DOMESTIC WASTEWATER TREATMENT IN PILOT-SCALE CONSTRUCTED WETLANDS IMPLEMENTED IN THE MIDDLE EAST TECHNICAL UNIVERSITY

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
THE MIDDLE EAST TECHNICAL UNIVERSITY

BY

ELIF ASUMAN KORKUSUZ

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY
IN
BIOTECHNOLOGY

SEPTEMBER 2004

Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Doctor of Philosophy.

Assoc. Prof. Dr. Dilek Sanin
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Doctor of Philosophy.

Assoc. Prof. Dr. Meryem Beklioğlu
Co-Supervisor

Assoc. Prof. Dr. Göksel N. Demirer
Supervisor

Examining Committee Members

Prof. Dr. Selçuk Soyupak	(ATILIM, CE)	
Assoc. Prof. Dr. Göksel N. Demirer	(METU, ENVE)	
Prof. Dr. İnci Eroğlu	(METU, CHE)	
Assoc. Prof. Dr. Sertaç Önde	(METU, BIOL)	
Dr. Günter Langergraber	(SIG-BOKU)	

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name : Elif Asuman Korkusuz

Signature :

ABSTRACT

"DOMESTIC WASTEWATER TREATMENT IN PILOT-SCALE CONSTRUCTED WETLANDS IMPLEMENTED IN THE MIDDLE EAST TECHNICAL UNIVERSITY"

Korkusuz, Elif Asuman

Ph.D, Department of Biotechnology

Supervisor: Assoc. Prof. Dr. Göksel N. Demirer

Co-Supervisor : Assoc. Prof. Dr. Meryem Beklioğlu

September 2004, 260 Pages

To foster the practical development of constructed wetlands used for wastewater treatment in Turkey, a pilot-scale subsurface constructed wetland system (90 m^2) was designed to treat the domestic wastewater produced by 60 PE living in the residential area of METU. In summer 2001, two parallel sets of hybrid wetland systems (vertical flow connected with horizontal flow) with identical design configuration, but with different fill media (blast furnace granulated iron slag and gravel) were built on the old sludge-drying bed of the abandoned wastewater treatment plant of METU, which has not been operating since the 1990s. Wetland cells were planted with common reed (*Phragmites australis*).

The main objective of this research was to quantify the effect of different filter media on the removal performance of subsurface flow constructed wetlands in the prevailing climate of Ankara. Thus, slag-filled and gravel-filled vertical flow

wetlands were operated identically with pre-settled domestic wastewater (3 $m^3.d^{-1}$) at a hydraulic loading rate of 110 $mm.d^{-1}$ for 12 months, intermittently.

According to the first year results, annual average removal efficiencies for the slag and gravel wetland cells were as follows: TSS (63% & 59%), COD (47% & 44%), NH_4^+-N (88% & 53%), TN (44% & 39%), PO_4^{3-}-P (44% & 1%) and TP (45% & 4%). The slag-filled vertical flow system removed phosphorus and ammonium efficiently than the gravel-filled system due to the differences in physical structures and chemical compositions of the fill media, and the different aerobic and anaerobic environments within the wetland cells. These results indicated that the well-designed constructed wetlands could also be used for secondary and tertiary treatment in Turkey, successfully.

Keywords: Domestic wastewater treatment, subsurface flow constructed wetland, *Phragmites australis*, nutrient removal, blast furnace slag.

ÖZ

"EVSEL ATIKSULARIN ORTA DOĞU TEKNİK ÜNİVERSİTESİ'NDE UYGULANAN PİLOT ÖLÇEKLİ EKİLMİŞ SULAKALANLARDA ARITIMI"

Korkusuz, Elif Asuman
Doktora, Biyoteknoloji Bölümü
Tez Danışmanı: Doç.Dr. Göksel N. Demirer
Yardımcı Tez Danışmanı: Doç.Dr. Meryem Beklioğlu

Eylül 2004, 260 Sayfa

Eevsel atıksu arıtmak üzere kullanılan ekilmiş sulakalanların Türkiye'de de pratik olarak uygulanmaya başlamasına katkıda bulunmak üzere, ODTÜKENT'te yaşayanlara ait atıksuyun birkısmını (60 PE) arıtmak üzere pilot-ölçekli yüzeyaltı akışlı ekilmiş sulakalan sistemi (90 m^2) tasarlanmıştır. 2001 yaz mevsiminde, 1990'lı senelerden beri kullanılmayan ODTÜ Atıksu Arıtma Tesisi'nin eski çamur kurutma yatağı üzerinde birbirine paralel, benzer tasarım konfigürasyonuna sahip iki adet hibrit sulakalan sistemi (düşey akışlı + yatay akışlı), farklı dolgu malzemesi (yüksek fırın demir granüle cürufu ve çakıl) kullanılarak oluşturulmuşlardır. Sulakalanların hepsine kamış (*Phragmites australis)* dikilmiştir.

Bu araştırmanın temel amacı, ekilmiş sulakalanlarda kullanılan farklı dolgu malzemelerinin kirleticilerin giderimine olan etkisini Ankara ikliminde belirlemeyi hedeflemektedir. Bu nedenle, 12 ay boyunca çakıl ve cüruf dolu düşey akışlı sulakalan yataklarının herbirine, ön çökeltmeden geçirilmiş 3m^3 hacmindeki evsel atıksu, 110 $mm.d^{-1}$ hidrolik yükleme hızı sağlanacak şekilde günde bir kez verilmiştir.

İlk yıl izleme çalışmaları sonuçlarına göre cürüflu ve çakıllı düşey akışlı sulakalan yataklarının yılllık ortalama giderim verimlilikleri sırasıyla: AKM (%63; %59), KOİ (%47; %44), NH_4^+-N (8%8; %53), TN (%44; %39), PO_4^{3-}-P (%44; %1) ve TP (%45; %4) olmuştur. Demir cüruflu düşey akışlı sistem, dolgu malzemelerinin fiziksel ve kimyasal yapılarındaki farklılıklardan, ve sulakalan yatakları içinde sağladıkları farklı oksijenli ve oksijensiz ortamlardan dolayı, çakıllı sistemden daha fazla fosfor ve amonyum gidermiştir. Bu sonuçlar, ekilmiş sulakalanların Türkiye'de de ikincil ve üçüncül atıksu arıtımında başarılı bir şekilde uygulanabileceğini işaret etmektedir.

Anahtar Kelimeler: Evsel atıksu arıtımı, yüzeyaltı akışlı ekilmiş sulakalan, *Phragmites australis*, besin giderimi, yüksek fırın cürufu.

To my beloved parents and teachers

ACKNOWLEDGMENTS

I would like to express my deepest gratitude to my supervisor Assoc. Prof. Dr. Göksel N. Demirer and co-supervisor Assoc. Prof. Dr. Meryem Beklioğlu Yerli for their guidance, advice, criticism, encouragements, insight and also believing in me throughout the research. I gratefully appreciate Prof. Dr. Selçuk Soyupak, Prof. Dr. İnci Eroğlu, Assoc. Prof. Dr. Sertaç Önde, Assoc. Prof. Dr. İlhami Tüzün, Dr. Günter Langergraber for their useful advice, critical reviewing and comments of my dissertation while serving on my committee. I would also like to appreciate Assoc. Prof. Dr. Ahmet Cevdet Yalçıner, Dr. Sheldon Tarre, Dr. Jan Vymazal, Dr. Johannes Laber, Dr. Ayfer Yediler and all the wetland researchers who answered my questions patiently, shared their valuable experiences and opinions, and encouraged me throughout the research.

This work was partially funded by the METU Research Coordination and Industrial Liaison Office (AFP-2001-07-02-00-31). I wish to thank all the staffs of the offices under the General Secretariat of the Middle East Technical University for their help during the study. Thanks are also extended to the KARDEMİR Iron and Stell Co. for providing the blast furnace slag for free and to the General Directorate of the Rural Services, Ankara, for providing the meteorological data. I also thank all the staff members of the Department of Environmental Engineering of METU.

The technical assistance and friendship of Murat Taşdemir throughout my lab and field studies is gratefully acknowledged. Special thanks are due to all my dear friends for their love, understanding, full support, and encouragements.

I extend thanks more than I can express to my family for their love, support and understanding throughout my many years of graduate study. I wish to express my gratitude for my special father who spent many hours tirelessly helping me with all the hard field work. Without you all, this study would never be possible.

TABLE OF CONTENTS

LIST OF TABLES

TABLE

LIST OF FIGURES

FIGURE

LIST OF ABREVIATIONS

METU	The Middle East Technical University
IUCN	International Union for the Conservation of Nature and Natural Resources
CW	Constructed Wetland
TSS	Total Suspended Solids
BOD_5	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
P	Phosphorus
TP	Total Phosphorus
PO_4^{3-}-P	Ortho-phosphate Phosphorus
N	Nitrogen
TN	Total Nitrogen
NH_4^+-N	Ammonium-nitrogen
NO_3^--N	Nitrate-nitrogen
TKN	Total Kjeldahl Nitrogen
Org-N	Organic-nitrogen
TCB	Total Coliform Bacteria
FWS	Free Water Surface Wetland
VSB	Vegetated Submerged Bed Wetland
SSF	Subsurface Flow
HF	Horizontal Flow
VF	Vertical Flow
RE	Removal Efficiency (%)
V	Volume (m^3)
C	Pollutant Concentration ($mg.L^{-1}$)
C_{in}	Influent Concentration ($mg.L^{-1}$)
C_{out}	Effluent Concentration ($mg.L^{-1}$)

t	Time (d)
ΔT	Time between two Measurements (d)
A	Surface Area of the Wetland Cell (m^2)
HRT	Hydraulic Retention Time (d)
HLR	Hydraulic Loading Rate ($m.d^{-1}$)
L:W	Length to Width Ratio
K_f	Permeability Coefficient
q	Amount of P-adsorbed per unit of Media (mg $P.kg^{-1}$ sample)
Ci	Initial Concentration ($mg.L^{-1}$)
Cf	Final Concentration of P or Equilibrium Concentration ($mg.L^{-1}$)
M	Mass of Dry-Weight of the Substrate (kg)
ρ_{part}	Particle Density of the Substrate ($g.cm^{-3}$)
ρ_{bulk}	Bulk Density of the Substrate ($g.cm^{-3}$)
α	Porosity of the Fill Media (unitless)
Q_{in}	Flowrate of the Wastewater entering the Wetland ($m^3.d^{-1}$),
Q_{out}	Flowrate of the treated Water exiting the Wetland ($m^3.d^{-1}$)
Q_{stored}	Flowrate of Wastewater stored in the Voids of the Substrate ($m^3.d^{-1}$)
I	Amount of Water entering the Wetland via Surface Inflow ($m^3.d^{-1}$)
P	Amount of Water entering the Wetland through Precipitation ($m^3.d^{-1}$)
ET	Loss of Water through Evapotranspiration from the Wetland ($m^3.d^{-1}$)
k	Areal Removal Rate Constant of Pollutant ($m.d^{-1}$)
k_T	Areal Removal Rate Constant at T°C ($m.d^{-1}$)
k_{20}	Areal Removal Rate Constant at 20T°C ($m.d^{-1}$)
Ar	The Van't Hoff–Arrhenius Coefficient
R	A Gas Constant (8.314 $J.mol^{-1}.K^{-1}$)
T	Temperature (°C)
θ	Temperature Coefficient, Theta value (dimensionless)
$Mass_{in}$	Mass of the Pollutant in the Influent ($g.d^{-1}$)
$Mass_{out}$	Mass of the Pollutant in the Effluent ($g.d^{-1}$)
ANOVA	Analysis of Variance

$F_{0.95}$	%95 Confidence Limit
dF	Degree of Freedom
dN	Sample Size
P>	Probability

CHAPTER 1

INTRODUCTION

1.1. General

In recent years, the amount of wastewater produced from several anthropogenic activities has increased as a result of the improvement of people's living standards, unplanned industrialization, and urbanization practices. Even though industrialized countries can treat their wastewater in a suitable way, there are still discharges of untreated wastewater in developing countries, which adversely affect the quality of the environment. As a result, people of developing countries are still facing the environmental and related health problems including waterborne diseases even in the 21st century. Since most of the conventional wastewater treatment systems are very energy intensive and expensive for developing countries; effective but simple, cheap and reliable, wastewater treatment alternatives are needed.

Being low-cost and low-technology systems, eco-technological systems like "constructed wetlands" (CWs) are now standing as the potential alternative or supplementary systems for the treatment of municipal, industrial, agricultural wastewater, as well as storm water (Moshiri, 1993; Kadlec and Brix, 1995; Kadlec and Knight, 1996; Cooper et al., 1996; Vymazal et al., 1998; Haberl, 1999; Kivaisi, 2001). Since the 1950s, constructed wetlands have been used effectively to treat different wastewaters with different configurations, scales and designs throughout the world. This was because of their nutrient capturing capacity, simplicity, low construction/ operation and maintenance cost, low energy demand, process stability, little excess sludge production, effectiveness and potential for creating biodiversity (Haberl, 1999). Constructed wetland technology is much more spread

in industrialized countries due to more stringent discharge standards, finance availability, change in tendency to use natural and/or decentralized wastewater treatment systems and to the existing pool of experience and knowledge based on science and practical work.

Even though the potential for application of wetland technology in the developing world is enormous, the rate of adoption of wetlands technology for wastewater treatment in those countries has been slow (Neue et al., 1997). Recently, a variety of applications for CW technology for water quality improvement were initiated in developing countries like China, Kenya, Mexico, Nepal, Nicaragua, Tanzania, Uganda, India, Morocco, Iran, Thailand, and Egypt as a result of the transfer of the knowledge, technical collaboration and co-operation by the developed countries (Haberl, 1999; Kivaisi, 2001; Njau et al., 2003).

However, Denny (1997) critically discussed the implementation of the CW technology in developing countries by the developed world 'advisors'. He found that aid programs from developed countries tend to favor the more overt technologies that have commercial spin-off for the donors. Additionally, Denny (1997) asserted that most of these advisors were unable to transfer their conceptual thinking to the realities and cultures of the developing countries. Thus, rather than assisting developing countries to improve their own CW technologies, the tendency has been to translocate "northern" designs to tropical environments. Moreover, Gopal (1999) has identified the current limitations to widespread adoption of CW technology for wastewater treatment in developing countries as they have limited knowledge and experience with CW design and management.

In this regard, developing countries should carefully consider if the CW technology is an appropriate option for water quality enhancement for their countries. Clearly, these countries interested in implementing wetland technology must identify their own specific research needs and develop appropriate strategies based on local parameters (Kivaisi, 2001). A clear understanding of the biological, hydraulic and

chemical processes involved are essential (Woods and Hensman, 1989; Denny, 1997). Most importantly, careful economic analysis must be conducted to determine whether constructed wetland treatment technology can be feasibly developed for a given project location or not (Kadlec and Knight, 1996; Batchelor and Loots, 1997; Gopal, 1999). In order to assess the feasibility of utilizing sustainable wetland technologies in developing countries, a coordinated multidisciplinary approach involving environmental and social scientists, engineers and policymakers are required (Kivaisi, 2001).

Similar to other developing countries, there is a great need for simpler, cheaper, and more reliable, effective and practical wastewater treatment alternatives in Turkey (DPT, 5th Five Year Progress Plan, 1985-1989). As the current wastewater treatment strategies in Turkey have been examined (Table 1.1), it can be seen that only 11% of the Turkish community has been provided with proper conventional wastewater treatment plant facilities. This is mainly due to high costs of conventional treatment processes and lack of law enforcement in Turkey.

Table 1.1. The current infrastructure services of Turkey

Infrastructure Service	**Population provided with Infrastructure (%)**	**Population not provided with Infrastructure (%)**
Sewerage System	55	45
Wastewater Treatment System	11	89

Reference: Environmental Inventory of the Municipality, Bulletin of the State Statistical Institute, 2000.

Compared to high-cost conventional mechanical treatment systems, constructed wetland technology is cheaper, more easily operated, more efficient to maintain. Moreover, minimal fossil fuel is required; and no chemicals are necessary (Kadlec and Knight, 1996). Implementing low-technology systems like constructed wetlands can also be a proper solution for treatment of different types of wastewater in Turkey. However, there have not been any full-scale constructed wetland applications in Turkey until 2003, except for a few laboratory scale experimental studies on constructed wetlands (Akça et al., 1998; Ayaz and Akça, 2000; Ayaz and Akça, 2001).

In this context, some of the researchers of the Departments of Biotechnology, Environmental Engineering and Biology at METU decided to conduct an interdisciplinary study on constructed wetlands in 2000. As a result, a project called "Domestic Wastewater Treatment in Pilot-Scale Constructed Wetlands at METU" was developed. The project was partially funded by the METU Research Coordination and Industrial Liaison Office (AFP-2001-07-02-00-31).

Within the framework of the above-mentioned project, a pilot-scale subsurface constructed wetland system (90 m^2) was designed to treat 6 $m^3.d^{-1}$ of the domestic wastewater produced by the residents of ODTÜKENT, where the students and academicians of METU reside. In summer 2001, two parallel sets of the hybrid constructed wetland systems with identical design configuration, but with different fill media were built on the sludge drying bed of the abandoned wastewater treatment plant, which has not been operating since the 1990s. Since vertical flow subsurface constructed wetlands with intermittent feeding are now state of the art in Europe due to their various advantages over the other type of systems (Haberl et al., 1995; Cooper, 1999), the first stage of the hybrid systems at METU was designed also as vertical flow constructed wetlands. In order to improve the treatment efficiency of the whole system, the second stage was designed as horizontal flow subsurface constructed wetlands that were connected in series to the vertical flow wetlands.

Even though the subsurface constructed wetlands have been mainly used for the removal of BOD, COD, TSS and coliform bacteria; there is a growing interest in their use for nutrient (nitrogen and phosphorus) removal (Kadlec and Knight, 1996). For an efficient removal of nutrients in constructed wetlands, use of substrates with higher adsorption capacity, larger surface area and higher porosity have also been suggested as very significant (IWA, 2000). Therefore, batch-scale phosphorus adsorption experiments were conducted to determine the suitable fill media to be used in wetlands of METU, in the first phase of the research. The blast furnace granulated slag (BFGS) obtained from the KARDEMİR Iron and Steel

Company, Karabük, Turkey, provided the best results in terms of phosphorus sorption capacity. Sand and gravel, the performances of which has been already reported for several types of wastewater in literature (Cooper and Findlater, 1990; Crites et al., 1995; Platzer, 2000; IWA, 2000), have also been investigated as fill media to compare the treatment performances of slag as a fill media in constructed wetlands of METU. Thus, the fill media of one the hybrid systems comprised of different sizes of gravel and sand; whereas the other one comprised of gravel, sand and granulated slag.

The wetland system was planted with common reed (*Phragmites australis*), which has been successfully used in several constructed wetland applications (Crites et al., 1995; IWA, 2000, Kivaisi, 2001). The shoots of reeds have been transferred from the natural reed beds of the METU campus. The domestic wastewater, which was diverted from the manhole to the sedimentation tanks, was subjected to settling before being applied to the constructed wetlands for 12 months (July 2002 and July 2003). Meanwhile, a water quality monitoring study was performed to determine the treatment performances of these wetlands. Generally, the domestic wastewater had a low strength and had lower biodegradability (due to higher COD:BOD_5 ratio) when compared to literature values given by Metcalf and Eddy (1991). Gathering the meteorological data from the Research Institute of Köy Hizmetleri, water budget could be calculated. Using the monitoring data, kinetic parameters were estimated and compared to the literature values. After stopping the operation of the wetlands, substrate and the plant samples were taken from both of the vertical flow wetlands. These samples were analyzed for determination of COD, BOD5, TSS, nitrogen and phosphorus species, nutrients and heavy metals. A detailed mass balance approach was conducted to examine the fate of nutrients in the wetlands operated on the METU campus.

The design, implementation and operation of the constructed wetlands implemented at METU were based on the local resources and needs of Turkey in terms of wastewater treatment. To the best of our knowledge, these were the first

pilot-scale subsurface outdoor constructed wetlands applied in Turkey for domestic wastewater treatment and operated under authentic conditions. Therefore, the knowledge and experience that was acquired during the course of this study was expected to be one of the leading studies for implementation of the pilot-scale constructed wetlands in Turkey. The research results obtained from this ecotechnological approach for water quality improvement in Turkey can also be useful for designers in other developing countries where similar climate conditions are prevailing.

1.2. Objectives of the Study

The main objective of this dissertation was to improve and evaluate basic design and operation criteria for domestic wastewater treatment in subsurface flow constructed wetlands in Turkey. Assessment of the performance and limitations of this system for secondary treatment of domestic wastewater in Turkey was also undertaken. Moreover, this dissertation aimed to quantify the effect of different substrates (fill media) on the treatment performance of the constructed wetlands operated identically in the prevailing climate of Ankara.

This dissertation covered the followings:

- A detailed literature survey on the constructed wetlands,
- Screening level batch-scale adsorption experiments to determine the suitable local fill media to be used in the pilot-scale subsurface constructed wetlands for enhanced nutrient removal,
- Design of a constructed wetland system for treatment of settled domestic wastewater of 60 persons daily,
- Construction of the primary settler, and vertical and horizontal subsurface flow pilot-scale constructed wetlands on the abandoned sludge drying bed of METU,
- Operation of the pilot-scale constructed wetlands for 12 months,

- Monitoring of the treatment performances of vertical flow subsurface constructed wetlands for 12 months (July 2002-July 2003),
- Conducting water budget calculations by using the daily average meteorological data (rain and evapotranspiration),
- Comparison of the treatment performances of vertical subsurface flow constructed wetlands operated under the same operational conditions by use of experimental and statistical analyses,
- Determination of areal removal rate constants of the contaminants and comparison of these values to literature values,
- Determination of the nitrogen and phosphorus content of the reed plants after an operation period of 12 months,
- Determination of the nutrients and metal contents of the reed plants, as well as the substrate samples (sand and slag) after an operation period of 12 months,
- Performing filter media extraction experiments to understand the phosphorus removal mechanisms in vertical flow wetlands,
- Developing nitrogen and phosphorus mass balances for the vertical subsurface constructed wetlands,
- Evaluation of the results,
- Recommendations for future studies.

The knowledge and experience acquired during the course of this study are expected to improve the level of understanding about constructed wetlands and to foster the practical development of the constructed wetland technology for water quality enhancement in Turkey.

1.3. Scope of the Study

The basic concepts regarding natural and constructed wetlands were discussed thoroughly in Chapter 2. The aim of this chapter was to clarify the basic questions related to the definitions, functions, values and types of constructed wetlands.

Moreover, the main removal mechanisms in constructed wetlands were also reviewed in this chapter.

Chapter 3, which is the "Materials and Methods", focused on the design approach used on the implementation of the pilot-scale constructed wetlands of METU. Additionally, all of the experimental procedures used within this study were presented in Chapter 3.

In Chapter 4, the results of the screening level batch-scale adsorption experiments were given. The physical characteristics of the filter media were described here. The meteorological data gathered from the nearest meteorological station of the Research Institute of the Rural Services, Ankara, and water budget calculations of the constructed wetlands of METU were also presented in this chapter. The experimental results of the monitoring study conducted between July 2002 and July 2003 were presented and discussed in this chapter. The kinetic parameters were calculated according to the outcomes of the monitoring study. Moreover, the data obtained from the experiments performed for determination of the contents of the harvested plants and substrate samples taken from the wetland cells presented and discussed. The phosphorus-extraction experiments conducted to understand the phosphorus retention mechanisms in the wetland cells were also submitted in this chapter. Finally, a mass balance approach was used to examine the fate of nutrients in the constructed wetlands implemented at METU.

The conclusions of the study as well as recommendations for future studies were presented in Chapter 5. The experiences gained during the implementation and operation phase of both of the pilot-scale constructed wetlands of METU were also given in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1. General Information on Natural Wetlands

From temporary shallow waterbodies to marshes and swamps, from lake margins (littorals) to large river floodplains, from coastal beaches and salt marshes to mangroves, from peat bogs and fens to coral reefs and beds of marine algae or seagrasses, a large spectrum of habitats are regarded as "wetlands". What brings all these diverse kinds of habitats together is that the land is so wet (or under water) for a part or whole of the year that the vegetation is quite distinct from that of the adjacent upland areas (Gopal, 1999).

Even though there are many different terms for description of the wetland systems, the most widely accepted definition was developed by the International Union for the Conservation of Nature and Natural Resources (IUCN) in the Ramsar Convention, in 1980. According to this convention, wetlands were defined as "any areas of swamp, pond, peat, or water, natural or artificial, permanent or temporary, stagnant or flowing water, including estuaries and marine water, the depth of which at low tide does not exceed 6 meters." (Mitsch and Gosselink, 1993).

Wetlands, which exist in every climate from the tropics to the frozen tundra and on every continent except Antarctica (Vymazal et al, 1998) and which comprise 7.7% of the Earth's landscape, or in other words a total surface area of 11.65 million km^2 (Patten, 1990), mean different things to different people with different backgrounds. To some, they are important habitats for numerous kinds of waterfowl and fish whereas to others they are the "kidneys of the earth". Sometimes

they have been called as "biological supermarkets" for the extensive food chain and rich biodiversity they support (Mitsch and Gosselink, 1993).

Both freshwater and saltwater wetlands, due to their transitional location and reducing conditions were found to have very significant roles in the natural cycling of organic and inorganic materials (Bastian and Hammer, 1993). In general, nutrient transformation in wetlands depends upon a large number of variables (Gopal, 1999), which include:

- hydrological regime,
- nutrient concentrations in the influent,
- nutrients already present in the system,
- the kind of vegetation (annual or perennial, submerged or emergent),
- sediments (mineral or organic), and
- other biota.

2.2. Functions of Natural Wetlands

All wetlands, other than peat bogs, are highly productive systems and support high biodiversity. Like other ecosystems, wetlands also perform many ecological functions. The hydrological, biological and biogeochemical functions impart them various values (Sather and Smith, 1984). Some of the values of these wetlands given by Vymazal et. al (1998) and Denny (1997) are summarized below:

- Water quality functions and water quality improvements (water supply for drinking and irrigation; particulate filtration; biodegradation of toxic compounds; human pathogen reductions; heavy metal stripping and accumulation; wastewater and stormwater treatment),
- Hydrological and hydraulic functions (erosion and flood control; recharge of groundwater aquifers; floodplain hydrodynamics),

- Climatic effects (buffering global warming; carbon fixation and CO_2 balance; micro-climatic influences),
- Biodiversity functions (wildlife enhancement; breeding grounds for waterfowl, fish and invertebrates like shrimps, crabs, oysters, clams, mussels; preservation of gene pools; conservation of flora and fauna),
- Mining activities (getting peat, sand, gravel),
- Usage of plants (staple food plants; grazing land; timber; paper production; roofing; agriculture, horticulture, fertilizers, fodder),
- Development of aquaculture and integrated systems (fishing, hunting, fish cultivation combined with rice production),
- Energy production (hydroelectric; solar energy; heat pumps; fuel as gas, solid and liquid),
- Educational uses (training; nature studies; research activities)
- Recreational and reclamational uses (sightseeing; sailing; swimming; canoeing).

Unfortunately, most of the above mentioned values were recognized recently by the developed world, which considered the natural wetlands for a long time as "wastelands" (Gopal, 1999) and used them as "convenient wastewater discharge sites" for as long as sewage has not been collected (Kadlec and Knight, 1996). Furthermore, they have were drained, ditched, covered, overfilled with toxins and nutrients for long periods (Mitsch and Gosselink, 1993).

As a result of the exponentially increasing demands of human expansion and resource exploitation, it has been recognized that natural wetland ecosystems cannot always function efficiently for desired objectives and stringent water quality standards. These and many other factors have led to the rapid development of "constructed wetlands" for wastewater treatment (Wetzel, 1993).

2.3. Constructed Wetlands for Waste Management and Water Quality Enhancement

Constructed wetland treatment systems are engineered and managed "natural systems" that are receiving increased worldwide attention for wastewater treatment and recycling (Bastian and Benforado, 1983; Reddy and Smith, 1987; Reed et al., 1988, Hammer, 1989; Cooper and Findlater, 1990; Etnier and Guterstam, 1991; Tchobanoglous and Burton, 1991; Vymazal et al., 1998; IWA, 2000; Njau et al., 2003). This appears to be, at least, in part, due to the growing interest on eco-technologies that supports more resource conservation and environmental protection, and greater reliance upon natural ecological processes and systems in preference to the more energy and chemical intensive "mechanical" (or conventional) waste management systems. Examples of the eco-technologies more extensively considered and used today to treat effectively and recycle polluted waters from point and non-point sources include:

- composting and direct land application of solid wastes (e.g. yard wastes) and sludges,
- a variety of land treatment systems (i.e., slow-rate irrigation, rapid infiltration, and overland flow-or grass filtration),
- pond systems,
- aquaculture and aquatic plant systems, and
- natural and constructed wetland systems (Bastian and Hammer, 1993).

2.4. Historical Development of Constructed Wetlands

The first work deliberately investigating wastewater treatment by wetland plants was conducted by Seidel (1955) at the Max Planck Institute in Plon, Germany. In 1952, Seidel explored the removal of phenols from wastewater by *Scirpus lacustris* and in 1956 began testing dairy wastewater treatment with *S. lacustris* (Bastian and Hammer, 1993). From 1955 through the late 1970s, Seidel published numerous studies on water and wastewater treatment with wetland plants (Seidel, 1955, 1961,

1976). One of her students, Kickuth, continued with the experimental work and popularized this concept with his co-workers in Europe, resulting in nearly 200 municipal and industrial waste treatment systems. Throughout the 1970s, in the U.S., land treatment alternatives were developed with the support of a significant research and development effort funded by the U.S. Environmental Protection Agency, the U.S. Army Corps of Engineers and other agencies (Bastian and Hammer, 1993).

In many parts of the countries, especially in Europe, there is a tendency to use conventional sewage and treatment in a wastewater treatment plant. Centralization was preferred until about 25 years ago, but high costs for sewerage and other technical and ecological disadvantages when applying central treatment plants caused a change so that on site technology has been more frequently taken into the consideration during the last 20 to 25 years (Haberl, 1995).

Today, due to the increased awareness for natural processes, the necessity of wastewater treatment in low density areas and demand for simple operation and maintenance (O/M) (Haberl, 1999), the use of constructed wetlands for wastewater management and water pollution control is becoming more popular and effective in many parts of the world (Reddy and Smith, 1987; Hammer and Pullin, 1989; Cooper and Findlater, 1990; Moshiri 1993, Bavor and Mitchell, 1994; Kadlec and Brix 1995, Kadlec and Knight, 1996; Cooper et al., 1996; Vymazal et al., 1998; IWA 2000, Kivaisi, 2001; Naylor et al., 2003; Njau et al., 2003).

2.5. Classification of Constructed Wetlands

Early studies of the process dynamics, movements, cycling and reservoirs for nutrients, metals, micronutrients, and trace elements established the theoretical basis for later studies of wetlands transformations of various types of wastewater (Bastian and Hammer, 1993). As a result, treatment wetland systems have been designed and constructed to utilize the natural processes involving wetland

vegetation, soils, and their associated microbial assemblages to assist in treating wastewater (Vymazal et al., 1998). There are various design configurations of constructed wetlands (Haberl, 1999) and they can be classified according to the following items:

- Life form of the dominating macrophytes (free-floating, emergent, submerged),
- Flow pattern in the wetland systems (free water surface flow; subsurface flow: horizontal and vertical),
- Type of configurations of the wetland cells (hybrid systems, one-stage, multi-stage systems),
- Type of wastewater to be treated,
- Treatment level of wastewater (primary, secondary or tertiary),
- Type of pretreatment,
- Influent and effluent structures,
- Type of substrate (gravel, soil, sand, etc.), and
- Type of loading (continuous or intermittent loading).

All the treatment wetland systems can be classified differently according to the different classification systems (Haberl, 1995). Commonly used classification systems are described by Haberl et al. (1983), Kraft (1985), Steiner and Freeman (1990), Börner (1992) and Brix (1993). The detailed information of these systems is summarized in the following sections.

2.5.1. Constructed Wetlands Based on the Dominant Macrophyte

Aquatic plants, which are the most visible and recognizable diagnostic feature of a wetland, contribute to the nutrient transformation by abetting in the physical, chemical and microbial processes besides removing nutrients for their own growth. They offer mechanical resistance to the flow, increase the retention time, and facilitate settling of suspended particulates. They improve conductance of the water through the soil as the roots grow and create spaces after their death. The plants add

organic matter into the water as well as providing a large surface area for microbial growth. Many aquatic plants actively transport oxygen to the anaerobic layers of soil (Armstrong and Armstrong, 1990; Brix, 1993; Allen, 1997) and thus help in oxidation and precipitation of heavy metals on the root surfaces (Dunhabin et al., 1988, Steinberg and Coonrod, 1994).

The submerged macrophytes directly oxygenate the water column. The emergent and free floating macrophytes shade out the water surface and prevent the growth of algae. Free-floating plants can completely eliminate oxygen in the water column leading to enhancement of reduction reactions. The algae contribute much to the wastewater purification processes as in the oxidation ponds. The absorption of nutrients by macrophytes varies with the species and is related to their growth under different conditions (Gopal, 1999).

There are three systems according to the life form of the dominating macrophyte (Brix, 1993): i) Free floating macrophyte-based system, ii) Submergent macrophyte-based system, iii) Rooted emergent macrophyte-based system.

2.5.1.1. Free-Floating Macrophyte Based System

These macrophytes are highly diverse in life-form and habits that they live in, ranging from large plants with rosettes of aerial and/or floating leaves and well developed submerged roots like water hyacinth (*Eichhornia crassipes*) to minute surface floating plants with few or no roots like duckweeds (*Lemna, Spirodella, Wolffia* sp.) (Brix and Schierup, 1989). The schematic presentation of the free-floating macrophyte based system is given in Figure 2.1.

The water hyacinth is one of the most productive plants in the world. It can be used both for tertiary treatment purposes and integrated secondary and tertiary treatment systems for BOD and nutrient removal. Water hyacinth based wastewater treatment systems have been developed to be successfully applied in the tropics and the

subtropics, the process design criteria of which was published by Reed et al. (1988) and Weber and Tchobanoglous (1986).

The dense cover of water hyacinths can effectively reduce the effects of wind mixing and minimize thermal mixing in the systems. The shading provided by the plant cover can restrict algal growth and their roots can impede the horizontal movement of particulate matter resulting in well-documented suspended solids removal (Dinges, 1982). Also, they provide good conditions for microbial attachment and nitrification (Reddy et al., 1989). But they are severely affected by frost, and their growth rate is greatly reduced at temperatures below 10°C (Brix, 1993).

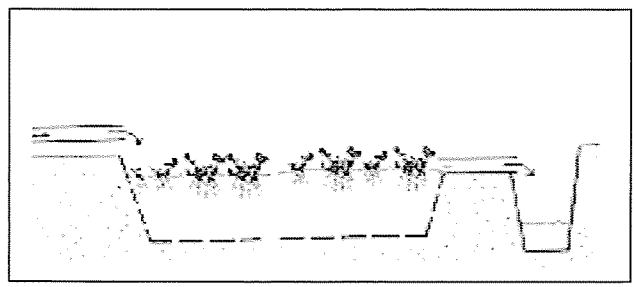

Figure 2.1. Free-floating macrophyte based system (Brix, 1993)

Duckweeds have been investigated much less than water hyacinths for use in wastewater treatment. Since they lack extensive root systems and thus provide a smaller surface area for attached microbial growth, they play less direct role in the treatment process. However, they have much wider geographical range than water hyacinths, as they are able to grow at temperatures as low as 1-3°C. They are used for secondary treatment purposes. The dense cover of duckweeds inhibits both the oxygen entering the water by diffusion and the photosynthetic production by phytoplankton due to poor light penetration. The water consequently becomes largely anaerobic, which in turn favors denitrification. The nutrition value of harvested biomass contains twice as much protein, fat, nitrogen and phosphorus as compared with that of water hyacinth (Brix, 1993).

2.5.1.2. Submerged Macrophyte-Based Systems

Submerged aquatic macrophytes have their photosynthetic tissue entirely submerged. The morphology and ecology of the species vary from small, rosette type, low-productivity species growing only in oligotrophic waters (e.g., *Isotes lacustris* and *Lobelia dortmanna*) to larger eloided-type, high productivity species growing in eutrophic waters (e.g., *Elodea canadensis*, *Potamogeton crispus*) Usually the flowers are exposed to the atmosphere. The illustration of the submerged macrophyte based system is given in Figure 2.2.

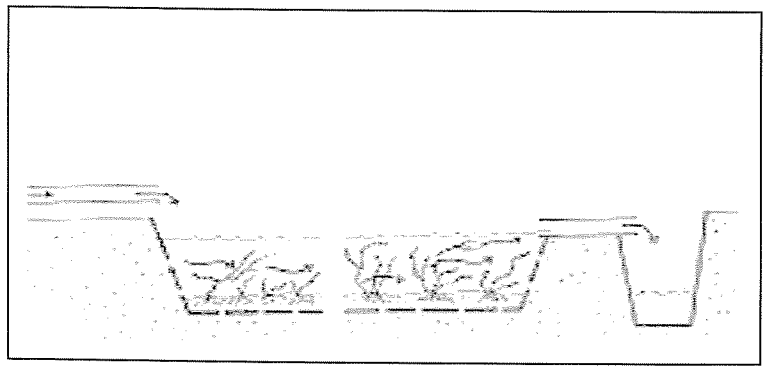

Figure 2.2. Submerged macrophyte based systems (Brix, 1993)

Submerged aquatic plants are able to assimilate nutrients from polluted waters but in well-oxygenated condition. Therefore, they are used for polishing secondarily treated water. Since these macrophytes deplete dissolved inorganic carbon in the water and increase the dissolved oxygen concentration during the periods of high productivity, pH of the water increases. This results in creating optimal conditions for volatilization of ammonia and chemical precipitation of phosphorus. Species like egeria (*Egeria densa*), elodea (*Elodea canadensis* and *Elodea nuttallii*), hornworth (*Ceratophyllum demersum*) and hydrilla (*Hydrilla verticillata*) are the most promising submerged macrophytes used in wastewater treatment (Brix, 1993; Vymazal et al., 1998).

2.5.1.3. Emergent Aquatic Macrophyte-Based Systems

They are the dominant life forms in wetlands and marshes, growing within a water-table ranging from 50 cm below the soil surface to a water depth of 150 cm or more. In general, they produce aerial stems and leaves and have an extensive root and rhizome system. The depth penetration of the root system and thereby the exploitation of sediment volume is different for different species (Brix, 1993). Some of the species of this group are *Phragmites* (common reed), *Scirpus* (bulrush) and *Typha* (cattail). The schematic presentation of the emergent aquatic macrophyte based system is given in Figure 2.3.

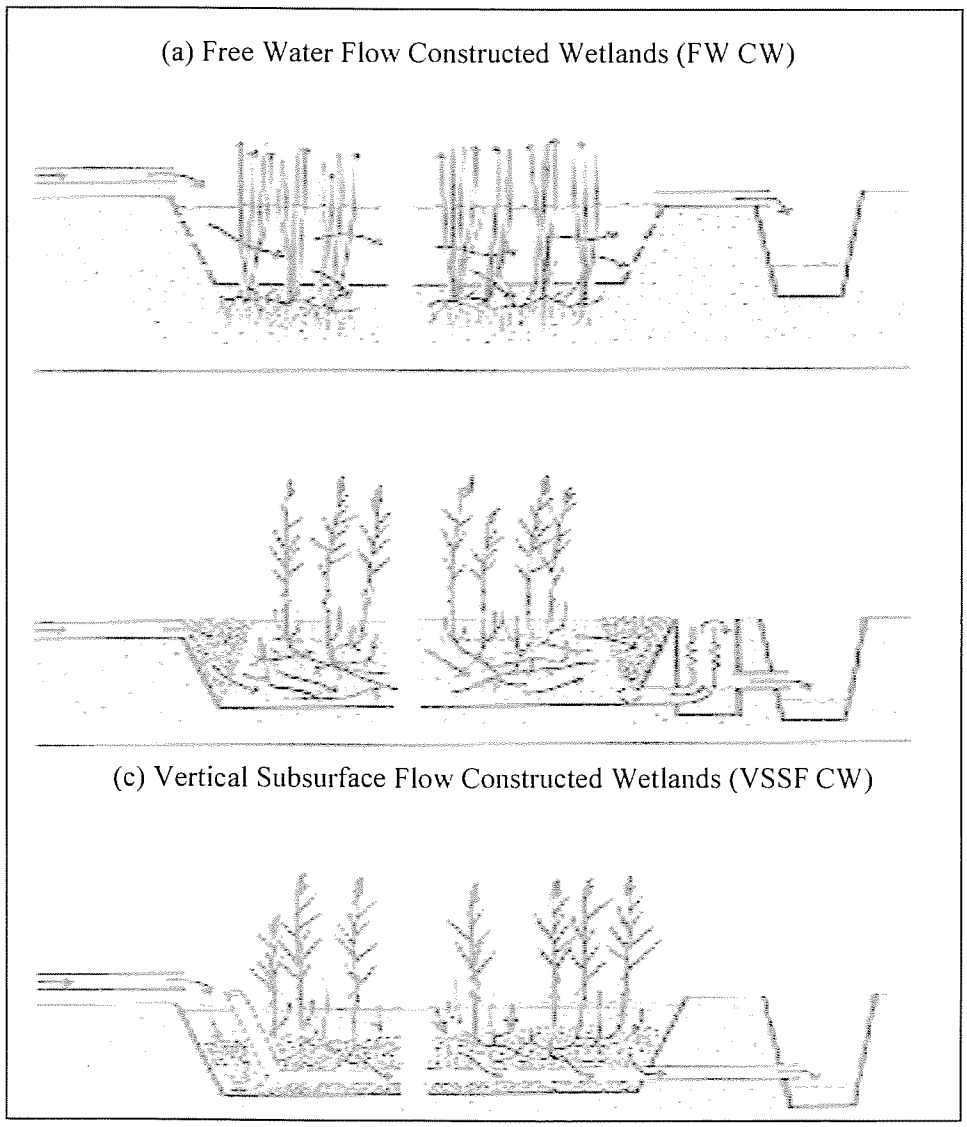

Figure 2.3. Emergent macrophyte-based systems (Brix, 1993)

Some of the characteristics of most commonly used emergent species in wastewater treatment are compared in Table 2.1, whereas the properties of some of the aquatic macrophyte species are summarized in Table 2.2.

Table 2.1. Properties of some emergent macrophyte species

Properties	**Emergent Species**		
	Typha (cattail)	*Scirpus* (bulrush)	*Phragmites* (common reed)
Distribution	worldwide	worldwide	worldwide
Optimum pH	4-10	4-9	2-8
Root penetration	0.3 m (in gravel)	0.6m (in gravel)	0.4 m (in gravel)
Annual Yield	14 (dw) tons / acre	9 (dw) tons / acre	18 (dw) tons / acre
Tissue C % (dw)	45	-	45
Tissue N % (dw)	1.4	1.8	2.0
Tissue P % (dw)	0.2	0.2	0.2
Tissue Solid (%dw)	30	30	40
Growth	rapid, via rhizomes, spreads laterally, dense cover in 1 year with plant spacing 0.6 m	moderate, dense cover in 1 year with plant spacing 0.3-0.6 m	very rapid, via rhizomes, spreads laterally 1m/year, very dense cover in 1 year with plant spacing 0.6 m
Hydroperiod	can be permenantly inundated > 0.3 m, tolerate drought	can be permenantly inundated < 1 m, tolerate drought	can be permenantly inundated > 1.0 m, tolerate drought
Common Use	in Free Water Surface & Subsurface Flow CWs in US	in Subsurface Flow CWs in US	in Free Water Surface & Subsurface Flow CWs in US and in Europe

Reference: Crites, 1995.

Table 2.2. Properties of aquatic plant species

SPECIES	**BIOMASS (ton/ha)**	**GROWTH (ton/ha.year)**	**N CONTENT (%)**	**P CONTENT (%)**
FREE-FLOATING				
Eichhornia	20-24	60-110	1.0-4.0	0.14-1.2
Lemna	1.3-3.5	6-26	2.0-7.0	0.2-2
Pistia	6-11	50-80	1.2-4.0	0.15-1.2
Hydrocotyle	7-11	30-60	1.5-4.5	0.2-1.3
Salvinia	2-3	9-45	2.0-5.0	0.2-0.9
SUBMERGED				
Myriophyllum	0.5-9	5-90	3.1-6.4	1.3-2.7
Enteromorpha	2	10-20	-	-
Elodea	-	13-47	2.6-7.3	0.46-2.3
EMERGENT				
Phragmites	6-37	10-60	1.8-2.1	0.2-0.3
Typha	4.3-22.5	8-61	0.5-2.4	0.1-0.4
Scirpus	-	20-46	0.8-2.7	0.1-0.3
Juncus	2.2	53	1.5	0.2

Reference: Gumbricht, 1993.

2.5.1.4. Planting Techniques

Plants can be introduced to a wetland by transplanting roots, rhizomes, tubers, seedling, or mature plants; by broadcasting seeds obtained commercially or from other sites; by importing substrate and its seed bank from nearby wetlands; or by relying completely on the seed bank of the original site. However, there should be no exotic plant introduction to the area (Mitsch and Gosselink, 1993).

If planting stocks rather than the site seed banks are used, it is most desirable to choose plants from the wild stock rather than the nurseries since the former are generally better adapted to the environmental conditions they will face in the constructed wetland. The plants should come from nearby if possible and should be planted within 36 hours of collection. If nursery plants are used, they should be from the same general climatic conditions and should be shipped rapidly to minimize losses. If seeds and seed banks are used for wetland vegetation, several precautions must be taken. The seed banks should be evaluated for the seed viability and the species present. The use of seed banks from other nearby sites can be an effective way of developing wetland plants in a constructed wetland if the hydrologic conditions in the new wetland are similar. When seeds are used directly to vegetate a wetland, they must be collected when they are ripe and stratified (Mitsch and Gosselink, 1993).

2.5.2. Constructed Wetlands Defined by the Flow Pattern

There are two types of constructed wetland based on the primary water flow pattern for the design of macrophyte based constructed wetlands. These are (i) free-water-surface (FWS) wetlands (the majority of water flows above the soil surface) (ii) subsurface flow (SSF) or vegetated submerged bed (VSB) wetlands (all flow is directed through the rooting media with no overland flow). Some of the design parameters for FWS and VSB constructed wetlands are summarized in Table 2.3.

Table 2.3. Constructed wetlands design parameters

Design Factors for Constructed Wetlands	Recommended Design Values	
	FWS	VSB
Organic loading (kg BOD.ha^{-1}.d^{-1})	80-110	80 - 120
Nitrogen Loading (kg.ha^{-1}.d^{-1})	TN < 60	TN < 60
Hydraulic Retention Time (d)	5-14	2 - 10
Hydraulic Loading Rate (cm.d^{-1})	2.5-5	6 – 8
Water Depth (cm)	<10 (warm months) <45 (cold months)	30 - 90
Aspect Ratio (Length:Width)	2:1, 4:1, 10:1	0.25:1, 5:1
Area Requirement (m^2. m^{-3}.d^{-1})	20-140	10-70
Configuration	multiple cells in series and in parallel	multiple cells in parallel

Reference: Reed, 1992; Knight, 1992.

2.5.2.1. Free Water Surface (FWS) Constructed Wetlands

In this type of wetland systems, the water surface is exposed to the atmosphere; the bed contains emergent aquatic vegetation; a layer of soil to serve as a rooting media; a liner if necessary to protect the groundwater and appropriate inlet and outlet structures. The water depth in this type of wetland can range from a few centimeters to ≥0.8 m, depending on the use of the wetland. A normal operating depth of 0.3 m is typical. Design flows for these FWS wetlands range from less than 4 m^3.d^{-1} to over 75000 m^3.d^{-1} (Crites, 1995).

However, there are other FWS configurations used for wastewater treatment. Some of the beds used for wastewater treatment may contain both emergent macrophytes and floating plants. Or, they may have open-water areas, which permit atmospheric reaeration and contain submerged plants. They may also contain islands for habitat purposes (Kreissl and Brown, 2000). FWS CWs with dominant removal mechanisms are illustrated in Figure 2.4.

