the point of the lowest mean absolute error (MAE) value.

In general, the larger ε, the smaller is the number of support vectors and thus the sparser the representation of the solution. However, if ε is too large, it can deteriorate the accuracy of the training data set (Cao et al., 2003). According to Figure 2(b), parameter ε was fixed at 0.1.

Furthermore, γ of the RBF kernel was set to 0.2 according to Equation 11 (Chang and Lin, 2001; Dong et al., 2005).

$$\gamma = \frac{1}{n}$$ (11)

where:

γ = parameter of the kernel function; and

n = number of variables in the input data.

TABLE 2

Correlation coefficients from a correlation analysis comprising input (column headings) and target (row headings) variables.

Variable	Turbidity (NTU)	Redox potential (mV)	pH (-)	Conductivity (μS)	Temperature (°C)	Dissolved oxygen (mg L⁻¹)
BOD[a] (mg L⁻¹)	0.413	-0.338	-0.271	0.254	-0.120	-0.074

Variable	Conductivity (μS)	Turbidity (NTU)	Temperature (°C)	Redox potential (mV)	Dissolved oxygen (mg L⁻¹)	pH (-)
SS[b] (mg L⁻¹)	0.930	0.509	-0.322	-0.308	-0.127	0.013

[a]five-day @ 20 °C N-Allylthiourea biochemical oxygen demand; [b]suspended solids.
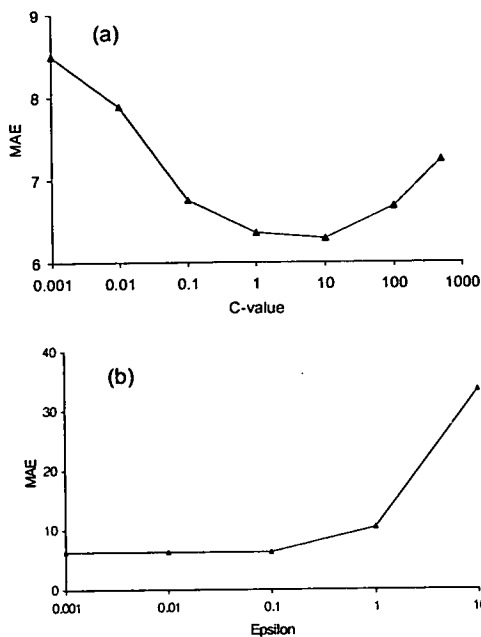
Figure 2. (a) C-value (ε=0.1), and (b) epsilon (C=10) versus mean absolute error (MAE) of the training set based on five-fold cross-validation.

In the SOM model, the map size is the most important factor to detect the differences of data. If the map is too small, it might not explain some important differences. On the contrary, it is possible to over-train the models (Leflaive *et al.*, 2005). After creating maps with several different map sizes, the optimum map size, which has lower errors for both QE and TE, was

chosen. For example, when predicting the BOD of Filter 8, the map size comprised 2304 units as shown in Table 3.

TABLE 3
Quantization error (QE) and topographic error (TE) for different self-organizing map sizes.

Map size	608	1508	2006	2304	2613	2911
QE	0.038	0.017	0.008	0.007	0.005	0.004
TE	0.108	0.091	0.124	0.091	0.148	0.120

Table 4 summarizes the findings of an input variable combination optimization exercise. The purpose was to identify the optimum combination of input variables by estimating both BOD and SS with as few input variables as possible to reduce the prediction error, sampling costs and effort. Therefore, the data set contained the following input variables in order of priority based on a correlation analysis (Table 2): turbidity, redox potential, pH, conductivity and outflow water temperature in terms of correlation with BOD; and conductivity, turbidity, outflow water temperature, redox potential and DO in terms of correlation with SS.

In the KNN model, best prediction results were obtained with five input variables for both BOD and SS. However, applying the

TABLE 4
Optimization of input attribute combinations for Filter 8: k-nearest-neighbors (KNN), support vector machine (SVM) and self-organizing map (SOM) applied to predict the five-day @ 20°C N-Allylthiourea biochemical oxygen demand (BOD) (mg L^{-1}) and the suspended solids (SS) (mg L^{-1}) concentrations. The training and test data sets contained the following input variables: 1 = turbidity (NTU); 2 = redox potential (mV); 3 = pH (-); 4 = conductivity (μS); 5 = outflow water temperature (°C) 6 = dissolved oxygen (mg L^{-1}). The figures for the best combinations of variables are underlined.