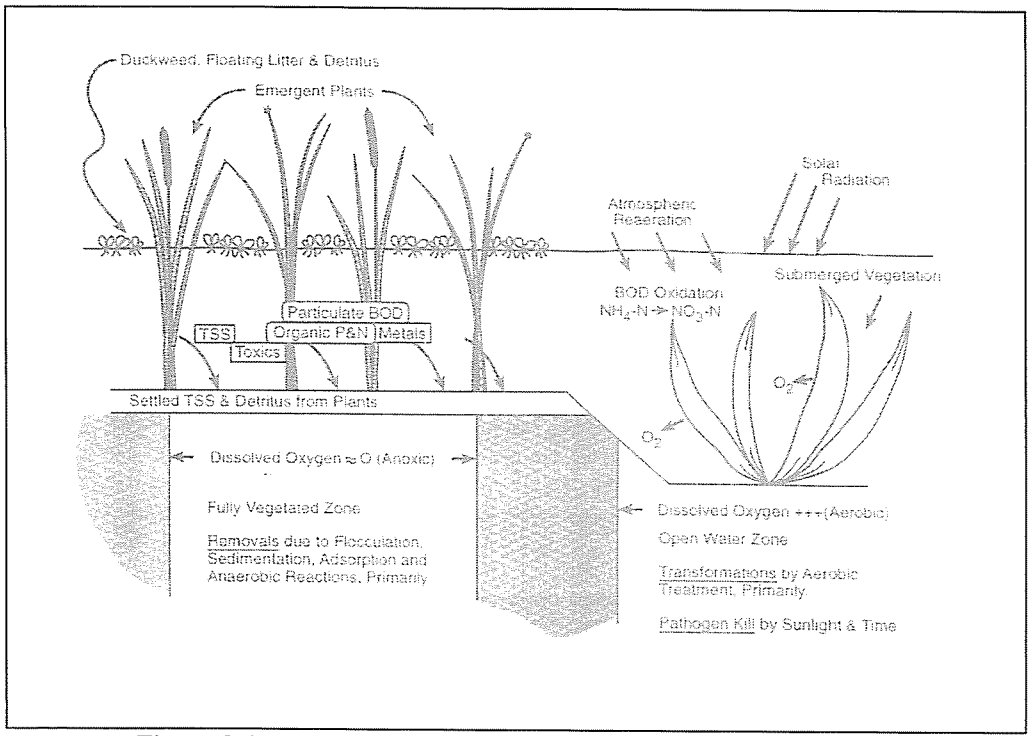

Figure 2.4. FWS constructed wetland with dominant mechanisms (Kreissl and Brown, 2000)

2.5.2.2. Subsurface Flow (SSF) Constructed Wetlands

In this case, the excavated basin is filled with a porous media, usually gravel, and the water level is maintained below the top of the gravel. Emergent aquatic plants are planted in the top surface of the media. A liner is used, if the protection of the groundwater is important. The depth of media is typically 0.3-0.6 m. Existing systems of this type range from those serving single-family dwellings to large-scale municipal systems (Crites, 1995). Nowadays, constructed wetlands are common alternative treatment systems in Europe in rural areas and over 95% of these wetlands are subsurface flow wetlands. In the following years, the number of these systems is expected to be over 10,000 only in Europe (Platzer, 2000). A general view of subsurface constructed wetlands is given in Figure 2.5.

There are mainly two types of flow directions used in these systems. These are horizontal flow (HF) and vertical up/down flow (VF). The important design and performance parameters published in the Abwasser Technische Vereinigung

Guidelines A 262 (ATV, 1998) for the treatment of municipal wastewater in reed plants in Germany are given in Table 2.4 (Gschlössl and Stuible, 2000).

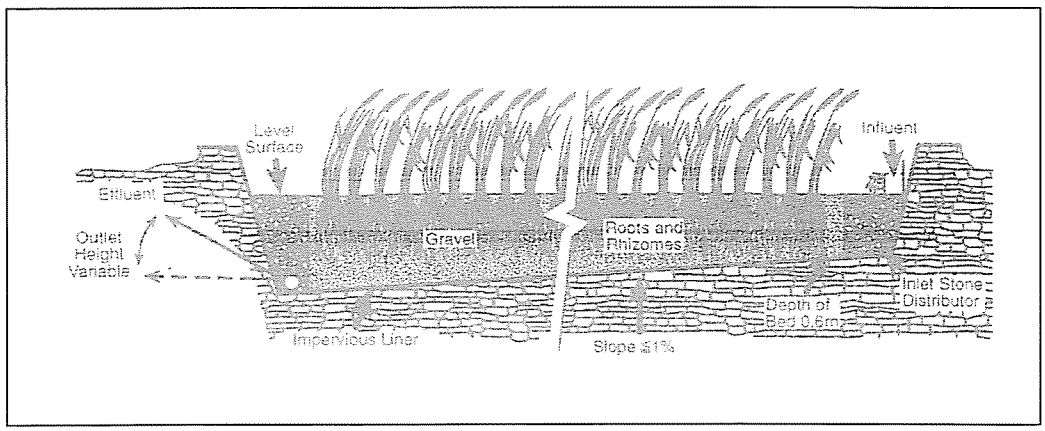

Figure 2.5. Subsurface constructed wetland (Kreissl and Brown, 2000).

Table 2.4. Important design and performance parameters for constructed wetlands published in Germany

Parameter	Horizontal Flow (HF) Subsurface Wetlands	Vertical Flow (VF) Subsurface Wetlands
Pre-sedimentation	Required	Required
Substrate	Sand, Fine Gravel	Sand, Fine Gravel
Permeability Coefficient (K_f), $m.s^{-1}$	10^{-3}-10^{-4}	10^{-3}-10^{-4}
Depth of Reed Bed, cm	≥ 50	≥ 80
Specific Area, m^2/pe	≥ 5	≥ 2.5
Maximum Load, $mm.d^{-1}$ (Dry Weather Flow)	40	60
Plants	*Phragmites*	*Phragmites*

Reference: ATV, 1998.

The details of the constructed wetland systems are presented below.

Horizontal Flow Beds

Initially the main interest was in horizontal-flow systems because they were simple and promised low construction and operational costs. There are many fine examples of HF systems for secondary treatment and even in cold seasons, because of their ability to filter, they proved very satisfactory where the standards required only BOD_5, TSS and bacteria removal (Cooper, 1999). These systems can remove nutrients at average efficiencies of 40-60% (Haberl et al., 1999).

However, there has been a growing interest in achieving fully-nitrified effluents. Tertiary treatment HF systems produce well-nitrified effluents (Green, 1997; Cooper et al., 1996) but secondary treatment HF systems cannot do this because of their limited oxygen transfer capacity (Cooper, 1999). Particular studies (Brix, 1990; Armstrong and Armstrong, 1990; Haberl and Perfler, 1990) have shown that roots of different macrophytes do release oxygen to the rhizosphere but unfortunately much less than needed for degradation and nitrification (Haberl et al., 1999). Concerning the hydraulic conductivity the greatest problem occur in soil-based systems (Haberl and Perfler, 1990).

Vertical Flow Beds

Originally developed by Seidel (1967), VF systems have been in operation in Europe for approximately 20 years in Germany, The Netherlands, Austria and the UK (Haider, 1983, 1994a; Greiner and De Jong, 1984; Boutin 1987; Radoux, 1987; Burka and Lawrance, 1990; Lienard et al., 1990). The Seidel-System is characterized as a relatively shallow vertical flow bed (~30 cm) and continuous feeding of alternatively operated beds in parallel in a first stage and a HF regime in the second stage. Brix (1992) gave an overview of Seidel systems in Europe. Cooper (1996) has developed design criteria for desired nitrification in VF constructed wetlands based on the oxygen demand, according to his experiments and theoretical approaches.

The latest generation of constructed wetlands in Europe has been developed as vertical flow system with intermittent loading (Haberl et al., 1999). The reason for growing interest in using vertical flow systems are (i) they have much greater oxygen transfer capacity resulting in good nitrification, (ii) they are considerably smaller (1-2 m^2/pe) than the HF system which need 5-10 m^2/pe for secondary treatment, (iii) they can efficiently remove BOD_5, COD and bacteria (Cooper, 1999).

An extremely important aspect of VF constructed wetlands is the potential risk of soil clogging which provokes a general failure of the system (Platzer, 2000). First only a few authors reported about this aspect (Cooper and Green, 1994; Platzer and Mauch, 1997). Currently there are various research projects in Germany and Austria concerning this problem (Goetz and Winter, 2000; Laber, 2000, Langergraber et al., 2003).

2.6. Advantages of Wetlands over Conventional Wastewater Treatment Systems

Constructed wetlands are designed to take advantage of many of the same processes that occur in natural wetlands, but do so within a more controlled environment. Some of these systems have been designed and operated with the sole purpose of treating wastewater, while others have been implemented with multiple use objectives in mind, such as using treated wastewater effluent as a water source for the creation and restoration wetland habitat for wildlife and environmental enhancement (Bastian, 1993; Kadlec and Brix 1995, Kadlec and Knight, 1996).

Haberl (1999) has summarized the main advantages of the constructed wetlands over traditional treatment plants. These are as follows:

- utilization of natural processes,
- simple construction,
- simple O/M,
- low energy maintenance,
- little excess sludge production,
- cost effectiveness,
- process stability,
- increase in biodiversity,
- utilization of the harvested aquatic plants for a variety of purposes (biomass, biogas, animal feed, fertilizer, using stems for thatching, matting, fencing, etc.).

2.7. Constructed Wetland Applications

The use of constructed wetlands for sewage treatment at different levels is commonly well known. However, they have also been applied for the treatment purpose of different types of wastewater. Some of these applications include treatment of wastewater originating from several industries, agricultural activities, landfills, surface runoff, acid mine drainage, sludge dewatering, etc. Some of these applications are given in Table 2.5. In order to understand the current trend for constructed wetlands, the current literature has been reviewed and classified according to the type of treated wastewater (Table 2.6, 2.7, 2.8). In the following sections, the applicability of wetland treatment technology is discussed.

2.7.1. Constructed Wetlands for Sewage Treatment

During the early years (pre-1985) of the development of the constructed wetland technology, virtually all emphasis was on the secondary and tertiary treatment of domestic and municipal wastewater after mechanical pretreatment. Since then, there are an expanding number of applications used for sewage treatment throughout the world (IWA, 2000). The number of subsurface flow constructed wetlands in operation in Europe is at present around 5000. In Germany alone, nearly 3500 systems are in operation (Börner et al., 1998). Many systems are also in operation in Denmark (200-400), the UK (400-600), Austria (around 160), Czech Republic (around 80), Poland (around 50), Slovenia (around 20) and Norway (around 10).

In general, most European SSF treatment wetlands are designed to treat domestic or municipal wastewater from sources less than 500 population equivalent (PE). However, most systems are designed for small sources of pollution (less than 50 PE) and many systems are designed for single households. Only a small number of systems were designed for larger sources of pollution (>1000 PE) (IWA, 2000).

Table 2.5. Use of constructed wetlands for different purposes

Date of Application	Type of treated wastewater	Scale	References
1952	Phenol Wastewater	Experimental	Seidel, 1955, 1965, 1966**
1956	Dairy Wastewater	Experimental	Seidel, 1976**
1956	Livestock Wastewater	Experimental	Seidel, 1961*
1965	Sludge Dewatering	Experimental	Bittman and Seidel, 1967**
1968	Reduction of Lake Eutrophication	Operational	Karpati et al., 1968**
1973	Textile Mill Wastewater	Experimental	Widyanto, 1975**
1974	Sludge Dewatering	Operational	Neurohr, 1983**
1975	Petroleum Refinery Wastewater	Operational	Litchfield, 1989*
1975	Photographic Laboratory Wastewater	Experimental	Wolverton, 1976**
1978	Acid Mine Drainage	Experimental	Huntsman, 1978*
1979	Fish Rearing Pond Discharge	Operational	Hammer and Rogers, 1980*
1980	Electroplating Wastewater	Experimental	Schroff, 1982**
1980	Piggery Effluent	Experimental	Finlayson et al., 1987**
1981	Heavy Metals Removal	Experimental	Gersberg et al., 1984**
1981	Tannery Wastewater	Experimental	Prasad et al., 1984**
1982	Reduction of Lake Eutrophication	Operational	Reddy, 1982*
1982	Urban Stormwater Runoff	Operational	Silverman, 1989*
1982	Pesticides	Experimental	Gudekar et al., 1984**
1982	Sugar Refinery Wastewater	Experimental	Yeoh., 1983**
1982	Benzene and its Derivatives	Experimental	Wolverton et al., 1984**
1983	Rubber Industry Effluent	Operational	John, 1984**
1983	Pulp and Paper Mill Wastewater	Experimental	Thut, 1989*
1985	Photochemical Laboratory Wastewater	Experimental	Wolverton, 1987*
1985	Seafood Processing Wastewater	Experimental	Guida & Kugelman, 1989**
1986	Potato Starch Industry Effluent	Experimental	De Zeeuw et al., 1990**
1986	Ash Pond Seapage	Operational	Brodie et al., 1989**
1986	Cyanides and Chlorphenols	Experimental	Wolverton etal., 1988**
1987	Thermally affected Wastewater	Operational	Ailstock, 1989**
1988	Compost Leachate	Operational	Pauly, 1990**
1988	Landfill Leachate	Experimental	Trautman and Porter, 1988*
1988	Livestock Wastewater	Operational	Hammer and Pullin, 1989*
1989	Reduction of Lake Eutrophication	Operational	Szilagyi, 1990*
1990	Harbor Dredged Materials	Experimental	Pauly, 1990*
1991	Pulp and Paper Mill Wastewater	Operational	Thut, 1991*
1992	Bakery Wastewater	Operational	Vymazal, 1994**
1993	Highway Runoff	Operational	Swift a Landsdown, 1994**
1994	Abattoir wastewater	Operational	Vymazal, 1995**
1994	Glycol contaminated Runoff	Operational	

Reference:*cited in Bastian and Hammer, (1993); ** cited in Vymazal et al., (1998).

Table 2.6. Distribution and percentage of the studies on constructed wetlands used for several purposes (1994-2000)

Type of Treated Wastewater in Constructed Wetlands	Number of Studies	Percentage (%)
Municipal	106	31.5
Leachate	12	3.6
Acid Mine Drainage	8	2.4
Surface Runoff	24	8.1
Sludge Dewatering	5	1.5
Industrial	35	10.5
Restoration and Rehabilitation, Prevention of Eutrophication	42	12.5
Agro-Industrial	38	11.3
Reviews, Suggestions, Design Criteria	64	19.1

References: Water Science and Technology, Vol: 35(5) 1997 and Vol: 40(3) 1999; *Proceedings of 7th International Conference on Wetland Systems for Water Pollution Control*, Florida, 2000.

Even though developed countries widely used constructed wetland technology for treatment of domestic wastewater under various conditions successfully; there is a growing interest in use of constructed wetlands in developing countries. However, there is limited information on the level of development of wetland technology in those countries. It appears that in some countries, basic research is being carried out, while in others, the technology has reached pilot and full-scale levels for various applications (Kivaisi, 2001). Morocco, Egypt, Iran, Thailand, Uganda, Nepal and India are some of the developing countries, where several researchers recently have conducted studies on treatment of domestic wastewater in constructed wetlands, recently.

For example, Mandi et al. (1998) conducted a study on the purification of domestic wastewater under semi-arid conditions in Morocco. Reed beds planted with *Phragmites australis* had a COD removal of 48–62%, TSS of 58–67% and a parasitic removal of 71–95% at a hydraulic load of 0.86–1.44 $m^3.d^{-1}$. Further experiments were carried out to improve the removal performances of the reed beds. In Egypt, Stotts et al. (1998) achieved a 100% removal of parasitic ova from domestic wastewater intended for agriculture use. In Iran, a subsurface flow reed bed *(P. australis)* of 150 m^2 was tested for treating municipal wastewater. At an organic loading of 200 $kg.ha^{-1}.d^{-1}$, which is higher than previously recommended

(<133 $kg.ha^{-1}.d^{-1}$) (Metcalf and Eddy, 1991), removal efficiencies of 86%, 90%, 89%, 34%, 56% and 99% for COD, BOD_5, TSS, TN, TP, and fecal coliform bacteria, were obtained, respectively. No clogging problems were experienced (Badkoubi et al., 1998).

In Thailand, Koottatep and Polprasert (1997) experimented with *Typha augustifolia* on removal of nitrogen from primary treated sewage in SF beds. With 8 weeks harvesting intervals at 5 days retention time, a maximum of 7.5 $kg.ha^{-1}.d^{-1}$ nitrogen uptake by the plants was obtained. This was accompanied by a TN removal of 84–86%. In Uganda, Okurut et al. (1998) demonstrated the viability of indigenous *C. papyrus* and *P. mauritian*s in pilot-scale CWs treating municipal wastewater. In the *C. papyrus* systems, average mass removal rates for COD, TSS, NH_4^+-N, TN and PO_4^{3-}-P were 15.32, 6.62, 6.5, 1.06, 0.06 $g.m^{-2}.d^{-1}$, respectively. In *P. mauritianus* systems, the removal rates for the same parameters were 2.25, 0.9, 0.66, 0.65, and 0.058 $g.m^{-2}.d^{-1}$, respectively. The level of BOD and TSS in the effluents were below 20 and 25 $mg.L^{-1}$.

The potential of CWs for application by small communities for wastewater treatment has been examined in Nepal (Laber et al., 1999). A hybrid system comprising of HF and VF beds (140 m^2 HF and 120 m^2 VF) with *Phragmites karka* were tested for one year on full scale for treatment of hospital wastewater. At a hydraulic loading rate of 107 $mm.d^{-1}$, removal efficiencies for COD, BOD_5, NH_4^+-N, TP, total coliforms, *Escherichia coli*, *Streptococcus* and TSS were 93%, 97%, 99.7%, 74%, 99.99%, 99.995, 99.97%, and 98%, respectively.

In India, a subsurface horizontal flow CW with indigenous *Phragmites karka* covering an area of 41.8 m^2 was installed in 1997 for treatment of domestic wastewater at Vikram University, India. The system was reported to perform well with BOD_5, TSS, NH_4^+-N, and TP removal of 65%, 78%, 78%, 56–65%, respectively (Billore et al., 1999).

2.7.2. Constructed Wetlands for Industrial Wastewater Treatment

The use of constructed wetlands to treat industrial wastewater has increased significantly over the past ten years. Unlike the municipal wastewater discharges, which usually have a consistent composition, industrial wastewater often have a variety of components of varying degrees of biodegradability and toxicity, thus necessitating different treatment modalities and strategies (Davies et al., 1990). However, due to the toxic constituents, not all the industries can discharge their effluent into the constructed wetlands (Husband et al., 2000).

On going studies are concentrated on the removal of industry-specific contaminants unique to the generated effluent of a particular industrial operation (Husband, 2000).

Some of the constructed wetland applications for industrial wastewater treatment include (Ferraro and Kadlec, 2000):

- leachate control of effluent from landfills,
- water from power plants,
- abandoned and active mines,
- remediation of polluted groundwater and surface water in hazardous waste industry,
- remediation of hydrocarbon effluents in the petrochemical industry,
- remediation and control of effluents from the pulp and paper industry, and
- remediation and control of effluents from food industries.

The distribution of the recent studies on industrial wastewater treatment between 1994-2000 is presented in Table 2.7.

Table 2.7. Distribution of recent studies on industrial wastewater treatment (1994-2000)

Type of Industrial Wastewater	Total Number of Applications	Distribution of Studies (%)
Petro-Chemical	6	20.70
Pulp and Paper	3	10.34
Heavy Metal Treatment	7	24.14
Radionuclides	2	6.89
Laboratory Wastewater	1	3.45
Olive Oil Wastewater	1	3.45
Explosives	1	3.45
Smelter Effluent	1	3.45
Textile	1	3.45
Sugar Beet	2	6.89
Potato Processing Industry	2	6.89
Chlorinated Alkenes	1	3.45
Chemical Manufacturing Plant	1	3.45

References: *Water Science and Technology*, Vol: 35(5), 1997 and Vol: 40(3) 1999; *Proceedings of 7th International Conference on Wetland Systems for Water Pollution Control*, Florida, 2000.

2.7.3. Constructed Wetlands for Agro-Industrial Wastewater Treatment

Wastewater from intensive agricultural activities (cattle feedlots, piggeries, dairies, swine barns and similar activities) typically has significantly higher concentrations of organic matter and nutrients than treated municipal effluent. The high pollutant loads can contribute to water management problems if wastes are allowed to discharge directly to receiving water. Agricultural wastes must be treated prior to disposal and constructed wetlands in association with stabilization ponds have been suggested as a potential treatment option prior to land application (Geary and Moore, 1999).

In most cases, a FWS wetland will be the cost-effective choice for treatment of this wastewater, since the smaller land area and other potential advantages of the SF are not usually essential in an agricultural setting. However, the SF may still be desirable for year-round operations in cold climates because of the enhanced thermal protection provided by this system (Crites et al., 1995). Despite its

temperature dependence, the constructed wetland is essential in removal of organic matter and pathogen even in colder months. However, refractory organic and heavy metal removal is important all year long (Lemos and Antunes, 2000). Hammer (1992); Watson et al. (1993) and Gale and Reddy, (1995) showed the effective use of constructed wetlands in the treatment of agro-industrial wastewater including stock-breeding. The distribution of agro-industrial wastewater treatments in constructed wetlands is given in Table 2.8.

Table 2.8. Distribution of the recent studies on agro-industrial wastewater treatment (1994-2000)

Type of Agro-Industrial Wastewater	Total Number of Applications	Distribution of Studies (%)
Animal Wastewater	6	19.35
Swine Wastewater	6	19.35
Dairy Wastewater	10	32.26
Agricultural Wastewater	5	16.13
Pesticide containing Wastewater	1	3.24
Slaughterhouse	3	9.67

References: *Water Science and Technology*, Vol: 35(5) 1997 and Vol: 40(3) 1999; *Proceedings of 7th International Conference on Wetland Systems for Water Pollution Control*, Florida, 2000.

2.7.4. Constructed Wetlands for Agricultural Runoff

Agricultural non-point source pollution is considered to be the largest single category resulting in the water deterioration. Since the agricultural applications of fertilizers and pesticides have increased dramatically since the middle 1960s, agrochemical contamination of surface and groundwater has become a serious environmental concern. Since the mid-1980s, a variety of state and federal programs have been used to promote wetland restoration (Crumpton, 2000) since wetlands can play important roles as filters for nutrient discharged from agricultural areas into the ecosystems (Romero et al., 1999). Some studies were done to understand the potential role of free water restored wetlands for water pollution control in agricultural areas for nitrogen removal (Comin et al., 1997; Romero et al., 1999).

2.7.5. Constructed Wetlands for Stormwater Runoff

Wetlands are essential part of nature's stormwater management system. Important wetland functions include natural restorative processes, which improves water quality while being cost-effective; conveyance and storage of stormwater, which dampens effects of flooding; reduction of flood flows and velocity of stormwater, which reduces erosion and increases sedimentation; and modification of pollutants typically carried in stormwater. Although detention ponds to reduce stormwater pollutant concentration in urban catchments are increasingly being used (Bavor and Mitchell, 1994), there is a great amount of interest in incorporation of natural wetlands and constructed wetlands into stormwater management systems (Steven, 1998; Kao and Wu, 1999; Roser and Bavor, 1994; Sakadevan and Bavor, 1998). The reason of the preference of constructed wetlands over the detention ponds is the effective removal capacity of constructed wetlands for treatment of particulate-bound pollutants such as metals, nutrients and microorganisms (Bavor, 2000).

2.7.6. Constructed Wetlands for Highway Runoff

The environmental impacts of road runoff are of increasing concern. Construction of impermeable roads and efficient drainage systems increase the peak discharges from storms, which causes stream-bed erosion and increased flood risk. Runoff quality is highly variable and depends on the amount of pollutants on the road and dilution by each particular storm event (Munger et al., 1995; Nuttall et al., 1997). Pollutants accumulated on the road surface from vehicle wear, emissions, and accidental spillage are transported into runoff. These pollutants include sediments, metals, salts, hydrocarbon, pesticides and herbicides. The quality of road runoff also has impacts on receiving waterbodies. Adsorbed pollutants can have acute or chronic ecotoxicological affects (Pontier et al., 2000).

Traditionally, these have been prevented with balancing ponds and wet or dry detention basins, until recently (Luker and Montague, 1994). The use of

constructed wetlands for the treatment of highway runoff is a relatively new technology although it has been established in the US for several years (Kadlec and Knight, 1996). The focus on fulfilling the objectives of Agenda 21 in Europe and the UK has encouraged the adoption of wetlands as method of sustainable environmental management. Initial recommendations for the use of pre-treatment structures including oil separators, silt traps and settlement basins were listed.

The related monitoring studies for the treatment of highway runoff via constructed wetlands show effective removals of suspended solids, as well as heavy metals like copper, chromium, nicel, zinc, lead, and iron (Sakadevan et al., 1999; Shutes et al., 2000; Pontier et al., 2000). But still, there are no established design criteria for constructed wetlands for treatment of highway runoff, since road runoff is an intermittent and highly variable feedstock (Pontier, 2000).

2.7.7. Constructed Wetlands for Landfill Leachates

Leachates generated in municipal and industrial landfills can be a major source of surface water and groundwater pollution. They are often difficult to handle due to their nature (e.g., toxic, containing high levels of contaminants, high or low pHs, saline, etc.) variations in quality and quantity (Higgins, 2000). As a result of inherent variability in composition, no two landfills produce the same quality of leachate. Not only do leachate composition vary day-to-day, but they are also affected by time, regional climatic patterns, and characteristics of the refuse including their depth and permeability (McBean and Rover, 1999; Martin et al., 1999).

The transport of landfill leachates to local conventional wastewater treatment plants or treatment in on-site facilities is usually expensive. Therefore, landfill managers are seeking for cost effective, reliable, flexible on-site technologies for pre-treatment and on/off-site disposals such as direct discharge of treated effluent into surface waters (Martin et al., 1999). As a result, over the past few years, the use of

constructed wetlands to treat leachates from municipal and industrial landfills has become a treatment modality (Maehlum, 1998; Martin and Johnson, 1995; Robinson, 1998, Sanford, 1998; Surface et al., 1993).

Constructed wetlands provide good removals of BOD_5, TSS, heavy metals (e.g., Cu, Cr, Al, Cd, Fe, Pb, Ni, etc.), organics including volatile organic compounds and pathogens from the leachates in the range of >60-90%. Even though they are widely used in cold climates, winter operability sometimes presents problems and they only remove part of the nutrients with reductions averaging only in the 30-60% range (Higgins, 2000).

Constructed wetlands used for leachate treatment differ in their configurations and types as (i) subsurface flow wetlands (Cooper and Hobson, 1989; Staubitz et al., 1989; Birkbeck et al., 1990; Surface et al., 1993), (ii) surface flow wetlands (Martin and Moshiri, 1994; Martin et al., 1993; Schwarz et al., 1993; Keeley et al., 1992), (iii) cold climate systems (Maehlum, 1998; Pries, 1995) and (iv) reed beds (Robinson, 1990; Urbanc-Bercic, 1994; Bulc et al., 1997; Agropsowicz, 1991). Due to their variability of leachate composition and a lack of design data, case-by-case design elements and evaluation are necessary for the implementation of the constructed wetlands for the treatment of the landfill leachates (Husband et al., 2000).

2.7.8. Constructed Wetlands for Acid Mine Drainage

Acid mine drainage (AMD) is a wide spread environmental problem associated with both active and abandoned mining operations. With ever increasing environmental awareness and legislation, there is a growing demand for remediation measures to minimize the environmental impact of AMD (Prior and Whitehead, 2000). Over the last 20 years, several different passive technologies, including constructed wetlands, and limestone drains, have been employed to abate the impact of acidic discharges on freshwater streams. Through a variety of

physical, chemical biological processes, these wetlands are effective in reducing acidity and removing up to >99% of iron and aluminum from AMD, but they only remove between 20 to 30% or less of manganese loading. Even though problems may occur with these wetland systems, current studies indicate that overall they are more cost effective and ecological beneficial than conventional chemical treatments (Brenner, 2000).

2.7.9. Constructed Wetlands for Sludge Dewatering

Although far less numerous than constructed wetlands for wastewater treatment, vertical flow constructed wetlands have been employed for dewatering sludges for over 30 years. Such wetlands, in which common reed is planted in soil, sand or gravel, appear to offer both economic and environmental advantages over alternative methods of sludge dewatering. They are far more effective than sand bed drying, they do not require chemical flocculants, centrifuges or belt presses (Edwards et al., 2000).

For small rural sewage treatment works, in such dewatering operations sludge is fed onto the vertical flow reed bed periodically. It becomes dewatered by percolation through the preceding sludge layers and the matrix by evapotranspiration through the reed roots, stems and leaves, and by evaporation from the sludge surface. Movement of the stems in the wind keeps open the drainage passages down through the sludge layer. With slow percolation of oxygen into the sludge layer, both via the reed plants and their root zone, and by diffusion through the air-sludge interface, the sludge gradually becomes oxidized with a reduction in volatile solids and an increase in percentage ash or fixed solids. With gradual loss of moisture, the percentage total solids of the dewatering sludge can build up towards 50% (De Maesener, 1997).

Reinhofer and Berghold (1994) showed that for a specific area of about 0.15-0.25 m^2/pe a sludge volume reduction of 80-90% and a dewatering capacity of about

35% dry matter is possible. Pauly (1994) succeeded in dewatering sludge even up to 60% dry matter. Moreover, he could achieve good hygienic quality of the end-product. Even though most of the full-scale experience on reed bed dewatering comes from Denmark (Nielsen 1990, 1995), there are also both full and pilot-scale applications for sludge dewatering in other countries like France (Lienard et al., 1990, 1995), U.S. (Kim, 1997), UK (Nuttall et al., 1997; Cooper and Willoughby, 1999), Germany (Platzer, 2000) and Poland (Obarska-Pempkowiak, 2000).

2.8. Constructed Wetland Studies in Turkey

In Turkey, one of the earliest batch-scale studies evaluated the growth rate and removal performances of different aquatic plant species like *Cyperus ssp., Canna sp.,* and *Paspalum paspalodes*, which were receiving different types of wastewater (Ayaz and Saygın, 1996). Akça et al. (1998) conducted to evaluate the removal performances of duckweed (*Lemna minor*) to treat anaerobically post treated landfill leachate in a tank with a volume of 9.6 L. Even though average COD and TKN removal efficiencies were obtained as 61% and 27%, respectively; the plants died after almost 2 months of the start-up. However, a subsurface flow sand bed constructed wetland planted with a mixture of rooted plants (*Cyperus* and *Lolium*) to treat the same wastewater, 50%, 40% and 70% removal of COD, TKN and TP was achieved at the end of a 4 months operation, respectively. Other experimental studies were carried out in a batch-scale subsurface constructed wetland with a volume of 25 L and planted with bulrush (*Scirpus sp.*) to treat the domestic wastewater taken from the İstanbul Sewerage System. For a 2 month period, average removal efficiencies of COD, TKN, TP and Cd were found as 74%, 75%, 68% and 95%, respectively (Akça et al., 1998).

In another study, Ayaz and Akça, 2000 evaluated the performance of a pilot-scale constructed wetland (2 polyester tanks of 0.3 m x 1.5 m x 3.5 m) planted with *Cyperus* plants. Primarily settled domestic wastewater from the campus of TUBITAK Marmara Research Center was pumped into the tanks filled with gravel

of 0-5 mm ensuring the subsurface flow conditions. Wastewater was recycled periodically between the two tanks and the treatment performance was monitored under different loading rates in a 12 month of period. The average COD removal efficiency of 90% was observed at an average loading rate of 122 g $COD.m^{-2}.d^{-1}$, whereas removal efficiencies for TSS, TKN, TN and PO_4^{3-}-P were 95%, 77%, 61% and 39%, respectively.

One of the constructed wetland studies was also performed on the campus of TUBITAK Marmara Research Center, where the batch and continuous flow experiments were conducted. The batch-experimental system consisted of 12 pairs of the serial connected tanks each with a surface area of 1 m^2 and filled with materials such as gravel, peat and perlite. Seven of them were planted with *Phragmites, Cyperus, Rush, Iris, Lolium, Canna* and *Paspalum*, whereas the remaining five were not planted. Each set was filled with sewage once a day and wastewater was recycled periodically. The plant species *Iris* and *Canna* showed the best performances for COD removal and for N-removal, respectively. The average removal efficiencies of COD, TSS, TKN, TN and PO_4^{3-}-P efficiencies were found as 88%, 97%, 85%, 83% and 60%, respectively (Ayaz and Akça, 2001).

A pilot-scale reed bed plant was constructed by Küçük et al. (2003) to evaluate the COD, NH_4^+-N, PO_4^{3-}-P and Total Chromium removal performance of a horizontal flow constructed wetland receiving biologically treated tannery effluent. *Typha domingensis* and *Phragmites australis* were selected as plant types for evaluations. The reed bed system was operated in batch and continuous modes. The impact of wetland design criteria, operational conditions and inlet NH_4^+-N concentrations of the wetland system on the removal of COD, NH_4^+-N, PO_4^{3-}-P, TSS and Total Chromium was investigated.

The horizontal flow reed bed planted with *Typha domingensis* and operated continuously at different hydraulic loading rates removed 31% COD, 50% NH_4^+-N, 83% PO_4^{3-}-P, and 55% Cr, respectively. During the batch operation of the reed bed,

the removal efficiencies of NH_4^+-N and PO_4^{3-}-P increased with the increase in the batch period, while removal efficiencies in terms of COD decreased. The highest NH_4^+-N and PO_4^{3-}-P removal efficiencies were achieved as 82% for and 83% at a batch period of 14 days, respectively. The COD and NH_4^+-N removal efficiencies of the horizontal flow reed bed planted with *Phragmites australis* and operated continuously at an optimum HRT of 8 days were found as 30% and 95%, respectively. The reed bed system provided good treatment performance at higher NH_4^+-N loading rates. The NH_4^+-N and COD removal efficiencies of the system at a HRT of 7 days and initial 20 $mg.L^{-1}$ NH_4^+-N concentration were almost 99% and 40%, respectively (Küçük et al., 2003).

In the framework of "Integrated Preventive Environmental Management Project for Municipalities – IPEMM", which was carried out by Chamber of Environmental Engineers (CEE) in Turkey, and supported by the Swiss Agency for Development and Cooperation, constructed wetlands to treat municipal wastewater of 40 $m^3.d^{-1}$ were designed and implemented in Viranşehir, Şanlıurfa, in 2003. These subsurface flow reed beds consisted of two of the parallel hybrid systems planted with *P.australis* at a density of 4 $shoots.m^{-2}$. The hybrid systems consisted of a horizontal subsurface flow wetland (150 m^2) connected to a vertical subsurface flow constructed wetland (75 m^2), in series. These wetlands were filled with local substrates (basalt and volcanic slag) and operated intermittently at a loading rate of 0.100 $m.d^{-1}$. This study was one of the pioneer studies in terms of municipal wastewater treatment in Turkey, which was carried out in cooperation of the technical staff of CEE and the Municipality of Viranşehir (Yıldız et al., 2004).

In 2003, the General Directorate of the Köy Hizmetleri has also started dealing with the Natural Treatment Systems to treat the wastewater produced in rural areas of Turkey. They started to implement subsurface flow constructed wetlands to treat the primarily settled domestic wastewater in the following villages of Turkey with a changing population of 100-1500 PE: Ankara-Haymana-Dikilitaş Köyü, İzmir-Torbalı-Korucuk Köyü, Adana-Yüreğir-Yeniyayla Köyü, Mersin-Merkez-Musalı

Köyü, Mersin-Erdemli-Sarıyer Köyü, Karaman-Merkez-Kızılyaka Köyü, Manisa-Akhisar-Sakarkaya Köyü, Isparta-Eğirdir-Ağılköy, Tekirdağ-Merkez-Dedecik Köyü, Tekirdağ-Malkara-Çavuşköy, Kahramanmaraş-Pazarcık-Çiğdemtepe Köyü, Kilis-Merkez-Beşikkaya Köyü, Isparta-Eğirdir-Sorkuncak Köyü, Uşak-Merkez-Hocalar Köyü, Burdur-Çeltikçi-Tekke, Burdur-Merkez-İğdeli, Aksaray-Sarıyahşi-Yaylak, Tokat-Turhal-Yeniceler, Tokat-Zile-Uzunöz, Isparta-Merkez-Aliköy, Niğde-Merkez-Fesleğen.

2.9. Cost Estimations for Constructed Wetlands

Construction of a new wetland involves careful consideration of a number of criteria, including a realistic look at the expected cost. The amount of funding available, the period of time, and the limits and rules concerning expenditure are questions to be dealt with early in the planning stages of a constructed wetland (Mitsch and Gosselink, 1993). System costs will obviously vary widely according to the site-specific issues (Kent, 1994). The major elements to be considered:

- Planning, engineering, and legal issues;
- Land acquisition and easements;
- Construction (including site preparation, excavation, trenching, placement of soil, planting, drainage and piping, inlet and outlet structures, pretreatment devices, placement of fill, riprap and crushed stone, erosion control measures, mulching and seeding, general landscaping, construction supervision and inspection);
- Operation and Maintenance (including monitoring, inspection, cleaning, disposal of waste materials); and
- Monitoring whether construction objectives are being met

Due to these numerous factors and the many different ways of conducting or contracting the work, it is not possible to give a "rule of thumb" for the estimation of the costs of a constructed wetland for water quality enhancement. In this regard,

variation in construction cost may range from about 1.5 US$/m^2 to over 20 US$/m^2 of land (Hochheimer et al., 1991).

2.10. Removal Mechanisms in Constructed Wetlands

Several physical, chemical and biological processes occur within the wetlands. In the following sections, the removal mechanisms for suspended solids, organic compounds, phosphorus and nitrogen are explained, respectively. There are also some biogeochemical indicators for determination of the fate of C, N, P and toxic organic compounds in constructed wetlands (Reddy and D'Angelo, 1997). A list of processes and respective biogeochemical indicators are listed in Table 2.9.

2.10.1. Suspended Solids Removal

Suspended solids are one manifestation of natural wetland processes, as well as being common contaminants in feed waters. A number of natural wetland processes produce particulate matter: the death of invertebrates, the fragmentation of detritus from plants and algae, and the formation of chemical precipitates such as iron flocs. Bacteria and fungi can colonize these materials and add to their mass. Since wetland systems have long hydraulic residence times, generally several days or longer, particulate matter usually has sufficient time to settle and become trapped in litter or dead zones (IWA, 2000).

Generally, suspended solids of natural and surface flow constructed wetlands are typically near neutral buoyancy, flocculent, and easily disturbed. However, the existence of a subsurface air-water interface causes sediment processing in the subsurface flow wetland to differ considerably from that in surface flow wetlands. Macrophyte leaf and seed litter are mostly contained on the surface of the bed and do not interact with the water flowing in the interstices below. Most vertebrates and invertebrates do not interact with the water. Resuspension is not caused by wind or vertebrate activities (IWA, 2000).

Table 2.9. Processes and biogeochemical indicators for determination of the fate of C, N, P and toxic organic compounds in constructed wetlands

C, N or P	Processes	Biogeochemical Indicators
CARBON		
	Mineralization	$DIC+CH_4$ in porewater Soil Oxygen Demand (SOD) CBOD Microbial Biomass C Extracellular Enzymes (Cellulases) Plant Litter Composition (Lignocellulose index; C/N, C/P ratio) Soil Redox Potential and pH Electron Acceptor availability
NITROGEN		
	Mineralization	NH_4^+-N+ NO_3^--N (Dissolved and exchangeable) Microbial Biomass N Extracellular Enzymes (Proteases, Peptidase) Plant Litter Composition (C, N, and P content) Soil Redox Potential and pH
	Nitrification	NH_4^+-N DO
	Ammonia Volatilization	NH_4^+-N (Dissolved and exchangeable) pH Alkalinity Temperature
	Denitrification	NO_3^--N Microbial Biomass C Extracellular Enzymes (Proteases, Peptidase) Plant Litter Composition Dissolved Organic Carbon Redox Potential
PHOSPHORUS		
	Mineralization	Bicarbonate Extractable P Microbial Biomass P Extracellular Enzymes (Phosphatase) Plant Litter Composition (C, N, and P content) Redox Potential
	Adsorption/Desorption	Soil Organic Matter Oxalate Extractable Fe and Al HCL-extractable Ca and Mg Particle Size Distribution (clay, silt and sand) Redox Potential and pH Algal Species Composition
TOXIC ORGANIC COMPOUNDS		
	Mineralization	Parameters shown for Carbon
	Adsorption/Desorption	Organic Matter Content (Particulate and Dissolved) Redox Potential and pH

Reference: Reddy and D'Angelo, 1997.

Higher velocities can dislodge adhering or deposited material, which forms the basis for the back-washing method of filter regeneration. Generation of particulate material can occur via all the mechanisms, which occur in surface flow wetlands. Below-ground macrophyte parts - roots and rhizomes - die, decay and produce fine detrital fragments. Many other organisms are present in the bed that can contribute to TSS via the same route: algae, fungi and bacteria all die and contribute particulate matter to the water flowing in the pore space. These microorganisms are unevenly distributed spatially within the gravel bed, with more organisms located near the inlet and near the bottom (Bavor et al., 1988).

Non-settling/colloidal solids are removed by bacterial decomposition, adsorption to the wetland media and plant root system (Stowell et al., 1981). The extensive root system adds surface area to the wetland media, which reduces water velocity and reinforces settling and filtration in the root network. However, plant effects are usually observed after three years of establishment in many of the wetlands (Brix, 1997; Tanner, 2001).

However, many particulate processes do operate in the water-filled voids. Particles settle into stagnant micropockets or are strained by flow constrictions. They can also impinge on substrate granules and stick as a result of several possible interparticle adhesion forces. These physical processes are termed "granular medium filtration" (Metcalf and Eddy, 1991).

In a subsurface flow wetland, the end result of subsurface biological and vegetative activity is the build-up of solids within the pore spaces of the medium. That build-up is larger near the inlet and larger near the top of the bed (Tanner and Sukias, 1994; Kadlec and Watson 1993). A significant portion of the pore volume can be blocked by accumulated organic matter, which can result in increased hydraulic gradients and decreased retention times (Tanner and Sukias, 1994). The deposits consist of low-intensity bio-solids together with fine mineral particulates, which can have a very low bulk density. Partial clogging can reduce the hydraulic

conductivity of the media and result in surface overflow (Reed et al., 1995). In many systems, to prevent clogging, the majority of settleable solids are removed in a mechanical pretreatment unit (e.g. sedimentation or Imhoff tanks) before the wastewater is discharged to the actual wetland system.

2.10.2. Organic Compounds Removal

Treatment efficiency of the constructed wetlands for the removal of organics (BOD_5, COD) is generally high (Cooper and Findlater 1990, Bavor and Mitchell 1994, Kadlec and Brix, 1995; Vymazal at al., 1998). In wetland systems, settleable organics are rapidly removed under quiescent conditions by deposition and filtration. Organic compounds are degraded biologically both aerobically as well as anaerobically by heterotrophs and autotrophs in the wetland systems depending on the oxygen concentration in the bed. Nearly all biological degradation takes place within bacterial films present on solid surfaces, including sediments, soils, fill medium, litter and live submerged plant parts (IWA, 2000).

Depending on the wetland design, the oxygen required for aerobic degradation can be supplied by diffusion, convection and oxygen leakage from the macrophyte roots into the rhizosphere. Thus, treatment efficiency of the constructed wetlands for the removal of organics is generally highly dependent on the oxygen concentration in the bed; the wetland design; treatment conditions; the characteristics of the fill medium (Cooper and Findlater, 1990, Bavor and Mitchell, 1994, Kadlec and Brix, 1995; Vymazal et al., 1998) Uptake of organic matter by the macrophytes is negligible compared to biological degradation (Watson et al., 1989; Cooper et al., 1996).

2.10.3. Phosphorus Removal

Excessive phosphorus loading from manmade sources is commonly linked to eutrophication of lakes and streams (Hillbricht Ilkowska et al., 1995). Phosphorus

is contributed by agricultural runoff and erosion from agricultural land, urban runoff and wastewater effluent (Brooks et al., 2001). Phosphorous is typically present in the wastewater as orthophosphate, dehydrated orthophosphate (polyphosphate) and organic phosphorous, which are present in solution, in particles or detritus, or in the bodies of aquatic organisms. Biological oxidation results in the conversion of most phosphorous to the orthophosphate forms (Cooper et al., 1996).

Orthophosphates such as PO_4^{-3}, HPO_4^{-2}, $H_2PO_4^{-}$, H_3PO_4 are available for biological uptake without further breakdown. The polyphosphates undergo hydrolysis in aqueous solutions and revert to the orthophosphates forms. The hydrolysis is a very slow process. The organic phosphorous is an important constituent of industrial wastes and less important in most domestic wastewater. The average total phosphorous concentration in domestic raw wastewater is about 10 $mg.L^{-1}$, where 30-50% of the TP comes from the sanitary wastes, while the remaining 70-50% is from phosphate builders in detergents. In most cases, the effluent standards range from 0.1 to 2.0 $mg.L^{-1}$. However, the TP concentration of 10 $mg.L^{-1}$ in the raw wastewater is generally reduced to about 9 $mg.L^{-1}$ in primary treatment units and to 8 $mg.L^{-1}$ in secondary units of conventional treatment systems (Lee and Lin, 1999).

Over the last two decades several studies have reported on the potential use of wetlands for removal of nutrients, including P from wastewater (Reddy and Smith, 1987; Mitsch and Cronk, 1992; Moshiri, 1993; Kadlec and Knight, 1996; IWA, 2000; Headley et al., 2003). P removal has been variable at best (Watson et al., 1989; Mann, 1990; Jenssen et al., 1993; Greenway and Woolley, 1999) because constructed wetland matrix materials are often selected based on local availability and particle size for reduced clogging, without consideration for their capacity for P removal (Watson et al., 1989; Mann, 1990). The factors affecting the phosphorus removal in constructed wetlands can be summarized as follows:

- Presence of metals like Fe, Al and Ca (Zhu et al., 1997),
- pH (Nichols, 1983),

- Dissolved oxygen (DO) concentrations in the filter media (Reddy and D'Angelo, 1997),
- Phosphorus concentration in the solution (Stober et al., 1997),
- Organic matter in the filter media (Sakadevan and Bavor, 1998),
- Particle size of the filter material (Reed at al., 1995),
- Temperature effect especially in cold-climates (Reddy and D'Angelo, 1997),
- Time (Brady, 1990).

Phosphorus removal in wetlands takes place due to the following processes (Pant et al., 2001):

- retention by root bed media (Tanner et al., 1998),
- plant uptake (Greenway and Woolley, 1999),
- storage in accumulating organic matter (Verhoven and Van der Toorn, 1990),
- accretions of wetland soils (Kadlec, 1997),
- microbial immobilization (Newbold et al., 1983; Reddy et al., 1999), and
- precipitation in the water column (Reddy et al., 1987; Diaz et al., 1994).

In subsurface flow (SSF) constructed wetlands, the main mechanisms for P removal are adsorption, complexation and precipitation, storage, plant absorption (plant uptake), and biotic assimilation (Watson et al., 1989). Detailed information related to these mechanisms were submitted in the following sections.

2.10.3.1. Adsorption and Precipitation Mechanisms

Adsorption is a process, by which a molecule becomes concentrated onto the surface of a solid phase. There are two forms of adsorption: chemical and physical. Chemical adsorption, or chemisorption, involves formation of a chemical bond, which can range from complete ionic to complete covelent, between the adsorbate and substrate (Nix, 1999). Chemical adsorption predominates in lower concentrations, but as the concentration increases and adsorption sites becomes saturated, physical adsorption (bonding by Van der Waals and electrostatic forces),

becomes more important (Faust and Aly, 1987; Nix, 1999). These types of adsorption involves weaker bonds, with no significant redistribution of electron density (Nichols, 1983).