Input variables	Number of test data sets	KNN		SVM		SOM	
		MASE[a]	r[2b]	MASE[a]	r[2b]	MASE[a]	r[2b]
BOD prediction							
1	60	1.42	0.394	1.35	0.621	_0.29_	0.998
1+2	60	1.49	0.394	1.27	0.621	0.30	0.988
1+2+3	60	1.51	0.330	1.09	0.639	0.34	0.984
1+2+3+4	60	1.34	0.342	0.95	0.699	0.46	0.955
1+2+3+4+5	60	_1.01_	0.680	_0.94_	0.720	0.41	0.947
SS prediction							
4	64	0.55	0.936	0.38	0.959	_0.29_	0.999
4+1	64	0.44	0.943	0.40	0.950	0.30	0.992
4+1+5	64	_0.37_	0.948	0.39	0.950	0.31	0.980
4+1+5+2	64	0.39	0.955	0.39	0.954	0.31	0.969
4+1+5+2+6	64	0.39	0.951	_0.36_	0.949	0.39	0.956

[a]mean absolute scaled error; [b]prediction coefficient of determination.

8

SOM model, the BOD and SS predictions were most accurate with the single input variable turbidity and conductivity, respectively. The best combination of variables for each model is highlighted (underlined figures) in Table 4. Consequently, input variable combinations for each model were determined on the basis of this information.

3.4. TRAINING DATA SETS OF NEW AND MATURE SYSTEMS

The performance of sustainable urban drainage systems including constructed treatment wetlands is known to change significantly over time. A high level of treatment performance a few weeks after commissioning is followed by a rapid decline a few months later, before an equilibrium is reached after about a year (Scholz, 2003b). However, it can be argued that most engineered wetland systems in the urban water area never reach an equilibrium that is comparable to natural systems because they are frequently being disturbed by high fluctuations of inflow water quality (e.g., gritting and salting in the winter) and operational changes to the system (e.g., temporary flooding of the wetlands) as described elsewhere (Garcia *et al.*, 2004; Gernaey *et al.*, 2004; Scholz, 2003b; Scholz, 2004). The machine learning models used for this research take data fluctuations within the first year of operation into account, because two years of data are used for a very broad range of input variables.

3.5. COMPARISON OF APPLICATIONS

The prediction results of the outflow BOD and outflow SS using KNN, SVM and SOM models are summarized in Table 5. Figures 3 and 4 visualize the BOD and SS prediction performances of the KNN, SVM and SOM models for Filter 8 (typical UK reed bed, according to Scholz (2004)).

The results show that the BOD and SS concentrations are reasonably well predicted with given input variables. Despite the greater variability of SS in contrast to BOD (Scholz, 2004), SS has a smaller MASE value between measured and predicted
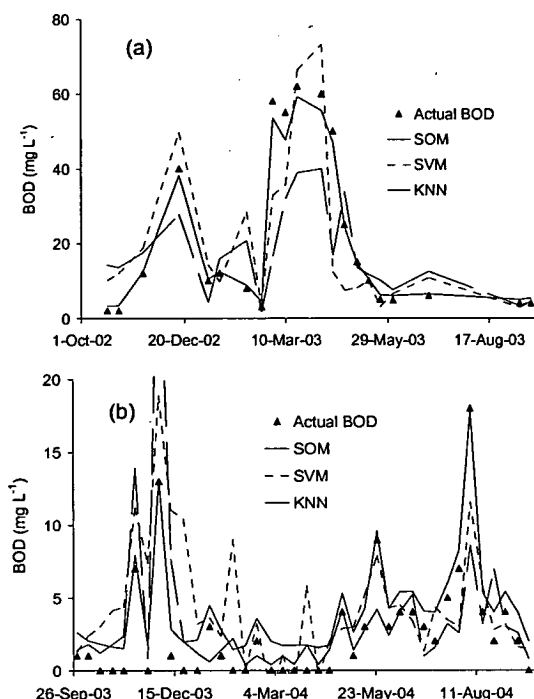
concentrations in comparison to BOD (Table 4 and 5).