Adsorption may actually be considered a unique form of precipitation, which is when anions and cations combine to form a solid (Nichols, 1983). Phosphates react with soluble aluminum, iron and manganese to form insoluble hydroxy-phosphates, in reactions similar to the forms shown below (Brady, 1990):

$$Al^{3+} + H_2PO_4^- + 2H_2O \leftrightarrow Al(OH)_2H_2PO_4 \downarrow + 2H^+ \qquad \text{Eqn(2.1)}$$

Phosphates react more extensively with the insoluble hydrous-oxides of these metals (e.g. gibbsite, $Al_2O_3 \cdot 3H_2O$, and goethite, $Fe_2O_3 \cdot 3H_2O$), again forming insoluble hydroxyl- phosphates (Brady, 1990). A typical reaction is given below:

$$Al_2O_3 \cdot 3H_2O + H_2PO_4^- \leftrightarrow 2Al(OH)_2H_2PO_4 \downarrow + 2OH^- \qquad \text{Eqn(2.2)}$$

In addition to precipitation and adsorption reactions, phosphates can participate in anion exchange with positively charged oxides on soil particles, a reversible process that holds the phosphate loosely. The reaction demonstrated by Brady (1990) is presented below:

$$Al(OH)_2{}^+OH^- + H_2PO_4^- \leftrightarrow Al(OH)_2{}^+H_2PO_4^- + OH^- \qquad \text{Eqn(2.3)}$$

Under aerobic, neutral to acidic circumstances (1<pH<7), Fe (III) binds inorganic phosphates in stable complexes. If the soil turns anaerobic (redox potentials < +250 mV) as a result of flooding, Fe(III) oxide–hydroxides are reduced to Fe(II) oxide–hydroxide, with release of free Fe(II) (aq) and phosphate (Ponnamperuma et al., 1967) through microorganism enzymatic catalysis (Jones 1985; Lovley et al., 1991). When the reduced soil re-oxidizes and the 'free Fe' re-precipitates, the regenerated Fe(III) oxide–hydroxides have a more amorphous structure with increased sorption capacity (McCallister and Logan, 1978; Lijklema, 1980; Redshaw et al., 1990). This sorptivity decreases with time, as the amorphous precipitate slowly becomes more crystalline.

Under basic to neutral conditions (7<pH<14), adsorption of phosphates to calcium occurs, in which the P is precipitated as insoluble Ca-P. Reaction between calcium and dihydrogen-phosphate to produce tricalcium phosphate, $Ca_3(PO_4)_2$, is presented below (Brady, 1990):

$$3Ca^{3+} + 2H_2PO_4 \leftrightarrow Ca_3(PO_4)_2\downarrow + 4H^+ \qquad \text{Eqn(2.4)}$$

Although this compound is quite insoluble, it may be converted further to even more insoluble products such as hydroxyapatite (HAp) $[3Ca_3(PO_4)_2].Ca(OH)_2]$ over time (Brady, 1990). Moreover, Johansson (1999) described another reaction with calcium and monohydrogen phosphate:

$$Ca^{2+} + 3HPO_4^{2-} + H_2O \leftrightarrow Ca_5(PO_4)_3{\cdot}OH\downarrow + 4H^+ \qquad \text{Eqn(2.5)}$$

Apart from the reversible nature of the adsorption, as soon as the soil redox or base status change, adsorption is also subject to saturation. Each soil has only a certain adsorption capacity and as soon as all adsorption sites will be occupied, no further adsorption will occur (Kadlec, 1985). However, fixation of phosphate in the matrix of clay minerals and complexation of phosphates with metals, have a much slower rate but are not so easily subject to saturation. Since the previously adsorbed P is precipitated, the adsorption sites become available again for adsorption of new P (Verhoeven and Meulemann, 1999). Moreover, Geller (1998) emphasized that the sorption capacity in artificial wetlands is not generally limited because of the input of Ca, Fe, and Al by wastewater.

2.10.3.2. Plant Uptake

Vegetation in the wetland acts as a temporary storage for nutrients. Particularly at the start of the growing season, large quantities of nutrients are taken up by the root system. If the vegetation is not harvested, most of these nutrients end up as litter. In autumn and winter, a large part of the nutrients will be gradually released again through leaching and organic matter mineralization. Only a small part of the nutrients taken up by the vegetation remains in addition to long-term storage in

aggrandizing wood or rhizome material (Brix, 1994). If the vegetation is harvested, the amount of nutrients released in autumn and winter is substantially lower. Harvesting the vegetation at the right moment in late summer (before re-translocation of nutrients to the root system occurs, but after the senescence of the plants has started so that they will survive the mowing) can substantially contribute to the nutrient removal capacity of a wetland (Brix, 1994; Kadlec and Knight, 1996).

Investigating the partitioning of P in planted wetlands, Lantzke et al. (1999) showed that VFWs in their initial phase can reduce TP concentrations by more than 90%, storing most of the influent P (70%) in plants. Afterwards plant biomass becomes P-saturated after a relatively short time and is not such an effective option, because aboveground biomass contains a relatively small pool of P (Sorrel and Orr, 1993). Sharma (1992) reported a TP removal of 15–22 $g.m^{-2}$ from a standing crop with one annual harvest.

However, according to Vymazal et al. (1999), the amount of P-removed by emergent vegetation forms only a small fraction of the TP removed in a constructed wetland. Plants absorb phosphorous through their roots and transport it to the growing tissues. The uptake capacity of P in the macrophytes is lower as compared to nitrogen, as P-concentrations in plant tissues are much lower than that of nitrogen (Brix, 1994; Vymazal 1995).

2.10.3.3. Storage

Phosphorus storage in accumulating organic matter is a sustainable mechanism for removing P from the wastewater. Plant derived litter is low in N and P just after death, as the plants re-translocate part of the nutrients during senescence. The microbes decaying the carbon rich litter may take up large amounts of nutrients from the aqueous environment (immobilization), which will be released several months to years later. In most wetlands, part of the organic matter is broken down

at such a slow rate that it accumulates as soil organic matter. The N and P contained in this organic matter accumulate along with it and forms a significant 'removal' process in many wastewater wetlands (Verhoeven and Meuleman, 1999).

2.10.3.4. Biofilm

The biofilm contributes to P removal by incorporating P into biomass for cell synthesis, maintenance, and energy transport. But, part of the P is also stored for subsequent use by the microorganisms. (Lee and Lin, 1999). Phosphorous may be released from cells under anoxic conditions (Metcalf and Eddy, 1991). In the wetlands, the microbial uptake is the smallest process among the other removal processes. Thus, the microbes have minimal effect on the removal of P in the wetlands (IWA, 2000).

2.10.4. Nitrogen Removal

Nitrogen in wastewater exists commonly in the form of organic nitrogen, ammonia (NH_4^+-N), nitrite (NO_2^--N), nitrate (NO_3^--N) and gaseous nitrogen (N_2O-N and N_2). All these forms of N are biochemically interconvertible and are components of N-cycle. Their treatment is of interest for many reasons. For example, N-compounds, particularly ammonia, can exert a significant oxygen demand through biological nitrification and may cause exhaustion of dissolved oxygen concentrations in receiving waters. Unionized ammonia can be toxic to aquatic organisms and readily reacts with chlorine. High nitrate levels in water supplies have been reported to cause methemoglobinemia in infants. Therefore, the need for N-control in wastewater effluents has generally been recognized and many treatment processes have been developed to remove N from the wastewater stream (Lee and Lin, 1999).

The organic nitrogen of the wastewater includes both soluble and particulate forms. The soluble organic nitrogen is mainly in the form of urea and amino acids

(proteins, peptides, nucleic acids). There are also numerous synthetic organic materials producing organic nitrogen. The main sources are from human excreta, kitchen litter, and food processing wastes. Typical domestic wastewater contains 20 $mg.L^{-1}$ of organic nitrogen and 15 $mg.L^{-1}$ of inorganic nitrogen. In wetland systems, the initial removal of organic nitrogen as TSS is usually quite rapid. Microbial processes convert particulate organic nitrogen via decomposition into new biomass and ammonium. Soluble organic nitrogen is partially transformed to ammonium by microorganisms, with 13 $mg.L^{-1}$ of organic nitrogen remaining in the secondary effluent of the wastewater treatment plants (Lee and Lin, 1999; Reed et al., 1995).

There are different types of methodologies to determine the nitrogen species of the wastewater. Generally, the organic nitrogen (Org-N), total kjeldahl nitrogen (TKN), total inorganic nitrogen (TIN), and total nitrogen (TN) could be calculated by the following equations (Vymazal, 1998):

$$Org\text{-}N = TKN - NH_4^+\text{-}N \qquad \text{Eqn (2.6)}$$

$$TIN = NH_4^+\text{-}N + NO_2^-\text{-}N + NO_3^-\text{-}N \qquad \text{Eqn (2.7)}$$

$$TN = Org\text{-}N + TIN \qquad \text{Eqn (2.8)}$$

The removal mechanisms for N in constructed wetlands are manifold and include volatilization, ammonification, nitrification/denitrification, plant uptake and matrix adsorption (Figure 2.6). Numerous studies have proven that the major removal mechanism in most of the constructed wetlands is microbial nitrification/denitrification. In systems with free-floating macrophytes ammonia volatilization can significantly contribute to nitrogen reduction (Vymazal 1998).

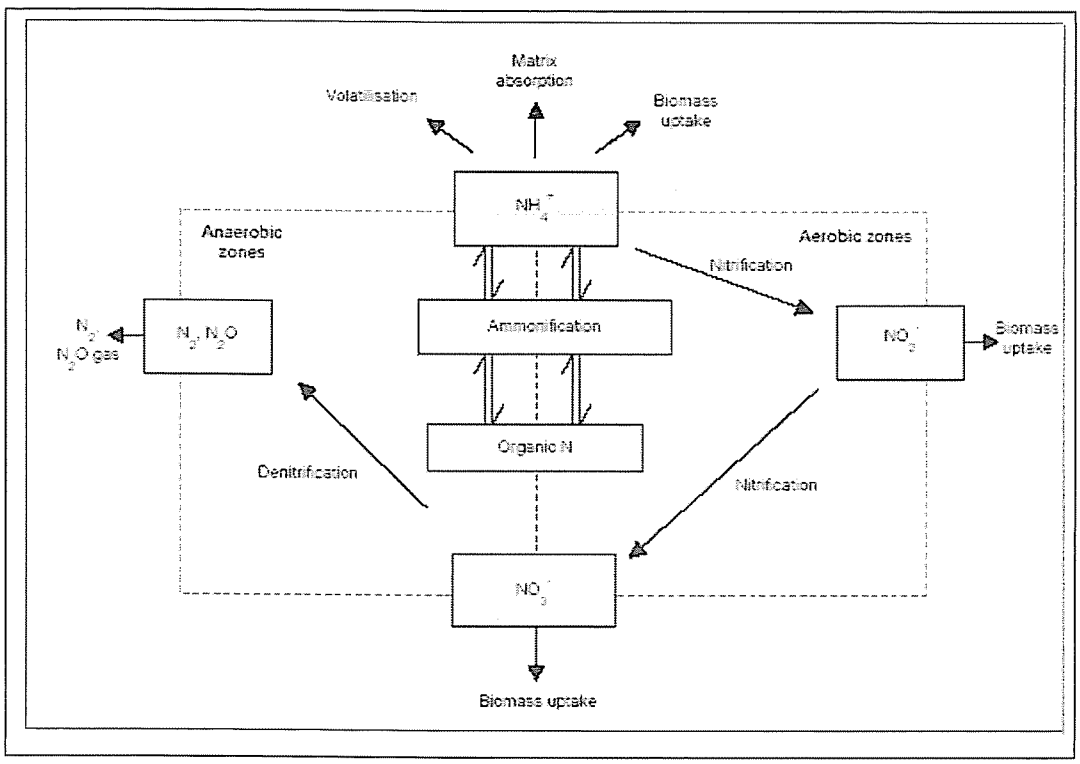

Figure 2.6. Nitrogen transformations in a constructed wetland treatment system (taken from Cooper et al., 1996)

2.10.4.1. Ammonia Volatilization

Ammonia is a weak base and exists in equilibrium with the ammonium ion as shown in Equation 2.9. The concentration of species is pH dependent and significant concentrations of ammonia (NH_3) occur only at pH values above 8.

NH_3 (aq) + H_2O ➔ NH_4^+ +OH Eqn (2.9)

Indeed, Reddy and Patrick (1984) pointed out that loss of ammonia through volatilization from flooded soils and sediments are insignificant if the pH value is below 7.5. At pH of 9.3, the ratio between ammonia and ammonium ion is 1:1 and the losses via volatilization are significant (Vymazal et al., 1998).

2.10.4.2. Ammonification

Ammonification (mineralization) is the biological transformation of organic N into inorganic N, especially NH_4^+-N (Vymazal, 2002). Mineralization rates are fastest in

the oxygenated zone, and decrease as mineralization switches from aerobic to facultative anaerobic and obligate anaerobic microflora. The rate of ammonification in wetlands is dependent on temperature, pH value, C/N ratio of the residue, available nutrients in the system, and soil conditions such as texture and structure (Reddy and Patrick 1984). The optimum pH range for the ammonification process is between 6.5 and 8.5. In saturated soils, pH is buffered around the neutrality, whereas under well-drained conditions, the pH value of the soil may decrease as a result of nitrate accumulation and production of H^+ ions during mineralization (Patrick and Wyatt, 1964). Reddy et al. (1979) concluded from the literature data that the rate of aerobic ammonification doubles with temperature increase of 10°C.

Ammonium nitrogen can be removed mainly through nitrification conducted by aerobic nitrifying bacteria. Since both of the processes (ammonification and nitrification) occur under aerobic conditions, they compete for available oxygen (Vymazal, 2002). According to Kadlec and Knight (1996), ammonification proceeds kinetically more rapidly than nitrification.

Vymazal (1999) suggested that ammonification seems to be the most temperature dependent process of those involved in nitrogen transformations in constructed wetlands. In the constructed wetlands, the plant detritus and other occurring materials in the wetland can also be a source of organic nitrogen, resulting in a seasonal release of ammonia as a result of decomposition (Reed et al., 1995). However, in real true natural plant systems, it is rare that there is excess nitrogen as nitrogen or ammonium. It has always been a rate-limiting nutrient (IWA, 2000).

2.10.4.3. Nitrification

Nitrification is the biological oxidation of ammonium to nitrate with nitrite as an intermediate in the reaction sequence. Nitrification is a chemoautotrophic process. In contrast to heterotrophic bacteria, the aerobic autotrophic nitrifiers derive energy from the oxidation of ammonia and nitrite and carbon dioxide is used as carbon

source for synthesis of new cells. These organisms require O_2 during ammonium-N oxidation to nitrite and NO_2^--N oxidation to NO_3^--N. Oxidation of ammonium to nitrate is a two-step process (Lee and Lin, 1999):

$$55\ NH_4^+ + 76\ O_2 + 109\ HCO_3^- \Rightarrow C_5H_7NO_2 + 54\ NO_2^- + 104\ H_2CO_3 + 57\ H_2O \quad \text{Eqn (2.10)}$$

$$400\ NO_2^- + NH_4^+ + 4\ H_2CO_3 + HCO_3^- + 195\ O_2 \Rightarrow C_5H_7NO_2 + 400\ NO_3^- + 3\ H_2O \quad \text{Eqn (2.11)}$$

$$NH_4^+ + 1.83\ O_2 + 1.98\ HCO_3^- \Rightarrow 0.021\ C_5H_7NO_2 + 0.98\ NO_3^- + 1.88\ H_2CO_3 + 1.041\ H_2O \quad \text{Eqn (2.12)}$$

The first step, which is the oxidation of ammonium to nitrite, is carried out by bacteria, mostly by the *Nitrosomonas* genera. The second step in the process of nitrification, which is the oxidation of nitrite to nitrate, is performed by bacteria mostly by the *Nitrobacter* genera. In contrast to ammonia-oxidizing bacteria, nitrite-oxidizing bacteria, or at least some species, can grow mixotrophically on nitrite and a carbon source, or are even able to grow in the absence of oxygen (Bock et al., 1986).

The growth rate for nitrifying bacteria is much less than that of heterotrophic bacteria. Nitrifying bacteria have a longer generation time of at least 10-30 hours. They are also much more sensitive to environmental conditions as well as to growth inhibitors. The growth rate for nitrite oxidizers is lower than that for the ammonia oxidizers, since they get much more electrons from their substrate that nitrifiers get from nitrite. In domestic wastewater treatment the rate limitation is oxygen, the faster growing heterotrophs take all available oxygen resources. Nitrites do not accumulate in wastewater system because the facultative bacteria can use nitrite instead of oxygen as their terminal electron acceptor to continue to metabolize carbon.

According to thermodynamics, the yields for *Nitrosomonas* and *Nitrobacter* are 0.29 mg VSS.mg^{-1} NH_4^+-N and 0,084 mg VSS.mg^{-1} NO_2^--N. So, considering the two-step nitrification reactions, the yield for *Nitrosomonas* and *Nitrobacter* is 0.15 mg cells.mg^{-1} NH_4^+-N and 0.02 mg cells.mg^{-1} NO_2^--N, respectively (Haug and McCarty, 1972). According to the nitrification equations, to oxidize 1 mg.L^{-1} of

NH_4^+N to NO_3^--N, approximately 4.3 $mg.L^{-1}$ of oxygen is required, whereas 8.64 $mg.L^{-1}$ of bicarbonate is utilized. Due the release of protons and alkalinity destruction during biological nitrification, there is a drop in pH values.

Vymazal (1985) summarizes that nitrification is influenced by temperature, pH value, alkalinity of the water, inorganic carbon source, microbial population and concentrations of ammonium-N and dissolved oxygen. However, quantification of these and other factors influencing the growth of nitrifiers has been difficult (Metcalf and Eddy, 1991). The optimum temperature for nitrification in pure cultures ranges from 25°C to 35°C and in soils from 30°C to 40°C. Lower temperatures (below 15°C) have a greater effect on nitrification rate, compared to temperatures between 15°C and 35°C. Cooper et al (1996) pointed out that the minimum temperatures for growth of *Nitrosomonas* and *Nitrobacter* are 5°C and 4°C, respectively. Reported data show a wide range of optimum pH of 7.0 to 9.5 with maximum activity at approximately pH of 8.5. Below pH of 7.0, adverse effects on ammonia oxidation become pronounced (Lee and Lin, 1999).

Dissolved oxygen concentrations above 1 $mg.L^{-1}$ are essential for nitrification to occur. If DO levels drop below this value, oxygen becomes the limiting nutrient and nitrification slows or ceases (Metcalf and Eddy, 1991). For gravel bed systems, compared to soil bed systems, the higher porosity allows more oxygen transfer to the substratum and more biomass accumulates inside the substratum, both of which are helpful for nitrification. It was reported that Root Zone Effects (RZE) might exist in vegetated constructed wetland systems, which could enhance nitrification by transferring oxygen to the root zone areas (Yang et al., 2001). There are varying reports about the quantity of plant root zone oxygen release. Brix et al. (1996) found an oxygen input of 20 mg $O_2.m^{-2}.d^{-1}$; where Gries et al. (1990) and Armstrong et al. (1990) measured oxygen releases that were higher (2–12 g $O_2.m^{-2}.d^{-1}$). One may explain these differences by the short-term nature of the measurements. More reliable data can only be given by long-term investigations (Luederitz et al., 2001).

More recently, Brix (1998) showed that the common reed species has a potential oxygen transfer of 2 g $O_2.m^{-2}.d^{-1}$ to the root zone, which mainly is utilized by the roots and rhizomes themselves. Since the wetland species are adapted to minimize oxygen loss from the roots, it is therefore not likely that wetland plants would be able to supply the rhizosphere with the amount of oxygen needed for RZE. Regardless of the magnitude of the oxygen release to the rhizosphere, the aerobic conditions are restricted to the micro zones adjacent to the fine lateral roots and most of the bed remains anoxic or anaerobic. Nitrification of ammonium in light sewage demands approximately 12 g $O_2.m^{-2}.d^{-1}$ assuming an area use of 5 m^2/PE. So, the potential oxygen transferred to the root zone is only one third of the need. In the case where nitrification is required, it is better to secure a better oxygen supply to the wetland matrix by lowering the loading rate (Brix, 1998).

In an intermittently–loaded vertical flow system, oxygenation in the wetland matrix is increased several fold compared to the horizontal subsurface flow systems (Brix and Schierup, 1990). During the loading period, air is forced out of the substrate and during effluent discharge; atmospheric oxygen is drawn into the pore spaces of the substrate. When the bed is dried, the oxygenation rate increases. But the minute wastewater is passed through the bed, the oxygen concentration in the beds drops to low values. Therefore, the intermittently loaded vertical flow wetland systems are generally able to provide good nitrification of the wastewater (Brix, 1998).

2.10.4.4. Denitrification

The first anoxic oxidation process to occur after oxygen depletion is the reduction of nitrate to molecular nitrogen or nitrogen gases, which is called denitrification. Denitrification is a bacterial process in which nitrogen oxides (in ionic and gaseous forms) serve as the terminal electron acceptor for respiratory electron transport, which is necessary for chemoheterotrophs. Electrons are transferred from an electron-donating substrate (usually, but not exclusively, organic compounds) through several carrier systems to a more reduced N form, such as di-nitrogen gas,

N_2. The resultant free energy is conserved in ATP following phosphorylation and is used by denitrifying organisms to support respiration. Denitrification is illustrated by the following equation:

$$6\ (CH_2O) + 4\ NO_3^- \Rightarrow 6\ CO_2 + 2\ N_2 + 6\ H_2O \qquad \text{Eqn (2.13)}$$

This reaction is irreversible and occurs in the presence of available organic substrate only under anaerobic or anoxic conditions (Eh = +350 to +100mV), where nitrogen is used as an electron acceptor in place of oxygen (Vymazal et al., 1998).

Vymazal (1995) summarizes the environmental factors known to influence denitrification rates including the absence of O_2, redox potential, soil moisture, temperature, pH value, the presence of denitrifiers, soil type, organic matter and the presence of overlying water. Cooper et al. (1996) pointed out that the presence of DO supress the enzyme needed for denitrification and is a critical parameter. Complete denitrification implies conversion to N_2 gas, although a certain amount of NOx is usually reduced only to nitrous oxide.

The quantity of N_2O versus N_2 evolved during denitrification is difficult and complex to predict. The ratio is affected by oxygen concentrations, assimilible carbon concentrations, pH value, temperature and nitrate to ammonia ratio in the denitrifying system. The optimum pH for denitrification lies between pH of 7-8; however, alkalinity produced during denitrification can result in a slight rise in pH. Denitrification is also strongly temperature dependent and proceeds at very slow rates, if the temperature fall below 5°C (Vymazal et al., 1998).

2.10.4.5. Plant Uptake

The potential rate of nutrient uptake by plant is limited by its net productivity (growth rate) and the concentrations of nutrients in the plant tissue. Nutrient storage is similarly dependent on plant tissue nutrient concentrations, and also on the ultimate potential for biomass accumulation (maximum standing crop). Thus,

desirable traits of plant used for nutrient assimilation and storage would include rapid growth, high nutrient content in tissues and a high biomass per unit area (Reddy and Debusk, 1987). Emergent macrophytes in constructed wetlands can remove 10-16% of the total removed nitrogen from the wastewater (Gersberg et al., 1985; Dusek et al., 1997).

Generally, the effects of the macrophytes, particularly common reed, in constructed wetlands on nitrogen removal can be also summarized as follows:

- A dense stand of plants can improve nutrient removal by plant uptake.
- Macrophytes may secrete root exudates rich in organic carbon (Brix, 1997), which in turn can increase the denitrification rate and the overall TN removal efficiency of the constructed wetland system.
- The abundance of plant roots, especially in the upper layers of the wetlands, can provide an organic carbon source as dead roots breakdown and decay.
- The large surface area of a healthy root system can also facilitate the establishment of a rich and productive community of attached microorganisms.
- The above-ground biomass of reeds may supply organic carbon to the system through the breakdown and decay of dead leaf and stem material on the surface of the reed bed, eventually leaching to the water column (Bayley et al., 2002). Release of the organic nitrogen back to the water phase can significantly result in a seasonal increase in the effluent values of ammonium-N (Yang et al., 2001; Reed et al., 1995). However, if there are relatively high N loadings to a constructed wetland, then either the uptake by growth or release by decomposition will be relatively insignificant. But, if the wetlands are natural or very low loaded, then the plants can play a significant role in the N budget.
- The plant root zone oxygen release may enhance microbial oxidation of COD and reduced forms of N in gravel bed constructed wetlands (Tanner et al., 1999).

2.10.4.6. Matrix Adsorption

In a reduced state ammonium-N is stable and can be adsorbed onto active cation exchange sites of the bed matrix. However, the ion exchange of NH_4^+-N on cation exchange sites of the matrix is not considered to be a long-term sink for NH_4^+-N removal. Rather, sorption of NH_4^+-N is presumed to be rapidly reversible. As the NH_4^+-N is lost from the system via nitrification, the exchange equilibria is expected to redistribute itself. Thus, the sorbed NH_4^+-N in a continuous flow system will be in equilibrium with NH_4^+-N in solution. Only intermittent loading of a system will show rapid removals of NH_4^+-N by adsorption mechanisms due to depletion of NH_4^+-N on the sorption sites during rest periods. The Freundlich equation can be used to model NH_4^+-N sorption (Cooper et al., 1996).

During a rest phase of the wetland, nitrates formed from ammonia ions adsorbed by the filter material are subsequently washed out at the start of the next feeding phase (Guilloteeau et al., 1993). However, these concentrations can be low and the overall effect appears as a slight decrease in TN removal efficiencies.

2.11. Reaction Kinetics for Constructed Wetlands

In most cases, wetlands are almost exclusively designed based on hydrological and sizing considerations (Wood, 1995). So, in order to be able to improve wetland designs with higher removal efficiencies, mathematical models have been derived based on assumptions describing removal processes and variables affecting those processes (Goulet, 2001). A large number of wetland systems have shown an exponential decrease in pollutant concentration level with distance through the wetland from inlet to the outlet. Some pollutant concentrations decline to near zero values while others level off to background concentrations (Brix, 1998).

This observation is consistent with a first-order removal model, with the removal rate being proportional to the pollutant concentration. The removal can thus

empirically be described with first order plug-flow kinetics with (a zero-order return) what is this term zero-order return and has an exponentially declining pattern (Kadlec and Knight, 1996). This approach has been widely applied to biochemical oxygen demand, nutrients, and total suspended solids (Dortch, 1996; Kadlec and Knight, 1996).

The simplest model that summarizes this behavior is a first-order reaction with a zero-order return is as follows (Kadlec and Knight, 1996):

$$J = k\,(C - C^*) \qquad \text{Eqn (2.14)}$$

where:

J = Constituent reduction rate ($g.m^{-2}.d^{-1}$),

k = First-order areal rate constant ($m.d^{-1}$),

C = Constituent concentration ($g.L^{-1}$), and

C* = Background constituent concentration ($g.L^{-1}$).

Combining the basic equation for a plug-flow model (Reed at al, 1988) with the water mass balance, an exponential relation between inlet and outlet concentrations can be described by integration of the previous equation (Kadlec and Knight, 1996):

$$k = \frac{Q}{A} \ln \frac{(Ci - C^*)}{(Ce - C^*)} \qquad \text{Eqn (2.15)}$$

where:

k = First-order areal rate constant ($m.d^{-1}$),

Q = Input discharge to the wetland ($m^3.d^{-1}$),

A = Surface area of the wetland (m^2),

Q/A = Hydraulic loading rate ($m.d^{-1}$),

C_i = Inlet concentration ($mg.L^{-1}$),

C_e = Outlet concentration ($mg.L^{-1}$), and

C* = Background concentration ($mg.L^{-1}$).

The area-based first order rate constant derived using the above equations is typically based on time-averaged data to eliminate variability due to short-term variation of inflow and outflow quality and changing flow patterns. Thus, monthly or longer averaging periods should be used for data analysis (Knight et al., 2000). Few studies have tested first-order removal models on a seasonal basis (Flanagan et al., 1994). Most studies only consider the summer period when biological productivity and removal rate constants are high (e.g. Kadlec, 2000). However, in cold climates, there are significant seasonal changes in temperature. The water temperature affects the removal of some of the constituents because the areal rate constant decreases as the temperature declines. At high temperatures, areal rate constant is high and wetlands should require lower hydraulic loading rates to treat the pollutants than at colder temperatures. In the winter, areal rate constant is low because the water temperature is around 4°C and therefore, the hydraulic loading rate required to retain a given amount of pollutants should be higher (Goulet, 2001). This effect can be modeled as a modified Arrhenius equation as follows (Reddy and Burgoon, 1996, Kadlec and Knight, 1996):

$$k = Ar * e^{(E/RT)} \qquad \text{Eqn (2.16)}$$

where:

Ar = The Van't Hoff–Arrhenius coefficient,

E = The activation energy ($J.mol^{-1}.K^{-1}$),

R = A gas constant (8.314 $J.mol^{-1}.K^{-1}$), and

T = Temperature in degree Kelvin.

Converting the temperature to degrees and assuming a water temperature of 20°C, the equation becomes:

$$k_T = k_{20}\,\theta^{(T-20)} \qquad \text{Eqn (2.17)}$$

where:

k_{20} = k at 20 °C ($m.d^{-1}$),

k_T = k at T°C ($m.d^{-1}$),

θ = Temperature coefficient, Theta value (dimensionless), and

T = Water temperature (°C).

While the hydraulic flow pattern in a wetland treatment system is typically intermediate between complete mix and plug flow (approximated by three complete-mix tanks in series; Kadlec, 1994), the area-based, first-order rate constant k ($m.d^{-1}$) derived using the above equations is a conservative estimate. Thus, there is an increased awareness that other variables need to be included in removal models (Goulet, 2001).

The background concentrations of the water quality parameters and the temperature coefficients observed in some of the constructed wetlands were summarized in Table 2.10. As long as k values are used to predict wetland treatment performance for a wetland with similar hydraulic loads, these rate constants and coefficients can be used for design. Otherwise, the rate constant must be corrected for the degree of mixing based on knowledge from the data-generating wetland (Kadlec and Knight, 1996). Thus, this empirical model should be used with great caution (Brix, 1998).

Table 2.10. Background concentration values (C*) and temperature coefficients (θ) for areal removal rate constants (k)

Parameter	**Background Values (C*)**	k **($m.yr^{-1}$)**	**θ (unitless)**
BOD_5 ($mg.L^{-1}$)	3.5+0.053 $C_{initial}$	34-180	1.00
TSS ($mg.L^{-1}$)	5.1+0.16 $C_{initial}$	1000	1.00
Organic Nitrogen ($mg.L^{-1}$)	1.5	17-35	1.05
NH_4^+-N ($mg.L^{-1}$)	0	18-34	1.04
NO_3^--N ($mg.L^{-1}$)	0	35-50	1.09
TN ($mg.L^{-1}$)	1.5	22-27	1.05
TP ($mg.L^{-1}$)	0.02-1	12	1.00
F.coli (CFU/100 mL)	300	75	1.00

Reference: Kadlec and Knight, 1996.

2.12. Fill Media used in Constructed Wetlands for Enhanced Phosphorus Removal

It has been well established that soluble phosphate can be removed in subsurface constructed wetlands if well designed (Reddy and Smith, 1987; Mitsch and Cronk, 1992; Moshiri, 1993; Kadlec and Knight, 1996; Pant et. al., 2001). Generally, phosphate retention is dependent upon the influent water quality, hydraulic loading rate, type of root media (Pant et. al., 2001) and the calcium, aluminum and iron content of the substrate (Vymazal, 1998; Pant et. al., 2001). The materials like pea gravel, crushed stones, and sand that are commonly used as substrates in the subsurface constructed wetlands usually do not contain high concentrations of these elements. Thus, the removal of phosphate is generally low and varies widely among systems due to different materials used. As Vymazal et al. (1998) stated the removal might be enhanced by the use of materials with higher concentrations of calcium, aluminum, or iron (limestone gravel, spoil from mining, sand with higher iron content).

One of the eco-technological means of attaining sufficiently low P concentrations in the wetlands is the use of specialized substrates with physical and chemical properties conducive to P removal, while maintaining sufficient permeability (House et al., 1994). The various physico-chemical properties (including pH; amorphous and poorly crystalline Al and Fe oxides) of these root bed media influence the P adsorption phenomena onto their surfaces (Froelich, 1988; Zhu et al., 1997; Reddy et al., 1999). If naturally occurring, inexpensive materials like *shale, dolomite,* and/or *sand* can effectively remove P through adsorption, their use as root bed media could enhance the efficiency of constructed wetlands to remove P from effluents (Pant et al., 2001).

As well as the naturally occurring ones, specialized substrates used to improve the P retention of constructed wetlands are *pumice, sand, LWA,* (commercial light weight aggregates, Johanson, 1996; Maehlum and Stalnacke, 1999), *LECA* (a

reactive porous media, Zhu et al., 2002) and industrial wastes such as *blast furnace slag* (a byproduct of limestone, coke, and iron ore, Rustige et al., 2002), *wollastonite* (a calcium metasilicate, Brooks et al 2000), *fly ash* (Jenssen et al., 1993; Mann and Bavor, 1993; Nur Onar et al., 1996)(Brooks et al., 2001), *zeolite*, *pelleted clay* either alone or in combination with soils (Sakadevan and Bavor, 1998), *alum,* and *calcite* (Ann et al., 1999) (Pant et al., 2001).

2.13. Production of Blast Furnace Granulated Slag

In the production of iron; iron ore, iron scrap, and fluxes (limestone and/or dolomite) are charged into a blast furnace at temperatures above 1500°C along with coke for fuel. The coke is combusted to produce carbon monoxide, which reduces the iron ore to a molten iron product. Blast furnace slag (BFS) is a nonmetallic co-product produced in the process. BFS consists primarily of silicates, alumino-silicates, and calcium-alumina-silicates. It also contains minor amounts of manganese, iron and sulfur compounds and trace quantities of heavy metals (Mann and Bavor, 1993).

The physical structure and gradation of granulated slag depend on the chemical composition of the slag, its temperature at the time of water quenching, and the method of production. Treatment with controlled quantities of water during the cooling increases the vesicular nature of slag, producing a light-weight, porous medium. This type of slag has good hydraulic conductivity and numerous sites for adsorption. When crushed or milled to very fine cement-sized particles, granulated blast furnace slag has been used as a raw material for cement production and as an aggregate and insulating material. Granulated slag has also been used as sand-blasting shot materials. In recent years, the use of granulated slag in constructed wetlands for removal of P was questioned by some of the wetland researchers (Mann and Bavor, 1993; Sakadevan and Bavor, 1998; Johansson, 1999).

CHAPTER 3

MATERIALS AND METHODS

3.1. Characterization of the Domestic Wastewater

The characterization of the wastewater, which was fed to the wetlands, was performed in this part of the study. Raw domestic wastewater was collected three times (on 15, 20, 26 June 2002) from one of the manholes, which was carrying the domestic wastewater of ODTÜKENT and surface runoff. The same manhole was used to supply wastewater to the constructed wetlands during the entire study. After collecting the samples as described in Standard Methods (AWWA, 1999), they were brought to the Chemistry Laboratory of the Department of Environmental Engineering of METU and analyzed on the same day.

In the laboratory, one liter of wastewater was poured into a beaker and placed onto a magnetic stirrer, whereas another one liter of wastewater was poured into an Imhoff cone and let settle for two hours to remove primarily settleable solids. The stirred wastewater samples represented the raw domestic wastewater without any treatment. Wastewater samples were transferred from the beaker and the Imhoff cone with an automatic pipette (Biohit CT14081, ISOLAB 1-5 mL, Germany). On the same day, wastewater samples were analyzed in duplicates for the chemical oxygen demand (COD), total suspended solids (TSS), total phosphorus (TP), ortho-phosphate phosphorus (PO_4^{3-}-P), ammonium nitrogen (NH_4^+-N), nitrate nitrogen (NO_3^--N), and total nitrogen (TN), respectively. Those analyses were performed according to the Standard Methods (AWWA, 1999). The experimental methodologies and the instruments used for the analysis will be explained in the following section in detail.

3.2. Analytical Methods

All the wastewater analyses conducted during this research were performed in the Chemistry Laboratory of the Department of Environmental Engineering of METU. The analytical methods (AWWA, 1999) and the instruments used within this dissertation were tabulated in Table 3.1 and Table 3.2, respectively. The calibration curves were prepared several times and renewed periodically as described in Standard Methods (AWWA, 1999). Some of the calibration curves that were used for the analyses of NH_4^+-N, NO_3^--N, TN, PO_4^{3-}-P and TP were presented in Appendix A.1. (Figure A.1-A.11), respectively.

Table 3.1. Analytical methods

Parameter	Methods and Method No
Biochemical Oxygen Demand, BOD_5	Oxygen Demand (Biochemical), Titration (5210)
Chemical Oxygen Demand, COD	Micro COD, Hack Method (0-1,500 $mg.L^{-1}$) (5220)
Total Suspended Phosphorous, TP	Persulfate Digestion Method (0-1.5 $mg.L^{-1}$) (4500-P)
Orthophosphate, PO_4^{3-}-P	Ascorbic Acid Method (0-1.5 $mg.L^{-1}$) (4500-P-E)
Total Nitrogen, TN	Persulfate Digestion Method (0.1-1 $mg.L^{-1}$) (4500-N)
Ammonium Nitrogen, NH_4^+-N	Direct Nesslerization Method (0-1.2 $mg.L^{-1}$)
Nitrate Nitrogen, NO_3^--N	Brucine Method (0.1-1 $mg.L^{-1}$) (4500-NO_3^-)
Total Suspended Solids, TSS	Vacuum Filtration (Milipore 0.45μm, 47 mm Cellulose Filter Paper) (2540-D)

Reference: Standard Methods for the Examination of Water and Wastewater, 1999.

The wastewater samples were analyzed for BOD_5, COD, phosphorus and nitrogen without any filtration. For each of the water quality parameter, samples were analyzed in duplicates or in triplicates. Conductivity and pH were measured in fresh samples using electrodes and pH/mV meters (Appendix A, Figure A.11-A.12; Table A.1-A.2). All the glassware used in these experiments was always cleaned as described in Standard Methods (AWWA, 1999). The wastewater samples were analyzed on the sampling day (in 24 hour). Otherwise, the water samples were stored at +4°C without adding any chemicals for one day for chemical analyses.

Table 3.2. Instruments used for analyses

Parameter	Instruments and Model
Conductivity	Conductivity meter, Orion Model115 (precision ±1%)
pH	pH/mV meter, EM78X EMAF
BOD_5	BOD glass bottles, Incubator
COD	HACH Reactor, HACH p/N 45600-02 Spectrophotometer
TP	Pressure Cooker, Milton Ray Spectronic 20 D Spectrophotometer
PO_4^{3-}-P	Milton Ray Spectronic 20 D Spectrophotometer
TN	Water Bath, Milton Ray Spectronic 20 D Spectrophotometer
NH_4^+-N	Milton Ray Spectronic 20 D Spectrophotometer
NO_3^--N	Water Bath, Milton Ray Spectronic 20 D Spectrophotometer
TSS	Vacuum Pump, 0523-V4-G21 DX GAST-MFG Cooperation, HERAEM Oven @105°C, Dessicator

3.3. Filter Media Selection

As explained in the Section 2.12, different types of fill media can be used to enhance the nutrient removal performance of the constructed wetlands. To question whether phosphate could be removed efficiently in the constructed wetlands implemented at METU using a special substrate of Turkish origin, natural materials and locally produced adequate industrial by-products were sought. Smaller particle size, larger surface area, higher phosphorus adsorption capacity, higher porosity and cost-effectiveness were the criteria for selecting the candidate filter materials. According to these criteria, perlite (produced in Ankara), volcanic slag (naturally found in Erzurum), pumice (mined in İzmir Cumaovası) and blast furnace granulated iron slag (a waste material of KARDEMİR Iron and Steel Company, Karabük) were chosen as candidate materials.

Pumice stone can be obtained from some provinces of Turkey (Ürgüp, Nevşehir, Kayseri, Niğde, Bitlis, Ağrı, Iğdır, Van, Uşak, Kula, Isparta, etc.). In this study, the pumice mined in İzmir Cumaovası was chosen as a possible fill medium to be evaluated in the proposed constructed wetlands due to its lower transportation cost. Samples of granulated and powdered pumice were transported from İzmir to Ankara. Since the size of the powdered pumice was in micron range, due to its

clogging potential in the wetlands, it was eliminated. Thus, the screening level experiments have been conducted only for granulated pumice with a particle size of 0-3 mm.

In Turkey, there are several iron and steel processing industries. KARDEMİR Iron and Steel Industry Limited Company, which is located in Karabük, is one of those industries. Similar to other iron and steel companies, different forms of slags (including the granulated BFS) are produced in KARDEMİR during its process. Within this study, the granulated BFS co-produced in KARDEMİR Iron and Steel Industry was brought to Ankara and used for the experiments.

However, comparing their advantages and disadvantages of the above-mentioned candidate materials, it was decided to compare the phosphorus sorption capacities of pumice mined in İzmir and blast furnace granulated slag co-produced in KARDEMİR Iron and Steel Company. Detailed information for pumice and granulated slag were given in Section 4.2. The sand and gravel, which were used in several types of constructed wetlands in the literature (Cooper, 1990; Crites and Reed, 1995; Laber et al., 2000) were selected as the control filter media in the constructed wetlands implemented at METU.

3.4. Batch-Scale Phosphorus Adsorption Experiments

Sorption isotherm tests can provide a good comparison of candidate materials to be used as filter media in constructed wetlands. In these tests, phosphorus can be removed from solution by either precipitation of phosphates or adsorption onto the media surface. The differences between removal of phosphorus by adsorption and precipitation were discussed by Nichols (1983). It is difficult to distinguish between the two processes since both of the forms are removed from the bulk solution by filtration. X-ray fluorescence and scanning electron microscopy can be used to detect the forms of the removed phosphorus (Johansson and Gustafsson, 2000; Drizo et al., 1999; Baker et al., 1998). However, it was considered beyond the

scope of this screening level work. Thus, removal of phosphorus (as a combination of adsorption and precipitation) was determined as the decrease in dissolved reactive phosphorus in solution after applying the procedure given below.

Batch shake tests were used to compare the adsorption capacities of pumice and granulated slag and to determine the better local media for phosphorus removal in constructed wetlands. The phosphorus removal capacities of pumice mined in İzmir Cumaovası and blast furnace granulated slag produced in KARDEMİR were determined according to the adsorption studies described in Baker et al., (1998); Johansson (1997); Zhu et al., (1997) and Sakadevan and Bavor (1998).

The phosphorus sorption capacities of slag and sand samples were investigated using phosphorus solutions ranging from 0 to 320 $mg.L^{-1}$, where the phosphorus solution was prepared using the salt of KH_2PO_4. Potassium phosphate monobasic (KH_2PO_4) salt is a strong electrolyte and it dissociates in solution producing HPO_4^{2}, $H_2PO_4^{-}$ and PO_4^{3-} ions, which are immediately available for reactions (Brooks et al., 2000). These are the main P-forms that are biologically available and thus contribute to eutrophication in waterbodies. Initially, both pumice and granulated slag were dried at 105°C for 24 hours to remove humidity. Then, six 8 g samples of both of the materials were placed in acid-washed Erlenmeyer flasks (300 mL), which contained a 250 mL P-solution with the following concentrations: 0, 20, 40, 80, 160, and 320 $mg.L^{-1}$. Even though 320 $mg.L^{-1}$ is a much higher concentration than that of typical phosphorus concentrations of domestic wastewater, the use of it was necessary to establish an adsorption isotherm for identifying differences between samples of pumice and slag at higher P concentrations.

Erlenmeyer flasks were equilibrated by shaking (200 rpm) at a room temperature of 22°C for 24 hours. The suspensions were filtered through 0.45 μm filter paper and the concentrations of the filtrates were analyzed according to the Ascorbic Acid Spectrophotometric Method No: 4500-P (AWWA, 1999). Replicate analyses were conducted for each of the phosphorus concentration. The amount of phosphorus

removed by each of the candidate filter media was calculated according to following equation:

$$q = \frac{(Ci - Cf) \times V}{M} \qquad \text{Eqn (3.1)}$$

where:

q = Amount of phosphorus adsorbed per unit of media (mg $P.kg^{-1}$ sample)

Ci = Initial concentration of phosphorus ($mg.L^{-1}$)

Cf = Final concentration of phosphorus or equilibrium concentration ($mg.L^{-1}$)

V = Volume of phosphate solution added to flask (0.250 L)

M = Mass of dry weight of the media (slag or pumice) (0.008 kg)

After performing the screening-level adsorption experiments, it was found that the phosphorus adsorption capacity of the blast furnace slag was slightly better than that of the pumice (see Section 4.3. for details). Therefore, it was decided to use the slag in one of the hybrid wetlands constructed at METU. To compare the P-adsorption capacity of the slag provided from Karabük to the literature values, using the same experimental procedure as described above, further batch-scale adsorption experiments were performed only for slag using the KH_2PO_4 concentrations of 0, 4, 8, 20 $mg.L^{-1}$ and raw domestic wastewater with a concentration of 10 mg $P.L^{-1}$. The range of phosphorus concentrations was selected to reflect the concentrations of typical domestic wastewater (6-20 $mg.L^{-1}$) according to Metcalf and Eddy (1991) and Kadlec and Knight (1996).

3.5. Determination of the Physical Characteristics of the Filter Media

The particle density, bulk density and porosity of the blast furnace granulated slag were determined according to the procedures described in the Unit Operations and Unit Processes Laboratory Manual published by Association of Environmental Engineering Professors (1984). The related procedures are provided below.

Particle Density

For determination of the particle density of slag, a pycnometer of 50 mL was weighed, which was dried at 105 °C for at least one hour ($M_1 \pm 0.0005$ g). Firstly, the pycnometer was filled with distilled water of known temperature. All bubbles were removed carefully by shaking the pycnometer. Secondly, the pycnometer filled with water was weighed ($M_2 \pm 0.0005$ g). Afterwards, the pycnometer was dried again at 105°C and filled with a dried sample of slag (22.7210 g), partially. The weigh of pycnometer which is partially filled with slag, was again determined ($M_3 \pm 0.0005$ g). Then, the remaining volume of the pycnometer was filled with water of the same temperature. Lastly, the pycnometer was weighed again ($M_4 \pm 0.0005$ g).

The particle density was calculated by following below equation, where w was accepted as the density of water (0.9982 $g.cm^{-3}$) at the temperature of the laboratory (20°C).

$$\rho_{part} = \frac{(M_3 - M_1)}{\frac{(M_2 - M_1) - (M_4 - M_3)}{w}} \qquad \text{Eqn (3.2)}$$

Bulk Density

The bulk density is the unit weight of a dry soil sample (including air spaces) per unit volume. To determine the bulk density of slag, a pycnometer of 50 mL (V) was weighed, which was dried at 105 °C for at least one hour ($M_1 \pm 0.0005$ g). Then, this pycnometer was filled with 50 mL of slag, which was dried before in oven at 105°C to remove humidity. Afterwards, the pycnometer filled with slag was weighed ($M_2 \pm 0.0005$ g). The particle density was calculated by following below equation:

$$\rho_{bulk} = \frac{[M_2 - M_1]}{V} \qquad \text{Eqn(3.3)}$$

Porosity

Two 500 mL graduated cylinders were used in porosity determination. In one cylinder, slag with a dry volume of 200 mL was measured. In the other cylinder, exactly 250 mL of water (V_1) was placed. The known volume of slag (200 mL) was poured slowly into the cylinder that contained 250 mL of water. The total apparent volume of the slag and water (V_2) were observed and recorded. Then to simulate fluidization of the particles, the top was plugged tightly with a rubber stopper and the cylinder was rapidly inverted a number of times, then the particles were allowed to settle. The apparent volume of slag was then measured (V_3). The porosity (α) was calculated from below equation:

$$\alpha = \frac{(V_3 - (V_2 - V_1))}{V_3} \qquad \text{Eqn(3.2)}$$

where:

V_1 = The volume of water (mL),

V_2 = The apparent total volume of sand + water (mL),

V_3 = The volume of dried slag (mL).