Figure 3. Five-day @ 20°C N-Allylthiourea biochemical oxygen demand (BOD) of the outflow of Filter 8 predicted by k-nearest-neighbors (KNN), support vector machine (SVM) and self-organizing map (SOM) for (a) the first year (22/09/02 – 21/09/03), and (b) the second year (22/09/03 – 21/09/04) of wetland operation. The entry (32.6, 3-Dec-03) for the KNN prediction is beyond the displayed range.
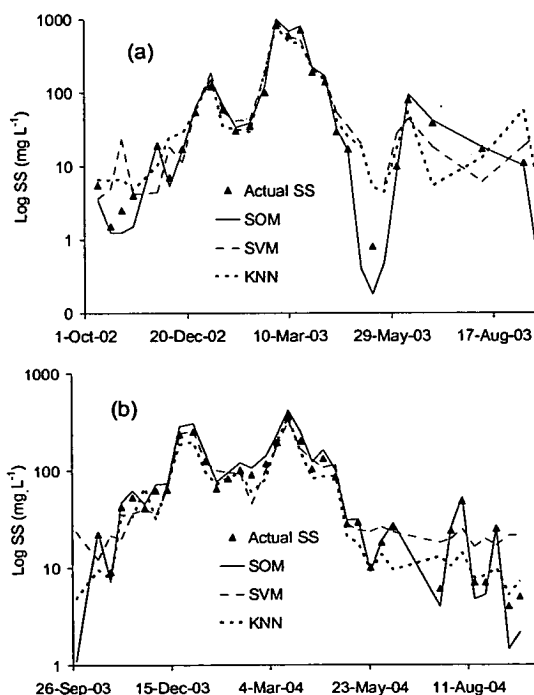

Figure 4. Suspended solids (SS) curve predicted by k-nearest-neighbors (KNN), support vector machine (SVM) and self-organizing map (SOM) for (a) the first year (22/09/02 – 21/09/03), and (b) the second year (22/09/03 – 21/09/04) of wetland operation.

The MASE from the BOD prediction with SOM, SVM and KNN are 0.36, 0.84 and 0.79, respectively. While the performance of the SVM model was not superior to that of KNN, the SOM model gave excellent prediction performance values compared to the other models (Table 6; Figures 3 and 4). To ensure the statistical significance of these findings, the prediction results were compared with each other and analyzed by using an analysis of variance (ANOVA). The ANOVA threshold for statistically significant findings is P<0.05. It follows that pairs of MASE associated with P≥0.05 can be regarded as similar. The analysis showed that the MASE of the SOM model were statistically different from those of SVM and KNN. However, the MASE of SVM and KNN were similar to each other, showing that the corresponding P-value was higher than 0.05. From the findings, it can be concluded that the SOM model outperformed the KNN and SVM models.

Figure 5 shows the regression analysis between measured and predicted BOD, and measured and predicted SS for Filter 8 using the SOM model. The associated data set contained turbidity and conductivity for both BOD and SS predictions. The application of linear trendlines results in very good fits for both target variables; the prediction coefficients of determination are 0.998 and 0.999 for BOD and SS, respectively.

Concerning the supervised and unsupervised methods, a previous study has shown that the prediction accuracy of unsupervised neural networks is lower than the one for supervised networks, as generally expected (Lee *et al.*, 2005). However, this result indicated that the SOM model is superior to the SVM model. Moreover, the SOM model

TABLE 5

Constructed treatment wetlands: k-nearest-neighbors (KNN), support vector machine (SVM) and self-organizing map (SOM) applied to predict the five-day @ 20°C N-Allylthiourea biochemical oxygen demand (BOD) (mg L^{-1}) and the suspended solids (SS) (mg L^{-1}) concentrations