Sieve Analysis

Moreover, the particle-size distribution was measured by sieving slag and sand through seven different mesh sizes, ranging from 0.149-9.5 mm different mesh sizes. For sieve analysis, representative samples of sand and slag was taken. The samples were firstly dried in the oven (105°C) for at least 1 hour and weighed (±0.0005 g). The largest sieve size, through which all particles can pass, was found. Then the smallest sieve size, through which none of the particles pass, was found. Five different sieves having sizes in between of these two extremes were placed onto the

sieving machine and samples were sieved for five minutes. Then, the fractions retaining on each sieve was weighed (±0.0005 g). Afterwards, the cumulative percent of sample by weight passing through each sieve size was calculated by subtracting cumulative percentage remaining values from 100%. Sieve size versus cumulative percentage passing values was plotted for both sand and slag. The uniformity coefficients were determined as follows:

Uniformity Coefficient= d_{60}/d_{10} Eqn (3.5)

where:

d_{60}= Particle size corresponding to the cumulative percentage value of 60%,

d_{10}= Particle size corresponding to the cumulative percentage value of 10%.

3.6. Field Studies at METU

In this section, detailed information related to the field application (site-selection, design, implementation, plantation, etc.) and operation phase of the pilot-scale constructed wetlands implemented at METU were presented.

3.6.1. Location of the Pilot-Scale Constructed Wetlands

METU campus was selected as the site of implementation of this study. The abandoned Wastewater Treatment Plant of METU was the most suitable spot. The necessary permission was taken from the General Secretary of METU to construct the wetlands on the sludge drying bed of this abandoned treatment plant.

The abandoned sludge drying bed was made of concrete and has dimensions of 20 m x 50 m x 2.5 m (width x length x depth). Within the sludge bed, there exist several filter layers of total of 2 m. Within these layers, an old drainage system made of concrete still exists. From the top to the bottom, the cross-section of the layer was as follows:

- Old Sludge (~30 cm)
- Fine sand (~20 cm)
- Coarse gravel (~50 cm)
- Compacted soil layer (~100 cm)

Upon request, pumping out part a portion of the domestic wastewater from the combined sewer system of METU to the proposed wetlands, was also granted by the General Secretary. The sewer carried the domestic wastewater produced in ODTÜKENT. In this regard, the infrastructure plan of the METU was examined to determine the nearest manhole to the abandoned sludge drying bed. Several visits had to be performed to the site since the locations of the new manholes were not shown in this plan. The nearest manhole, from which a certain amount of domestic wastewater could be pumped out via a submerged pump and diverted to the to the sedimentation tanks during the research, was situated at about 60 m distance to the sludge drying bed. As the name implied, a submerged wastewater pump can only function in a water column of around 60 cm. Thus, a wall of 1 m was put up using bricks at the bottom of the chosen manhole, so that the incoming raw wastewater could firstly accumulate there till a water height of 1 m has been reached, and then could continue to flow through the sewer line (Figure 3.1). The details of this submersible pump and its operation mode will be given in the Section 3.10.

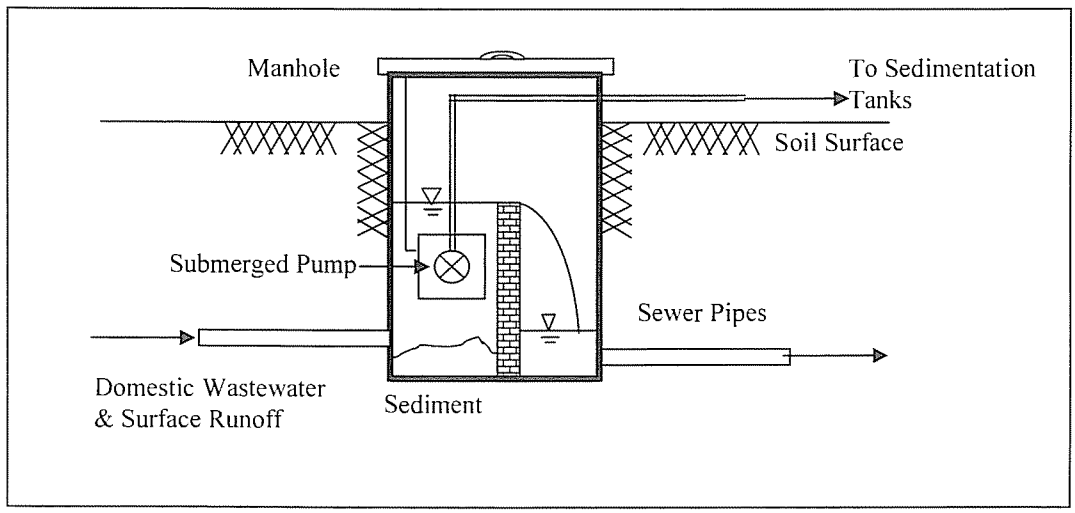

Figure 3.1. Cross-Section of the manhole

3.6.2. Configuration of the Constructed Wetlands

In the early 1980s, when subsurface flow constructed wetlands were introduced, the wetland systems usually consisted of only one bed. However, hydraulic problems and the need of higher effluent qualities led to a changed approach so that usually a multicell configuration was used (IWA, 2000). Thus, in this research, it was decided to implement two parallel sets of hybrid system with similar design configuration, but with different filter media. It was also decided to operate both of the hybrid systems identically under the same operational conditions (same influent discharge rate, same hydraulic loading rate, same plant density, etc.) in order to quantify the differences of the treatment performances of both systems. One hybrid system was planned to consist of a combination of two subsurface flow constructed wetlands, each of which would have different flow regime and different cross-sections.

Vertical flow subsurface constructed wetlands with intermittent feeding are now state of the art in Europe due to its advantages over the other type of systems: high removal efficiencies for BOD_5 and suspended solids; more equal root distribution and water-root contact; higher nitrification capacity, fewer problems of bad odor and proliferation of insects; etc. (Haberl et al., 1995; Cooper, 1999). Therefore, the first stage of the hybrid systems of METU was designed as a subsurface constructed wetland with vertical flow (Figure A.14 & A.15). In order to improve the overall treatment efficiency of the whole hybrid system, especially in terms of nitrogen, it was also planned to connect horizontal flow subsurface constructed wetlands (Figure A.16.& A.17) to the vertical downflow constructed wetlands in series, where due to the anaerobic conditions the denitrification process could also be achieved.

3.6.3. Sizing of the Constructed Wetlands

The wetlands used in this study were implemented at pilot-scale level with 60 PE capacity. According to the statistics conducted by the State Statistical Institute

(DİE), one person produces approximately 100 $L.d^{-1}$ of wastewater in Turkey. So, a wastewater flowrate of 6 $m^3.d^{-1}$ was used in the hybrid wetland systems. A vertical flow constructed wetland connected with a horizontal flow type of subsurface wetland constituted a hybrid system. The surface area of the wetlands was determined by using the equation 2.11 (see Appendix A.2 for detailed explanations and calculations). The total surface area of each of the hybrid system was calculated as 45 m^2. The area of the horizontal flow constructed wetlands was selected as half of the area (15 m^2) of the vertical flow wetland (30 m^2).

According to the sorption experiments, it was decided to use blast furnace granulated slag as filter media to be used in one of the hybrid systems, in addition to gravel and sand. The depths of the wetlands were chosen as 60 cm, which is a recommended depth for constructed wetlands in the literature (Table 2.3). The design data for the wetlands were presented in Table 3.3. The plan view of the constructed wetlands was illustrated in Figure A.18.

Table 3.3. Properties of the implemented pilot-scale subsurface flow wetlands

Parameters	Pilot-Scale Constructed Subsurface Wetlands			
	# 1	# 3	# 2	# 4
Flow Type	VF	HF	VF	HF
Fill Medium	Sand and Gravel	Sand and Gravel	Blast furnace granulated slag	Blast furnace granulated slag
Width (m)	4.40	3.70	4.60	3.30
Length (m)	6.30	3.80	6.40	4.20
Depth of the Fill Medium (m)	0.60	0.60	0.60	0.60
Area (m^2)	~30	~14	~30	~14
Discharge ($m^3.d^{-1}$)	3	3	3	3
Hydraulic Loading Rate ($m.d^{-1}$)*	0.11	0.22	0.11	0.22
Plant Density ($reed.m^{-2}$)	9	9	9	9
Plant Type	*Phragmites australis*	*Phragmites australis*	*Phragmites australis*	*Phragmites australis*

Constructed Wetland #1 & #3 constituted the gravel hybrid wetland system;
Constructed Wetland #2 & #4 constituted the granulated slag hybrid wetland system.
* Volume of wastewater applied daily to the unit area of the wetland ($m^3/m^2/d$).

3.6.4. Excavation Work

As the first step of construction, the old sludge drying bed was excavated about 100 cm with a caterpillar (Figure A.19). The excavated soil (about 100 m^3) was transferred onto the unused part of the sludge drying bed and was compacted.

3.6.5. Sealing of the Constructed Wetlands

Constructed wetlands require sealing to prevent the contamination of groundwater or to prevent groundwater from infiltrating into the wetland. Depending on the characteristics of the selected area for implementation of pilot-scale wetlands, an impermeable layer (e.g., lower density polyethylene, clay, bentonite, geotextile, etc.) can be used to seal the bottom of constructed wetlands (IWA, 2000).

Constructed wetlands used in this study were sealed by using a roll of nylon with a width of 10 m and length of 42 m. Nylon was selected due to its low price (Figure A.20). At the site, necessary amount of nylon was cut off according to the dimensions of the wetlands and then laid down. A slope of 1% was created at the bottom of the constructed wetlands of METU to allow easier water collection.

3.6.6. Cross-Sections of the Constructed Wetlands

A layer of 15 cm gravel with a diameter of 15-30 mm was placed on the top of the nylon layer. The depth of the overlying fill medium for all of the wetlands was about 30 cm. In one of the systems, the overlying layer was composed of washed gravel, the diameter of which varied between 7-15 mm (Figure A.14 & A.16). The other hybrid system was filled with the sieved blast furnace granulated slag with the diameter of 0-3 mm (Figure A.15 & A.17). A 15 cm of fine sand mixed with a 0-3 mm sized rough sand was placed as the initial rooting media for the common reed at the top of the fill medium layer of each of the wetlands,. Both of the vertical flow

wetlands had a freeboard of at least 30 cm, whereas both of the horizontal flow wetlands had a freeboard of 90 cm. Some of the pictures that was taken while the filter material were placed were presented in Figure A.21.

3.6.7. Sedimentation Tanks

In order to store and settle the domestic wastewater diverted from the nearest manhole, the use of two of the sedimentation tanks was planned. Upon approval of the Directory of the Heat Management of the METU, two identical, cylindrical, old water boilers were used as sedimentation tanks (Height: 3.10 m; Diameter: 1.35 m; Volume: 4.12 m^3; Effective Volume: 3.61 m^3).

After performing the necessary cleaning and modifications, the sedimentation tanks were ready to use (Figure A.22). Both of the sedimentation tanks had an outlet at the bottom for sludge removal. There were openings with a diameter of 30 cm at the top of the tanks for aeration. Both of the tanks was connected to each other with a pipe with a diameter of 4 cm, placed at 20 cm above the bottom so that the domestic wastewater could accumulate in each of the tanks equally. After settling the wastewater was directed to the vertical downflow wetlands with a PVC pipe of a 50 mm diameter. There were also sampling ports installed to the tanks, from which wastewater samples were taken during the monitoring period.

At the site, the tanks were placed vertically on concrete blocks (Figure A.23). The platform was about 1 m above the surface of the vertical flow constructed wetland so that the settled wastewater could flow by the gravitational force. The total wastewater head was at least 2.5 m during the operation period.

3.6.8. Inlet and Outlet Structures

Perforated PVC pipes were used to distribute the wastewater evenly onto the vertical flow wetland beds. Original PVC pipes have a diameter of 50 mm and length of 1 m. Since perforated PVC pipes were not available, 7 mm holes were

drilled at every 20 cm of the PVC pipes, to provide an equal downflow distribution. On each of the vertical flow wetland cells, three 6 m length perforated PVC pipes were installed in parallel by the use of metallic holders. Metallic holders (Y in shape) held these pipes at a height of 25 cm above the top surface of the vertical flow constructed wetlands. At every 1.5 m of the length of the wetland cell, a metallic holder was placed so that 12 holders were used for each of the vertical flow wetlands (Figure A.24).

To collect the treated wastewater, elastical polyethylene drainflex pipes of a diameter of 100 mm were placed within the gravel layer (15/30 mm) in all of the wetlands. The drainflex pipes with small openings were already available in the Turkish market. At a distance of 1 m, four 8 m drainflex pipes were placed within the gravel layer (15/30 mm) in both of the vertical flow wetlands. Part of these drainflex pipes (around 2 m) outstayed in the air above the filter medium for aeration and cleaning purposes. The end points of the drainflex pipes were connected to each other via solid PVC pipes of 100 mm diameter at the lower part of the vertical flow wetlands. There was only one open end on this collector to direct the collected treated water to the horizontal flow subsurface wetland cell. Remaining drainflex pipes were cut down in small pieces (80 cm) and placed vertically like chimney at every 2 m distance of the vertical flow wetland cells for providing the lower layers with oxygen.

An inlet zone formed by coarse stones served as an inlet arrangement in both of the horizontal flow subsurface constructed wetlands, whereas the effluent of these wetlands were again drained via two of drainflex pipes of 1 m. The coarse stones (100-200 mm) were obtained from the former trickling filter of the old wastewater treatment plant of the METU. The freely drained water was used to irrigate the grasses existing on the old sludge drying bed.

3.6.9. Plantation of the Constructed Wetland Cells

The aquatic plants to be used in constructed wetlands should be native to the local area in order to prevent the unwanted spread of the plant. Common reed *(Phragmites australis)*, which has been successfully used in constructed wetland applications for treatment of several type of wastewater (Crites, 19995), can be easily obtained on the METU campus. Thus, all of the pilot-scale constructed wetlands were planted with the shoots of the *Phragmites australis*, which were transferred from the natural reed beds on the campus (Figure A.25).

The reeds transplanted at a density of 9 seedlings.m^{-2} by the workers of the Directory of the Forestation and Plantation Works, METU, on 26th June 2001. Before applying the wastewater to the system, reeds were irrigated daily with tap water for at least 40 days in order to establish good plant adaptation (Figure A.26). However, the reeds withered in the pilot-scale wetlands due to mainly the following constraints:

- Insufficient root structure of the reeds to adapt themselves to their new environment because of extra cutting of the roots of the transferred plants;
- Unexpected weather conditions (extreme drought period experienced in 2001) resulted in insufficient water saturation conditions in the wetland cells;
- Insufficient nutrient supply due to the late application of the domestic wastewater to the wetland beds;
- Wrong handling due to being inexperienced with reed transplantation to the constructed wetlands.

Hence, it was decided to replant the cells once more in the spring of 2002. Therefore, the formerly planned operation and monitoring period had to be shifted to early summer of 2002. In this regard, at the end of the October 2001, the workers of the Directory of the Forestation and Plantation Works of METU have transplanted thousand of the reed seedlings into the tubes filled with local soil (see

Figure A.27). At the beginning, these plants were placed in the garden of this directory and stayed outside until May 2002. Meanwhile, 300 of the planted tubes were transferred into the greenhouse of METU at the end of January 2002 in order to ensure the growth of some of the common reed seedlings and also to check whether the transplantation were done in an adequate way (see Figure A.27). The indoor air temperature of the greenhouse was about 25°C and the workers of the greenhouse irrigated the plants for about 3 months, regularly.

At the beginning, the stems of the reeds placed in the greenhouse looked like dehumidified and had a color of yellow. However, one month later, about 250 of 300 reed stems have turned to green and also gave new shoots. At the end of the March 2002, due to the harsh field conditions, in order to prevent the plants from getting frozen, it was decided to build a small greenhouse. This greenhouse was created using a nylon ceiling over the reeds (~700), which were standing outside in the garden of the Directory of the Forestation and Plantation Works of METU. About 650 of 700 reed stems standing outside also gave new shoots. In general, about 80% of 1000 reed seedlings indicated successful plant growth.

In the third week of May 2002, as the air temperatures increased, all the reed tubes were transferred to the field by a tractor with the help of the workers of METU (Figure A.28). Each of the wetland cells were transplanted with the reeds with a height of 30-50 cm resulting in a plant density of 9 seedlings.m^{-2}, on 17th May and 18th May 2002 (Figure A.28).

The reed shoots were transplanted in the holes with a depth of 30 cm and a diameter of a 20 cm with the same reed density of 9 reed.m^{-2} were digged systematically in each of the wetland cells in order to transplant. Neither the roots, nor the upper sites of the reeds were cut. The plastic reed tubes filled with soil were scratched with a knife and the soil-plant combination was placed carefully in the holes as shown in Figure A.29. Since the upper section of each wetland cell constituted of sand, the holes transplanted with reeds were again covered with sand.

Reeds were irrigated with tap water brought to the site with the old water storage tank in order to establish a good plant adaptation. The newly planted reed shoots had a successful adaptation and a good growth in the pilot-scale constructed wetland cells (Figure A.29).

Since the project team has not preferred the application of the primarily treated domestic wastewater to the wetlands without providing a good plant establishment; the proposed operation and monitoring period had to be shifted. Having provided a successful plant adaptation (Figure A.30), the operation of the wetland beds has started in June 2002.

3.6.10. Operation Schedule

A control panel was designed for controlling the wastewater flow line between the manhole, sedimentation tanks and the upper wetland cells. In 2002, the control panel and the pumps had to be renewed due to some problems faced within the system under the field conditions in winter time. Even though the control panel itself had its own protection, in order to protect the control panel from the sun; rain and snow; an extra old control panel housing has been obtained in METU and the control panel was placed in it. Afterwards, it was installed nearby the manhole at the field. The control panel consisted of contactors, fuses, clemens, termics and timers. It has been designed to provide the operation of the below described system:

Operation Schedule:

06:00	Submergible pump in the manhole turns on when the timer sends a signal.
06:00-09:00	Pump is on and sends the wastewater to the sedimentation tanks.
09:00	When the water level in the sedimentation tanks is at maximum, the level sensor A sends a signal to the contactor and pump is turned off.
09:00-11:00	Suspended solids of the wastewater settle down in the sedimentation tanks for two hours.

11:00 Timer sends a signal to the selenoid valve to let it open and let the settled wastewater be flushed onto the vertical downflow subsurface constructed wetland cells.

13:00 When the water level in the sedimentation tanks is at minimum, the level sensor B sends a signal to the contactor and selonoid valve is turned off.

The pump and the solenoid valve would not operate until the following morning unless the schedule is changed. During the whole monitoring period, the Presettled wastewater was applied only once a day to the vertical flow subsurface constructed wetlands at METU. The photo of the control panel is given in Figure A.31.

In order to maintain the desired conditions for the entire system, a submerged drainage pump (WILO TP-R10M) with a steel housing was bought. The new pump was chosen considering the headloss between the manhole and the sedimentation tanks, and also the other constraints. The headloss was calculated according to the William Hazen equation for 70 m plastic pipe with a diameter (D) of 0.040 m; a pumping capacity (Q) of $3m^3.h^{-1}$ and a value of William Hazen coefficient (C_{WH}) of 140 for plastic pipes. The formula is presented below:

$$H = [10.67*L*Q^{1.852}]/[D^{4.87}*C_{WH}{}^{1.852}] \qquad \text{Eqn (3.6)}$$

where:

L = Length of the pipe; m

Q = Pump capacity; m^3/sec

D = Diameter of the pipe, m

C_{WH} = William Hazen coefficient

The calculated headloss using the William Hazen coefficient is about 1 m. Total headloss was calculated as 7.5 m including the water head difference of 6.5 m. So, the pump with the following characteristics were chosen for the mentioned purpose:

Power: 0.75 kW

Outlet diameter: R 1 $^{1/2"}$

Monophase, 220 V

Maximum pump lift: 18 $m^3.h^{-1}$

Pump head: 10 m

Headloss: 7.30 m

The pump was placed in a cylindrical tank with a diameter of 40 cm, height of 50 cm. It has identical holes all around its surface in order to allow the flow of fluid wastewater, but to prevent the entrance of the big solid particles carried by wastewater with submerged pump. Afterwards, this tank was installed in the manhole and the electric cables were connected to the control panel.

In 2001, two of the submerged pumps used for discharging the constructed wetland cells effluents were borrowed from the Directory of the Heat Management of the METU and placed into the system. Even though the pumps were operating in 2001 properly, they were broken in June 2002.

Since the purchase of two of the new pumps became a must, two submersible pumps (WILO TM W 32/11 HD) were bought and intalled into the system. The characteristics of the pumps are as follows:

Outlet diameter: R 1 $^{1/4"}$

Monophase, 220 V

Maximum pump lift: 16 $m^3.h^{-1}$

Pump head: 9 m

3.6.11. Construction Cost of the Wetland System

This work was partially funded by the METU Research Coordination and Industrial Liaison Office (AFP-2001-07-02-00-31). The total construction cost of the project was minimized because of recycling of some of the old materials and donations. For example, even though blast furnace granulated slag has a cost of $6 (US)/tones, due to personal contacts, the total amount of slag was donated by KARDEMİR. Only the transportation of the slag from Karabük to METU was paid.

The expenses for the application part of the wetlands have been listed in Table 3.4. However, the expenses for conducting the monitoring study (e.g. chemicals, laboratory equipments, etc.), maintenance cost, etc. was not shown here.

Table 3.4. Expenses of the project

Expenses	Quantity	Unit Cost	Total Cost
Excavation	12 hours	$20.00 (US)/hr	$240.0 (US)
Nylon	10 m x 42 m	$2.50 (US)/m	$105.0 (US)
Sand	30 m^3	$11.00 (US)/$m^3$	$330.0 (US)
Gravel	32 m^3	$11.00 (US)/$m^3$	$330.0 (US)
Transportation of slag	32 tonnes	$7.30 (US)/tones	$235.0 (US)
Drainflex and PVC pipes	200 m (Total)	$1.60 (US)/m	$320.0 (US)
Submersible Pumps	3	$120.00(US)/each	$360.0 (US)
Control Panel and Connections	---	---	$500.0 (US)
Workers	33	$12.0 (US)/8 hr	$395.0 (US)
TOTAL			**$2,815.0 (US)**

In Europe, the construction cost of a subsurface flow constructed wetland for a population of 20 PE varies between 100 and 150 Euro/m^2; whereas the annual operation and maintenance cost is about 150 Euro/PE (Günter Langergaber, personal communication). For METU case, the construction cost can be approximated to $100 (US)/PE if the expenses not shown in Table 3.4 (e.g. cost of the sedimentation tanks) were considered. Even though the annual O/M cost was not calculated in this study, it should be taken into account while planning to implement constructed wetlands on the field.

3.7. Meteorological Data

The daily meteorological data (air temperature, precipitation and evaporation) were gathered from the nearest meteorological station located at the Research Institute of the Köy Hizmetleri, situated to the west of the abandoned wastewater treatment plant of METU. The daily average rain and evaporation data were examined and used for the water budget calculations of the constructed wetlands; whereas the ambient air temperature data were evaluated to understand the effect of temperature on the efficiency of the wetlands.

3.8. Water Budget Calculations

For constructed subsurface flow wetlands, the wastewater applied to the cells and atmospheric precipitations received by the wetland cells are the main water inputs, whereas the treated water going out of the wetland and evapotranspiration are the output discharge values (Wynn and Liehr, 2001). Since the cells are generally lined, it is assumed that there is no groundwater exchanges so that the infiltration term can be excluded from the water budget calculations. If the constructed wetland receives water through surface runoff, it should be also considered as an input term in the water budget equation. The water budget of the wetland can be described as:

$$Q_{out} = Q_{in} + I + P - ET - Q_{stored} \qquad \text{Eqn (3.7)}$$

where:

Q_{out} = The quantity of treated water exiting the wetland ($m^3.d^{-1}$),

Q_{in} = The quantity of wastewater entering the wetland ($m^3.d^{-1}$),

Q_{stored} = The quantity of wastewater stored in the porous parts of the wetland substrate ($m^3.d^{-1}$),

I = The amount of water entering the wetland through surface inflow ($m^3.d^{-1}$),

P = The quantity of water entering the wetland area through precipitation ($m^3.d^{-1}$),

ET = The loss of water through evapotranspiration from the wetland area ($m^3.d^{-1}$).

The inflow through precipitation can be calculated by multiplying the surface area of the wetland by the precipitation data obtained from the nearest meteorology station. Evapotranspiration values can be calculated according to Thornthwaite's method, which takes into account the daily average air temperature of the local area. This method was used for terrestrial ecosystems and has been applied with some success to the wetlands (Mitsch, 1991). Moreover, the daily evaporation values can be approximated to the evapotranspiration values since the evapotranspiration rate of the reed plants is almost equal to the evaporation rate (IWA, 2000).

The inflow and outflow concentrations of the organics and nutrients to be treated in the constructed wetlands are affected by additional water inputs and outputs (like precipitation, evapotranspiration, groundwater infiltration, etc.) other than the fluctuations in the wastewater. Precipitation dilutes the pollutant concentrations within the wetland so that the measured effluent values are actually lower than the actual ones. On the contrary, evaporation and evapotranspiration concentrate the pollutant concentrations in the wetlands due to the decrease in the water amount so that the measured effluent values are higher than that of the actual ones (IWA, 2000). Therefore, in this study, daily average outflow discharges have been calculated by adding the difference of the evaporation and rain values (mm) multiplied with the area of vertical subsurface constructed wetland (30 m^2) to the daily measured inflow values of 3 $m^3.d^{-1}$. The correction factors have been calculated by dividing the calculated outflow values by the measured daily inflow values.

3.9. Water Quality Monitoring Study

Even though the wetlands of METU were constructed in year 2001, the reed plants could not indicate successful adaptation in 2001. Therefore, the wetland cells had to be replanted in May 2002. The primarily treated wastewater was not applied to the system until a successful plant adaptation was obtained as explained in Section 3.6.9. At the end of the June 2002, it was observed that the plants adapted themselves to the wetland substrates as they grew well and covered the surface area of the wetland cells homogeneously. So, the primarily treated wastewater was applied to the wetland cells firstly in the early July 2002. Parallel to the wastewater application, the monitoring study was started.

Even though it was planned to monitor the whole treatment performance of the hybrid systems, due to some operational problems, only the treatment performances of the vertical flow subsurface constructed wetlands were monitored. The influent and effluent water samples of the vertical flow constructed wetlands were taken

biweekly between July 2002 and July 2003. The effluent was sampled 15 minutes later than the influent samples were taken. Temperature, conductivity, pH, COD, TSS, TP, PO_4^{3-}-P, NH_4^+-N, NO_3^--N, and TN values of the influent and effluent water samples were monitored. Water samples were taken properly as described in Standard Methods (AWWA, 1999) and brought to the Chemistry Laboratory of the Department of Environmental Engineering of METU in 15 minutes. Chemical analyses were performed on the same day as explained in Section 3.2.

3.10. Treatment Performances of the Constructed Wetlands

The data obtained from the monitoring study (July 2002-July 2003) that was conducted for the vertical flow pilot-scale constructed wetlands of METU were analyzed. The influent and effluent concentrations of the pollutants (TSS, COD, PO_4^{3-}-P, TP, NH_4^+-N, NO_3^--N, TN) for each of the vertical subsurface flow constructed wetland of METU were shown graphically (Figures: Sampling date vs. Influent and Effluent Pollutant Concentrations). Moreover, the concentration-based removal efficiencies of these wetlands were calculated and illustrated (Figures: Sampling Date vs. Removal Efficiencies (%)) Concentration based percent removal efficiencies (RE%) were calculated according to the following equation:

$$RE\% = [C_{in}-C_{out}]*100/C_{in} \qquad \text{Eqn (3.8)}$$

Using the effluent concentrations of the pollutants and hydraulic loading rate, loading rates for each of the pollutants were calculated using the below given equation and presented in graphical forms (Figures: Pollutant Loading Rate vs. Effluent Concentrations) with linear regression analysis:

$$\text{Pollutant Loading Rate } (g.m^{-2}.d^{-1}) = (C_{in})*(Q_{in}/A) \qquad \text{Eqn (3.9)}$$

Additionally, area-adjusted removal rates for each of the pollutants were calculated according to the following equation assuming Total Q_{in}= Total Q_{out}. These values were plotted against loading rates (Figures: Pollutant Loading Rates vs. Area-adjusted Removal Rates) with linear regression analysis:

$$\text{Area-adjusted Removal Rate } (g.m^{-2}.d^{-1}) = [(Q_{in}*C_{in}) - (Q_{out}*C_{out})] /A \quad \text{Eqn (3.10)}$$
$$= [(Mass_{in}-Mass_{out})] /A$$
$$= HLR*[C_{in} - C_{out}]$$

where:

Q_{in} = Water flow rate entering the wetland ($m^3.d^{-1}$),

C_{in} = Inlet concentration ($mg.L^{-1}$),

C_{out} = Outlet concentration ($mg.L^{-1}$),

A = Surface area of the wetland (m^2),

HLR = Hydraulic Loading Rate ($m.d^{-1}$),

$Mass_{in}$ = Mass of the pollutant in the influent ($g.d^{-1}$), and

$Mass_{out}$ = Mass of the pollutant in the effluent ($g.d^{-1}$).

For the above-given calculations, a constant inflow and outflow rate of 3 $m^3.d^{-1}$; an area of 30 m^2 and a hydraulic loading rate of 0.1 $m.d^{-1}$ for each of the vertical flow subsurface pilot-scale constructed wetland of METU were taken into consideration. In order to compare the treatment performances of the constructed wetlands of METU with the constructed wetland applications of the other countries, the literature was reviewed and the performance data of those studies were presented in Section 4.7.

3.11.Determinations of the Kinetic Parameters

Using the first-order plug flow equation (Eqn 2.15) as given in the Section 2.11, the areal-removal rate constants of each of the pollutants were calculated for both of the wetlands considering the influent and effluent concentrations of the pollutants. Relationship between the loading rates and areal-removal rate constants were demonstrated graphically. Moreover, the literature was reviewed and the areal-removal rate constants were compared to each other.

3.12. Analyses for Determination of the Plant Content

In May 2002, the reed plants in the tubes were ready for planting into the constructed wetlands. To determine the growth rate of the reeds, some of the tubes were chosen randomly; brought to the laboratory and the stems were removed from the soil. The roots were washed with tap water to remove the attached microorganisms and soil particles. The wet and dry weight of the reed samples were measured and recorded. After one year period of operation, the heights of the reed plants in the wetland cells were recorded randomly on the field in July 2003 (Figure A.32).

Considering the initial and final average height of the reed plants, the average growth rate of the reeds in terms of $mm.d^{-1}$ was calculated as follows:

Growth Rate of the Reds ($mm.d^{-1}$) = (Avg. Final Height – Avg. Initial Height) / ΔT Eqn (3.11)

where;

Avg. Final Height = The average height of the randomly selected reeds grown in the wetland cells in July 2003 (cm)

Avg. Initial Height = The average height of the randomly selected reeds before planting into the wetland cells in May 2002 (cm)

ΔT = Time between two measurements (day)
(in this case approximately 13 months = 400 days)

To differentiate the role of the plants in the overall nutrient uptake capacities of the constructed wetlands, it was planned to perform plant analysis to determine the contents of the plant biomass. In this regard, random square plots with dimensions of 0.25 m x 0.25 m were determined on the wetland cells. Below-ground and above-ground plant biomass samples within these plots were harvested from the wetland substrates (Figure A.33). The plants were brought to the Chemistry Laboratory of the Department of Environmental Engineering of METU. Firstly, the

wet-weight of the below-ground (roots and rhizomes) and above-ground (stems and leaves) parts of the harvested reeds were measured. Secondly, the harvested above-ground plant biomass; rhizomes and roots were dried at 60°C for 48 hours and weighed for dry-weight biomass (Figure A.34). Afterwards, they were grounded to pass a mesh of 2 mm. All the harvested samples were digested in acid solutions and analyzed for seven parallels for TN and TP to determine the nitrogen and phosphorus content of the plants (Figure A.35). The same TN and TP procedures were performed as explained in Table 3.1. According to the results of the above-mentioned experiments, the total TN and TP mass removed by the plants in each of the wetland cells were calculated.

To understand the effect of the season on the TN, Fe, Cu, Mg, Mn, Na, K, and Ca content of the reed biomass of the wetland cells, sample reeds were harvested once more from the wetland cells on November 2003, as described above. However, these plant samples could not be analyzed in the Chemistry Laboratory of the Department of Environmental Engineering of METU for Fe, Cu, Mg, Mn, Na, K, and Ca. Hence, they were sent to the Department of Agriculture of the Ege University, İzmir, for these analyses. In the Ege University, TN, Fe, Cu, Mg, Mn, Na, K, and Ca content of the above-ground and below grounds of the reeds were determined according to the methodologies described by Kacar (1972).

3.13. Determination of the Contents of the Substrate

It was aimed to understand what kind of nutrients, metals and other compounds were accumulated in the filter media of both of the wetlands of METU. Therefore, substrate samples (sand, slag and gravel) were taken from several points of the vertical flow wetland cells (Figure A.36) at the beginning (May 2002) and at the end of the operation period (July 2003 and November 2003). All the fresh substrate samples were brought to the laboratory and stored in the dark at +4°C until analysis. Necessary amounts of the sand and slag samples (~1 kg) taken in July

2003 and November 2003 from both of the wetland cells, as well as the fresh slag and sand samples, were sent to the Soil Laboratory of the Department of Agriculture of the Ege University, İzmir.

The soil analyses were performed according to the methodologies adopted by Kacar (1972). The samples were analyzed for some compounds in the Soil Laboratory of the Ege University. These compounds were as follows: TN, TP, P available for plants, total Na, Na available for plants, total K, K available for plants, total Ca, Ca available for plants, Mg, and heavy metal (Fe, Mn, Zn, Cu, Pb, Cr, Sn, Cd, Hg, Ni).

3.14. Chemical Extraction Experiments for Phosphorus Determination

Phosphorus retention in the subsurface flow constructed wetlands is primarily via adsorption, absorption and precipitation (Mann, 1990; Kadlec and Knight, 1996). However, it is difficult to differentiate between these phosphorus fate-mechanisms only by looking at the inflow and outflow phosphorus concentrations of the constructed wetlands. These fate-mechanisms involved in the sorption/release of P within the wetlands filled with special substrates are not very well known (Johansson and Gustafsson, 2000). These mechanisms are, however, important for the practical use of the filter materials. Therefore, a more detailed knowledge of these mechanisms might facilitate estimations of the longevity of the materials with respect to P sorption (Johansson and Gustafsson, 2000) and also would question if the sorbed P is available for plants when the filter materials of the wetlands were reused afterwards as fertilizers or soil conditioners for the agricultural purposes.

Fractionation of P-forms in the filter media can provide an opportunity to understand which forms of ions in the filter media sorbed the P and what kind of transfer dynamics were between these ions and phosphorus (Zhu et al., 2002). Identification of the phosphorus forms in soils/sediments/wetland substrates may be achieved by chemical extraction. Various chemical fractionation schemes have been proposed in the literature (e.g. Chang and Jackson, 1957; Hieltjes and

Lijklema, 1980; Williams et al., 1971; Hartikainen, 1979; Stuanes and Nilsson, 1987 cited in Zhu et al., 2002). All based upon the assumptions that certain reagents will extract discreet forms of phosphorus (Sovik and Klove, 2002).

In this dissertation, the chemical extraction methodology proposed by Chang and Jackson (1957) and modified by Hartikainen (1979) was used in this study to fractionate the inorganic phosphorus forms retained by sand and slag layers of the wetlands. This was a suitable method for the media with high Ca content (Zhu et al., 2002). The experiments were conducted in the Chemistry Laboratory of Department of Environmental Engineering of METU. The method involved sequential extraction of the soil samples, where each chemical removed its discrete form of inorganic phosphorus (Sovik and Klove, 2002).

The substrate (sand and slag) samples were taken from the vertical subsurface flow constructed wetlands of METU at the beginning (in May 2002; used as blank) and end of the monitoring period (in July 2003). Both the fresh and wastewater applied samples were brought to the laboratory and dried at 105°C for 12 hours. Sand and slag samples were weighed and one gram of each sample was placed into the Erlenmeyer flasks with a volume of 50 mL. The firstly used extractant (NH_4Cl) was also added to the flasks and flasks were placed into the shaker at 25°C. The extraction scheme was shown in Table 3.5.

Table 3.5. Chemical phosphorus extraction scheme for 1 g of filter material

Phosphorus-Fraction	**Extractant**	**Treatment**
Loosely-bounded P	1 M NH_4Cl	50 mL extractant, shaken for 1 hr
Al-Bounded P	0.5 M NH_4F	50 mL extractant, shaken for 1 hr
Fe-Bounded P	0.1 M NaOH	50 mL extractant, shaken for 18 hr
Ca-Bounded P	1 M H_2SO_4	50 mL extractant, shaken for 1 hr
Occluded P	KCl-$C_6H_8O_6$-EDTA	50 mL extractant, shaken for 1 hr

The extractant from each step was centrifuged. The supernatant was filtered through 0.45 μm membrane filter and decanted into a vial. The soil (slag and sand samples) was washed with 2 x 25 mL saturated NaCl solution between the extraction steps to get rid off any phosphorus that had re-adsorbed back onto the soil from solution (Headley et al., 2002). The amount of phosphorus in the supernatant was measured using Ascorbic Acid Method (AWWA, 1999).

For each of the extraction step, five parallels were used (Figure A.37). Sample blanks, consisting of blank slag that was not used in the reed beds, were also run through the sequential extraction with each of batch samples. The sample blank values were then subtracted from the sample values to take into account any pre-existing phosphorus on the raw slag, or that was dissolved from the internal structure of the slag during extraction.

3.15. Mass Balance Approach for the Constructed Wetlands

As Breen (1990) mentioned, a number of authors (Heliotis and De Witt, 1983; Howard Williams, 1985; Middlebrooks, 1987) have been critical of the "green box" approach of many constructed wetland treatment studies because it failed to identify which components and mechanisms were important in determining the level of performance. In general, they considered that a "mass balance (or material balance) approach" was required. The fundamental approach was to show the changes occurring in the wetlands by the mass balance analysis. The following was a general form of a mass balance equation (Kuo, 1999):

[Rate of Mass **Accumulated**] = [Rate of Mass **In**] - [Rate of Mass **Out**]
± [Rate of Mass **Generated** or **Destroyed**] Eqn(3.12)

In order to investigate particular aspects of constructed wetlands treating wastewater, several authors (Heliotis and De Witt, 1983; Howard Williams, 1985; Middlebrooks, 1987) advised to design experiments like substratum characterization and specific experiments that clarify the nutrient removal

mechanisms. In this regard, a simple mass balance method was proposed by Breen (1990) to examine the fate of nutrients in constructed wetlands. Under this approach, a reed bed was divided into a series of interactive compartments (water, substratum, microbiota, flora and fauna), each representing a store of nutrients (Breen, 1990). By measuring the mass change in the size of these storages over time, the relative importance of each compartment could be determined and the dominant removal processes could be identified. For a conservative material, assuming steady state conditions and first order rates, changes in the output mass (y) could be described by using the equation given by (Howard-Williams, 1985):

$$y = x - [k_1 - k_2]\, x \qquad \text{Eqn (3.13)}$$

where:

y = output mass over a certain time period,
x = input mass over a certain time period,
k_1 = composite uptake rate coefficients (where for wetlands, k_1 processes are sedimentation, precipitation, adsorption, absorption, production, denitrification, uptake by plants, biological assimilation, etc.),
k_2 = composite release rate coefficients (where for wetlands, k_2 processes are suspension, dissolution, desorption, decomposition, respiration, etc.).

Simply monitoring influent and outflow concentrations ($mg.L^{-1}$) of the water pollutants and discharge of the wastewater to the wetlands over a period of time, x and y, thus, the change in storage $[k_1-k_2]x$ for the whole system could be determined. Moreover, changes in the storage of individual components could be similarly described and measured (Breen, 1990). Similarly, TSS, COD, PO_4^{3-}-P, TP, NH_4^+-N, NO_3^--N and TN mass balances for both of the vertical flow reed beds were constructed in this study by using the influent and effluent concentrations monitored for 12 months. Both of the reed beds were conceptually partitioned into the following compartments to differentiate the importance of the fate mechanisms that were responsible for removal of TN and TP as Headley et al., (2002):

1. Influent loading,
2. Effluent loading,
3. Change in plant biomass (above-ground and below-ground), and
4. Change in substrate.

A fifth, unmeasured compartment (detritus, microbiota, other) was assumed to have accumulated the difference between Compartment 1 and Compartments 2-4. The data of the first and second compartments were gathered from monitoring studies (Section 4.7); whereas for the third compartment the data were taken from the section called "Analysis for Determination of Plant Contents" (Section 4.8); and for the fourth compartment from the sections called "Determination of the Contents of Substrates" (Section 4.9) and "Chemical Extraction Experiments for Phosphorus Determination" (Section 4.10), respectively.

3.16. Statistical Analyses

For all the experiments that were performed within this dissertation, at least two replicates were used except for mentioned otherwise. Average and mean values, as well as the standard deviations, were calculated using SigmaPlot ™ and Excel XP Microsoft Office™ softwares. Linear regression analyses were also performed using the above-mentioned softwares, whenever it was necessary.

For differentiating the treatment performances of the slag system and gravel system, discriminant function analyses were performed. One-way ANOVA at a significance level of 0.05 was applied to the removal efficiencies calculated from the data of the monitoring period of July 2002-July 2003 for each of the water quality parameter. These analyses were conducted by using a sub-programme of Excel XP of Microsoft Office™ Software. The statistical results were presented in the following form: (ANOVA; $F_{0.95}(dF;dN)$; P) where $F_{0.95}$= %95 confidence limit; dF=degree of freedom; dN=sample size; P>0.05 nonsignificance (accept null hypothesis).

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Characteristics of the Wastewater treated in the Constructed Wetlands

The characteristics of the raw domestic wastewater before entering the primary sedimentation tanks and after primary treatment were summarized in Table 4.1 and 4.2, respectively.

Table 4.1. The Characteristics of the raw domestic wastewater of METU before primary treatment

DWW	BOD_5	COD	PO_4^{-3}-P	TP	NH_4^+-N	NO_3^--N	TN	TSS
Min ($mg.L^{-1}$)	40	221	2.60	5.98	14.0	0.13	28.1	80
Max ($mg.L^{-1}$)	90	348	4.34	6.19	29.5	0.91	50.9	125
Average ($mg.L^{-1}$)	65	279	3.34	6.14	23.9	0.60	34.7	102
Median ($mg.L^{-1}$)	70	274	3.20	6.19	26.3	0.68	30.7	102
ST DEV ($mg.L^{-1}$)	30	52	0.74	0.11	6.17	0.34	9.23	22

Table 4.2. The Characteristic of the domestic wastewater of METU after primary treatment

DWW	BOD_5	COD	PO_4^{-3}-P	TP	NH_4^+-N	NO_3^--N	TN	TSS
Min ($mg.L^{-1}$)	40	108	2.97	3.59	15.1	0.00	12.4	24
Max ($mg.L^{-1}$)	100	307	8.03	8.46	34.5	3.22	52.1	140
Average ($mg.L^{-1}$)	50	228	4.62	6.77	24.6	1.21	30.3	48
Median ($mg.L^{-1}$)	60	261	4.44	7.08	23.9	0.67	32.0	36
ST DEV ($mg.L^{-1}$)	35	68	1.37	1.56	6.51	1.08	12.4	32

As can bee seen from Tables 4.1 and 4.2, COD and TN values of the wastewater slightly decreased after the primary treatment upon sedimentation. TSS

concentrations decreased by a removal efficiency of about 50%. A reduction of COD about 50 $mg.L^{-1}$ in the raw wastewater during primary sedimentation was accounted for by the 50% removal of TSS.

This indicated that primary treatment was exclusively sedimentation and there was little or no biological breakdown occurred. Since the wastewater was kept for 2-3 hours in the sedimentation tanks, anaerobic degradation was minimized. The increase in the concentrations of PO_4^{3-}-P and TP in the primary treatment might have been attributed to the hydrolysis of the polyphosphates to small sized orthophosphates.

The literature for the characteristics of the domestic wastewater fed to the constructed wetlands for different countries and data for METU were given in Table 4.3. Generally, the average concentrations of all the pollutants recorded in the raw domestic wastewater of METU were lower than that of the literature given by Vymazal et al (1998); but similar to that of the typical values of domestic wastewater given by Metcalf and Eddy (1991) (see Table 4.3). However, BOD_5 value of the wastewater of METU (65 ± 30 $mg.L^{-1}$) was comparably lower than the typical BOD_5 value of raw domestic wastewater (220 $mg.L^{-1}$) cited in Metcalf and Eddy (1991).

Moreover, the COD:BOD_5 ratio of the wastewater of METU was about 4.3, which was higher than that of the literature value of 1.14 (Metcalf and Eddy, 1991). Thus, it could be concluded that the domestic wastewater of the METU had a low biodegradability and could be classified as "low strength" wastewater. These differences might have been due to the differences in the water usage habit of the inhabitants of METU and also to the dilution of wastewater with precipitation.

Table 4.3. Domestic wastewater characterizations gathered from several researches

Countries	Parameters ($mg.L^{-1}$)						
	BOD_5	COD	$COD:BOD_5$	TSS	TP	NH_4^+-N	TN
Germany[b]	248	430	1.73	-	15.9	80.5	115
France[b]	215	495	2.30	225	8.5	25.0	46.0
METU old WWTP[e]	153	340	2.22	333	2.91	16.1	19.7
Turkey[f]	147	288	1.96	145	13.0	-	50.0
Nepal[c]	110	325	2.95	83	-	33.0	-
Poland[a]	110	283	2.57	140	7.7	-	46.1
Slovenia[a]	107	200	1.87	-	-	28.7	-
Germany-Baviera[a]	106	234	2.21	-	-	-	-
Denmark and UK[a]	97	264	2.72	99	8.6	21.0	36.6
Czech Republic[a]	87	211	2.42	65	6.6	28.1	46.4
North America[a]	28	-	-	48	4.41	5.9	18.9
Sweden[a]	801	-	-	-	5.03	-	25.3
Belgium[b]	54	168	3.11	60	4.60	-	16.9
Typical DWW Values[d]	220	250	1.14	100	8.0	25.0	40.0
This Study (Raw DWW)	65	280	4.30	102	6.14	24.0	34.7

References: [a]Vymazal et al., (2000); [b]Vymazal et al., (1998); [c]Shreshta et al., (2000); [d]Metcalf and Eddy, (1991), [e]METU ENVE, (1989); [f]Özbey, (1988) .

4.2. Properties of the Pumice and Blast Furnace Granulated Slag

General information of the granulated pumice mined in İzmir Cumaovası and the blast furnace slag co-produced in KARDEMİR Iron and Steel Co. were given in Section 2.13. The chemical composition of the granulated BFS of KARDEMİR Ltd.Co. and the granulated BFS slag that were used by wetland researchers in other countries were presented in Table 4.4.

All the granulated BFS has almost the same chemical composition although they were produced in different companies and countries (Table 4.4). The little variations in compositions of BFS cultivated in the different countries were probably attributed to with careful selection and careful blend of the raw materials by the producers. Generally, all the slag samples presented in Table 4.4 were rich in SiO_2 and CaO, followed by Al_2O_3 and MgO. The slag of KARDEMİR has slightly

lower CaO content (33.53%) and slightly higher SiO_2 content (41.79%) if compared to other slag samples. Higher Ca and Al contents of the slags favor the phosphorus adsorption (Johansson, 1999). However, slags with almost same compositions can show varying adsorption capacities and physico-chemical characteristics as stated by Bailey et al. (1999). Detailed information on the adsorption capacities and physical characteristics of these slags were presented in the following sections (see Section 4.3. and 4.4)

Table 4.4. Compositions of the blast furnace slag produced in iron and steel companies

Composition (%)	Blast Furnace Granulated Slag			
	Kardemir Iron and Steel Co., Turkey*	**Steel Works in Oxelösund, Sweden****	**ECO Stahl GmbH., Germany*****	**Australian Steel Mills Ltd., Australia********
FeO	0.64	0.30	0.24	<1-3
Fe_2O_3	-		-	-
SiO_2	41.79	35.50	35.00	32-37
MnO	2.35		0.42	<1.00
Al_2O_3	12.47	9.60	11.50	13-16
CaO	33.53	35.00	38.60	38-43
MgO	6.55	13.70	10.30	5-8
S	0.81	1.40	1.50	<0.10
Na_2O	-	-	0.37	<0.50
K_2O	1.24	1.30	0.63	<1.00
TiO_2	0.45	1.70	1.00	-
Bazite	0.75	1.00	-	-

Reference: *KARDEMİR Iron and Steel Ltd.Co., 2001. **Johansson, 1999. ***Grüneberg and Kern, 2001. ****Sakadevan and Bavor, 1998.

4.3. Sorption Isotherm Studies

The aim of this screening level adsorption experiments was to choose a substratum with a higher P-adsorption capacity so that it could be used as a fill medium in some of the pilot-scale constructed wetland of METU. In this regard, phosphate sorption capacities of pumice mined in İzmir and blast furnace granulated slag obtained from KARDEMİR Iron and Steel Ltd. Co. were determined by performing

the P-sorption experiments as described in Section 3.3. The initial and final (equilibrium) P-concentrations, as well as the P-sorption capacities for both pumice and slag were summarized in Appendix B (Table B.1). The adsorption capacities (expressed as mg $P.kg^{-1}$ sample) were calculated from the change in the P concentration of the contact solution during the shaking period according to the Equation 3.1 (see Section 3.4). Phosphorus sorptions were plotted as a function of the initial phosphorus concentrations of the solutions (Figure B.1).

Generally, pumice and slag samples showed similar P-adsorption capacities. There was a direct relationship between the initial P-concentration and the adsorption capacities of both of slag and pumice samples (as the initial P-concentration increased, the P-adsorption capacity increased). Even though both samples showed similar trends, the blast furnace granulated slag samples of KARDEMİR Iron and Steel Co. showed slightly higher P-retention capacities compared to the pumice mined in İzmir Cumaovası (Figure B.1). As the initial P-concentrations of the solutions changed between 0-320 $mg.L^{-1}$, the P-adsorption capacities for pumice and slag varied between 0-8,300 mg $P.kg^{-1}$ and 0-9,150 mg $P.kg^{-1}$, respectively (Figure B.1). These differences in the P-retention capacities of slag and pumice could be related to their different chemical compositions and different physical properties, such as surface area and surface structures, resulting in different amounts of reactive Ca, Fe and Al (Zhu et al, 2002).

As stated by Stober et al., (1997), direct relationship between the P-concentrations and adsorption capacities depend on the prevailing reactions of the adsorption and precipitation mechanisms (Equations 2.1-2.5 given in Section 2.10.3.1). According to these equations, as the P-concentration in the solution increases, the reactions move to right-hand site to restore equilibrium. Since the phosphorus is readily removed from the solution, it is converted further to even more insoluble products such as hydroxyl-apatites (HAp) (Brady, 1990).

It is well known that a certain supersaturation is needed to precipitate HAp (Abbona and Franchini-Angela, 1995; Lundager-Madsen et al., 1995). To initiate HAp precipitation a high activation energy is needed, especially if no other Ca-phosphates are present that can serve as "seeds" for HAp formation. In a companion study conducted by Johansson and Gustafsson (2000), clear evidence for HAp precipitation in the blast slag materials were found. Thus, for slag and pumice samples, it could be stated that Ca-P were already present in the solutions, which served as seeds for HAp formation and thus resulting in further sorption capacities as the initial P-concentrations of the solutions were increased (Figure B.1). The extent of HAp formation is critically dependent on factors such as degree of supersaturation, pH and PO_4^{3-} concentration of the solution (Johansson and Gustaffson, 2000). Unfortunately, since the pH of the solutions that were used in the sorption studies conducted in this research was not measured, it was difficult to interpret exactly on the effect of pH in the sorption mechanisms.

In the literature, there are also some P-sorption studies on the use of slag as filter medium in filter beds and constructed wetlands for P-removal (Mann and Bavor, 1993; Sakadevan and Bavor 1998; Baker et al., 1998; Bailey et al. 1999; Johansson 1999; Johansson and Gustafsson, 2000). Mann and Bavor (1993) reported an adsorption capacity of 420 mg $P.kg^{-1}$ for a slag that was considered to have good potential for application in a constructed wetland, while Sakadevan and Bavor reported an adsorption capacity of 44,000 mg $P.kg^{-1}$ for their slag. Crolla et al. (2000) reported adsorption capacities ranging from 3,900 to 17,000 mg $P.kg^{-1}$ for a number of slags tested. However, it was difficult to compare the results found in this study with those published in the literature due to the variations in sorption studies (intermittent flow or continuous flow, wastewater type, phosphorus concentrations, shaking time, etc.) chemical compositions or size distributions of the candidate filter material.

Nevertheless, the P-sorption studies conducted by Johansson (1999) were similar to the sorption studies performed in this research. Moreover, the chemical

compositions of the slag samples (provided from Oxelösund) used by Johansson (1999) and in this study were very similar, especially in terms of Ca, Al and Fe (see Table 4.3). In both of the studies, the P-sorption capacities of the slag samples were determined by performing almost the same experimental procedure and the same P-solution. However, the range of initial P-concentrations (0-20 $mg.L^{-1}$) was different in the experiments performed by Johansson (1999). The range of P-concentrations (0-20 $mg.L^{-1}$) was selected to reflect the P-concentrations found in the typical domestic wastewater (Metcalf and Eddy, 1991; Kadlec and Knight, 1996).

In this context, using the same experimental procedure as described in this study (Section 3.4.) and by Johansson (1999), further batch-scale adsorption experiments were performed only for slag (provided from KARDEMİR) using the KH_2PO_4 concentrations of 0, 4, 8, 20 $mg.L^{-1}$ and raw domestic wastewater with a concentration of 10 mg $P.L^{-1}$. The results were tabulated in Table B.1. According to the findings of these sorption studies, the granulated slag (particle diameter < 3mm) of KARDEMİR Ltd. Co. showed relatively higher P-sorption capacities than that of granulated slag (particle diameter < 4 mm) produced in Oxelösund, Sweden (Johansson, 1999). At an equilibrium phosphorus concentration of 5 $mg.L^{-1}$, the P-sorption capacity for slag produced in KARDEMİR Ltd. Co was around 400 mg $P.kg^{-1}$slag (Table B1); whereas it was around 100 mg $P.kg^{-1}$slag for the slag produced in Oxelösund (Johansson, 1999).

The differences in the P-sorption capacities could be again related to the differences in the chemical and physical properties (Zhu et al., 2002). However, both studies indicated that coarse-grained blast furnace granulated slag (diameter< 4 mm) could be considered as suitable materials for P-sorption in ecologically-engineered treatment plants like constructed wetlands due to its physical and chemical properties conducive to P removal (House et al., 1994).

Similarly, in this study, blast furnace granulated slag provided from KARDEMİR Iron and Steel Ltd. Co. showed higher P-adsorption capacities in the sorption

isotherm studies if compared to pumice. Moreover, it was a cheaper waste material. Hence, BFS of KARDEMİR was preferred to be used in some of the wetlands of METU. Hence, it was carried forward for further studies and characterization.

4.4. Physical Characteristics of Slag and Sand

Physical properties of slag were determined as described in the Section 3.5. The particle-size distribution of slag and sand was given in Appendix B (Table B.2 and Figure B.2). The particle-size distribution of the tested materials showed variations. Granulated slag had more finer textures if compared to sand (Figure B.2). This could suggest that the fine-grained slag could have lower hydraulic conductivity than that of sand. Materials with lower permeability (hydraulic conductivity) retard the movement of water, hence allowing longer periods of time for sorption to occur (Johansson, 1999).

Unfortunately, in this research, the hydraulic conductivity could not be measured neither in the field, nor in the laboratory. However, during the operation period (12 months), there was not any clogging problem or surface overflow in the constructed wetlands of METU, which are the indicators of inappropriate selection of the filter material (Vymazal et al., 1998). The characteristics of the slag and sand that were used in this study, as well as the literature values, were presented in Table 4.4.

The particle density and the bulk density of the slag gathered from KARDEMİR Iron and Steel Co. were lower than that of the literature values (Table 4.4). However, the porosity value of the slag used in this study falled within the range given in the literature. The variations could be due to the differences in chemical and physical compositions of the slags produced in different places with different methods. Particle density, bulk density and the porosity values of the sand used in wetlands of METU were highly comparable to the literature values (Table B.3).

4.5. Meteorological Data for the Constructed Wetlands

The daily average meteorological data (temperature, precipitation, evaporation) recorded on the sampling days were tabulated in Table 4.5. The daily average air temperature, precipitation and evaporation data for the period of July-October 2002 and November 2002-July 2003 were illustrated in Figure B.3 and B.4 (Appendix B), respectively. The monthly average temperature, precipitation and evaporation data taken on the sampling days for the period of July 2002 and July 2003 were calculated and illustrated in Figure B.5 (Appendix B).

Table 4.5. Daily meteorological average data recorded on the sampling days

Sampling Date	Mean Daily Ambient Air Temperature (°C)	Mean Daily Precipitation (mm)	Mean Daily Evaporation (mm)
15.06.2002	20.95	0	4.69
26.06.2002	23.80	0.5	5.85
12.07.2002	21.05	2.6	0.86
25.07.2002	19.62	0.2	5.12
06.08.2002	21.43	0.2	4.19
12.08.2002	26.47	0	5.53
20.08.2002	19.15	0	2.54
28.08.2002	18.15	0	4.63
03.09.2002	20.02	6.1	5.24
11.09.2002	16.82	0	2.92
02.10.2002	13.59	0.1	2.48
11.10.2002	17.05	0	1.72
15.10.2002	13.38	13.9	3.25
22.10.2002	8.71	0	1.74
31.10.2002	5.81	0	2.16
11.11.2002	6.62	4.7	0.5
28.11.2002	1.40	0.2	0.43
13.12.2002	-5.10	0	0
17.01.2003	1.37	0	0
02.02.2003	6.2	16.5	0
30.03.2003	4.52	0	0
02.04.2003	7.96	7.3	0
09.04.2003	1.77	0	1.65
17.04.2003	9.3	0	2.98
02.05.2003	17.54	0	4.7
18.05.2003	17.09	12.6	5.1
26.05.2003	14.45	0.1	3.3
06.06.2003	18.48	0	4.3
17.06.2003	23.47	0	5.9

Reference: Meteorology Station of General Directorate of Köy Hizmetleri, Eskişehir Yolu, Ankara.

In the period of July-October 2002, the calculated average ± st dev [min; max] data for air temperature, precipitation and evaporation were 7.25°C ± 8.16°C [-9.40°C; 24.34°C]; 1.37 mm ± 3.92 mm [0 mm; 31 mm] and 1.52 mm ± 2.15 mm [0 mm; 7.50 mm], respectively (Figure B.3). In the period of November 2002-July 2003, the calculated average ± st dev [min; max] data for air temperature, precipitation and evaporation were 18.68°C ± 4.62°C [3.97°C; 28.69°C]; 0.78 mm ± 2.37 mm [0 mm; 17 mm] and 3.82 mm ± 2.09 mm [0.18 mm; 14.67 mm], respectively (Figure B.4).

4.6. Water Budget Calculations of the Constructed Wetlands

According to the water budget equation (Eqn. 3.7), the outflow discharges of the wetlands of METU were calculated using the daily average precipitation, evapotranspiration and inflow data. The wetland systems of METU have been operated at a constant loading rate, thus, the inflow discharge values of both of the systems were well known ($3m^3.d^{-1}$). Unfortunately, since there was not any flowmeter to measure the outlet discharges of both of the wetlands of METU continuously; the actual outflow values could not be measured exactly for each day and in turn could not be compared with the calculated one.

Moreover, it has been suspected that there could be some leakages in the bottom of both of the wetlands bottoms although the bottom of the wetlands has been lined with nylon during the construction phase. Since both wetlands were operated as vertical subsurface flow, the wastewater was equally distributed on the surface area of the wetlands via perforated pipes. The wastewater passed through the entire depth of the wetland substrate in the vertical down-flow direction and reached the drainflex pipes at the wetland bottom. The treated water flowed through the solid PVC outlet pipe. If there were leakage at the bottom, the treated water would percolate deeper to the lower sections of the old sludge drying bed. In spite of any leakage, the treatment efficiency of the treated water flowing through the outlet

pipes of the wetlands was representing the overall treatment efficiency of the wetlands.

Measuring the hydraulic input and the hydraulic output of the wetland systems, one could show that evaporation and precipitation could affect the treatment performances of the planted wetlands so that the mass removal efficiency was significantly higher or lower than that of the observed levels. Since precipitation diluted the pollutant concentrations within the wetland, the measured effluent values were actually lower than the actual ones; whereas evapotranspiration concentrated the pollutant concentrations due to the decrease in the water amount so that the measured effluent values were higher that the actual ones (IWA, 2000).

The average rain and evaporation values (mm) gathered from the General Directorate of the Rural Services were tabulated in Appendix B (Table B.4) only for the sampling days (July 2002-July 2003). The daily average evaporation and rain values (m^3) were obtained by multiplying the daily average values of these parameters presented in Table 4.4, by the surface area (30 m^2) of vertical flow constructed wetland beds of METU. The daily average outflow discharges were calculated by adding the difference of the rain and evaporation values to the daily measured inflow values. The correction factors were calculated by dividing the calculated outflow discharge values by the measured daily inflow discharge values (Table B.4).

According to the correction factors of this study (Table B.4), the measured outflow concentrations can vary within a range of -5.9% and 16.5%. However, as the treatment performances of most of the treatment wetlands have not been presented in the literature considering these correction factors (IWA, 2000), the outflow concentrations measured in the laboratory have also been presented without any corrections in the further sections. Nevertheless, in the mass balance calculations, corrected outflow values (Q_{out}) were considered (see Appendix B, Table B.4).

4.7. Results of the Monitoring Study

The data obtained from the monitoring study, as well as corresponding calculations and discussion for the water quality parameters (TSS, COD, PO_4^{3-}-P, TP, NH_4^+-N, NO_3^--N, TN) for each of the vertical subsurface flow constructed wetland were presented in the following sections.

4.7.1. Total Suspended Solids (TSS) Removal

The manhole, from which the wastewater was pumped to the constructed wetlands, received both the domestic wastewater of ODTÜKENT and the rainwater including the surface runoff. Whenever there was precipitation, the characteristics of the wastewater varied accordingly. Observed day to day fluctuations in the water use also resulted in the variation of the suspended solids concentration.

The TSS concentration of the raw domestic wastewater (102.3 $mg.L^{-1}$) was similar to the TSS values of the domestic wastewater of the countries like Denmark (99 $mg.L^{-1}$) as given in Table 4.3. Even though the average TSS concentration of the raw domestic wastewater used in this study was lower than that of Poland and France (Table 4.3), it was in the range of TSS concentrations (100 $mg.L^{-1}$) reported by Metcalf and Eddy (1991).

According to the monitoring results given in Figure 4.1.a & b, the inlet TSS concentrations of both of the vertical subsurface flow constructed wetlands varied between 20-183 $mg.L^{-1}$ (74.72 ± 42.91 $mg.L^{-1}$). Generally, the influent TSS concentration indicated steep increases with the rain events encountered in the fall season since the surface runoff carried more sediment particles to the sewer system. The increase in influent TSS concentrations could also be related to the water use habits of the inhabitants.

The non-trapped influent solids, the surplus sludge and plant litter solids in the process of mineralization constitute the effluent of the wetlands (Börner et al., 1998). The effluent TSS concentrations of the slag and gravel systems of METU varied between 4-77 $mg.L^{-1}$ (26 ± 17 $mg.L^{-1}$) and 4-82 $mg.L^{-1}$ (32 ± 22 $mg.L^{-1}$), respectively, during the monitoring period (Figure 4.1.a&b). Concentration based TSS removal efficiencies of the slag system and gravel system varied between 4%-77% (63% ± 22%) and 4%-82 % (59% ± 20%), respectively (Figure 4.1.c). The effluent TSS concentrations of both of the slag and gravel systems gave similar responses to the variations of the inflow TSS concentrations (Figure 4.1.d). Furthermore, TSS removal performances of identically operated slag and gravel system did not significantly differ from each other statistically (1-way ANOVA; $F_{0.95}(1;96)=1.09$; $P>0.05$). Therefore, it could be stated that the differences in the size, compositions and porosities of the substrates of the slag and gravel system did not lead to significant effects on the TSS removal performances of the wetlands, which received settled wastewater with relatively low TSS concentrations (75 ± 43 $mg.L^{-1}$).

During the start-up period, the effluent TSS concentrations were very low (<10 $mg.L^{-1}$). However, TSS effluent concentrations increased in time. The decrease in the number of the heterotrophs living in the wetland cells,, due to the decrease in the air and water temperatures during fall and winter, might have resulted in lower biological TSS degradation. Suspended solids in the effluent of the constructed wetlands is a function not only of the treatment system, but also the weather conditions. For example after heavy rains or rapid snow smelt, the effluent could be turbid in the wetland systems (Börner et al., 1998). Hence, the increases in the effluent TSS concentrations (Figure 4.1.a&b) could also be related to the flushing of the trapped solids from the wetland fill media by the heavy rains in fall and snow smelt in winter. Moreover, this increase can be related to the mineralization of the reed plants in the fall and winter period (Naylor et al., 2002).

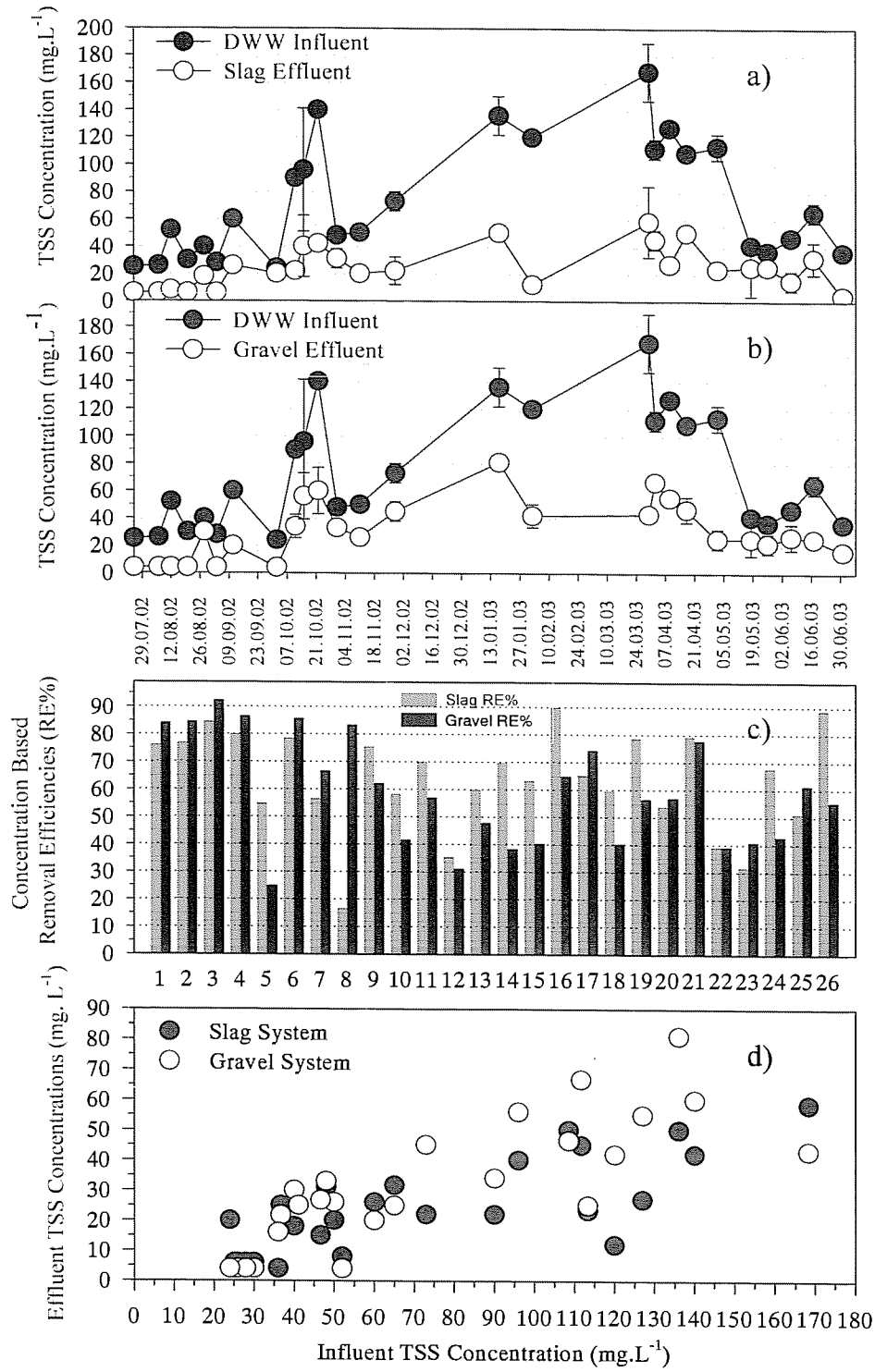

Figure 4.1. TSS a & b) time vs. influent and effluent concentrations ($mg.L^{-1}$) c) removal efficiencies (RE%) d) influent vs. effluent concentrations ($mg.L^{-1}$) of the slag and gravel wetland systems of METU

Accumulation of trapped suspended solids and significant quantities of plant litter are major threats for extended good performance of some wetland systems. Especially, hydraulic conductivity of the media in subsurface flow systems, which can be clogged easily can be reduced leading to surface overflow (Reed and Brown, 1995). Surface overflow was not observed in both of the wetlands during the operation period, which might be due the low organic content of the raw wastewater and efficient pretreatment of suspended solids by 50% before entering the wetlands. Throughout the monitoring period, average effluent TSS concentrations of both of the systems were below the Wastewater Treatment Plant Discharge Standards of Turkey (1991), which is 35 $mg.L^{-1}$ for treated domestic wastewater. Thus, it could be postulated that influent TSS values of 115 and 80 $mg.L^{-1}$ for slag and gravel systems resulted in compliance with the Wastewater Treatment Plant Discharge Standards for TSS (Figure 4.1.d). The influent TSS loading rates (see Eqn. 3.9) vs. the effluent TSS values for both systems were presented in Figures 4.2 and 4.3. The TSS loading rates for both systems varied between 2.0-18 $g.m^{-2}.d^{-1}$ (7.47 ± 4.29 $g.m^{-2}.d^{-1}$).

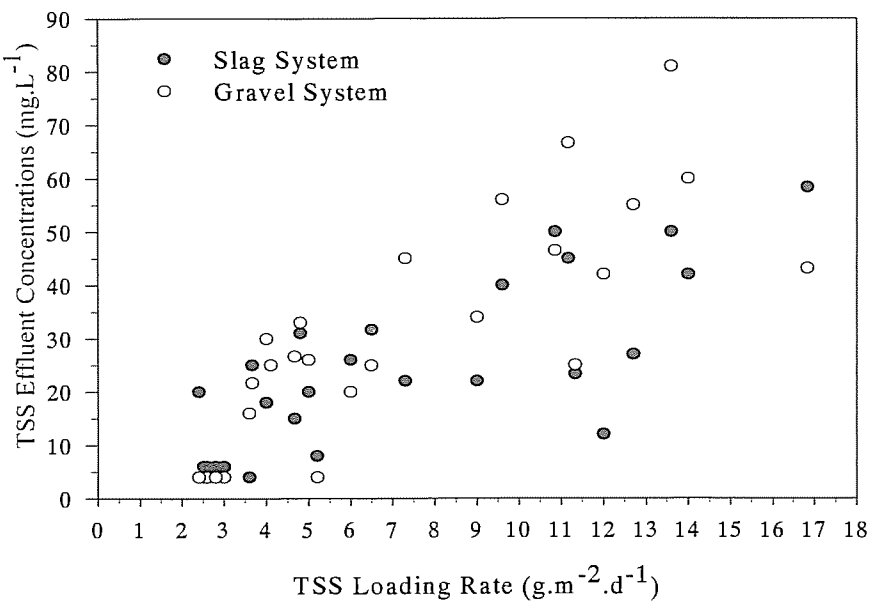

Figure 4.2. TSS loading rate ($g.m^{-2}.d^{-1}$) vs. effluent concentrations ($mg.L^{-1}$) of the pilot-scale constructed wetlands implemented at METU

For slag and gravel systems, the effluent TSS concentrations were dependent on the TSS loading rate (Figure 2). However, Brix (1998) stated that the effluent TSS concentrations were independent of the TSS loading rates in their wetland systems constructed in Denmark. This difference might be due to the variations in the characteristics of the wetland systems and the operational conditions (e.g. grain size of the filter media, HLR, type and strength of the wastewater, etc.). From the data in Figure 4.2, it can be stated that slag and gravel systems could be operated up to the loading rates of 11.5 $g.m^{-2}.d^{-1}$ and 8.5 $g.m^{-2}.d^{-1}$, respectively, to have effluent TSS concentrations below 35 $mg.L^{-1}$.

As opposed to the horizontal flow subsurface constructed wetlands, where most of the suspended solids are eliminated at the inlet end of the bed (Vymazal et. al., 1998), the total surface area of the vegetated beds plays an important role in the removal of TSS in vertical flow wetlands. The same was also found for this study (Figure 4.3). Both of the vertical flow wetland beds could remove TSS even at increased TSS loading rates. The correlation of the TSS loading rate and removal rate for the slag system was stronger when the regression analysis (R^2=0.9065) was considered and compared to that of the gravel system (R^2=0.8062). However, it should be noted that the effluent concentrations increased as loading rates increased for both systems (Figure 4.2).

In order to compare the TSS treatment performances of the VSF CW systems studied in this dissertation (Table 4.6) with the relevant literature from other countries for domestic wastewater treatment, the literature was reviewed and summarized in Table 4.7. As expected, as the influent TSS concentration of the wetland systems decreased, the effluent concentrations and the removal efficiencies also decreased. Average TSS removal efficiency of the wetlands used in this study (Table 4.6) was lower than that of the wetland studies given in Table 4.7. For all of the studies, the effluent concentrations were well below the discharge standard values given in European Union Directives.

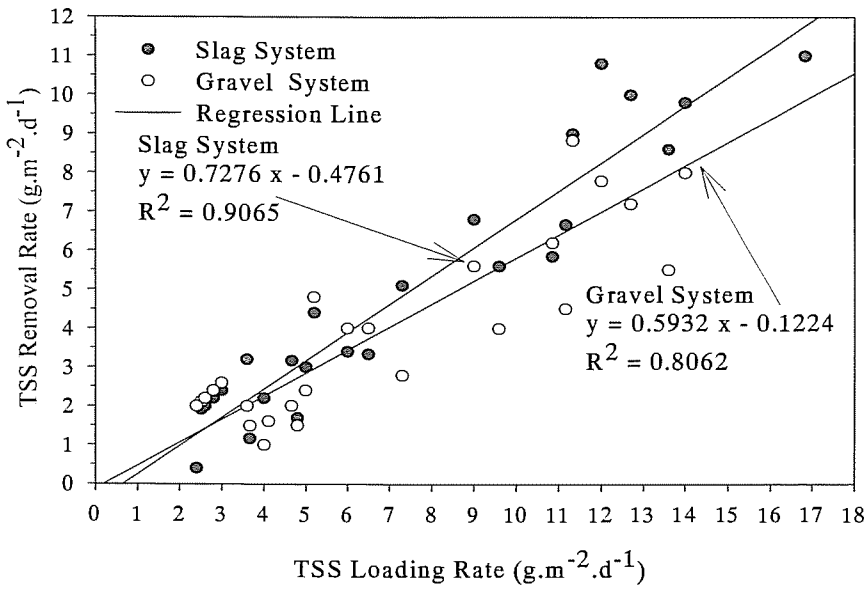

Figure 4.3. TSS loading rate ($g.m^{-2}.d^{-1}$) vs. removal rate ($g.m^{-2}.d^{-1}$) of the pilot-scale constructed wetlands implemented at METU

Table 4.6. TSS concentration values and removal efficiencies of the constructed wetlands implemented at METU

TSS	Influent ($mg.L^{-1}$)	Slag Out ($mg.L^{-1}$)	Gravel Out ($mg.L^{-1}$)	Slag System (RE%)	Gravel System (RE%)
Minimum	24.00	4.00	4.00	16.67	25.00
Maximum	168.30	58.34	81.00	90.00	92.31
Average	66.79	23.26	28.91	67.18	63.57
Median	49.00	22.00	25.51	69.93	61.89
St Dev.	42.77	15.59	21.80	19.42	21.68

Table 4.7. TSS influent and effluent concentrations of vertical flow constructed wetlands applied in other countries

Countries	TSS		
	Influent ($mg.L^{-1}$)	Effluent ($mg.L^{-1}$)	Removal Efficiency (%)
St Bohaire, France*	272	22	92
Oaklands, GB.*	169	20	88
Sobiechy, Poland*	98	24	76
Dhulikhel, Nepal*	159	2	99
Colecott, Ireland*	53	1	98
Austria**	121	10	92
Belgium**	60	15	75
France**	225	18	92

Reference: *O'Hogain (2002);**Vymazal et al., (1998).

The differences in the TSS removal efficiencies of the wetlands used in this study (Table 4.6) with other studies (Table 4.7) might have been due to the variations in the design criteria, operational and climate conditions, wetland configurations, the depth of the wetland bed, the type of the substrate and the plants used in wetlands. Lower TSS reductions could be related to the lower influent TSS values of the wetlands of METU.

Another possible reason for the lower percent TSS removal is the fact that the wetland systems of METU was operated for almost a year and therefore didn't reach the state of succession with less developed root system. A three-year old constructed wetland planted with emergent plants and having an extensive root system can enhance the TSS removal efficiency by providing a larger surface area, reducing the water velocity and reinforcing settling and filtration in the root network (Brix, 1997; Tanner, 2001). Hence, the observed TSS removal efficiencies of the slag and gravel systems could mostly be related to the processes of sedimentation, filtration, bacterial decomposition and adsorption to the wetland media (Stowell et al., 1981).

Moreover, both of the wetland cells didn't have a "filter cake" yet, which could improve filtration until clogging. Also, in METU, pre-settled domestic wastewater was used, where all of the easily settled TSS was removed before entering the wetlands. The remaining TSS was harder to remove, because of its smaller size. If the TSS removed during sedimentation was included into the TSS reduction, then percentage removal efficiency would be much higher. Thus, it could be misleading to compare the systems reporting the removal percentage efficiencies with and without pretreatment. However, it could be concluded that both the slag and gravel wetland systems showed acceptable TSS treatment performances throughout the monitoring period as they were in compliance with the Turkish Discharge Standards (1991).

4.7.2 Chemical Oxygen Demand (COD) Removal

The COD concentrations of the raw domestic wastewater pumped to the sedimentation tanks and of the primarily treated wastewater that was subsequently applied to the wetlands were presented in Tables 4.1 and 4.2, respectively (see Section 4.1). Even though the COD values of the raw domestic wastewater used in this study (280 $mg.L^{-1}$) were similar to that of the typical COD values reported by Metcalf and Eddy (1991), they were lower than that of the average COD values recorded in countries like Germany, France and Nepal (Table 4.3).

The inlet concentrations of both of the slag and gravel wetland systems varied between 85-446 $mg.L^{-1}$ (244 ± 108 $mg.L^{-1}$), during the monitoring study (Figure 4.4 a & b). The effluent COD concentrations of the slag and gravel systems varied between 28-257 $mg.L^{-1}$ (119.5 ± 63.66 $mg.L^{-1}$) and 11 to 290 $mg.L^{-1}$ (130.4 ± 67.4 $mg.L^{-1}$), respectively (Figure 4.4.a & b). The effluent concentrations were affected by the fluctuations of the influent COD concentrations, dilution of the wastewater by the rain water and seasonal changes.

As it was explained in Section 4.7.1 for TSS, the reason for the fluctuations in the COD influent values might have been the variations in the surface runoff (see Appendix B, Figure B.3 & B.4) and changes in the water consumption of the community. For example, the effect of precipitation on 18^{th} and 19^{th} of August, 2002 could be seen as a decrease in the influent COD value and also as a dilution effect in the effluent COD values of both of the constructed wetlands. With the start of the new semester, the students and other residences of the campus began to come back from their summer holidays. Therefore, an increase in the influent and effluent values was observed between the end of the August, 2002, and first two weeks of the October 2002. On 14^{th} October, 2002, due to the dilution caused by heavy rain, there was a sharp decrease in the influent COD values, and also coincided with the decrease of the ambient air temperature. It was observed that the COD influent values monitored in winter period were higher than that of the values of summer period.

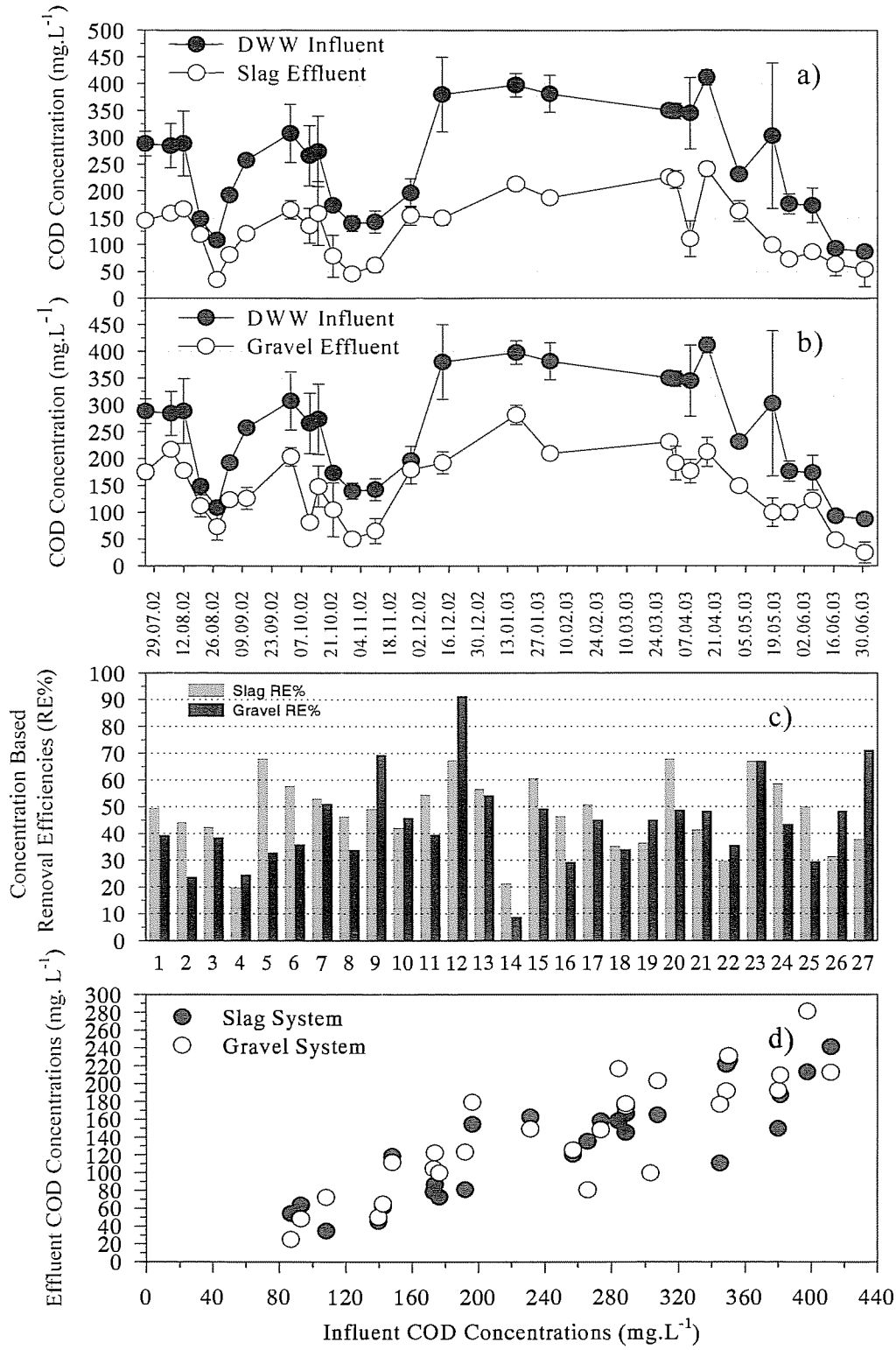

Figure 4.4. COD a & b) time vs. influent and effluent concentrations ($mg.L^{-1}$) c) removal efficiencies (RE%) d) influent vs. effluent concentrations ($mg.L^{-1}$) of the slag and gravel wetland systems of METU

Throughout the monitoring period, concentration based COD removal efficiencies of the slag system and gravel system varied between 20-68% (52.9 ± 20.4 %) and 8.8-71% (48.60 ± 22.2 %), respectively (Figure 4.4.c). Even though it was expected to have different COD removal performances for each of the wetland due to their different structures (chemical compositions of the fill media; pore volumes in each of the wetland cells; surface area of the substrates; oxygen transfer capacities, etc.), both of the wetlands did not significantly differ from each other statistically (One-way ANOVA; $F_{0.95}(1;90)=0.54$; $P>0.05$). This might have been due to the low organic content of the wastewater applied to the wetlands, which probably has not clogged the pores of the substrates with settled organics. It might have also been due to the sufficient oxygen diffusion into the wetland cells. It could be also stated that the COD removal in both of the wetlands were mainly due to the biological degradation and minor due to the plant uptake since one-year old wetlands of METU did not establish an extensive plant root network during the operation period. Throughout the monitoring period, the average effluent COD concentrations of both of the systems were around 125 $mg.L^{-1}$, which is the limit COD effluent discharge value stated in the Wastewater Treatment Plant Discharge Standards of Turkey (1991). It could be postulated that influent COD values of 240 and 217 $mg.L^{-1}$ for slag and gravel systems resulted in compliance with the Wastewater Treatment Plant Discharge Standards for COD, respectively (Figure 4.4.d).

For both systems, the influent and effluent COD concentration values, as well as the removal efficiencies are summarized in Table 4.8. The COD removal performance of some of the vertical subsurface flow constructed wetland systems applied in other countries for domestic wastewater treatment were presented in Table 4.9. It was obvious that the average influent COD concentration (244 ± 108 $mg.L^{-1}$) of this study was lower than all of the studies given in Table 4.9, except for Belgium (168 $mg.L^{-1}$). However, the average effluent COD values of this study were higher than that of the COD effluent values recorded in other studies given in Table 4.9.

Table 4.8. COD concentration values and removal efficiencies of the constructed wetlands implemented at METU

COD	Influent ($mg.L^{-1}$)	Slag Out ($mg.L^{-1}$)	Gravel Out ($mg.L^{-1}$)	Slag System (RE%)	Gravel System (RE%)
Minimum	87.00	34.50	25.00	19.93	8.83
Maximum	411.67	241.00	281.00	68.06	71.26
Average	250.69	131.01	143.31	52.93	48.60
Median	269.59	140.01	148.00	49.90	45.07
St Dev.	93.90	57.76	64.55	20.41	22.24

Table 4.9. COD influent and effluent concentrations of vertical flow constructed wetlands applied in other countries

Countries	COD		
	Influent ($mg.L^{-1}$)	Effluent ($mg.L^{-1}$)	Removal Efficiency (%)
St Bohaire, France*	748	112	85
Oaklands, GB.*	406	25	94
Sobiechy, Poland*	370	63	8
Dhulikhel, Nepal*	261	11	96
Colecott, Ireland*	462	55	88
Austria**	325	33	90
Belgium**	168	60	64
France**	495	92	81
Germany**	430	95	78

Reference: *O´Hogain (2002);**Vymazal et al., (1998).

This indicated a low biodegradable fraction in the COD as suggested by the low BOD values measured in the raw wastewater (see Section 4.1). If the wastewater has non-biodegradable or low-biodegradable pollutants more than the biodegradable pollutants, even though the conditions are suitable for microorganisms, the removal of COD would also be lower and be very difficult to bring the COD effluent values down to a value of 40-50 $mg.L^{-1}$ (IWA, 2000). It was also the case for the wetlands constructed at METU. Moreover, due to the higher amount of phosphorus because of detergents, the raw domestic wastewater of METU had low BOD values, which caused to a poor COD removal efficiency in both of the constructed wetlands implemented at METU.

The COD loading rates for both of the systems varied between 8.5-44.6 $g.m^{-2}.d^{-1}$ (24.41 ± 10.80 $g.m^{-2}.d^{-1}$) during the monitoring period (Figure 4.5). The effluent COD concentrations were largely dependent on the influent COD concentrations for both systems. Similar to the TSS case, the total surface area of the vegetated vertical subsurface flow wetlands was significant in terms of the COD removal. However, there is less information on the COD loading of the constructed wetlands in the literature (Vymazal, 2002). To have effluent COD concentration values below 125 $mg.L^{-1}$, slag and gravel systems using this wastewater could be loaded up to a rate of 24 and 22 $g.m^{-2}.d^{-1}$.

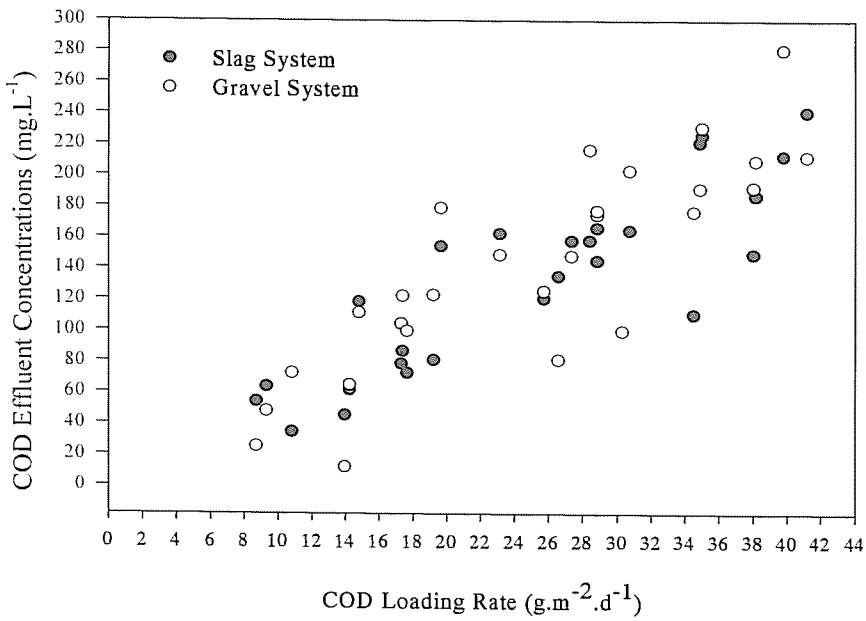

Figure 4.5. COD Loading Rate vs. Effluent Concentrations of the Pilot-Scale Constructed Wetlands of METU

The correlation between inflow loading rate and outflow removal rate for the slag system (Figure 4.6) indicated that the COD removal rate was slightly more dependent on the COD loading rate for the slag system (R^2=0.714) as compared to that of gravel system (R^2=0.626). This slight difference between the systems could be related to the differences of the biofilm dominating within the gravel and slag

substrates. In the slag system, it has been thought that the thickness of the biofilm was thinner on the granulated slag particles so that the pollutants responsible for COD were more available to the microorganisms due to better transport mechanisms. The larger surface area of the slag system might have increased wastewater retention time in the matrix as well as providing more active microorganisms as compared to gravel system. Thus, whenever there was a sharp increase in the COD applied to the slag system, due to the combination of slower hydraulic conductivity and increased microorganism biofilm contact, the slag system showed a slightly better capability of handling loads and removing the COD efficiently. The biofilm in the gravel system was probably thicker because of the bigger sizes of the larger pore size and smaller overall surface area, which might have resulted in difficulties of the transport of the COD to the microorganisms.

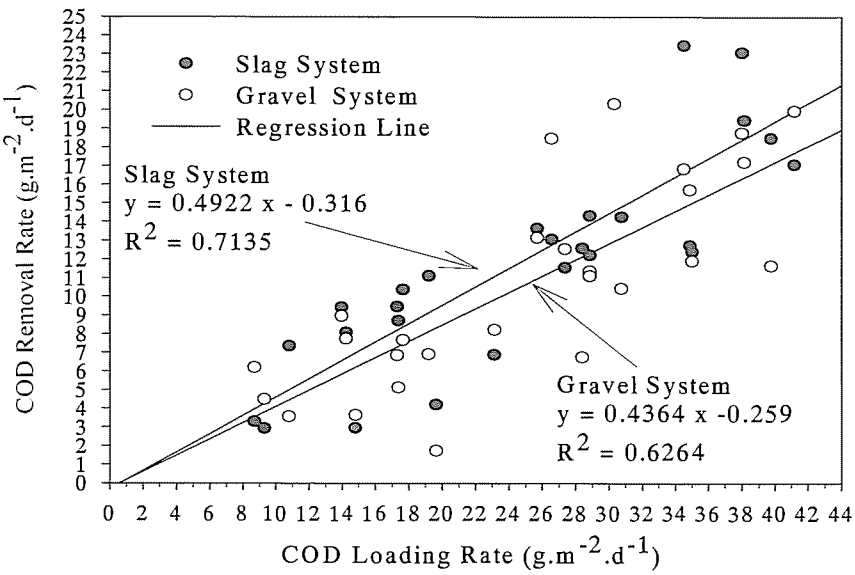

Figure 4.6. COD loading rate ($g.m^{-2}.d^{-1}$) vs. removal rate ($g.m^{-2}.d^{-1}$) of the pilot-scale constructed wetlands implemented at METU

4.7.3. Phosphorus (PO_4^{3-}-P and TP) Removal

The influent PO_4^{3-}-P concentrations of both of the vertical subsurface flow constructed wetlands implemented at METU varied between 2.10 and 8.05 $mg.L^{-1}$ (4.71 ± 1.54 $mg.L^{-1}$) (Figure 4.7. a & b). Even though the influent PO_4^{3-}-P concentrations were almost constant around 4-5 $mg.L^{-1}$ during July and August, 2002, some steep increases were observed in the influent PO_4^{3-}-P concentration values in October, February and April (Figure 4.7 a & b). Some of these jumps in influent PO_4^{3-}-P values were observed after rainy days (see Appendix B Figures B.3 & B.4). Those increases could be related to additional PO_4^{3-}-P originating from dust particles and also from fertilizers leachates applied to the gardens of ODTÜKENT, which may have been washed out with the surface runoff to the sewer system. For example, the comparably bigger peak seen on 9th September, 2002 coincided with the rainy period, which has lasted till 17th September, 2002. Moreover, during the same time, fall semester at METU started and thus the sewer system received larger loads of PO_4^{3-}-P to due to the heavy use of detergents for cleaning purposes and sanitary wastes.

The second significant jump in the influent PO_4^{3-}-P concentrations on 14th October, 2002 again coincided with precipitation, which was one of the heavier rains encountered during the whole monitoring period. Moreover, in February and April 2003, there were again significant increases in the influent PO_4^{3-}-P concentrations, both of which again coincided with heavier precipitation (see Appendix B Figures B.3 & B.4). The PO_4^{3-}-P influent concentrations of fall and winter time were higher than that of the spring concentrations. During the monitoring period, the PO_4^{3-}-P effluent concentrations of the slag and gravel system varied between 0.34-4.50 $mg.L^{-1}$ (2.36±1.25 $mg.L^{-1}$) and 2.32-7.20 $mg.L^{-1}$ (4.54±1.18 $mg.L^{-1}$), respectively (Figure 4.7. a & b).