Filter number	Number of test data sets	KNN		SVM		SOM	
		MASE[a]	$r^{2\,b}$	MASE[a]	r^{2b}	MASE[a]	r^{2b}
				BOD prediction			
3	55	1.02	0.461	0.98	0.384	0.77	0.997
4	58	1.01	0.681	1.07	0.713	0.17	0.994
5	59	0.58	0.696	0.67	0.666	0.35	0.994
6	61	0.76	0.798	0.83	0.643	0.44	0.997
7	58	0.78	0.609	0.77	0.503	0.85	0.999
8	60	1.01	0.680	0.94	0.720	0.29	0.998
9	57	0.76	0.544	0.90	0.431	0.20	0.998
10	60	0.71	0.744	0.87	0.513	0.41	0.999
11	59	0.79	0.645	0.96	0.451	0.37	0.985
12	115	0.88	0.342	0.87	0.213	0.24	0.997
3-12	642	0.79	0.550	0.84	0.463	0.36	0.888
				SS prediction			
3	60	0.49	0.973	0.33	0.966	0.17	0.999
4	61	0.38	0.957	0.28	0.954	0.08	0.998
5	60	0.66	0.938	0.28	0.978	0.20	0.999
6	64	0.57	0.941	0.32	0.940	0.17	0.998
7	57	0.32	0.892	0.38	0.883	0.08	0.995
8	64	0.37	0.948	0.36	0.949	0.29	0.999
9	62	0.53	0.882	0.51	0.883	0.54	0.996
10	65	0.48	0.922	0.51	0.949	0.62	0.998
11	64	0.42	0.839	0.36	0.895	0.48	0.999
12	113	0.83	0.803	0.68	0.770	0.47	0.953
3-12	670	0.54	0.844	0.43	0.883	0.31	0.932

[a]mean absolute scaled error; [b]prediction coefficient of determination.

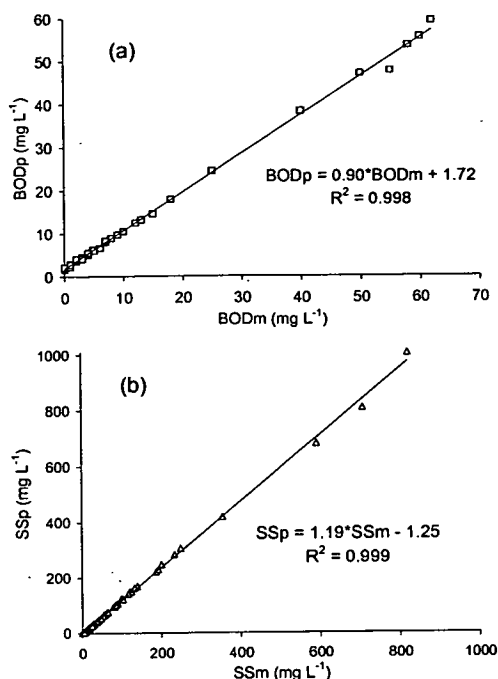provides better prediction results with smaller input variables.

Figure 5. Regression analysis (a) between the measured five-day @ 20°C N-Allylthiourea biochemical oxygen demand (BODm) and the predicted BOD (BODp) applying self-organizing map (SOM), and (b) between the measured suspended solids (SSm) and the predicted SS (SSp) applying the SOM model for Filter 8.

Basically, the outstanding performance of the SOM models is assumed to be attributed to the potential of clustering and classification of data. Particularly, in comparison with other neural networks, the SOM model was convenient for detecting the outliers, which are displayed in particular parts of the map without affecting the remaining parts, because each outlier takes its place in one unit of the map, and only the weights of that unit and its neighbors are affected (Cereghino et al., 2001; Leflaive et al., 2005).

Additionally, the SOM model showed its high performance in the visualization of relationships between variables for non-linear and complex biochemical data sets. Visualization gives better understanding of the relationships between most variables in biochemical processes. Figure 6 displays component planes on the trained map in grey scale.

The unified distance matrix (U-matrix) visualizes distances between neighboring map units, and helps to identify the cluster

structures of the map. Each component plane shows values for each variable with its corresponding unit. Cluster can be identified in the upper part of the U-matrix (Figure 6).
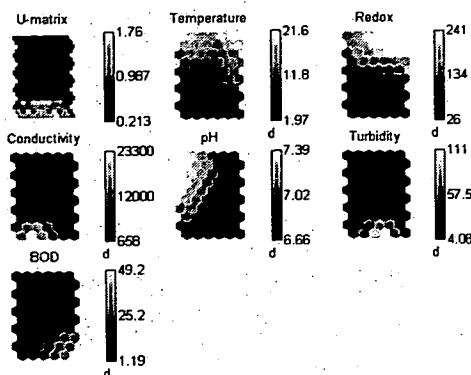

Figure 6. Visualization of variables (outflow water temperature (°C), redox potential (mV), conductivity (μS), pH (-), turbidity (NTU) and five-day @ 20°C N-Allylthiourea biochemical oxygen demand (BOD) (mg L^{-1})) on the self-organizing map trained to predict BOD of Filter 8. The map size is sixty units. The U-matrix is the unified distance matrix.

In the equivalent area of each component plane, the temperature and the redox potential are high. On the other hand, the conductivity, turbidity and BOD concentrations are low in the upper part of the planes. Figure 6 indicates that a high BOD is associated with a high temperature, high redox potential, low conductivity and low turbidity.

The likelihoods of correct predictions, if the effluent concentrations are either below or above the thresholds for secondary wastewater treatment, are also shown in Table 6. The BOD and SS concentrations for compliance are 20 and 30 mg L^{-1}, respectively (Scholz, 2003a).

TABLE 6

Correct prediction of compliance (%) for the estimation of the five-day @ 20°C N-Allylthiourea biochemical oxygen demand (BOD) (mg L^{-1}) and the suspended solids (SS) (mg L^{-1}) concentrations.

models	SOM[a]	SVM[b]	KNN[b]
BOD	97.0	87.9	87.2
SS	96.4	90.0	88.1

[a]self-organizing map; [b]support vector machine; [c]k-nearest neighbors.

The correct predictions of compliance were all >87%. The probabilities are therefore all at least by 0.37 higher in comparison to 'pure guessing (50%)'. Therefore, all

11

models are well suited for relatively highly variable water quality data sets such as those from constructed treatment wetlands.

4. Conclusions

This paper demonstrates to the reader the successful application of k-nearest neighbors (KNN), support vector machine (SVM) and self-organizing map (SOM) to typical 'black box' systems such as constructed treatment wetlands governed by biochemical processes. The KNN, SVM and SOM methodologies were successfully applied to predict water quality variables of constructed treatment wetlands. The five-day @ 20 C N-Allylthiourea biochemical oxygen demand (BOD) and suspended solids (SS) which are time-consuming and expensive to estimate, can be cost-effectively monitored (virtually in real time) by applying machine learning tools with input variables such as turbidity and conductivity. Their performances are encouraging, and the use of these models as management tools for the day-to-day process control is therefore recommended. Moreover, little domain knowledge is required to build a model, and the input variables can be optimized by trial and error. In terms of accuracy of prediction, the SOM model provided better performance using smaller input variables in comparison to both KNN and SVM models. Particularly, the SOM model demonstrated its potential to analyze the relationship between complex biochemical variables.

However, establishing the SOM model required more time due to the long searching process of the optimal map, compared to the KNN and SVM models. Thus, in addition to the accuracy of model predictions, the resource, which is required to build and test the model, should be considered when selecting the optimal model.

References

Aguilera, P. A., Frenich, A. G., Torres, J. A., Castro, H., Vidal J. L. M. and Canton, M.: 2001, 'Application of the Kohonen Neural Network in Coastal Water Management: Methodological Development for the Assessment and Prediction of Water Quality', *Water Res.* 35, 4053-4062.

Alpaydin, E.: 2004, *Introduction to Machine Learning*, MIT Press: Cambridge, USA.

Belanche, L., Valdes, J. J., Comas, J., Roda, I. R. and Poch, M.: 2000, 'Prediction of the Bulking Phenomenon in Wastewater Treatment Plants', *Artif. Intell. Eng.* 14, 307-317.

Carpenter, G. A. and Markuzon, N.: 1998, 'ARTMAP-IC and Medical Diagnosis: Instance Counting and Inconsistent Cases', *Neural Networks* 11, 323-336.

Cao, L. J. and Francis, E. H. Tay.: 2003, 'Support Vector Machine with Adaptive Parameters in Financial Time Series Forecasting', *IEEE Transactions on Neural Networks,* 14, 6.