As expected from theory, there was a good relationship between the PO_4^{3-}-P and TP concentration values of the wetlands constructed at METU. Since TP included all forms of phosphorus, TP concentrations were always bigger than PO_4^{3-}-P

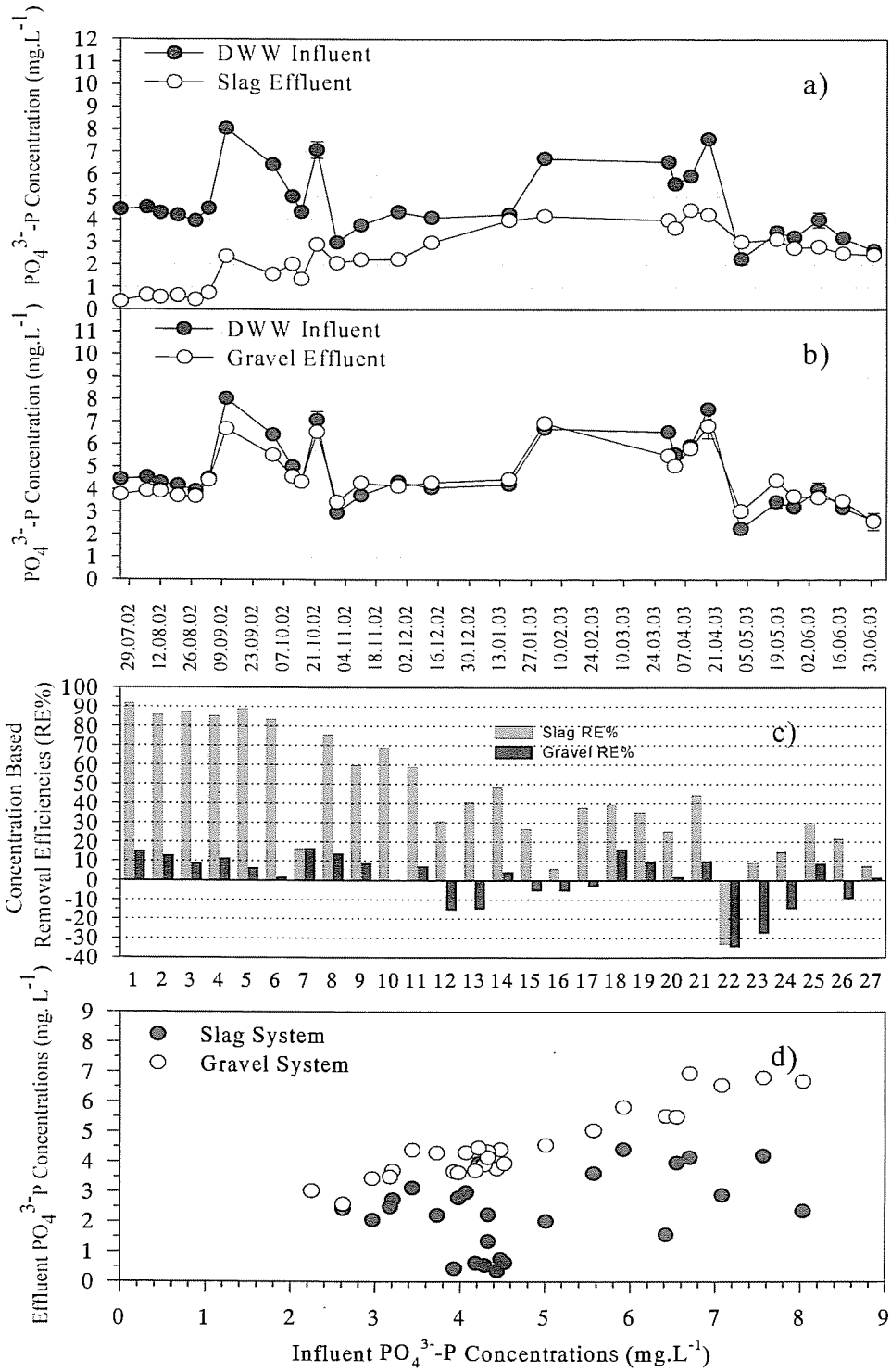

Figure 4.7. PO_4^{3-}-P a & b) time vs. influent and effluent concentrations ($mg.L^{-1}$) c) removal efficiencies (RE%) d) influent vs. effluent concentrations ($mg.L^{-1}$) of the slag and gravel wetland systems of METU

concentrations. The TP influent concentrations varied between 3.39-9.72 $mg.L^{-1}$ (6.45 ±1.80 $mg.L^{-1}$) reflecting the changes in seasons, water and detergent usage habits. The effluent P-concentrations of both of the systems (Figure 4.7. a & b and Figure 4.8. a & b) were almost constant and very low at the beginning of the operation period (independent of the influent concentrations). During the monitoring period, the TP effluent concentrations of the slag and gravel system varied between 0.26-3.34 $mg.L^{-1}$ (1.80 ± 0.96 $mg.L^{-1}$) and 3.79-7.47 $mg.L^{-1}$ (6.04 ± 1.04 $mg.L^{-1}$), respectively, (Figure 4.8. a & b). The TP effluent concentrations behaved in a similar fashion to that of the TP influent concentrations. However, TP effluent concentrations rose with the increase in P-loading rates and operation time.

Throughout the monitoring period, the PO_4^{3-}-P removal efficiencies of the slag system and gravel system ranged from -42.86% to 89.03% (44.31% ± 31%) and from -50.11 to 40.40 % (4.33 ± 16.58 %), respectively (Figure 4.7.c). The TP removal efficiencies of the slag system and gravel system ranged from -35.20% to 85.73% (44.85% ± 28.35 %) and from -50.11 to 40.40 % (4.33 ± 16.58 %), respectively (Figure 4.8.c). Slag and gravel systems differed significantly from each other in terms of P-removal (for PO_4^{3-}-P and TP, 1-way ANOVA results were $F_{0.95}(1;100)=77.05$; $P<0.001$ and $F_{0.95}(1;100)= 84.6$; $P<0.0001$, respectively).

The negative removal efficiencies corresponded to the apparent phosphate release in both of the wetland systems, even though the difference between influent and effluent P-concentrations was only about 1.0 $mg.L^{-1}$. The negative P-removal efficiencies of constructed wetlands could be explained in several ways. The increase in effluent P-concentrations of both systems after rain could be related to a combination of dilution and flushing effect on the wetland beds. In such cases, already adsorbed-P might have been washed down with the rainwater to the outlet pipes. The P-derivatives that was adsorbed in the matrix would only be "flushed out" when the P-concentration in the bulk solution were low, causing an equilibrium shift and desorption. So, the rainwater could have diluted the bulk solution of the wetland cells and resulted in desorption. Moreover, some of the P-releases coincided with the decrease of the ambient air temperature. As the air

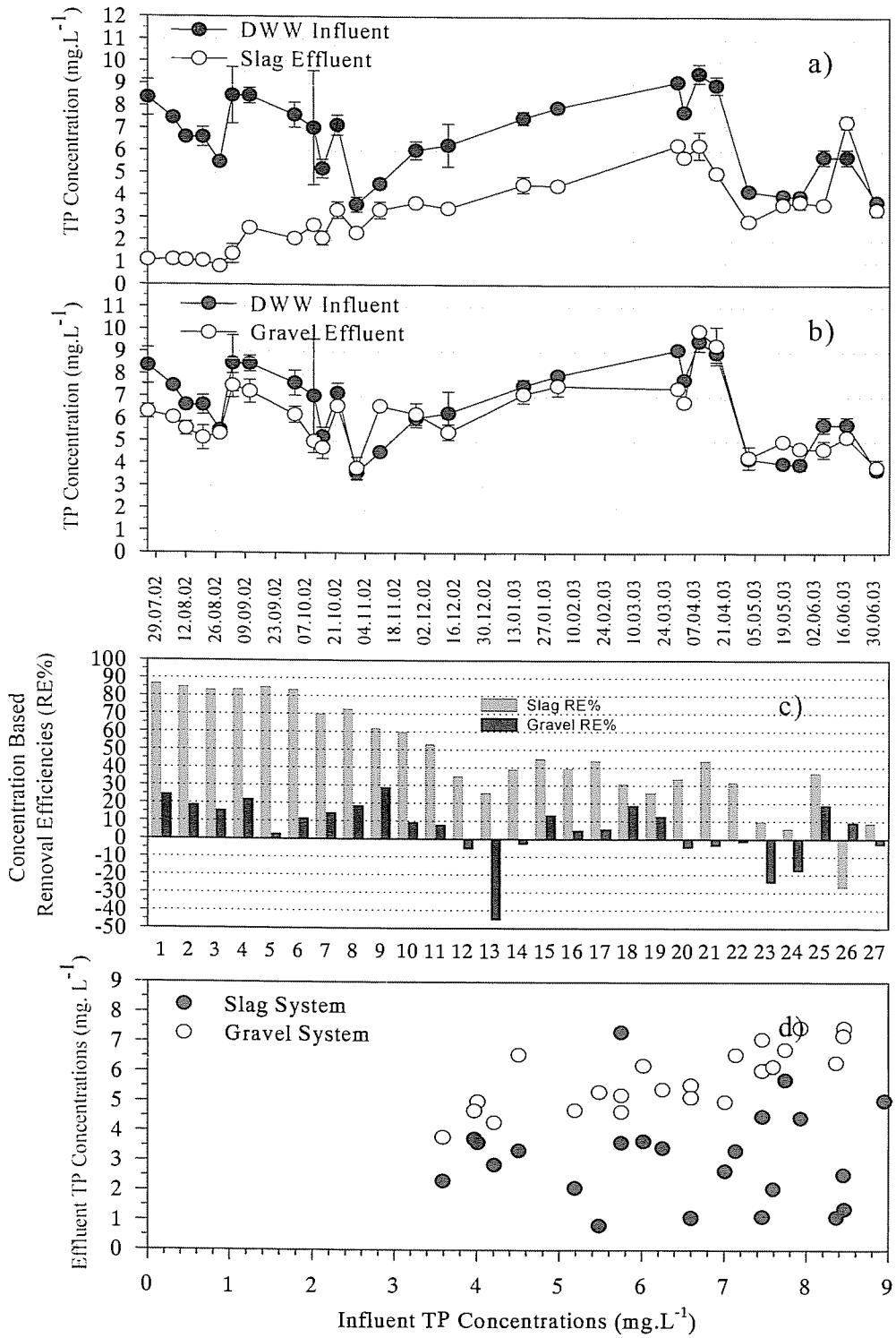

Figure 4.8. TP a & b) time vs. influent and effluent concentrations ($mg.L^{-1}$) c) removal efficiencies (RE%) d) influent vs. effluent concentrations ($mg.L^{-1}$) of the slag and gravel wetland systems of METU

temperature decreased and the fall season proceeded, the above sections of the reed plants were no longer green and the plants were storing carbon in their root section during the fall and winter. With the mineralization of the dead leaves, a portion of the P taken by the plants was supposed to return to the wetland substrate and to appear as an increase in the effluent P-concentrations (Vymazal et al., 1998; IWA, 2000), which resulted in negative P-removal efficiencies for both of the systems.

It is also well known that the emergent plants can change the pH values of the fill mediums by proton release during nutrition, exudation of organic acids and production of carbohydrates, CO_2 release by roots (Olsen et al., 1981). In vertical flow wetlands older than one year, effluent P-concentrations can also increase with the change of the oxidation-reduction behavior and reverse adsorption-precipitation mechanisms (Lantzke et al., 1999). Since the affinity of the fill medium for P depends on its contents and the pH of the environment (Naylor et al., 2003), the change in the pH values might have affected the P-retention capacities of the wetlands implemented at METU, negatively. Therefore, another explanation for the P-releases could be the decrease in the pH values of the wetlands constructed at METU, as the time proceeded (Appendix A, Figure A.12).

The constant effluent P-concentrations of the slag system at the beginning might be explained mainly by the higher adsorption capacity, where the slag substrate was fresh and the adsorption sites were free of P. Since the slag had higher calcium content (around 34%, see Table 4.4) and throughout the monitoring period the pH of the slag system ranged from 7.11 to 8.56 (7.67 ± 0.37) (Appendix A, Table A.1), it could be claimed that insoluble calcium-P compounds have precipitated and slowly converted to apatite (Sovik and Klove, 2002). In acid soils, P is mainly sorbed to Fe- and Al-oxide minerals. Even though slag had in its composition 12.47% of Al_2O_3 and 0.64% of Fe (Table 4.4), since the pH of the slag system did not fall below 7.11, it has been believed that the Al-P and Fe-P oxides were the least available form (Vymazal et al., 1998). Hence, the increase in the effluent P-concentrations of the slag system could also be related to a possible decrease in the free calcium ion concentrations.

The increase in the effluent P-concentrations of the slag system might also be explained by the saturation of the adsorption sites in time, as Kadlec (1985) stated. Additionally, the carbon chain of the detergents might have covered the adsorption sites so that the available adsorption sites could not be accessed by the P anymore in the slag system. The slag system with its smaller particle size could remove suspended solids efficiently. As the removed suspended solids included also organic-P, it was expected to have smaller difference in the effluent PO_4^{3-}-P and TP concentrations for both of the systems, as TP is the summation of the organic-P and PO_4^{3-}-P. However, the large difference between the effluent TP and PO_4^{3-}-P values indicated that the organic P-fraction was not only associated with suspended solids. This suggested that a significant fraction of the organic-P is in the domestic wastewater was residual organic detergents with phosphate groups attached to an alkyl carbon chain, which might be mainly removed by adsorption mechanism in the slag bed. As the time passed, the available adsorption sites of the slag medium might be covered with the carbon chain of the organic detergents, which entered the wetlands via the wastewater.

In the slag system, the dominant P removal mechanisms were believed to be adsorption and precipitation due to the physico-chemical characteristics of the slag. However, in the gravel system, the P removal mechanisms were thought to be mainly filtration, biological assimilation, plant uptake and partly the adsorption of P to the sand particles within the gravel system. Even though the top layer of the gravel bed covered with sand, the gravel system could not be described as a wetland cell with noticeable P-adsorption capacity, as the monitoring results implied.

For both of the wetlands of METU, the PO_4^{3-}-P and TP influent and effluent concentrations, as well as the removal efficiencies were summarized in Table 4.10 and 4.11, respectively. The literature values for PO_4^{3-}-P and TP were also presented in Table 4.12 and 4.13, respectively. The average PO_4^{3-}-P reductions of the slag system displayed higher efficiencies than those studies presented in Table 4.12,

whereas the average PO_4^{3-}-P reductions of the gravel system closely agreed with those studies. The slag system had lower effluent TP values than that of the vertical subsurface constructed wetlands in Belgium (Cadelli et al., 1998); in Austria (Haberl et al., 1998); in Germany (Börner et al., 1998) and in France (Lienard et al., 1998). Those studies were supposed to include the constructed wetland systems filled with gravel substrate, not with slag substrate. Moreover, the operational conditions differed. The slag system could reduce P better than that of those studies presented in Table 4.12 and 4.13.

Table 4.10. PO_4^{3-}-P concentration values and removal efficiencies of the constructed wetlands implemented at METU

PO_4^{3-}-P	Influent ($mg.L^{-1}$)	Slag Out ($mg.L^{-1}$)	Gravel Out ($mg.L^{-1}$)	Slag System (RE%)	Gravel System (RE%)
Minimum	2.25	0.03	2.58	-33.33	-34.67
Maximum	8.03	4.41	6.93	91.92	16.69
Average	4.59	2.28	4.54	44.11	0.91
Median	4.33	2.39	4.30	39.54	4.39
St Dev.	1.47	1.31	1.18	31.97	13.35

Table 4.11. TP concentration values and removal efficiencies of the constructed wetlands implemented at METU

TP	Influent ($mg.L^{-1}$)	Slag Out ($mg.L^{-1}$)	Gravel Out ($mg.L^{-1}$)	Slag System (RE%)	Gravel System (RE%)
Minimum	3.59	0.26	3.79	-27.30	-45.45
Maximum	9.47	7.32	9.94	86.78	28.96
Average	6.61	3.18	6.03	46.56	5.61
Median	6.81	3.34	6.04	43.91	9.44
St Dev.	1.78	1.82	1.50	29.10	16.27

Table 4.12. PO_4^{3-}-P influent and effluent concentrations of the vertical flow constructed wetlands applied in other countries

Countries	PO_4^{3-}-P		
	Influent ($mg.L^{-1}$)	Effluent ($mg.L^{-1}$)	Removal Efficiency (%)
France	6.4	5.3	17.2
Germany	11.4	3.8	66.7

Reference: Vymazal et al., (1998).

Table 4.13. TP influent and effluent concentrations of the vertical flow constructed wetlands applied in other countries

Countries	TP		
	Influent ($mg.L^{-1}$)	Effluent ($mg.L^{-1}$)	Removal Efficiency (%)
Austria	10.7	4	62.6
Belgium	4.6	3.5	23.9
France	8.5	5.8	31.8
Germany	15.9	4.8	69.8

Reference: Vymazal et al., (1998).

For the conventional treatment systems, there is no discharge standard value for orthophosphate in Turkish Regulations. The allowable discharge limit for TP is 2 $mg.L^{-1}$ according to the Wastewater Treatment Plant Discharge Standards of Turkey (1991). Even though it is very difficult to reduce the TP effluent concentrations below 8 $mg.L^{-1}$ after the secondary units of the conventional treatment systems (Lee and Lin, 1999), the slag wetland system used as a secondary treatment stage at METU had a very promising TP removal performance.

To understand the relation of effluent PO_4^{3-}-P concentrations to influent PO_4^{3-}-P concentrations, the data were plotted in Figure 4.7.c, whereas the effluent TP concentrations were plotted against influent TP concentrations in Figure 4.8.c. As the trends were compared to each other (see Figure 4.7.c and Figure 4.8.c), it might be postulated that both system had different phosphorus uptake mechanisms due to their different physico-chemical characteristics and differences in the adsorption capacities. Even though the slag system had a better PO_4^{3-}-P and TP removal performance than that of the gravel system, there wasn't a linear correlation between the influent and effluent PO_4^{3-}-P and TP concentrations for the slag system (Figure 4.9). This might be due to the decreasing slag performance in phosphate removal as the time proceeded and adsorption sites were being taken up.

Brix (1998) examined the TP removal performances of 90 Danish constructed reed beds. He has calculated the median values of 7.4 and 4.8 $mg.L^{-1}$ for influent and effluent TP concentrations, respectively. Similar to that of the gravel system in this study, the effluent TP concentrations were linearly related to the influent TP concentrations in the Danish study.

During the monitoring period, the PO_4^{3-}-P and TP loading rates for both of the systems varied between 0.21-0.80 $g.m^{-2}.d^{-1}$ (0.47 ± 0.15 $g.m^{-2}.d^{-1}$) and 0.34-0.97 $g.m^{-2}.d^{-1}$ (0.65 ± 0.18 $g.m^{-2}.d^{-1}$), respectively (Figure 4.9 and Figure 4.10). For the gravel system, the effluent PO_4^{3-}-P concentrations were linearly dependent on the PO_4^{3-}-P loading rates. However, for the slag system, there was not a linear correlation between the PO_4^{3-}-P loading rates and the effluent values, due to the variable P-removal performance of the slag system. Similarly, the effluent TP concentrations were linearly dependent on the TP loading rate for the gravel system. However, for the slag system, there was not a linear correlation between the loading rate and the effluent values, as explained above.

The slag system could remove PO_4^{3-}-P efficiently even as the loading rates increased (Figure 4.11) as the batch-scale adsorption experiments indicated (as the P concentration increased, the adsorption capacity increased, see Figure B.1). The linear correlation between PO_4^{3-}-P loading rate and PO_4^{3-}-P removal rate for gravel system (R^2=0.521) was better than that of the slag system (R^2=0.350). Similarly, the slag system could remove TP more efficiently than the gravel system, as the loading rates increased (Figure 4.12). However, the linear correlation of the TP loading rate and TP removal rate for gravel system (R^2=0.412) was stronger as compared to that of slag system (R^2=0.108).

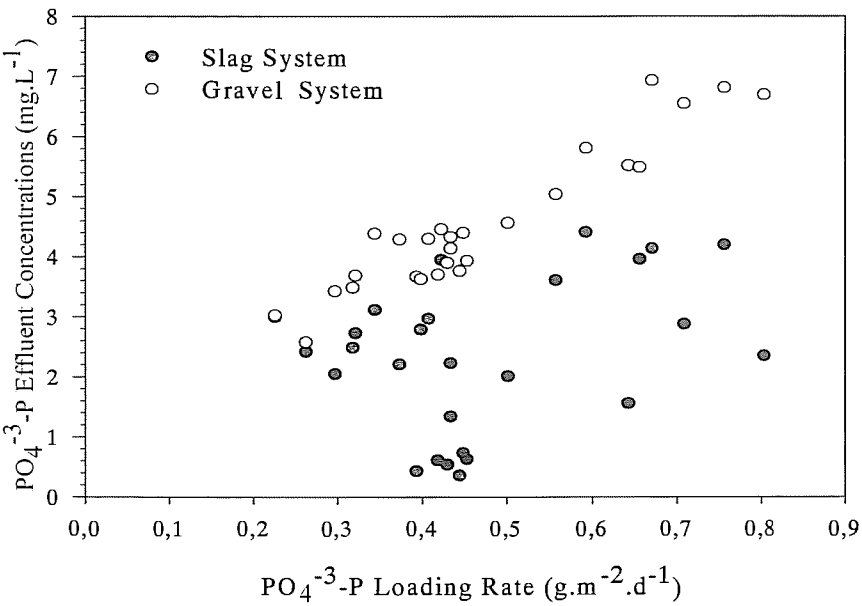

Figure 4.9. PO_4^{3-}-P loading rate ($g.m^{-2}.d^{-1}$) vs. effluent concentrations ($mg.L^{-1}$) of the pilot-scale constructed wetlands implemented at METU

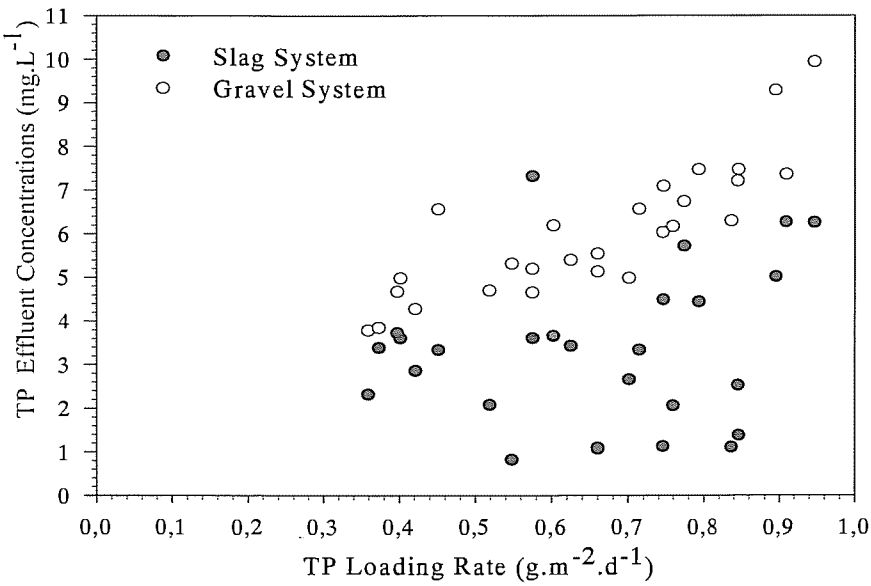

Figure 4.10. PO_4^{3-}-P loading rate ($g.m^{-2}.d^{-1}$) vs. effluent concentrations ($mg.L^{-1}$) of the pilot-scale constructed wetlands implemented at METU

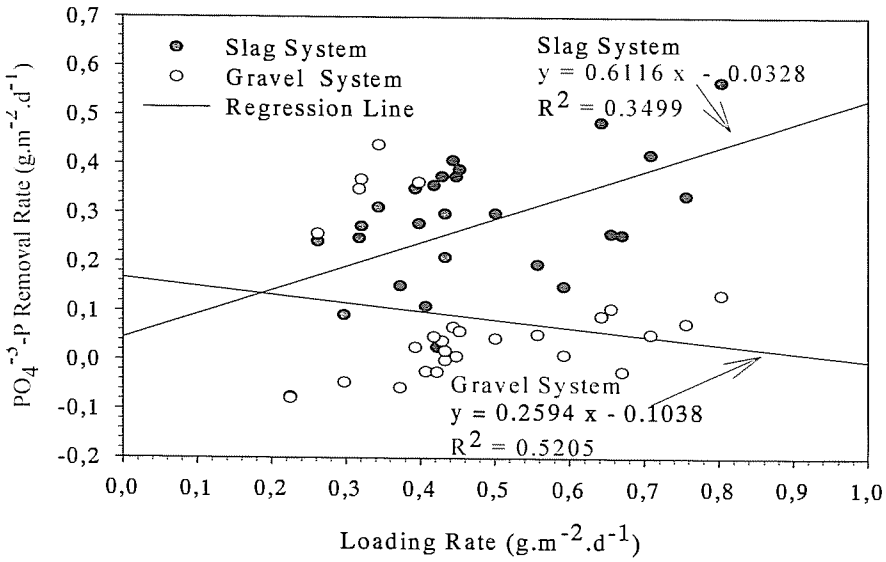

Figure 4.11. PO_4^{3-}-P loading rate ($g.m^{-2}.d^{-1}$) vs. removal rate ($g.m^{-2}.d^{-1}$) of the pilot-scale constructed wetlands implemented at METU

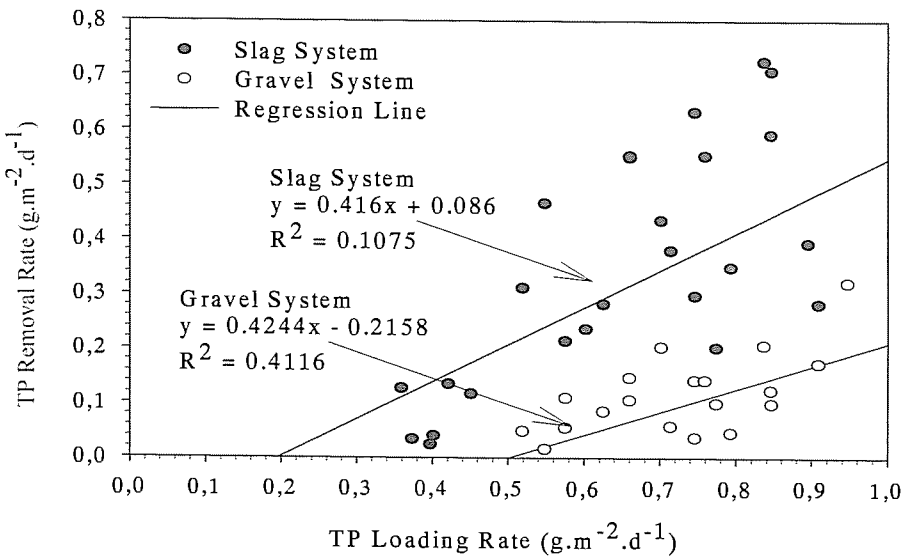

Figure 4.12. TP loading rate ($g.m^{-2}.d^{-1}$) vs. removal rate ($g.m^{-2}.d^{-1}$) of the pilot-scale constructed wetlands implemented at METU

4.7.4 Ammonium-Nitrogen (NH_4^+-N) Removal

The prevailing form of nitrogen in the wastewaters is ammonium due to the anaerobic nature of the wastewater. Ammonia is soluble and is largely produced by deamination of the organic nitrogen-containing compounds and by hydrolysis of excreted urea. At some water treatment plants ammonia is added in low concentrations (few $mg.L^{-1}$) to react with chlorine to form a combined chlorine residual (AWWA, 1999). Ammonium in the soil is either used by the plants or converted to nitrate by nitrifying bacteria. Mainly, NH_4^+-N is oxidized to nitrate by biological the nitrification only after most of the organic carbon has been removed from the wastewater (see Section 2.10.4 for detailed information).

The average NH_4^+-N concentration value of the raw domestic wastewater produced at METU (23.86 ± 6.17 $mg.L^{-1}$) was lower than that of the average NH_4^+-N concentration values of other studies (Table 4.3). The lower NH_4^+-N concentrations was due to the low strength of the wastewater produced at METU. During the monitoring period, the influent NH_4^+-N concentrations of both slag and gravel systems varied between 15.05-48.82 $mg.L^{-1}$ (26.37 ± 8.52 $mg.L^{-1}$); whereas the NH_4^+-N effluent concentrations varied between 0-21.2 $mg.L^{-1}$ (3.73 ± 4.39 $mg.L^{-1}$) and 3.2-22.8 $mg.L^{-1}$ (12 ± 5.15 $mg.L^{-1}$), respectively (Figure 4.13. a & b).

Concentration based NH_4^+-N removal efficiencies of the slag and gravel systems varied between 54%-100% (87.3% ± 12.4 %) and 26%-89.5 % (55.9 ± 15.1 %), respectively (Figure 4.13.c). Even though the NH_4^+-N removal performance of the slag system was statistically better than that of gravel system (1-way ANOVA; $F_{0.95}(1;100)=173.85$; $P<0.0001$), both of the systems (Table 4.14) indicated better nitrification as compared to other vertical flow wetland systems in other countries (Table 4.15). The slag system (from 27 ± 8.3 $mg.L^{-1}$ to 3.2 ± 3.2 $mg.L^{-1}$) displayed higher removals than that of the studies cited by Vymazal et al. (1998) and O'Hogain (2002); whereas the gravel system (from 27 ± 8.3 $mg.L^{-1}$ to 12 ± 5.5 $mg.L^{-1}$) displayed higher removals than that of recorded by Lienard et al., (1998) in France (25 $mg.L^{-1}$ to 18 $mg.L^{-1}$).

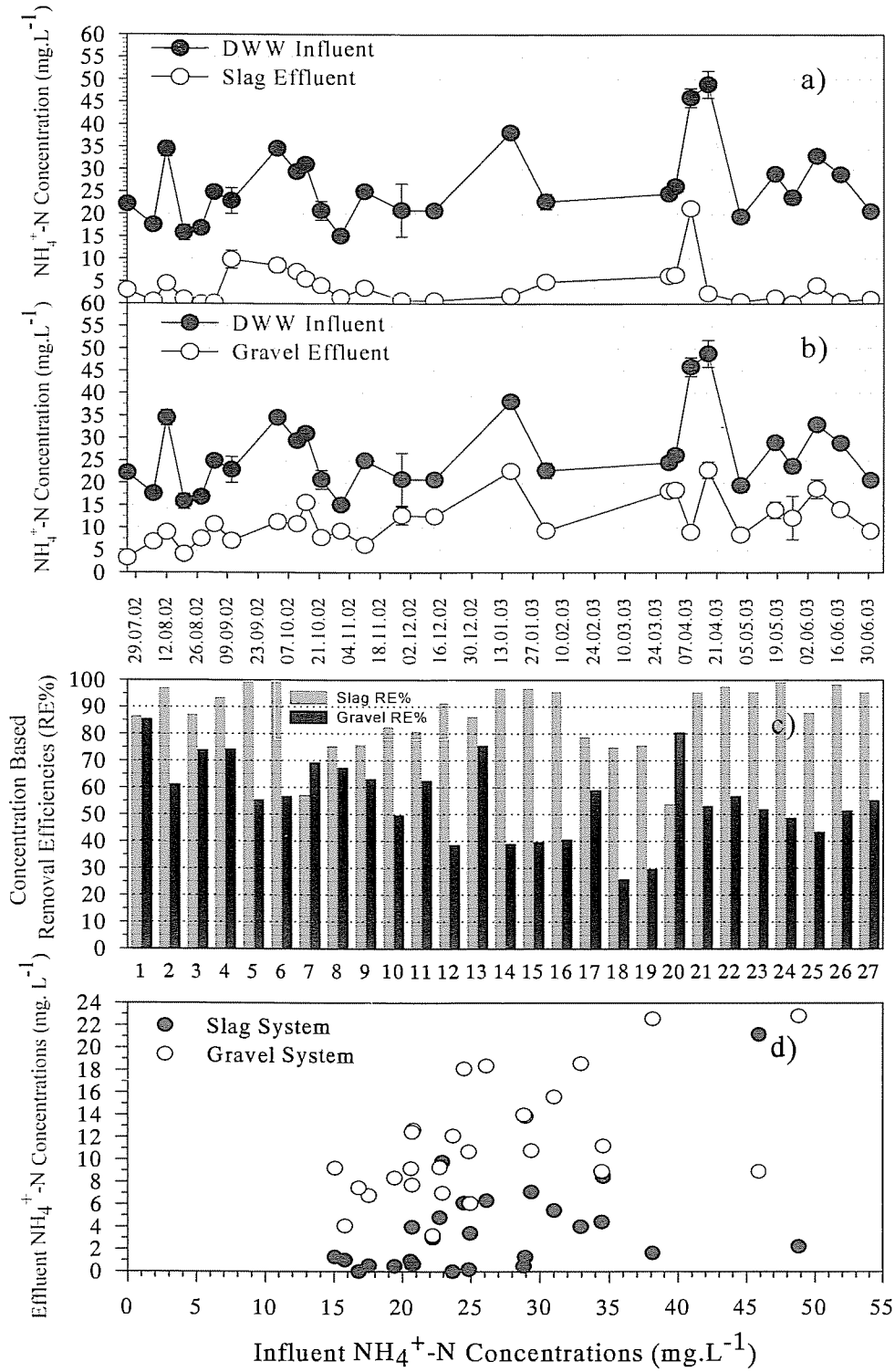

Figure 4.13. NH_4^+-N a & b) time vs. influent and effluent concentrations ($mg.L^{-1}$) c) removal efficiencies (RE%) d) influent vs. effluent concentrations ($mg.L^{-1}$) of the slag and gravel wetland systems of METU

Table 4.14. NH_4^+-N concentration values and removal efficiencies of the constructed wetlands implemented at METU

NH_4^+-N	Influent ($mg.L^{-1}$)	Slag Out ($mg.L^{-1}$)	Gravel Out ($mg.L^{-1}$)	Slag System (RE%)	Gravel System (RE%)
Minimum	15.05	0.01	3.22	53.84	25.95
Maximum	48.82	21.18	22.82	100.00	85.49
Average	26.37	3.73	11.49	87.25	55.93
Median	24.47	2.61	10.71	91.43	55.48
St Dev.	8.52	4.39	5.15	12.44	15.09

Table 4.15. NH_4^+-N influent and effluent concentrations of vertical constructed wetlands applied in other countries

Countries	NH_4^+-N		
	Influent ($mg.L^{-1}$)	Effluent ($mg.L^{-1}$)	Removal Efficiency (%)
St Bohaire. France*	44	27.72	37.0
Oaklands. GB.*	51	8.16	84.0
Sobiechy. Poland*	46	6.44	86.0
Dhulikhel. Nepal*	32	0.32	99.0
Colecott. Ireland*	45	14.85	67.0
Austria**	72	4.50	93.7
France**	25	18.0	28.0
Germany**	81	29.0	64.0

Reference: *O´Hogain (2002);**Vymazal et al., (1998).

The variation in the influent NH_4^+-N concentrations was related to the rain events and change in sewage characteristics due to varying population size on the campus and the flowrate. Almost most of the peaks in influent NH_4^+-N values were observed after the rainy days (see Appendix B, Figure B.3. & Figure B.4). Those increases could also have originated from the leachates of organic fertilizers applied to the gardens of ODTÜKENT, which might be washed out with surface runoff to the sewer system. In September 2002, with the start of the new semester at METU, there was a heavier load of NH_4^+-N to the sewer system due the increase in the wastewater production through the increase in showers, kitchen wastes, etc. (Figure 4.13. a & b). Afterwards, a steady decrease was observed in the influent NH_4^+-N values beginning on 14th October, 2002, which coincided with the heaviest rain of the monitoring period with a precipitation value of ~14 mm (see Appendix B, Figure B.3 & B.4). Thus, the dilution effect of this rain was pronounced in the influent NH_4^+-N concentration values.

The effluent NH_4^+-N concentrations of both of the slag and gravel wetland systems corresponded to the changes in the influent NH_4^+-N values (Figure 4.13. a & b). Even though there wasn't a good linear relationship between the influent and effluent NH_4^+-N values for both of the systems, from the linear regression equations it could be clearly stated that the slag system showed better NH_4^+-N treatment performance than that of gravel system, which was due to the differences of the nitrification abilities of the two systems (Figure 4.13.d).

Throughout the monitoring period, peak effluent NH_4^+-N concentration values were observed in both of the systems (Figure 4.13. a & b). This was probably the new establishment of the nitrifying population, where there might not have been enough bacteria to use up of all the ammonium. This could be also due to the increase in TN concentrations, which resulted in a lower nitrification capacity of the wetland beds.

During the fall and winter period, when the air temperature decreased, it was expected to observe some increases in the effluent NH_4^+-N concentrations due the mineralization of the organic-N of the above ground biomass of the reed plants as mentioned by Reed et al. (1995) and (Yang et al., 2001). Moreover, with lower air and water temperatures, the reduction in nitrification was expected which would lead to a decrease in NH_4^+-N removal performances. However, there wasn't significant decrease in NH_4^+-N removal performances of both of the wetlands of METU even the air temperature decreased. Since both gravel and slag were not cationic exchangers (Vymazal et al., 1998) and their surface area was relatively small compared with soil, it was plausible to believe that NH_4^+-N were not adsorbed in great quantities in both of the wetland matrix. Thus, the flushing effect of the rain was believed to be minimal.

The higher nitrification capacities of the intermittently operated wetland systems constructed at METU compared to other vertical flow wetland systems (Table 4.15) could be attributed to the enhanced oxygen transfer from the atmosphere to the wetland substrates (Brix, 1997). The higher nitrification capacities of the slag and

gravel systems might have also been attributed to the lower strength and biodegradability of the domestic wastewater treated in the wetlands (Table 4.3), which allowed the use of the available oxygen in the wetland cells for nitrification instead of carbon removal. In addition, the higher surface area of the slag granules as compared to the gravel probably might have enhanced more oxygen transfer to the slag granules covered with a larger biofilm.

The problem with smaller sized media is that they get easily clogged from heterotrophic bacteria degrading carbon (IWA, 2000). However, due to the low COD and TSS concentration of the wastewater, the smaller slag media did not clog from the heterotrophic bacteria and could do show off its real potential in nutrient removal. In both of the systems, vegetation might have slightly increased nitrification through the oxygenation of the substrate through the Root Zone Effect (Yang et al., 2001). Moreover, establishment of a healthy root system was also supposed to facilitate a rich and productive community of attached microorganisms by providing higher surface area (see for detailed information Section 2.4.10.3).

Throughout the monitoring period, the NH_4^+-N loading rates for both of the systems (Figure 4.14) changed between 1.46-4.77 $g.m^{-2}.d^{-1}$ (2.63 ± 0.83 $g.m^{-2}.d^{-1}$). The effluent NH_4^+-N concentrations were not linearly dependent on the NH_4^+-N loading rates for both of the slag and gravel systems. However, the slag system could remove NH_4^+-N efficiently even the loading rates have increased (Figure 4.15). There was a linear correlation between loading rate and removal rate for both wetland systems (for slag system $R^2 = 0.726$; for gravel system $R^2 = 0.635$). So, it could be concluded that the surface area of the wetland cells and the filter media played an important role in the removal of NH_4^+-N from wastewater fed to the slag and gravel systems.

Even though no standard exists for NH_4^+-N discharge in the Turkish Regulations, it is very well known that ammonia exerts a significant amount of oxygen demand through biological nitrification in the receiving waters, which can enhance the eutrophication. Moreover, unionized ammonia can be toxic to aquatic organisms

(Lee and Lin, 1999). Therefore, it is necessary to reduce the effluent NH_4^+-N values of treated waters to permissible levels from an environmental point of view. As the results indicated, well designed and operated constructed wetlands can be therefore a promising solution for the removal of ammonium.

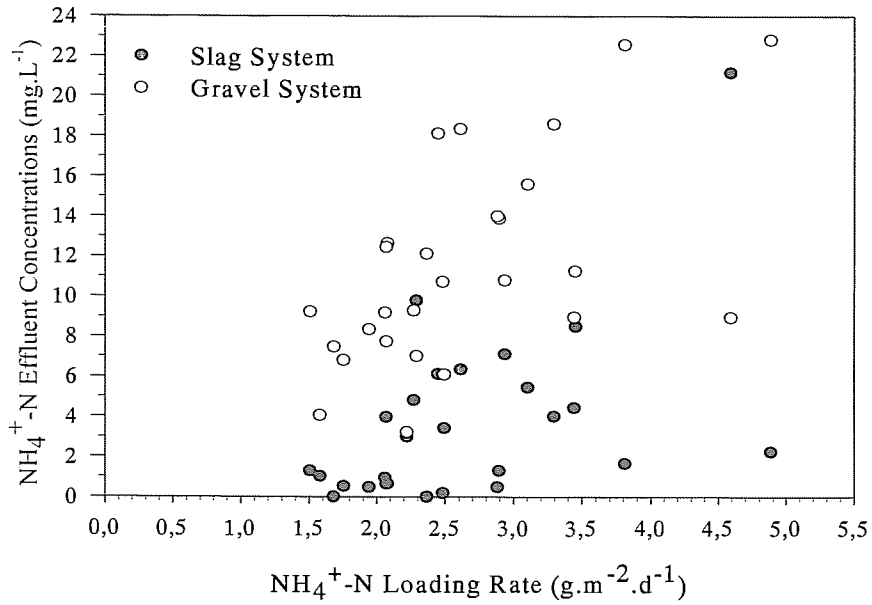

Figure 4.14. NH_4^+-N loading rate (g.m^{-2}.d^{-1}) vs. effluent concentrations (mg.L^{-1}) of the pilot-scale constructed wetlands implemented at METU

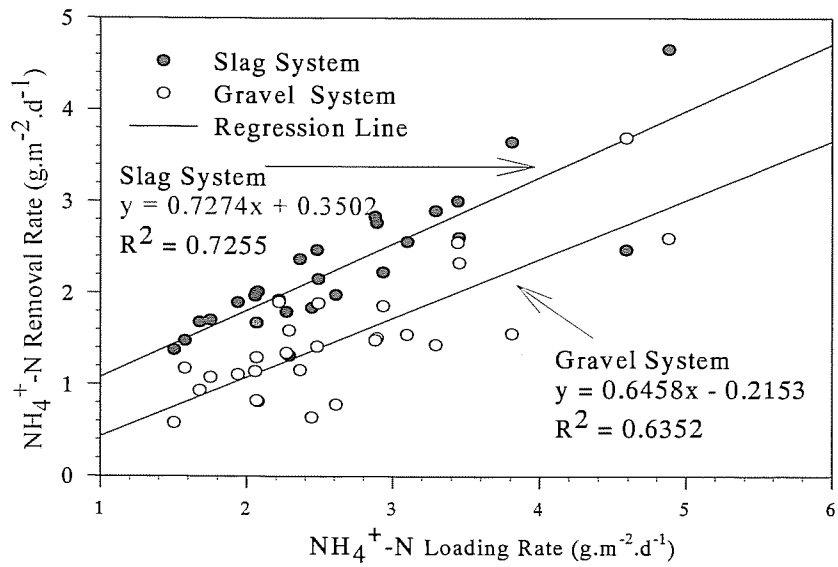

Figure 4.15. NH_4^+-N loading rate (g.m^{-2}.d^{-1}) vs. effluent concentrations (mg.L^{-1}) of the pilot-scale constructed wetlands implemented at METU

4.7.5. Nitrate Nitrogen (NO_3^--N) Removal

In vertical subsurface flow wetland systems, nitrification processes can be very efficient depending on the type of feeding and characteristics of wastewater. In order to have efficient nitrogen treatment, most of the biodegradable carbon has to be removed firstly from the wastewater, enabling the nitrifying bacteria to convert ammonium to nitrate. The produced nitrate can subsequently be reduced to nitrogen gas by biological denitrification. At higher loads to the wetlands, only suspended solid and carbon removal can be obtained, whereas at lower loads nitrification and denitrification can take place (IWA, 2000). Since the COD and TSS contents of the domestic wastewater of METU were relatively low if compared to the literature, thus, it was expected to have higher N-conversions in both slag and gravel systems.

Throughout the monitoring study, the primarily treated inlet NO_3^--N concentrations of both of the vertical subsurface flow constructed wetlands of METU varied between 0.0-6.44 $mg.L^{-1}$ (1.47 ± 1.81 $mg.L^{-1}$). Even though it was not usual to find NO_3^--N values in raw domestic wastewater because of the anaerobic nature, nitrate might arisen from the washout of nitrates in the air via the precipitation and nitrates brought to the sewer system via surface runoff. The initial nitrate concentrations might be due to the significant ingress of the run-off water (Lienard et. al., 1998).

Due to the nature of the nitrification process, there must be a relation between the influent NH_4^+-N, influent organic-N values and the effluent NO_3^--N values. In METU case, the amount of organic-N compounds bounded to the TSS were negligible, as TSS values were low. Thus, effluent NO_3^--N concentrations were plotted against the influent NH_4^+-N concentrations for the slag and gravel systems in Figure 4.16. a & b, respectively. The NO_3^--N effluent concentrations of the slag and gravel system ranged from 1.15 $mg.L^{-1}$ to 31.33 $mg.L^{-1}$ (14.33 ± 7.9 $mg.L^{-1}$) and from 0 $mg.L^{-1}$ to 33 $mg.L^{-1}$ (8.4 ±6.3$mg.L^{-1}$), respectively (Figure 4.16. a & b). For both of the systems, the effluent NO_3^--N concentrations reflected the changes of the NH_4^+-N influent concentrations. During the peak TN loads (usually after rain events), effluent NO_3^--N increased particularly in the slag system (Figure 4.16.c).

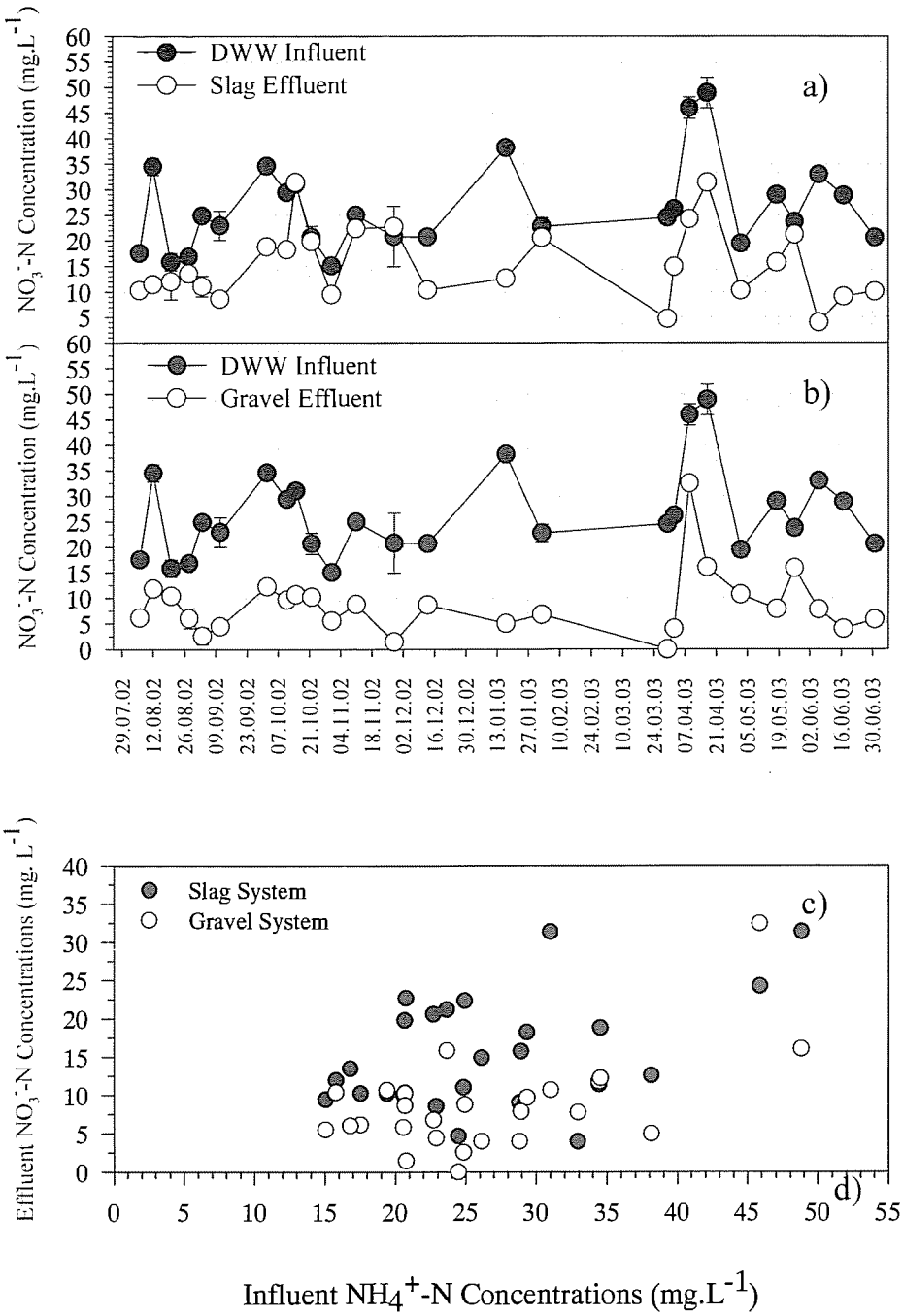

Figure 4.16. a & b) time vs. NH_4^+-N influent and NO_3^--N effluent concentrations ($mg.L^{-1}$) c) NH_4^+-N influent vs. NO_3^--N effluent concentrations ($mg.L^{-1}$) of the slag and gravel wetland systems of METU

The average pH values of the effluents of both of the gravel and slag systems were above 7.5 (see Appendix A, Table A.1), which might have created suitable conditions for nitrification within both of the wetland cells (IWA, 2000). Comparing the wetlands of METU for NO_3^--N production, the slag system had higher effluent NO_3^--N concentrations than that of the gravel system (1-way ANOVA; $F_{0.95}(1;100)=23.54$; $P<0.0001$). However, it did not necessarily mean that the nitrification in the slag system was more efficient than the gravel system since the denitrification rate was not clearly known. Though the higher effluent NH_4^+-N concentrations of the gravel system, it could be postulated that the gravel system had less nitrification capacity and could not convert the NH_4^+-N to NO_3^--N as the slag system could. The large surface area of the slag might have enhanced aerobic nitrification and depressed the anoxic denitrification processes. However, this might be an advantage for the gravel system, since the denitrifiers prefer a less oxygenated condition in the wetland substrate in order to convert the nitrified nitrate to nitrogen gas. In other words, the gravel system might have supported a better balance of aerobic and anaerobic or anoxic zones.

It is well known that the nitrification reaction is strongly temperature dependent and lower temperatures especially below 15°C can significantly reduce nitrification (Reddy and Patrick, 1984). As the temperature has decreased below 15°C in the fall and winter season (Figure B.4), the production of nitrate has also decreased in both of the systems due to the reduction of the nitrification rate. On the contrary, the NO_3^--N effluent concentrations for both of the systems started to increase with the increase of the air temperature in the spring season (Figure 4.16. a & b).

Due to the lower carbon and TSS content of the wastewater treated in the wetlands constructed at METU, both of the beds had higher NO_3^--N effluent concentrations (Table 4.16) as compared to other wetland studies (Table 4.17) cited by Lienard et al., (1998); but had lower concentrations than that of the nitrate concentrations of the constructed wetlands in Austria reported by Haberl et al., (1998). The results were comparable to the data taken from some of the wetlands of Germany, where

the average influent NO_3^--N concentration was 1.9 $mg.L^{-1}$ and the effluent value was 12 $mg.L^{-1}$ (Table 4.17). Average NO_3^--N effluent concentrations (14.33 ± 7.85 $mg.L^{-1}$) of the slag system were slightly higher than the German study, whereas the effluent NO_3^--N concentration of the gravel system (8.38 ± 6.34 $mg.L^{-1}$) was lower than this German study. Since the EU Nitrate Directive is still not valid for Turkey, there is not yet any NO_3^--N discharge standard for the treated wastewater effluents in Turkey.

Table 4.16. NO_3^--N concentration values of the constructed wetlands implemented at METU

NO_3^--N	Influent ($mg.L^{-1}$)	Slag Out ($mg.L^{-1}$)	Gravel Out ($mg.L^{-1}$)
Minimum	0.00	1.15	0.00
Maximum	6.44	31.33	32.44
Average	1.47	14.33	8.38
Median	1.00	12.26	7.74
St Dev.	1.81	7.85	6.30

Table 4.17. NO_3^--N influent and effluent concentrations of vertical constructed wetlands applied in other countries

Countries	NO_3^--N	
	Influent ($mg.L^{-1}$)	Effluent ($mg.L^{-1}$)
Austria	0.0	47.5
France	0.0	5.0
Germany	1.9	12.0

Reference: Vymazal et al., (1998).

For both of the systems, the NH_4^+-N loading rates changed between 1.50 and 4.88 $g.m^{-2}.d^{-1}$ (2.63 ± 0.86 $g.m^{-2}.d^{-1}$) (Figure 4.17). There was not a linear correlation between the influent NH_4^+-N loading rates and effluent NO_3^--N values for the slag and gravel systems (Figure 4.17). As Figure 4.18 indicated, the NO_3^--N produced in the gravel system was linearly dependent on the NH_4^+-N loading rate (R^2=0.560), whereas it was not valid for the slag system (R^2=0.0812). This indicated the importance of the total surface area of the particles used in the wetland substrates other than the wetland surface area. As the wastewater amount applied to the wetland cells increased, due to the porous nature of the slag particles, the wetted area might have been changed irregularly if compared to the gravel particles with

almost a constant surface area. However, without conducting further detailed research on nitrification and denitrification capacities of the wetland systems with different substrates, it was difficult to make a clear discussion.

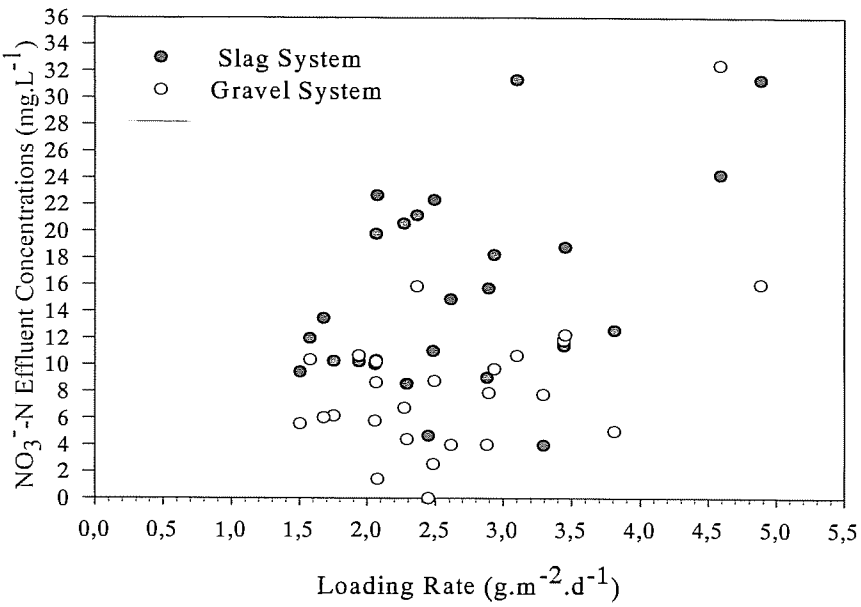

Figure 4.17. NH_4^+-N loading rate (g.m^{-2}.d^{-1}) vs. NO_3^--N effluent concentrations (mg.L^{-1}) of the pilot-scale constructed wetlands implemented at METU

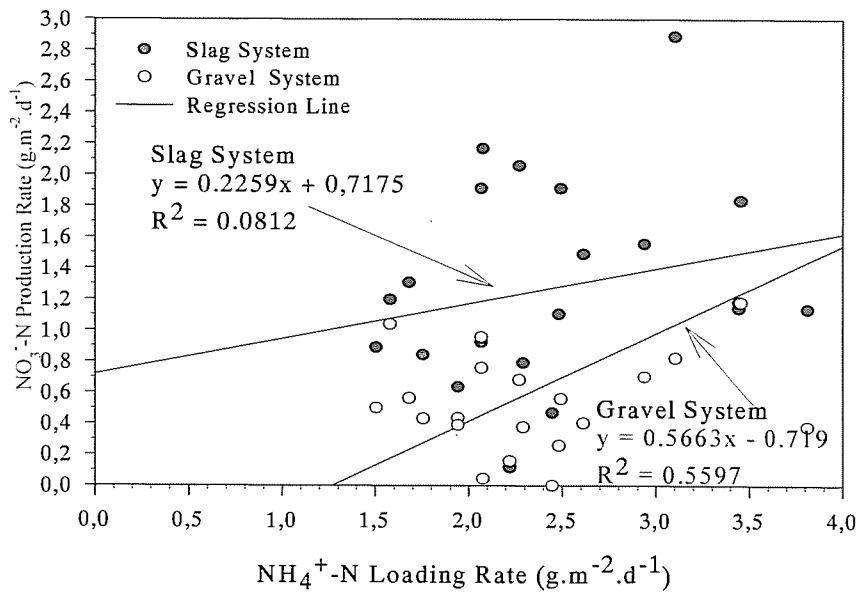

Figure 4.18. NH_4^+-N loading rate (g.m^{-2}.d^{-1}) vs. NO_3^--N Production Rate (g.m^{-2}.d^{-1}) of the pilot-scale constructed wetlands implemented at METU

4.7.6. Total Nitrogen (TN) Removal

The influent TN concentrations of the vertical subsurface flow constructed wetlands implemented at METU varied widely between 19.86 and 59.55 $mg.L^{-1}$ (34.75 ± 10.57 $mg.L^{-1}$) (Figure 4.19. a & b). The influent TN concentration values were almost the summation of influent NH_4^+-N and influent organic-N concentration values. Therefore, the influent TN concentrations of both of the wetlands reflected the changes in the influent NH_4^+-N and organic-N concentrations. Since the effluent organic-N concentrations were low due to the sufficient suspended solids removal, the effluent TN concentrations could be approximated to the sum of the effluent NH_4^+-N and effluent NO_3^--N concentration values for both of the wetlands. Hence, the variations of the effluent NH_4^+-N and NO_3^--N concentrations were reflected to the variations of the effluent TN concentrations of both of the slag and gravel system. Moreover, the variations in the influent TN concentration values were similar to that of the effluent TN concentration values of the wetland systems.

The TN effluent concentrations of the slag system (Figure 4.19.a) varied between 7.96-38.78 $mg.L^{-1}$ (18.54 ± 8.36 $mg.L^{-1}$), whereas they varied between 11.46-53.63 $mg.L^{-1}$ (20.90 ± 9.11 $mg.L^{-1}$) for the gravel system (Figure 4.19.b). The TN removal efficiencies of the slag and gravel systems ranged from 10.16% to 81.41 (45.47% ± 20.42 %) and from 8.72% to 62.08% (40.15% ± 13.06%), respectively (Figure 4.19.c). Comparing these two wetlands in terms of TN removal performances, both of them did not differ from each other statistically (1-way ANOVA; $F_{0.95}(1;100)=2.40$; $P>0.05$). Though there was a correlation between the influent and effluent TN concentrations of the gravel system ($R^2=0.692$); it was not the case for the slag system ($R^2=0.265$) (Figure 4.19.d).

The TN influent and effluent concentration values as well as the removal efficiencies for both of the systems were summarized in Table 4.18. Average TN reductions of the slag and gravel systems were comparable to other wetland studies presented in Table 4.19.

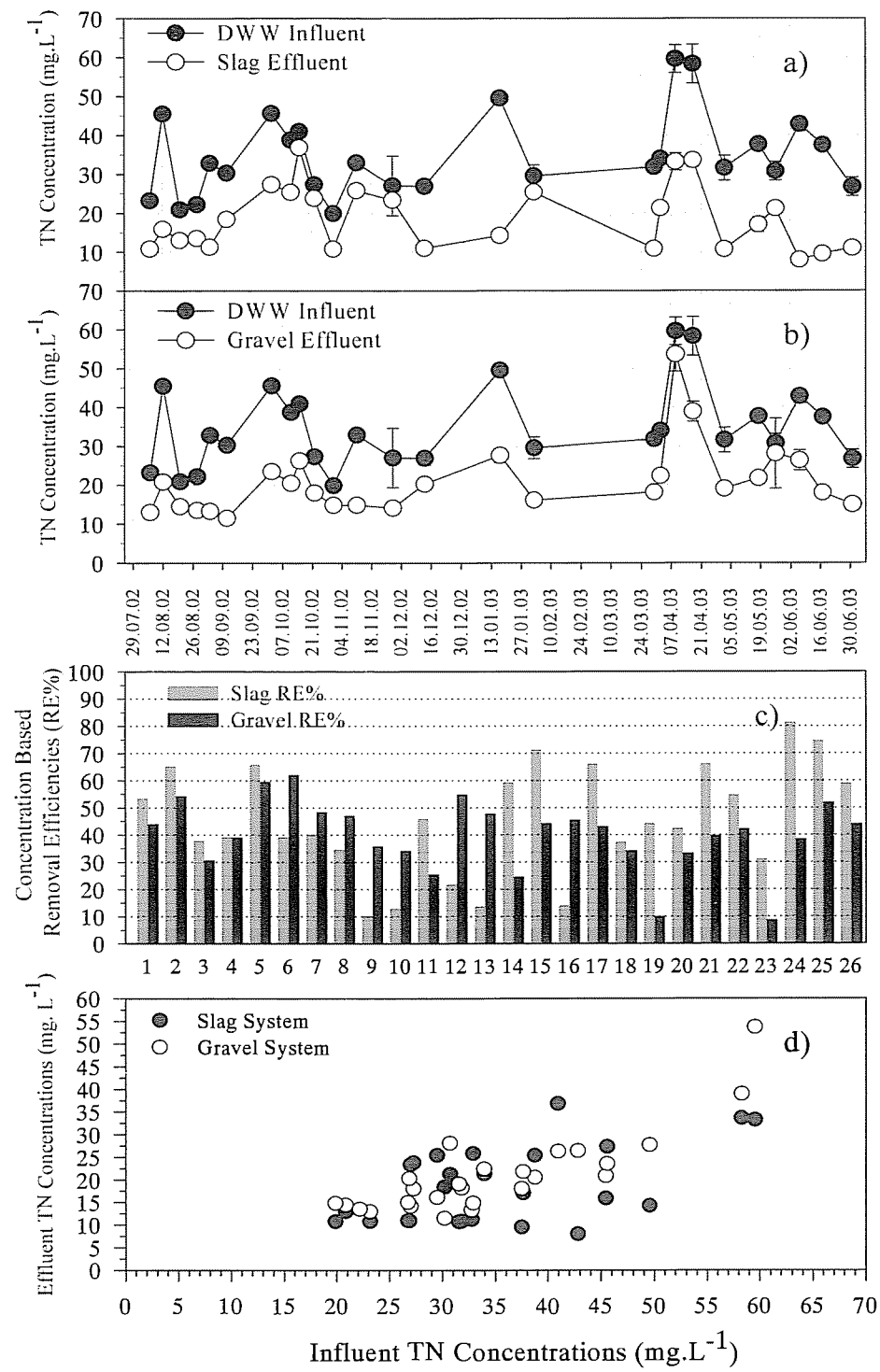

Figure 4.19. TN a & b) time vs. influent and effluent concentrations ($mg.L^{-1}$)

c) removal efficiencies (RE%) d) influent vs. effluent concentrations ($mg.L^{-1}$) of the slag and gravel wetland systems of METU

Table 4.18. TN concentration values and removal efficiencies of the constructed wetlands implemented at METU

TN	Influent ($mg.L^{-1}$)	Slag Out ($mg.L^{-1}$)	Gravel Out ($mg.L^{-1}$)	Slag System (RE%)	Gravel System (RE%)
Minimum	19.86	7.96	11.46	10.16	8.72
Maximum	59.55	36.78	53.63	81.41	62.08
Average	34.75	18.54	20.90	45.47	40.15
Median	32.29	16.42	18.58	43.35	42.62
St Dev.	10.57	8.36	9.11	20.42	13.06

Table 4.19. TN influent and effluent concentrations of vertical constructed wetlands applied in other countries

Countries	TN		
	Influent ($mg.L^{-1}$)	Effluent ($mg.L^{-1}$)	Removal Efficiency (%)
Austria	86.1	55.0	36.1
France	46.0	23.2	49.7
Germany	115.0	60.0	47.8

Reference: Vymazal et al., (1998).

The TN reductions in both of the systems were supposed to be mainly due to the denitrification process. Theoretically, the 60-75% of the removed TN is due to denitrification process. However, a part of the removed TN might be due to the plant assimilation, microbial growth (aerobic and anaerobic microorganisms, in addition to nitrifiers and denitrifiers), and suspended solids removal. The plants can assimilate less than 10% of the removed TN, whereas the microorganisms can use 15-25% of the TN for their growth. Through the filtration mechanism in wetland substrates, the nitrogen bound in the suspended solids can also be removed, which accounts for about 15-20% of the removed TN (IWA, 2000).

Throughout the monitoring period, the TN loading rates for both of the systems varied between 1.9 and 62.1 $g.m^{-2}.d^{-1}$ (3.42 ± 109 $g.m^{-2}.d^{-1}$). For the gravel system, the effluent TN concentrations were almost linearly dependent on the inflow TN loading rates (Figure 4.20). A study conducted by Brix (1998) indicated a linear relationship between the inlet and effluent concentrations of TN values of 90 constructed wetlands in Denmark. The regression coefficient of this Danish study

indicated a mean removal efficiency of ~50% for TN ($y = 0.49 x + 2.5$, $R^2 = 0.58$). This result was consistent with the result obtained for the gravel system, which have removed TN efficiently even as the TN loading rates increased (Figure 4.20). The linear correlation between the TN loading rate and the removal rate for slag system (R^2=0.4923) was stronger than that of the gravel system (R^2=0.2607), if the linear regression analysis has been considered (Figure 4.21).

According to Turkish Regulations, the allowable TN discharge value for treated wastewaters was 15 $mg.L^{-1}$. It could be postulated that to have TN effluent values below 15 $mg.L^{-1}$, the slag and the gravel systems could be loaded upto a TN loading rate of 2.7 $g.m^{-2}.d^{-1}$. Throughout the monitoring period, the average TN effluent values of both of the wetland systems were higher than the discharge standard. But, it should be emphasized that these values were obtained from one-staged wetland beds.

Different wetland configurations provide varying oxidation-reduction potential and different types of microflora, which result in enhanced denitrification capacities (Vymazal et al., 1998). In this regard, the wetlands implemented at METU were designed and constructed as hybrid systems (first stage vertical bed connected to second stage horizontal bed) to have efficient TN removal. However, due to some operational difficulties in the horizontal systems, only the removal performances of the vertical flow slag and gravel wetland beds could be monitored. If the effluent of the horizontal subsurface flow wetland beds could have been monitored regularly, it would be found that the horizontal flow wetlands could achieve denitrification resulting in higher overall TN removal efficiencies, as it was planned at the start of the research. However, the TN removal performances of both of the one-staged vertical flow wetlands of METU were still promising.

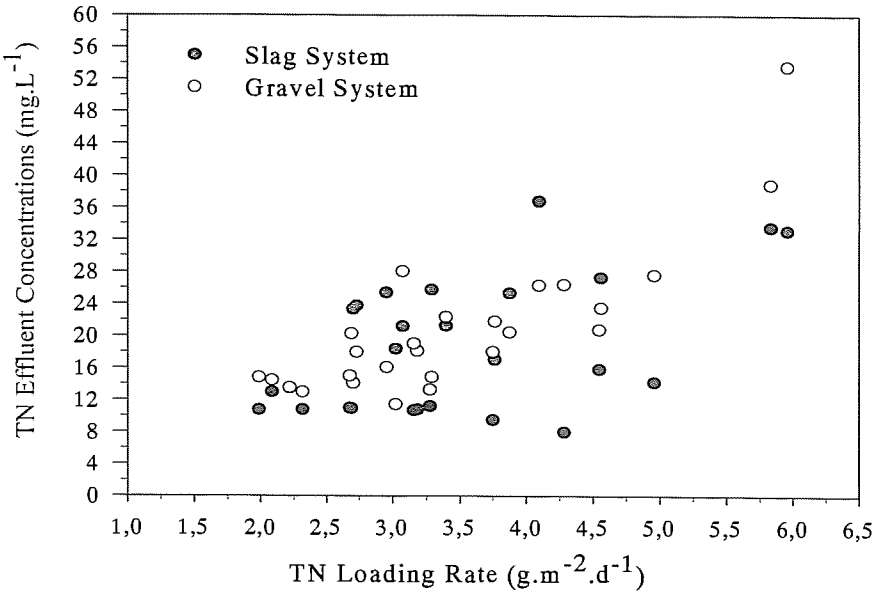

Figure 4.20. TN loading rate ($g.m^{-2}.d^{-1}$) vs. effluent concentrations ($mg.L^{-1}$) of the pilot-scale constructed wetlands implemented at METU

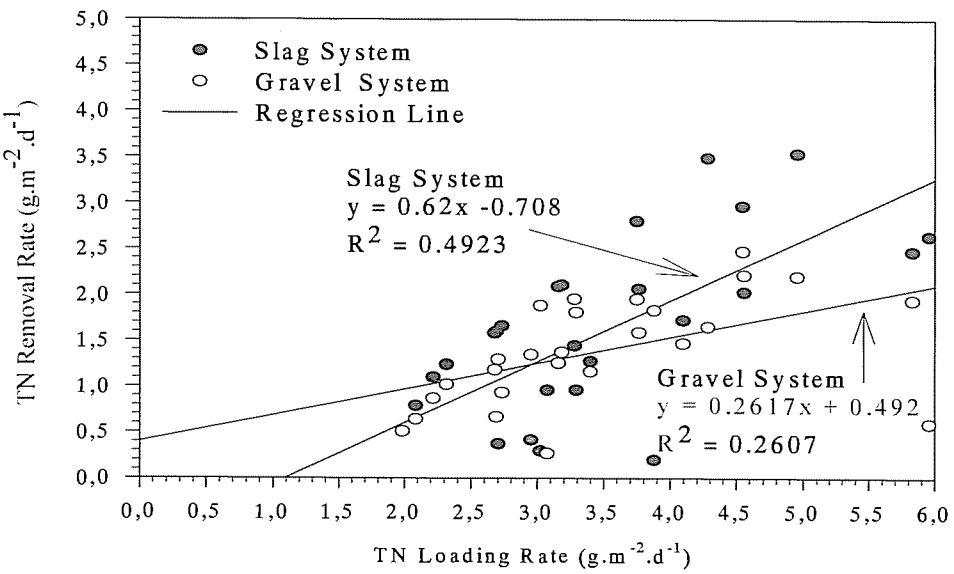

Figure 4.21. TN loading rate ($g.m^{-2}.d^{-1}$) vs. removal rate ($g.m^{-2}.d^{-1}$) of the pilot-scale constructed wetlands implemented at METU

4.7.7. Determination of the Kinetic Parameters

The areal removal rate constants were calculated according to the first order plug-flow kinetic equation (Eqn 2.15) as explained in detail in Section 2.11. The inlet and outlet concentrations of the pollutants, as well as the hydraulic loading rates applied to the systems were used in the calculations. The average, maximum, minimum, and standard deviation values of the areal removal rate constants ($m.d^{-1}$) were presented in Table 4.15 for the monitoring period of July 2002-July 2003. In order to be able to compare the areal rate constants for important water quality parameters of the constructed wetlands implemented at METU to that of the former wetland studies, literature were reviewed. These values ($m.d^{-1}$) were also listed in Table 4.20. Moreover, the calculated areal removal rate constants ($m.yr^{-1}$) of the wetland systems of METU were compared graphically (Figure 4.22) with the areal removal rate constants ($m.yr^{-1}$) found in literature. The loading rates versus removal rate constants for TSS, COD, PO_4^{3-}-P, TP, NH_4^+-N and TN of the wetland systems of METU were plotted in the following figures (Figure 4.23-28) for the monitoring period of July 2002-July 2003.

It can be stated that the average removal rate constants of TSS, COD, TP, NH_4^+-N, TN for the slag and gravel wetland systems were comparable to some of the vertical flow constructed wetland studies given in the literature, which were also treating domestic wastewater (Table 4.20). The COD removal rate constants (literature, slag system and gravel systems of METU) were almost the same. The average areal removal rate constant of TP for the slag system was much higher than that of the gravel system of METU and the literature. It was an expected result since the TP removal capacity of the slag system was higher than the gravel system (as the treatment efficiency increases, the areal removal rate constant also increases). Both of the systems had higher areal NH_4^+-N and TN removal rate constants if compared to the literature values. The higher standard deviations for the areal removal rate constants were thought to be due to the intersystem variability and intra-system stochastic effects during the monitoring period (IWA, 2000).

Table 4.20. The Areal rate constants of the water quality parameters

Parameter	Literature Review	July 2002-July 2003	
TSS	**k literature ($m.d^{-1}$)***	**k slag ($m.d^{-1}$)**	**k gravel ($m.d^{-1}$)**
AVG	0.057	0.117	0.109
MAX	0.178	0.230	0.256
MIN	0.019	0.018	0.029
STDEV	**	0.051	0.062
COD	**k literature ($m.d^{-1}$)**	**k slag ($m.d^{-1}$)**	**k gravel ($m.d^{-1}$)**
AVG	0.069	0.067	0.064
MAX	0.110	0.114	0.245
MIN	0.027	0.022	0.009
STDEV	**	0.027	0.046
PO_4^{3-}-P	**k literature ($m.d^{-1}$)**	**k slag ($m.d^{-1}$)**	**k gravel ($m.d^{-1}$)**
AVG	**	0.085	0.002
MAX	**	0.252	0.018
MIN	**	-0.028	-0.029
STDEV	**	0.077	0.013
TP	**k literature ($m.d^{-1}$)**	**k slag ($m.d^{-1}$)**	**k gravel ($m.d^{-1}$)**
AVG	0.0179	0.079	0.008
MAX	0.0330	0.202	0.041
MIN	0.0027	-0.024	-0.037
STDEV	**	0.068	0.017
NH_4^+-N	**k literature ($m.d^{-1}$)**	**k slag ($m.d^{-1}$)**	**k gravel ($m.d^{-1}$)**
AVG	0.069	0.287	0.085
MAX	0.110	0.493	0.164
MIN	0.027	0.000	0.030
STDEV	**	0.124	0.034
TN	**k literature ($m.d^{-1}$)**	**k slag ($m.d^{-1}$)**	**k gravel ($m.d^{-1}$)**
AVG	0.0328	0.068	0.054
MAX	0.1095	0.107	0.097
MIN	0.0137	0.041	0.037
STDEV	0.008	0.041	0.021

* *References*: Kadlec and Knight (1996); Vymazal et al., (1998); IWA (2000).

** Not available (for P removal, most of the references provided only the TP areal removal rate constant).

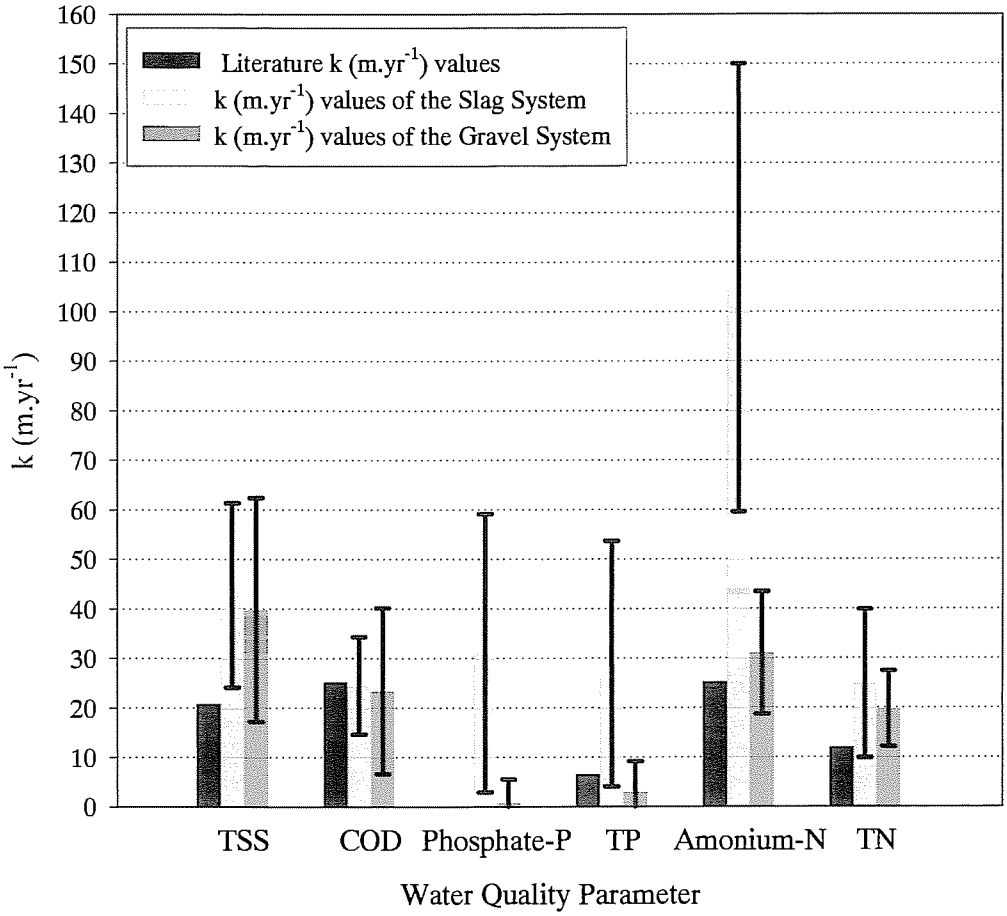

Figure 4.22. Comparison of the calculated and reviewed areal removal rate constants

In theory, the parameters of the first-order models are referred to as "rate constants", and therefore ideally are independent of the inlet concentration and loading rate (IWA, 2000). However, in several wetland studies, calculated rate constants generally increased with an increase in hydraulic loading rates and constituent's mass loading rates (Brix, 2002). Similarly, variations in the areal removal rate constants were observed as the mass loading rates varied for both slag and gravel systems (Figure 4.23-28). Moreover, the removal rate constants were not linearly dependent on the mass loading rates (Figures 4.23-28). This might have indicated that higher mass loading rates increased the area of the bed that was actually involved in the purification process and therefore the area specific degradation get more effective and varied with time (Brix, 1998). The variations in

the areal removal rate constants of some of the parameters could also be related to temperature effect since the removal of some of the constituents was affected by the water temperature (Goulet, 2001).

The simple first-order models work well on annual and seasonal average bases (IWA, 2000). The reasons might be explained as follows: First, there is nominal delay of one detention time between the entrance and the exit of a water parcel. Secondly, temporary increases and decreases in the wetland storages can easily affect instantaneous performance. The outlet concentrations therefore do not "track" the inlet concentrations (IWA, 2000). To understand the seasonal effects on the areal removal rate constants, winter and summer periods were compared to each other (Appendix B, Table B.5). Almost for all of the parameters, the areal removal rate constants of winter period (November 2002-July 2003) were lower than that of the summer period (July 2002-November 2002) indicating the temperature effect.

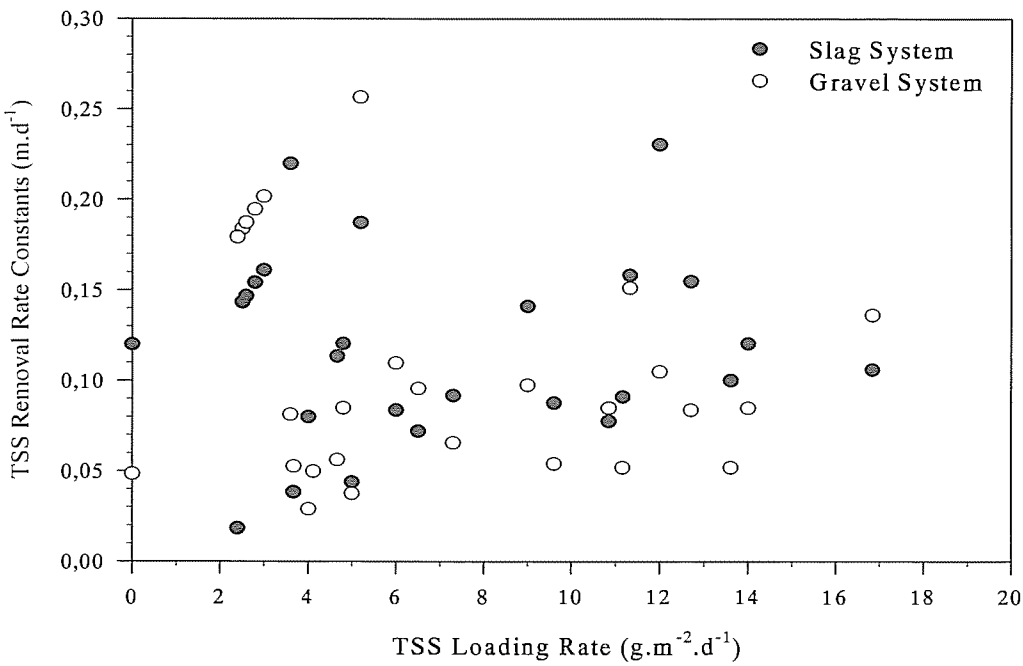

Figure 4.23. TSS loading rate ($g.m^{-2}.d^{-1}$) vs. areal removal rate constants ($m.d^{-1}$) of the pilot-scale constructed wetlands implemented at METU

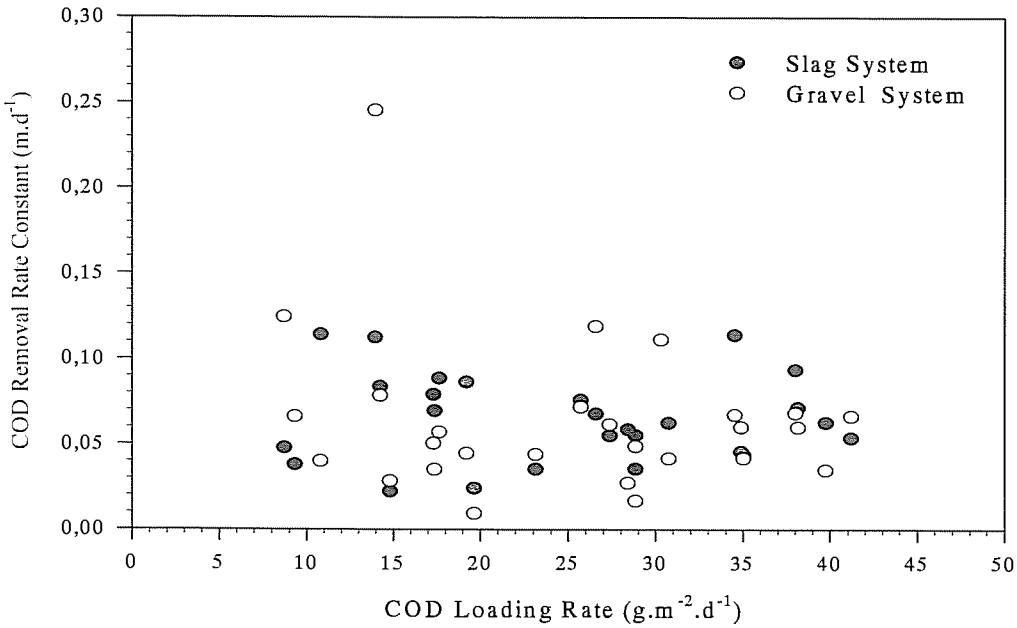

Figure 4.24. COD loading rate ($g.m^{-2}.d^{-1}$) vs. areal removal rate constants ($m.d^{-1}$) of the pilot-scale constructed wetlands implemented at METU

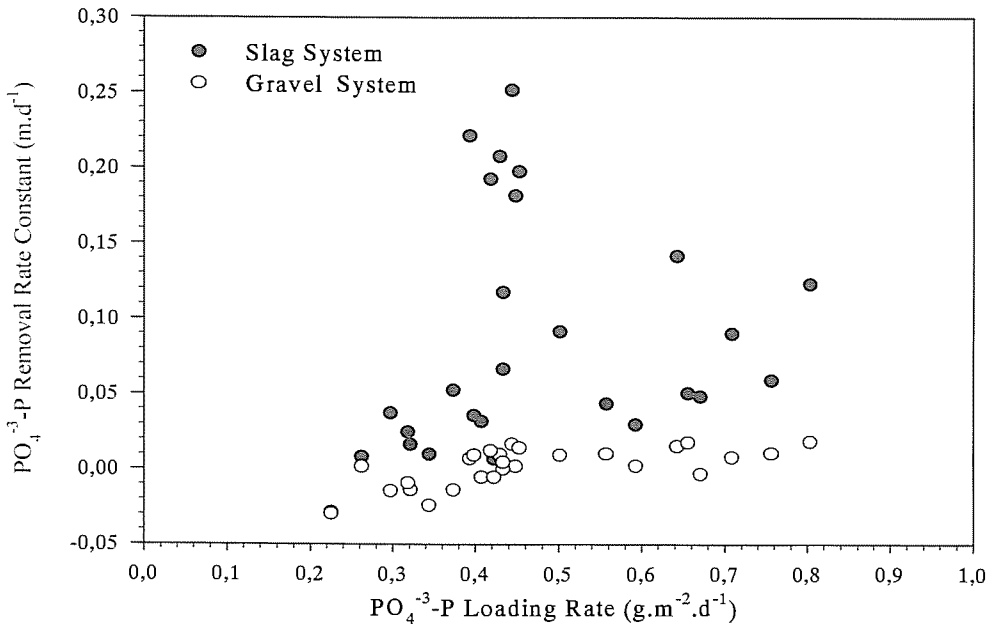

Figure 4.25. PO_4^{3-}-P loading rate ($g.m^{-2}.d^{-1}$) vs. areal removal rate constants ($m.d^{-1}$) of the pilot-scale constructed wetlands implemented at METU

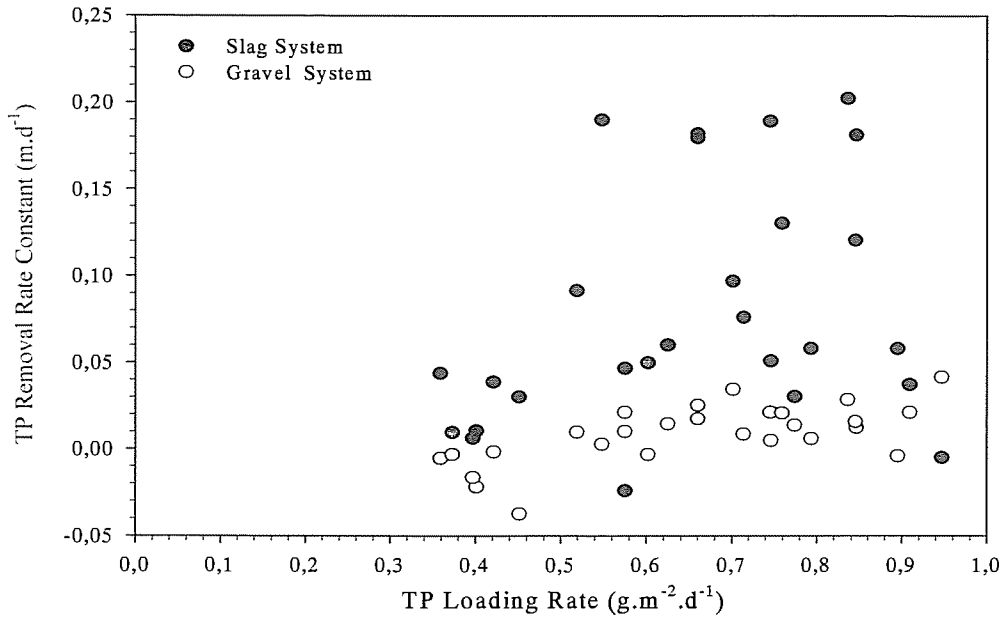

Figure 4.26. TP loading rate ($g.m^{-2}.d^{-1}$) vs. areal removal rate constants ($m.d^{-1}$) of the pilot-scale constructed wetlands implemented at METU

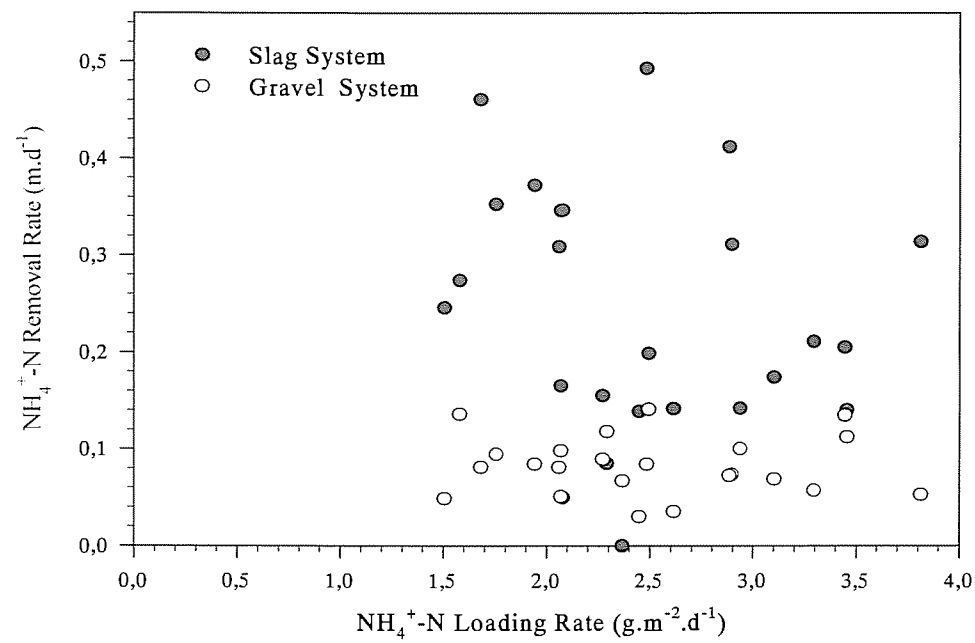

Figure 4.27. NH_4^+-N loading rate ($g.m^{-2}.d^{-1}$) vs. areal removal rate constants ($m.d^{-1}$) of the pilot-scale constructed wetlands implemented at METU

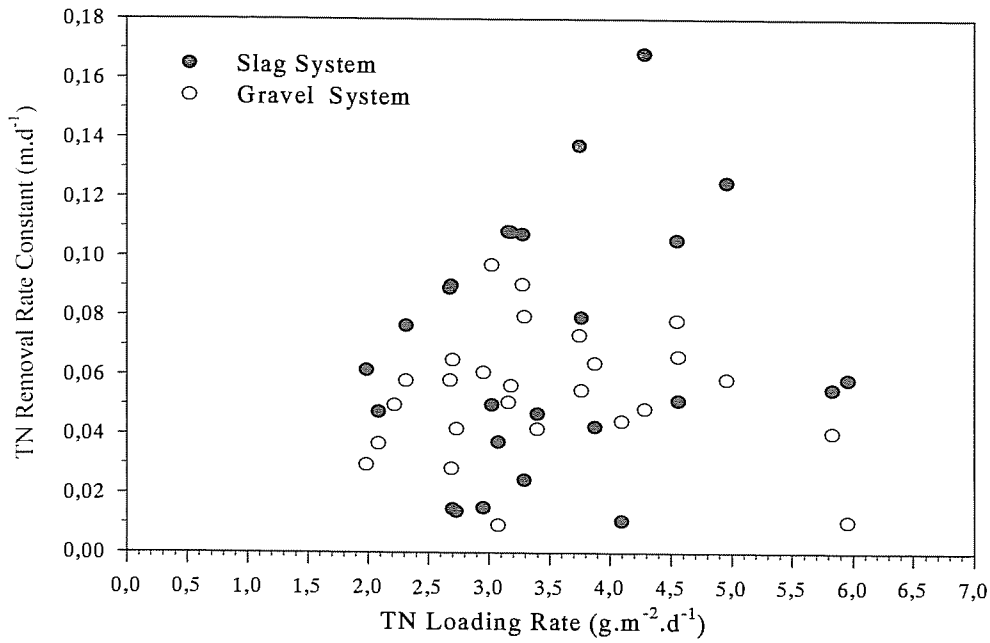

Figure 4.28. TN loading rate ($g.m^{-2}.d^{-1}$) vs. areal removal rate constants ($m.d^{-1}$) of the pilot-scale constructed wetlands implemented at METU

4.8. Analyses for Determination of the Plant Content

Before planting the reeds into the wetland cells (May 2002), the height and the weight of some of the seedlings were measured and recorded. Accordingly, the average weight (g) (± st dev) was 6.59 ± 1.60 g (sample size, n = 8). The weight of the plants varied between 4.98 g and 8.73 g. The above-ground height of the reed plants that were removed from the soil were measured in the laboratory. Moreover, the above-ground heights of the reeds were also measured randomly in the field before planting them into the wetland cells (May, 2002). According to these measurements, the average height (cm) (± st dev) of the plants was 39.45 ± 8.65 cm (n = 20), whereas the minimum and maximum height of the reeds were 25 cm and 55 cm, respectively. After an operation period of 12 months, the heights of the reed plants in the wetland cells were recorded randomly on the field (July 2003). These measurements were summarized in Table 4.21.

Table 4.21. Height of the reeds in vertical flow wetlands constructed at METU (July, 2003)

Type of VF Constructed Wetland of METU	Average Height (cm) ± St Dev (cm)*	Minimum-Maximum Height (cm)*
Gravel System	119.5 ± 17.7	89-170
Slag System	148.4 ± 22.4	106-192

*Sample Size (n) = 32

Using the Eqn (3.11), the growth rate of the reed plants in the wetland cells was calculated in terms of $mm.d^{-1}$. For the gravel system and slag system, the growth rates of the reed plants were 2.00 $mm.d^{-1}$ and 2.72 $mm.d^{-1}$, respectively. According to these results, it could be stated that the reed plants in the slag system were grown slightly faster than that of the plants in the gravel system.

In July 2003, the randomly harvested plants from both of the VF constructed wetlands of METU were brought to the laboratory. Moreover, in November 2003, some reed samples were harvested again from the wetland cells following the same procedure and brought to the laboratory. The wet-weight of the below-ground (roots and rhizomes) and above-ground (stems and leaves) parts of the harvested reed samples were determined both for 1 m^2 and 30 m^2 (total surface area of the VF constructed wetlands of METU) summarized in Table 4.22. The reductions of the wet-weight biomass to dry-weight biomass were also determined and presented in Table 4.23.

Table 4.22. Wet-weight of the reeds in vertical flow wetlands constructed at METU

Type of VF Constructed Wetland	GRAVEL SYSTEM		SLAG SYSTEM	
Harvesting Time (in 2003)	July	November	July	November
Above-Ground Wet-Weight ($kg.m^{-2}$)	4.024	4.247	7.008	4.313
Below-Ground Wet-Weight ($kg.m^{-2}$)	6.288	3.695	6.824	4.298
Total Biomass Wet-Weight ($kg.m^{-2}$)	**10.312**	**7.942**	**13.832**	**8.611**
Above-Ground Wet-Weight (kg. 30 m^{-2})	120.72	127.41	210.24	129.39
Below-Ground Wet-Weight (kg. 30 m^{-2})	188.64	110.85	204.72	128.94
Total Biomass Wet-Weight (kg. 30 m^{-2})	**309.36**	**238.26**	**414.96**	**258.33**

Table 4.23. Dry-weight to wet-weight ratios (%) of the reed samples

Type of VF Constructed Wetland	**GRAVEL SYSTEM**		**SLAG SYSTEM**	
Harvesting Time (in 2003)	**July**	**Nov.***	**July**	**Nov.***
Above-Ground Dry Weight:Wet-Weight (%)	52.9 ±3.2	64	54.9 ±11.1	34
Below-Ground Dry Weight:Wet-Weight (%)	56.6 ±5.7	51	54.0 ±14.9	56
Total Biomass Dry:Wet-Weight (%)	**54.2**	**57.5**	**54.5**	**45**

* The analyses were conducted in the Ege University. Since they only provided the mean data, the standard deviations could not be given here.

The above-ground and the below-ground biomasses of the slag system were higher than that of the gravel system for both of the harvesting times (July and November 2003). For both of the wetland systems, the macrophytes passed through an annual cycle of growth and died. This has resulted in a difference in the biomasses measured in July and November. The biomass values measured in July were reduced approximately by 30% in November.