Cereghino, R., Giraudel, J. L. and Compin, A.: 2001, 'Spatial Analysis of Stream Invertebrates Distribution in the Adour-Garonne Drainage Dasin (France) Using Kohonen Self-organizing Maps', *Ecol. Model.* 146, 167-180.

Chang, C.-C. and Lin, C.-J.: 2001, LIBSVM: a Library for Support Vector Machines. Software available at http://www.csie.ntu.edu.tw/~cjlin/libsvm.

Dong, B., Cao, C. and Lee, S. E.: 2005, 'Applying Support Vector Machines to Predict Building Energy Consumption in Tropical Region', *Energ. Build.* 37, 545-553.

Dong, N., Lu W. C., Chen N. Y., Zhu Y. C. and Chen K. X.: 2005, 'Using Support Vector Classification for SAR of Fentanyl Derivatives', *Acta Pharmacol. Sin.* 26, 107-112

Dubey, A., Realff, M. J., Lee, J. H. and Bommarius, A. S.: 2005, 'Support Vector Machines for Learning to Identify the Critical Position of a Protein', *J. Theor. Biol.* 234, 351-361.

Dubois, D. and Prade, H.: 1998, 'An Introduction to Fuzzy Systems', *Clin. Chim. Acta* 270, 3-29.

Duch, W. and Grudzinski, K.: 1999, 'Weighting and Selection of Features', *Proceedings of Intelligent Information Systems VIII Workshop*, Ustron, Poland. June 1999, pp. 32-36

Garcia, H. L. and Gonzalez, I. M.: 2004, 'Self-organizing Map and Clustering for Wastewater Treatment Monitoring. *Eng. Appl. Artif. Intel.* 17, 215-225.

Gernaey, K. V., Van Loosdrecht M. C. M., Henze, M., Lind, M. and Jørgensen, S. B.: 2004, 'Activated Sludge Wastewater Treatment Plant Modeling and Simulation: State of the Art', *Environ. Modell. Softw.* 19, 763-783.

Gevrey, M., Rimet, F., Park, Y. S., Giraudel, J. L., Ector, L. and Lek, S.: 2004, 'Water Quality Assessment Using Diatom Assemblages and Advanced Modelling Techniques', *Freshwater Boil.* 49, 208-220.

Grieu, S., Traore, A., Polit, M. and Colprim, J.: 2005, 'Prediction of Parameters Characterizing the State of a Pollution Removal Biologic Process', *Eng. Appl. Artif. Intel.* 18, 559-573. .

Hamed, M. M., Khalafallah, M. G. and Hassanien, E. A.: 2004, 'Prediction of Wastewater Treatment Plant Performance Using Artificial Neural Networks', *Environ. Model. Softw.* 19, 919-928.

Hand, D., Mannila, H., Smyth, P.: 2001, *Principles of Data Mining*, MIT-Press: Cambridge, USA.

Hong, Y-S. T., Rosen, M. R. and Bhamidimarri, R.: 2003, 'Analysis of a Municipal Wastewater Treatment Plant Using a Neural Network – Based Pattern Analysis', *Water Res.* 37, 1608-1618.

Hyndman, R. J. and Koehler, A. B.: 2005, 'Another Look at Measures of Forecast Accuracy', Monash Econometrics and Business Statistics Working Papers, 13/05.

Iovine, J: 1998, *Understanding Neural Networks*, Elsevier: Amsterdam, The Netherlands.

Joachims, T.: 1999, 'Making Large-scale SVM Learning Practical. Advances in Kernel Methods – Support Vector Learning', in B. Scholkopf, C. Burges and A. Smola (eds.), MIT-Press. Software available at http://svmlight.joachims.org.

Kohavi, R.: 1995, 'A Study of Cross-validation and Bootstrap for Accuracy Estimation and Model Selection', *Proceedings of the 14th International Joint Conference on Artificial Intelligence*, pp. 1137-1143.

Kohonen, T.: 2001, *Self-organizing Maps*, 3rd edition. Springer: Berlin, Germany.

Lee, K., Booth, D. and Alam, P.: 2005, 'A Comparison of Supervised and Unsupervised Neural Networks in Predicting Bankruptcy of Korean Firms', *Expert Syst. Appl.* 29, 1-16.

Leflaive, J., Cereghino, R., Danger, M., Lacroix, G. and Ten-Hage, L.: 2005, 'Assessment of Self-organizing Maps to Analyze Sole-carbon Source Utilization Profiles', *J. Microbiol. Meth.* 62, 89-102.

Liu, H.-X., Zhang, R.-S., Yao, X.-J., Liu, M.-C., Hu, Z.-D. and Fan, B.-T.: 2004, 'Prediction of Electrophoretic Mobility of Substituted Aromatic Acids in Different Aqueous-alcoholic Solvents by Capillary Zone Electrophoresis Based on Support Vector Machine', *Anal. Chim. Acta* 525, 31-41.

Lu, R.-S. and Lo, S.-L.: 2002, 'Diagnosing Reservoir Water Quality Using Self-organizing Maps and Fuzzy Theory', *Water Res.* 36, 2265-2274.

Lu, W.-Z. and Wang, W.-J.: 2005, 'Potential Assessment of the Support Vector Machine Method in Forecasting Ambient Air Pollutant Trends', *Chemosphere* 59, 693-701.

Maier, H. R., Morgan, N. and Chow, C. W. K.: 2004, 'Use of Artificial Neural Networks for Predicting Optimal Alum Doses and Treated Water Quality Parameters', *Environ. Model. Softw.* 19, 485-494.

Mohanty, S., Scholz, M. and Slater, M. J.: 2002, 'Neural Network Simulation of the Chemical Oxygen Demand Reduction in a Biological Activated Carbon Filter', *J. Ch. Inst. Wat. Environ. Manage.* 16, 58-64.

Mukherjee, A.: 1997, 'Self-organizing Neural Network for Identification of Natural Models', *J. Comput. Civil. Eng.* 11, 74-77.

Onkal-Engin, G., Demir, I. and Engin, S. N.: 2005, 'Determination of the Relationship between Sewage Odor and BOD by Neural Networks', *Environ. Model. Softw.* 20, 843-850.

Pai, P.-F. and Hong, W.-C.: 2005, 'Support Vector Machines with Simulated Annealing Algorithms in Electricity Load Forecasting', *Energ. Convers. Manage* 46, 2669-2688.

Ruiz-Jimenez, J., Priego-Capote, F., Garcia-Olmo, J. and Luque de Castro, M. D.: 2004, 'Use of Chemometrics and Mid Infrared Spectroscopy for the Selection of Extraction Alternatives to Reference Analytical Methods for Total Fat Isolation', *Anal. Chim. Acta* 525, 159-169.

Scholz, M.: 2003a, 'Case study: Design, Operation, Maintenance and Water Quality Management of Sustainable Storm Water Ponds for Roof Runoff', *Bioresource Technol.* 95, 269-279.

Scholz, M.: 2003b, 'Performance Predictions of Mature Experimental Constructed Wetlands which Treat Urban Water Receiving High Loads of Lead and Copper', *Water Res.* 37, 1270-1277.

Scholz M.: 2004, 'Treatment of Gully Pot Effluent Containing Nickel and Copper with Constructed Wetlands in a Cold Climate', *J. Chem. Technol. Biot.* 79, 153-162.

Scholz, M., Höhn, P. and Minall, R.: 2002, 'Mature Experimental Constructed Wetlands Treating Urban Water Receiving High Metal Lloads', *Biotechnol. Prog.* 18, 1257-1264.

Vapnik, V.: 1995, *The Nature of Statistics Learning Theory*, Springer-Verlag: New York, USA.

Verdenius, F. and Broeze, J.: 1999, 'Generalized and Instance-specific Modeling for Biological Systems. *Environ', Model. Softw.* 14, 339-348.

Vesanto, J., Himberg, J., Alhoniemi, E. and Parhankangas, J.: 1999, 'Self-organizing Map in Matlab: the SOM Toolbox', *Proceedings of the Matlab DSP Conference*, Espoo, Finland, Nov., pp. 35-40. Software available at http://www.cis.hut.fi/projects/somtoolbox/.

Werner, H. and Obach, M.: 2001, 'New Neural Network Types Estimating the Accuracy of Response for Ecological Modeling', *Ecol. Model.* 146. 289-298.