Combining the data given in Table 4.22 and 4.23, the dry-weight of the above-ground and the below-ground reeds in both of the wetlands were calculated for 1 m^2 and 30 m^2 (surface area of the wetlands) (Table 4.24). Summing up the above-ground and below-ground dry-weight biomasses, total dry-weight of the biomass was found.

Table 4.24. Dry-weight of the reeds in vertical flow wetlands constructed at METU

Type of VF Constructed Wetland	**GRAVEL SYSTEM**		**SLAG SYSTEM**	
Harvesting Time (in 2003)	**July**	**November**	**July**	**November**
Above-Ground Dry-Weight ($kg.m^{-2}$)	2.132	2.718	3.850	1.466
Below-Ground Dry-Weight ($kg.m^{-2}$)	3.560	1.884	3.685	2.407
Total Biomass Dry-Weight ($kg.m^{-2}.yr^{-1}$)	**5.691**	**4.602**	**7.535**	**3.873**
Above-Ground Dry-Weight (kg. 30 m^{-2})	63.96	81.54	115.50	43.98
Below-Ground Dry-Weight (kg. 30 m^{-2})	106.80	56.52	110.55	72.21
Total Biomass Dry-Weight (kg. 30 m^{-2})	**170.76**	**138.06**	**226.05**	**116.12**

In the literature, the below-ground biomass of *Phragmites australis* was given in the order of 2000 g dry matter.m^{-2}. However, a dense macrophyte stand would have a larger amount of below-ground biomass in the form of roots and rhizomes, often

in the range of 0.5-5.0 kg dry matter.m^{-2} (IWA, 2000). As the wetlands of METU had higher plant density (9 plant.m^{-2}) if compared to other wetland studies (4-6 plants.m^{-2}); both wetlands of METU could be accepted as reed beds with denser macrophyte stands. This idea could be supported also by the results given in Table 4.24. Accordingly, both of the wetlands of METU had below-ground biomass in the range of 1.88-3.69 kg dry matter.m^{-2} (July and November), which is in the range of 0.5-5.0 kg dry matter.m^{-2} as given in the literature. The above-ground biomass in the form of stem and leaves, however, has often a range of 0.4-3.5 kg dry matter.m^{-2} in the literature (Naylor et al., 2002). The above-ground biomass of the wetlands of METU ranged between 1.46 ad 3.85 kg dry matter.m^{-2} (Table 4.24), which was within the range of the figures given in the literature.

The TN and TP contents of the above-ground and below-ground plants were determined and given as percentage of the dry-weight biomass of the plants (Table 4.25). TN and TP contents of the plants of the slag system were higher than that of the gravel system. The nutrients (nitrogen and phosphorus) available for the plant roots and rhizomes in the filter media could enhance the nutrient uptake of the plants resulting in higher N and P contents (Vymazal et al., 1998). Thus, the higher TP content of the plants in the slag system could be explained by the higher P-adsorption capacity of the slag material if compared to gravel, as the adsorbed phosphorus in the filter media was taken by the plants. Moreover, the higher TN content could be related to the higher nitrate production of the slag system, where higher amount of mineralized nitrate compounds that were adsorbed by the filter media were more available for plant uptake that in the gravel system.

In the literature (Table 2.2), TN and TP content of the reed plant tissues varied between 1.8-2.1% and 0.2-0.3% of the total dry-weight biomass, respectively. Even though TP content of the plants in constructed wetlands of METU were generally comparable to the literature values, TN content was lower than that of the literature values (Table 4.25). These differences in the TN and TP contents of the plants could be related to the variations in the harvesting time, type of the wastewater

applied, the nutrient content of the wastewater, experimental analysis, filter media, type of constructed wetland, etc. (Vymazal et al., 1998).

Table 4.25. TN and TP percentages (± St Deviation %) of the dry-weight biomass of reed plants

Type of VF Constructed Wetland	**GRAVEL SYSTEM**		**SLAG SYSTEM**	
Harvesting Time (in 2003)	**July**	**November***	**July**	**November***
TN in Above-Ground Biomass	1.76 (±0.84)	1.29	2.80 (±0.48)	0.78
TN in Below-Ground Biomass	0.81 (±0.34)	0.70	1.24 (±0.12)	1.26
TN Average (DW %) of Total (Above-Ground + Below-Ground) Reed Biomass	**1.28**	**0.99**	**2.01**	**1.02**
TP in Above-Ground Biomass	0.33 (±0.03)	0.19	0.27 (±0.02)	0.21
TP in Below-Ground Biomass	0.22 ±0.02	0.34	0.17 ±0.02	0.49
TP Average (DW %) of Total (Above-Ground + Below Ground) Reed Biomass	**0.27**	**0.27**	**0.22**	**0.35**
TN:TP Ratio in Above-Ground Biomass	5.33	6.67	10.37	3.68
TN:TP in Below-Ground Biomass	3.68	2.05	7.29	2.56
TN:TP Ratio of Total (Above-Ground + Below Ground) Reed Biomass	**4.74**	**3.72**	**9.14**	**2.90**

* The analyses were conducted in the Ege University. Since they only provided the mean data, the standard deviations could not be given here.

Plant tissue composition (% dry weight) data indicated that N content of the plants harvested in November was lower than the N content of the plants harvested in July for both of the slag and gravel systems (Table 4.25). This reduction in N content could be explained with the N limitation in the wetland cells since the wastewater was not applied to the wetlands between July 2003 and November 2003. The plants could assimilate the mineralized N, which remained in the wetland substrate from the operation period (July 2002-July 2003) and released from the dead plant tissues between July-November 2003.

Even though the P content of the above-ground plants was decreased between initial (July) and final (November) harvests for both of the wetlands (Table 4.25), P content of the below-ground plants was increased, which is typical both for wetland

plants in natural stands and for those grown in hydroponic culture (Boyd, 1975; Breen, 1990). The TP increase in the root content of the harvested plants could be explained by the normal biorhythm of *Phragmites australis*, which usually translocates the storage products to the rhizomes and roots just before the end of the growing season (IWA, 2000), in other words before the start of winter. The yearly TN and TP uptake rates ($g.m^{-2}.yr^{-1}$ and $kg.30\ m^{-2}.yr^{-1}$) of the reeds within slag and gravel systems were calculated combining the data given in Table 4.24 and Table 4.25 and presented in Table 4.26.

Table 4.26. Total dry-weight of TN and TP removed by reeds in vertical flow wetlands constructed at METU

Type of VF Constructed Wetland	**GRAVEL SYSTEM**		**SLAG SYSTEM**	
Harvesting Time (in 2003)	**July**	**November**	**July**	**November**
TN in Above-Ground Biomass ($g.m^{-2}.yr^{-1}$)	37.523	35.008	107.80	11.493
TN in Below-Ground Biomass ($g.m^{-2}.yr^{-1}$)	28.836	13.188	45.69	30.328
TN Total (Above-Ground + Below-Ground) Dry-Reed Biomass ($g.m^{-2}.yr^{-1}$)	**66.359**	**48.196**	**153.49**	**41.821**
TN in Above-Ground Biomass ($kg.\ 30\ m^{-2}.yr^{-1}$)	1.125	1.050	3.234	0.345
TN in Below-Ground Biomass ($kg.\ 30\ m^{-2}.yr^{-1}$)	0.865	0.396	0.171	0.909
TN Total (Above-Ground + Below-Ground) Dry-Reed Biomass ($kg.30\ m^{-2}.yr^{-1}$)	**1.990**	**1.446**	**3.405**	**1.254**
TP in Above-Ground Biomass ($g.m^{-2}.yr^{-1}$)	7.030	5.245	10.395	3.122
TP in Below-Ground Biomass ($g.m^{-2}.yr^{-1}$)	7.830	6.443	6.264	11.818
TP Total (Above-Ground + Below-Ground) Dry-Reed Biomass ($g.m^{-2}.yr^{-1}$)	**14.860**	**11.688**	**16.659**	**14.490**
TP in Above-Ground Biomass ($kg.\ 30\ m^{-2}.yr^{-1}$)	0.211	0.157	0.312	0.094
TP in Below-Ground Biomass ($kg.\ 30\ m^{-2}.yr^{-1}$)	0.235	0.193	0.188	0.354
TP Total (Above-Ground + Below-Ground) Dry-Reed Biomass ($kg.30\ m^{-2}.yr^{-1}$)	**0.446**	**0.350**	**0.500**	**0.448**

In the literature, there are many reviews on nutrient contents in plant tissues grown in natural wetlands (Reddy and Debusk, 1987; Vymazal, 1995). However, only few data on nutrient contents of plants were reported for wastewater treatment wetlands (IWA, 2000). In Europe, TN and TP assimilation of reeds in constructed wetlands

have been found to be 16-65.2 $g.m^{-2}.yr^{-1}$ and 1.6-5.6 $g.m^{-2}.yr^{-1}$, respectively (Obarska-Pempkowiak, 1997). In the vertical flow gravel wetland system, TN assimilation capacity of the reeds changed from 66.4 $g.m^{-2}.yr^{-1}$ (July, 2003) to 48.2 $g.m^{-2}.yr^{-1}$ (November 2003) while it varied from 153.50 $g.m^{-2}.yr^{-1}$ (July, 2003) to 41.82 $g.m^{-2}.yr^{-1}$ (November, 2003) in the vertical flow slag wetland system (Table 4.26). Nitrogen uptake capacities of both of the systems were in agreement with data given by Obarska-Pempkowiak (1997). The decrease in the N-uptake capacity of the reeds in the slag and gravel system between two harvests (July and November) might have been due to the slow growth in above-ground biomass and consequently due to the die-off of the plants before winter.

In the vertical flow gravel and slag wetland systems (Table 4.26), TP assimilation capacity of the reeds ranged from 14.86 $g.m^{-2}.yr^{-1}$ (July, 2003) to 11.68 $g.m^{-2}.yr^{-1}$ (November, 2003) and from 16.66 $g.m^{-2}.yr^{-1}$ (July, 2003) to 14.50 $g.m^{-2}.yr^{-1}$ (November, 2003), respectively. Between two harvests (July-November), there was not a major change in the overall P-uptake capacities of the reeds (above-ground + below-ground) in both of the systems. However, there was a dramatic decrease in the P-content of the above-ground biomass and a dramatic increase in the P-content of the below-ground biomass of the slag system when season turned from summer to winter. *Phragmites australis* has been reported to be effective at conserving P through internal cycling and seasonal redistribution between above and below-ground parts (Fiala, 1978). Hocking (1989) also reported substantial seasonal cycling and conservation of P between the shoots and rhizomes of *Phragmites australis,* with the amount of P in rhizomes peaking in winter, and decreasing in spring. Similar outcomes from this study (Table 4.26) might have been observed due to the translocation of the P content of the above-ground biomass of the plants to the below-ground biomass as the season turned from summer (July) to winter (November). Moreover, it might be due to sloughing of the leaves from senescent shoots during the autumn (Headley et al., 2003).

The TP uptake capacity of the reeds in the slag system was higher than that of the gravel system for two of the harvest times, which could be related to the P-retained by slags that was available for uptake by plants (Johansson and Gustafsson, 2000). Phosphorus uptake capacities of the reeds in both of the wetland systems (Table 4.26) were higher than the values reviewed by Obarska-Pempkowiak (1997). This could be due to the denser plantation in wetlands of METU, which resulted in higher biomass per unit area, thus in higher P-uptake capacities (Table 4.26).

As well as the TN and TP content of the above-ground and below grounds of the reeds, Fe, Cu, Mg, Mn, Na, K, and Ca content (dry weight) were also determined in November in the Department of Agriculture of the Ege University, İzmir according to the methodology described by Kacar (1972) and presented in Table 4.27.

Table 4.27. Na, K and Metal contents of the reeds harvested in November 2003

	SLAG SYSTEM			GRAVEL SYSTEM		
ppm	**Below Ground**	**Above Ground**	**Total Biomass**	**Below Ground**	**Below Ground**	**Total Biomass**
Na	1300	700	2000	1900	800	2700
K	5100	5000	10100	5000	7500	12500
Fe	3795	334	4129	4162	484	4646
Cu	19207	46113	65320	38094	41306	79400
Mn	130	29	159	360	72	432
Mg	2842	1127	3969	6664	1568	8232
Ca	5000	3000	8000	28000	3000	31000

ppm= $mg.kg^{-1}$

Even though many metals become toxic to sensitive organisms at moderately low concentrations, a number of metals are biologically essential at trace concentrations for plants (IWA, 2000). Hence, most metals are more concentrated in some of the wetland plant species, which have a well-established ability for direct uptake of heavy metals (Vymazal et al., 1998). Accumulation may become sufficient to kill some of the plant species within just one growing season (Cooper et al., 1996). However, it was not the case for the reeds planted in the constructed wetlands of METU, which might have a number of tolerance mechanisms to prevent excessive metal uptake (Ross and Kaye, 1994).

Even though metals were found upto certain degrees in reed biomass of the wetlands of METU (Table 4.27), any plant kills were observed at least during the monitoring period of one year. The plant biomass of the gravel system stored higher amounts of Na, K, Fe, Cu, Mn, Mg and Ca than that of the slag system. Reed plants harvested from the slag and gravel systems accumulated higher levels of Na, Fe, Mn, Mg, and Ca in their below-ground parts than in their above-ground parts, which were also stated in numerous studies from natural and constructed wetlands (Vymazal, 1995).

Kadlec and Knight (1996) reported that wetland emergent plants from relatively unimpacted areas stored Mn between 200-600 $mg.kg^{-1}$. The Mn content in reed samples (Table 4.27) harvested from the gravel system (432 $mg.kg^{-1}$) agreed well with literature (Kadlec and Knight, 1996). However, in reed samples taken from the slag system (Table 4.27), Mn content (159 $mg.kg^{-1}$) was lower if compared to the values given by Kadlec and Knight, (1996). For both wetland systems, higher amounts of Cu and K were found in the above-ground reed biomass than in the below-ground reed biomass. Plants of the gravel system accumulated significantly higher amounts of Ca and Cu in their roots and rhizomes, if compared to the Ca and Cu content of the below-ground biomass of the slag system (Table 4.27).

Combining the data given in Table 4.24 and Table 4.27, the total amount of the stored Na, K and metals (Ca, Fe, Cu, Mn, and Mg) in the reeds harvested in November from the slag and gravel wetland system was calculated for per unit area and given in Table 4.28. Since the influent and effluent Na, K and metal concentrations of the domestic wastewater treated in the wetland cells constructed at METU were not monitored, a mass balance approach could not be used for the data given in Table 4.28. However, these data might be used to have a general idea about the levels of Na, K and some of the heavy metal adsorbed by the reed biomass in the constructed wetlands treating domestic wastewater and surface runoff (due to combined sewer of METU).

The amounts of nutrients that can be removed by harvesting were generally insignificant compared to the loading into the constructed wetlands with wastewater Brix (1994). However, Kadlec and Knight (1996) suggested harvesting the macrophytes of the constructed wetlands at the right moment in late summer so that it could substantially contribute to the nutrient removal capacity of a wetland. In some places, especially in developing countries, the plants of the wetlands are harvested and this biomass is used as fertilizer and fodder (Denny, 1997).

Table 4.28. Na, K and metal amounts stored in the reeds of the wetlands constructed at METU

Elements	SLAG SYSTEM		GRAVEL SYSTEM	
	Below-Ground	Above-Ground	Below-Ground	Above-Ground
Na ($g.m^{-2}$)	3.13	1.68	3.58	2.17
Na ($g.30\ m^{-2}$)	93.90	50.40	107.40	65.10
K ($g.m^{-2}$)	12.27	12.04	9.42	20.39
K ($g.30\ m^{-2}$)	368.10	361.20	282.60	611.70
Ca ($g.m^{-2}$)	12.04	7.22	52.75	8.15
Ca ($g.30\ m^{-2}$)	361.20	216.60	1582.50	244.62
Fe ($g.m^{-2}$)	9.14	0.80	7.84	1.32
Fe ($g.30\ m^{-2}$)	274.20	24.00	235.2	39.6
Cu ($g.m^{-2}$)	46.23	110.99	71.77	112.27
Cu ($g.30\ m^{-2}$)	1386.90	3329.7	2153.10	3368.1
Mn ($g.m^{-2}$)	0.31	0.07	0.68	0.20
Mn ($g.30\ m^{-2}$)	9.30	2.10	20.4	6.00
Mg ($g.m^{-2}$)	6.84	2.71	12.55	4.26
Mg ($g.30\ m^{-2}$)	205.2	81.3	376.50	127.80

For a few metals, biochemical transformations and chemical characteristics can lead to "biomagnification", a phenomenon in which increasing concentrations occurs in consumers along a food chain. Biomagnification can have devastating effects at top consumer levels, including humans (IWA, 2000). For this reason, the use of the plants that are harvested from the constructed wetlands as fertilizer and fodder should be considered carefully as they can have higher amounts of metals.

4.9. Determination of the Contents of the Substrate

To understand the effect of seasonal changes on the retained nutrients in the wetland cells, soil samples taken from the wetlands were sent to the Soil Laboratory of the Department of Agriculture of the Ege University, İzmir. They performed a more detailed analysis in order to determine the elements (including heavy metals) adsorbed by sand and slag samples (Table 4.29 and Table 4.30).

The amount of the nutrients adsorbed by the slag media decreased between two sampling period (July and November), which could be explained by desorption of the retained nutrients in the slag wetland (Table 4.29). It has been stated that a reduction in the concentration of the nutrients by uptake (plants and biofilm), flushing, or dilution can cause a release of nutrients that has already been adsorbed (Syers et al., 1973). Heavier precipitation, snow melt would cause a decrease in the nutrient concentration, initiating the release of nutrient that had accumulated in the wetland. The amount of released nutrients would depend on the age and the solubility of the precipitate. It would be released most easily from freshly precipitated crystals and adsorbed nutrient that has not yet penetrated particles (Brady, 1990). This may have significance for uncontrolled outdoor wetland systems, especially during precipitation and snow-melt events, and may be an explanation for the nutrient releases observed in the slag wetland between July and November 2003.

The processes of metal removal in constructed wetlands include sedimentation, filtration, adsorption, complexation, precipitation, cation exchange, plant uptake and microbially mediated reactions, especially oxidation and reduction (Watson et al., 1989). Metals are removed by cation exchange to wetland sediments, precipitation as sulphides and as other insoluble salts. The anaerobic sediments provide sulphate reduction to sulphide and facilitate chemical precipitation. As a result, good removals of metals were reported for operating wetlands (IWA, 2000).

Table 4.29. Content of the substrate samples taken in July and November 2003 from the wetlands constructed at METU (analyzed in the Soil Laboratory of the Ege University)

Contents of Substrates ($mg.kg^{-1}$)		GRAVEL SYSTEM		SLAG SYSTEM			SLAG SYSTEM	
	Fresh Sand (Blank)	Sand Sample taken in July	Sand Sample taken in November	Sand Sample taken in July	Sand Sample taken in November	Fresh Slag (Blank)	Slag Sample taken in July	Slag Sample taken in November
TN	0.200	0.364	0.294	0.378	0.518	0.392	0.364	0.350
P available for plants	2.66	13.34	6.53	12.77	11.09	1.87	12.14	6.96
Total Na	70.00	110.00	140.00	200.00	180.00	330.00	340.00	230.00
Na available for plants	20.00	40.00	60.00	50.00	70.00	50.00	160.00	80.00
Total K	140.00	150.00	150.00	480.00	470.00	1230.00	1080.00	490.00
K available for plants	30.00	30.00	30.00	100.00	80.00	470.00	180.00	80.00
Total Ca	2600.00	3200.00	4900.00	14100.00	13800.00	38000.00	40000.00	14100.00
Ca available for plants	1400.00	1200.00	1900.00	2000.00	2200.00	2700.00	3000.00	2000.00
Mg	392.00	461.00	402.00	588.00	618.00	343.00	833.00	549.00

Table 4.30. Heavy Metal content of the substrate samples taken in July and November 2003 from the wetlands constructed at METU (analyzed in the Ege University)

Contents of Substrates ($mg.kg^{-1}$)	Fresh Sand (Blank)	GRAVEL SYSTEM		SLAG SYSTEM		SLAG SYSTEM		
		Sand Sample taken in July	Sand Sample taken in Nov.	Sand Sample taken in July	Sand Sample taken in Nov.	Fresh Slag (Blank)	Slag Sample taken in July	Slag Sample taken in Nov.
Fe	0.31	0.06	0.43	0.61	0.43	0.06	0.18	0.12
Mn	0.95	1.53	0.78	1.93	1.56	1.18	2.62	1.33
Zn	50	2600	390	1780	980	282	1280	1020
Cu	0.05	1.1	0.15	0.9	0.35	0.4	0.2	1.1
Pb	84	101	99	122	152	99	88	95
Cr	367	352	181	214	107	64	166	410
Sn	Trace	Trace	Trace	Trace	Trace	Trace	0.01	Trace
Cd	0.60	0.67	0.69	0.65	0.71	0.61	0.61	0.80
Hg	2.8	2.9	2.3	2.8	3.2	2.0	2.8	3.8
Ni	448	364	210	293	93	71	220	620

Certain metals such as Cd and Zn have been shown to have a stronger affinity for the dissolved phase, whereas Pb tends to be predominantly particulate associated (Morrison et al., 1984). Similarly, in the slag system, the heavy metals were adsorbed upto certain degrees (Table 4.30). In literature, it was also noted that slags have been successfully used to remove heavy metals in the lab-scale constructed wetlands (Phytoremediation Inventory, 2003). However, since the metal concentrations of influent and effluent streams of both wetlands could not be monitored during the monitoring studies, a mass balance approach for metal retention could not be developed in this study.

Nevertheless, the metal uptake of the reed plants (Table 4.27) was significantly higher than the heavy metal retention capacity of the slag or sand media (Table 4.30). The higher metal uptake capacity of the reed biomass, especially of the below-ground tissues, might be due to precipitation of higher amounts of heavy metals on the larger surface area of the roots and rhizomes, through which the metals were absorbed to the plant tissues.

4.10. Chemical Extraction Experiments for Phosphorus Determination

The P-fractionation experiments aimed to investigate the P-retention mechanisms in order to explain how the inorganic phosphorus was sorbed to the blast furnace slag and sand in the wetlands. The results of the P-fractionation experiment performed in the Chemistry Laboratory of the Department of Environmental Engineering of METU were summarized in Table 4.31. The percent (%) distributions of different forms of sorbed phosphorus for each of the sample were calculated considering the data given in Table 4.31 and illustrated in Figure 4.29.

For the slag samples, the P-data found in the P-fractionation experiments (Table 4.31) were consistent with the P-data found in the screening level P-adsorption shake experiments (Table B.1). However, the results for the sand samples were

questionable since sand samples had higher P-sorption capacity than that of slag samples (Table 4.31). If the P-sorption capacity of the sand samples were as found in the P-extraction experiments; both wetlands had to show off higher P-removal efficiencies during the operation period, which was not valid especially for the gravel system.

Table 4.31. Chemical P-fractionation of the slag and sand samples (July 2003)

Phosphorus Forms (mg P.kg^{-1})	**Fresh Slag (Blank)**	**Slag taken from Slag System**	**Sand taken from Gravel System**	**Sand taken from Slag System**
Loosely-Bounded P	4.92±0.68*	42.17±7.28	68.45±10.04	35.20±8.21
	[4.06-5.60]**	[34.73-54.19]	[52.75-80.0]	[24.50-43.00]
Al-Bounded P	-	-	-	-
Fe-Bounded P	1.97±0.68	6.58±3.25	6.90±1.36	28.11±3.06
	[1.33-3.08]	[3.08-11.70]	[5.04-8.60]	[25.27-31.23]
Ca-Bounded P	11.90±0.81	36.93±12.30	366.80±19.31	547.56±40.68
	[11.20-12.60]	[18.90-44.80]	[350.00-387.90]	[500.50-605.50]
Occluded-P	-	-	-	-
TOTAL	**18.79**	**85.68**	**442.15**	**610.88**

*Average Values (mg P.kg^{-1}) ± Standard Deviations (mg P.kg^{-1}) for a sample size of n=5.
**Minimum and Maximum Values [mg P.kg^{-1}].

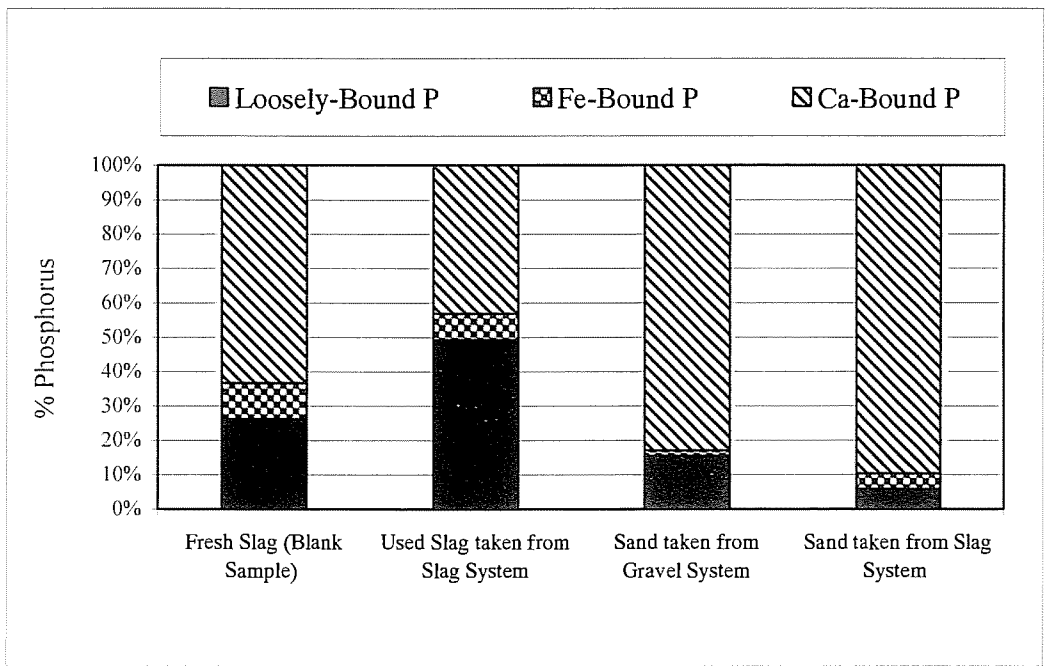

Figure 4.29. Distribution of the extracted P-forms for substrate samples (July 2003)

In this regard, it can be stated that the exact amount of P-sorbed by the sand samples could not be determined by the chemical extraction methodology proposed by Chang and Jackson (1957) and modified by Hartikainen (1979) that was used in this study. Similar findings were also recorded by Headley et al. (2003), who also performed P-extraction experiments for basaltic gravel and found higher P-adsorption values for the raw gravel than that of the gravel used in the reed beds. As noticed by Headley et al. (2003), the acidic extractants used in the methodology might have dissolved relatively large amounts of native-P from within the structure of the basaltic sand samples. As the fresh sand samples had a pH>8.15 and sand samples taken in July and November from the wetlands had a 7.9 >pH >7, sand samples were also basaltic. Hence, it was also thought that the acidic extractants used in the methodology modified by Hartikainen (1979) might have dissolved native-P from within the inner structure of the sand particles.

Moreover, Kacar (1972) indicated that when performing the Ascorbic Acid P-determination experiments using molybdate, the PO_4^{3-}-P compound reacts to form heteropoly complexes in acidic conditions (Eqn 4.1) and a characteristic molybdate blue color was observed:

$$H_3PO_4 + 12\ H_2MoO_4 \rightarrow H_3P(Mo_3O_{10})_4 + 12\ H_20 \qquad \text{Eqn(4.1)}$$

However, under certain conditions compounds like arsenic, silicium, bor, etc. reduce heteropoly complexes like P and a molybdate blue color appears. Since the concentration of P is related to the intensity of the blue colour, higher P-absorbance values are observed due to the interference of these compounds resulting in higher P-concentrations (Kacar, 1972). Similarly, some other compounds (e.g. silicium, etc.) originated from sand particles might have dissolved in the acidic extractants and reacted to form heteropoly complexes as described in Eqn 4.1 and might have resulted in higher P-fractions. Thus, it might be another possible explanation for questionable P-results for the sand samples. Nevertheless, the P-fractionation data (Figure 4.29) indicated that the formation of insoluble Ca compounds and incorporation into the more permanently removed P-compounds did play a major

role in the fixation of the P by sand if compared to the formation of Al and Fe-bound-P.

Calcium-containing alkaline slag has proved to have a high P-sorption capacity as shown earlier in batch and column experiments, but also in field investigations (Yamada et al., 1986; Mann and Bavor, 1993; Johansson, 1999 a, b; Sakadevan and Bavor, 1998). Adsorption and precipitation reactions with P were influenced in these wetland systems due to the varying pH values since pH influences availability of Fe, Al and Ca (Nichols, 1983). At low pH (3-4), Al and Fe are soluble, and reactions with these minerals predominate. As pH increases, the fixing capacity of Al and Fe is reduced and at near neutral and higher pHs, reactions with soluble Ca become more important (Brady, 1990; Richardson and Craft, 1993).

As P is known to bind with Ca at high pH, formation of calcium-phosphates was believed to be a major mechanism of P-removal by the slag systems (Baker et al., 2000). However, Johansson and Gustafsson (2000) studied P-removal by slag and showed that Ca concentration decreased with increasing P-addition. In support, they performed an ion activity determination to show that the removal mechanisms for blast furnace slag were precipitation of HAp, not other calcium phosphates. The results from the investigations of Johansson and Gustafsson (2000) indicated that direct HAp formation was the predominant P-removal mechanism when a model P-solution was added to slag materials.

Based on the chemical analysis of the slag samples (Table 4.4), the Ca content of the blast furnace granulated slag of KARDEMİR was very high (33%). Since slag was high in lime, it produced an effluent with high pH. The monitored pH values of the effluents of the slag wetland system varied between 7.11 and 8.56 and were higher than the influent pH values that varied between 7.2 and 8.06 (Appendix A, Figure A.1). Therefore, the higher P-removal capacity of slag system was also thought to be due to the higher amounts of easily leached Ca and seeds of hydroxyapatite (HAp) or related apatites (carbonate apatite, fluorapatite) that might have functioned as seeds.

Moreover, chemical fractionation depicted that the loosely-bound P (49.22%) and Ca-P (43.10%) were found to be the predominant forms of P-mineral for the slag samples taken from the slag wetland system in July 2003 (Figure 4.29); whereas for the fresh blast furnace granulated slag samples, the dominant P-forms were Ca-P (63.32%), loosely-bound P (26.18%) and Fe-P (10.50%), respectively. At least with the methods applied within this work, Al-bound P and occluded-P could not be observed for both slag and sand samples. Thus, it was thought that the slightly basic conditions in the slag system (average pH = 7.67±0.37, see Table A.1) have favored the formation of loosely-bound P and Ca-P compounds over Fe-P, Al-P products.

The higher Ca content of the fresh slag samples (Table 4.29) also supported the idea that there were already seeds of HAp in the slag produced in KARDEMİR so that P was easily precipitated with calcium. Joko (1984) and Van Dijk and Braakensiek (1984) reported that HAp was precipitated directly from solution when hydrated lime was added to wastewaters. The critical supersaturation limit in these earlier studies ranged from 10^{2}-$10^{2.5}$ times the HAp solubility, similar to that was found in the study conducted by Johansson and Gustafsson (2000).

The critical supersaturation limit is not likely to be constant but it would be related to certain other factors such as pH, contact time and the initial amount of Ca phosphates in the material. The slag samples indicated a pH effect on the critical supersaturation limit-a higher supersaturation is needed at lower pH (Johansson and Gustafsson 2000). As Joko (1984) indicated, the critical supersaturation limit can also be considerably lowered (implying a higher P removal effciency) if HAp seeds are initially present in the sorbent. Johansson and Gustafsson (2000) also stated that the alkalinity may be important in limiting the extent of HAp precipitation, as CO_3^{-2} ions may remove Ca^{2+} through calcite precipitation. Thus, Ca-containing materials may be less efficient P-retainers if the alkalinity is high.

This was also observed for the slag system implemented at METU. The pH values of the effluent of the slag wetland system (Table A.1) decreased in time which

might be due to the removal of Ca^{+2} by CO_3^{2-}. A possible decrease in the free calcium ions might have resulted in a decrease of the P-retention capacity of the slag system as the time passed. Since the Ca determination experiments accounted all of the Ca forms (Table 4.29), including the Ca^{+2} ions precipitated with CO_3^{2-}, there was not any significant decrease in the Ca amounts of the slag samples taken in July. Moreover, Geller (1998) emphasized that the sorption capacity in artificial wetlands is not generally limited because of the input of Ca, Fe, and Al by wastewater. In this regard, calcium ions of the wastewater might have also contributed to Ca content of the slag material.

The loosely-bound P fraction could consist mainly of adsorbed-P that is available for plant uptake. Adsorption of P occurs rapidly and is potentially reversible if a change takes place in the pH, redox potential or equilibrium P-concentration (Grobbelaar, and House, 1995; Hillbricht-Ilkowska et al., 1995). Therefore, the weakly-bound P fraction did not represent a permanently removed P pool. However, once P was held at the filter media surface by adsorption, it might become more permanently bound through inner-sphere complexation and precipitation reactions (Frossard et al., 1995; Sparks, 1995). In this way, weakly bound-P might gradually progress into the Ca-associated P fraction to be more permanently removed (Headley et al., 2003).

Detailed knowledge on the P-retention mechanisms of the slag materials used in the wetlands can elucidate the longevity and potential suitability as fertilizers or soil conditioners in the agriculture. Johansson and Hylander (1998) reported that P-retained by slag could be recovered to some extent by plants. Hylander et al. (1998) also showed in pot experiments with barley that P retained by slag was available for uptake by plants. However, without performing similar pot experiments and further investigations, it is difficult to state if the slag taken from the slag system that was operated at METU could be used as fertilizer efficiently.

4.11. Mass Balance Calculations for the Wetlands implemented at METU

Using the data obtained from the monitoring studies (July 2002-July 2003) for TSS, COD, PO_4^{3-}-P, TP, NH_4^+-N, NO_3^--N and TN, the total mass entering ($Mass_{in}$) and leaving ($Mass_{out}$) the wetland cells were calculated and tabulated in Appendix C (Table C.1-C-21). The sample calculations were also presented in Appendix C. The data given in Tables C.1-C.21 were summarized and presented in Table 4.32. The mean daily mass loading, removal and release rates ($g.m^{-2}.d^{-1}$) were calculated using the data of Table 4.32. by dividing first to the total surface area of the wetlands (30 m^2) and secondly to 365 day (monitoring period of 12 months). The calculated loading rates were given in Table 4.33. Since the data summarized in Table 4.33 were discussed in details in the related discussions of the findings the monitoring studies, no further discussion were done in here again.

Table 4.32. Summarized mass balance data for the water quality parameters

	VF CW SLAG SYSTEM			VF CW GRAVEL SYSTEM		
	Mass In (kg)	**Mass Out (kg)**	**Mass Removed (kg)**	**Mass In (kg)**	**Mass Out (kg)**	**Mass Removed (kg)**
TSS	73.20	26.84	46.32	73.20	36.26	36.94
COD	246.18	133.24	112.94	246.18	153.99	92.18
PO_4^{3-}-P	4.39	2.41	1.99	4.39	4.22	0.17
TP	5.93	3.42	2.51	5.93	5.50	0.43
NH_4^+-N	27.57	3.87	23.70	27.57	13.06	14.51
NO_3^--N	2.57	15.85	-13.28*	2.57	9.31	-6.74*
TN	36.06	18.51	17.55	36.06	20.86	15.20

*Negative values found in NO_3^--N indicated the production of NO_3^--N in both wetlands.

As Table 4.32 indicated, slag system has removed higher amounts of PO_4^{3-}-P, TP and NH_4^+-N compared to the vertical flow gravel system; whereas it has produced (generated) higher amounts of NO_3^--N. The statistical analyses (one-way ANOVA) given in Sections 4.7.1-4.7.5 pointed that both systems did not differ from each other statistically in terms of TSS, COD and TN removal efficiencies (%). Using the data given in Table 4.32, the percentage distribution (%) of $Mass_{out}$, the stored

or generated mass were calculated considering the $Mass_{in}$ as 100%. These percentage distributions for TSS, COD, PO_4^{3-}-P, TP, NH_4^+-N, NO_3^--N and TN were also given in Table 4.33.

Table 4.33. Mass loading and removal rates for the wetlands constructed at METU

	VF CW SLAG SYSTEM			VF CW GRAVEL SYSTEM		
Unit in: $g.m^{-2}.d^{-1}$	**Mass In**	**Mass Out**	**Mass Stored**	**Mass In**	**Mass Out**	**Mass Stored**
TSS	6.685	2.451	4.230	6.685	3.311	3.374
	**(100%)	(36.7%)	(63.3%)	(100%)	(49.5%)	(56.5%)
COD	22.482	12.168	10.314	22.482	14.063	8.418
	(100%)	(54.1%)	(45.9%)	(100%)	(37.4%)	(62.6%)
PO_4^{3-}-P	0.401	0.220	0.182	0.401	0.385	0.016
	(100%)	(54.9%)	(45.3%)	(100%)	(96.1%)	(3.9%)
TP	0.542	0.312	0.229	0.542	0.502	0.039
	(100%)	(57.7%)	(42.3%)	(100%)	(92.7%)	(7.3%)
NH_4^+-N	2.518	0.353	2.164	2.518	1.193	1.325
	(100%)	(54.1%)	(45.9%)	(100%)	(37.4%)	(62.6%)
NO_3^--N	0.235	1.447	-1.213	0.235	0.850	-0.616
	(100%)	(617%)	(-517%)	(100%)	(362%)	(-262%)
TN	3.293	1.690	1.603	3.293	1.905	1.388
	(100%)	(51.3%)	(48.7%)	(100%)	(57.8%)	(42.2%)

* Negative values found in NO_3^--N indicated the production of NO_3^--N in both wetlands.

** The values in parentheses are the calculated percentage distribution values.

A detailed mass balance approach was performed only for TP and TN, the aim of which was to determine the relative importance of each of these nutrients in different compartments (influent loading, effluent loading, plant uptake, substrate and other wetland compartments) of the constructed wetlands. In the following sections, the detailed TP and TN mass calculations for both of the wetlands of METU were presented.

4.11.1. Phosphorus Mass Balance

For the slag system, P-uptake rate by *P. australis* (above and below-ground) throughout the study was 0.0456 $g.m^{-2}.d^{-1}$ (Table 4.26) and for the gravel system it was 0.0407 $g.m^{-2}.d^{-1}$ (Table 4.26). Both of the uptake rates were almost 3 times higher than that of the values found by Headley et al., (2003). They studied the P-removal of nursery effluent with very low P concentrations (0.5 $mg.L^{-1}$) in the gravel wetlands implemented in Australia. Higher uptake rates of reeds in the wetlands of METU was thought to be normal as domestic wastewater that was applied to the reed beds had an average TP concentration of 6.61 ± 1.78 $mg.L^{-1}$, so that P were not limiting for the plants. For slag system of METU, the plants removed 19.92% of the P removed from the wetland cells. The above-ground plant biomass compartment (12.43%) was larger than the below-ground plant biomass compartment (7.49%) for the slag system. So, it was clear that absorption by plants could be an important removal mechanism depending on the conditions of the wetlands. As a result, plant biomass could be expected to influence system performance and nutrient absorption rate (Breen, 1990) depending on the type of macrophytes, density in the wetland cells, characteristics of the wastewater, hydraulic loading rate, type of wetland, climate, etc.

According to the results of the P-extraction and P-fractionation experiments done for the slag samples taken from the slag system in July (Section 4.10), the P remained in the slag material was around 70 $mg.kg^{-1}$. For an initial P concentration of ~7 $mg.L^{-1}$ that corresponded to the average P concentration of the domestic wastewater applied to the wetlands over 12 month, the adsorption capacity was determined as around 150 $mg.kg^{-1}$ (see Table B.1).

There might be several reasons, which might have caused this considerable difference between these two adsorption capacities (around 150 $mg.kg^{-1}$ and around 70 $mg.kg^{-1}$). It has been stated that a reduction in the concentration of phosphorus by uptake, flushing, or dilution could cause a release of phosphorus that has already

been adsorbed (Syers et al., 1973). The amount released would depend on the age and the solubility of the precipitate. It would be released most easily from freshly precipitated crystals and adsorbed phosphorus that had not yet penetrated particles (Brady, 1990). This might have significance for uncontrolled outdoor wetland systems like the wetlands operated in this study, especially during precipitation and snow-melt events, and also when the influent P concentrations had fluctuated. Even though the influence of organic matter (OM) on phosphorus adsorption is not well known, a negative relationship might have developed due to physical blockage of adsorption sites, or competition for sites by organic ions (Sakadevan and Bavor, 1998). On the other hand, some retention of phosphorus had been observed in association with organic matter, although most likely due to its Fe, Al and Ca content (Nichols 1983; Reed et al., 1995; Sakadevan and Bavor, 1998).

Taking into consideration the results of the P-extraction experiments, the weight of the slag used in the slag wetland system, the P-fixation compartment by slag was calculated as follows:

Mass of P fixed by Slag=(Bulk Density of Slag * Volume of Slag * P adsorbed by Slag) Eqn (4.2)

where:

Bulk Density of Slag = 1.067 $g.m^3$ (or 1067 $kg.m^{-3}$) (see Table 4.4)

Volume of Slag = Surface Area of the Slag System * Depth of Slag Layer

= 30 m^2 * 0.3 m

= 9 m^3

Weight of Slag Layer = Bulk Density of Sand * Volume of Sand

= 1067 $kg.m^{-3}$ * 9 m^3

= 9603 kg

P adsorbed by Slag = ~70 $mg.kg^{-1}$ (see Table 4.31)

TP adsorbed by Slag Layer in the Slag System = 9603 kg * 70 $mg.kg^{-1}$

= 672210 mg

So, the mass of the P-adsorbed by slag media (mostly as Ca-P and loosely-bound P) was found to be 0.672 kg, which accounted for 26.77% of the P removed in the slag system. Since not all the influent P was filterable reactive P and not all of this would have been PO_4^{3-}-P ion and available for adsorption (Breen, 1990), a portion of the influent P was in particular form, which would have been filtrated in the filter media. The amount of P filtrated in the slag system was calculated using the removed TSS data (46.32 kg) given in Table 4.32 and assuming 1.5 % of TSS removed from the system was due to P removed thorough sedimentation and filtration (Sheldon Tarre, personal communication). So, approximately 0.695 kg P was removed from the system, which accounted for 27.68% of the removed P in the slag system.

As Breen (1990) and Headley et al., (2003) suggested, the magnitude of the unaccounted-for compartment (desorption, release from the dead plants, uptake by biological assimilation, adsorption to the gravel and sand media, fixation to atmosphere as phosphin, etc.) was estimated by taking the difference between the influent loading rate and the sum of all other measured compartments. Even though it might include any cumulative errors from the measurements of all other compartments, since the other compartments could not be measured during the monitoring study, the unaccounted-for components had to be calculated as explained above. In this regard, the unaccounted-for compartment for the slag system was accounted for approximately +0.644 kg, which constituted +25.64% of the P removed from the slag system. A positive sign observed for the unaccounted-for compartment indicated the importance of the P removal mechanisms over P-generation mechanisms constituting this compartment. Similarly, Headley et al., (2003) found in their studies this compartment as ~30% of the P removed in their wetlands.

Since the unaccounted-for component (~26%) in the P data formed a significant P pool, further research should be carried out to measure and quantify the importance of seasonal litter accumulation and phosphine emissions as P removal pathways

within the constructed wetlands. In Hungary, Devai et al., (1988) measured substantial emissions of the gaseous form of P called phosphine from a constructed wetland. The release of reduced phosphine appeared to be microbially mediated. They attributed up to 50% of the deficit in a P mass balance to be due to phosphine losses. Thus, the phosphine losses might also be of significance in the reed beds of METU and contributing significantly to the unaccounted-for compartment. Moreover, since the adsorption of P to sand and gravel could not be measured with the experimental methodologies used within this dissertation thesis, adsorption/desorption to sand and gravel, as well as the sorption from slag granules, had also be evaluated within the unaccounted-for compartment for both of the wetland cells of METU.

However, the situation was different for gravel system, where almost all the removed TP (0.443 kg) was seemed to be due to a plant uptake that was calculated as 0.446 kg (Table 4.26). This result might include some cumulative errors (errors in weighing the plants, determination of TP content. etc.). However, when considering the amount of P filtrated in the gravel system, which was calculated using the removed TSS data (36.94 kg) given in Table 4.32 and assuming 1.5 % of TSS removed from the system was P (Sheldon Tarre personal communication), it could be estimated that approximately 0.554 kg P (0.0506 $g.m^{-2}.d^{-1}$) was removed from the gravel system through filtration. Nevertheless, these findings pointed out that the unaccounted-for compartment had also an important role among all the other compartments. This compartment was thought to include the P-removal mechanisms like adsorption and precipitation to the sand and gravel media; biotic assimilation; as well as the P-generating mechanisms like fixation to the atmosphere as phosphine; desorption; and release from the dead plant tissues; etc. In this regard, the TP mass balance for gravel system was established as follow:

$[Mass_{in}\text{-}Mass_{out}]$ = [Plant TP Uptake] + [Filtration] ± [Unaccounted-for Components] Eqn (4.3)

[5.93 kg -5.50 kg] = 0.443 kg + 0.554 kg ± [Unaccounted-for Components]

[Unaccounted-for Components] = – 0.567 kg (-0.0518 $g.m^{-2}.d^{-1}$)

So, the negative value of unaccounted-for component indicated that the P-generating mechanism like desorption, release from the dead tissues and microrganisms were more important than the P-removal mechanisms prevailing in the gravel system. The percentage distribution was calculated considering the mass loading (5.93 kg) to the gravel system as 100%. In this regard, the compartments namely plant P uptake, filtration and unaccounted-for components accounted for 7.47%, 9.34% and -9.56% of the $Mass_{in}$, respectively.

4.11.2. Nitrogen Mass Balance

For the slag system, N-uptake rate by the biomass of *Phragmites australis* (above and below-ground) over the entire 12 month study was 0.448 $g.m^{-2}.d^{-1}$ (Table 4.26) and for the gravel system it was 0.182 $g.m^{-2}.d^{-1}$ (Table 4.26). Plant N-uptake rate of the slag system was almost 3 times higher than that of the values found by Obarska-Pempkowiak et al., (1997), who reported plant N-uptake rate as 0.180 $g.m^{-2}.d^{-1}$. The plant-N uptake rate for the gravel system, however, was the same with the rate found by Obarska-Pempkowiak et al., (1997). For slag and gravel system of METU, the TN above-ground plant biomass compartments were higher than the TN below-ground plant biomass compartments for both of the wetland beds (Table 4.26). The N-absorption of the reeds in both of the systems was so high that the plant uptake compartments were significantly higher than the difference of the $Mass_{in}$ and $Mass_{out}$ compartments.

According to the results of the experiments that were conducted to determine the TN contents of the sand samples taken from the slag and gravel systems were 0.140 $mg.kg^{-1}$ and 0.164 $mg.kg^{-1}$ (Table 4.29), respectively. The approximate amount of the TN-fixed by the sand layer that was the top 10 cm of both of the wetland systems was calculated for slag and systems as follows:

Mass of N-fixed by Sand=(Bulk Density of Sand*Volume of Sand*N adsorbed by Sand) Eqn (4.4)

where:

Bulk Density of Sand = 1.500 $g.m^3$ (or 1500 $kg.m^{-3}$) (see Table 4.4)

Volume of Sand = Surface Area of the Wetland System * Depth of Sand Layer

= 30 m^2 * 0.1 m

= 3 m^3

Weight of Sand Layer= Bulk Density of Sand * Volume of Sand

Weight of Sand Layer = 1500 $kg.m^{-3}$ * 3 m^3 = 4500 kg

TN adsorbed by Sand in the Slag System = ~0.140 $mg.kg^{-1}$ (see Table 4.31)

TN adsorbed by Sand in the Gravel System = ~0.164 $mg.kg^{-1}$ (see Table 4.31)

so,

TN adsorbed by Sand Layer in the Slag System = 4500 kg * 0.140 $mg.kg^{-1}$

= 630 mg

TN adsorbed by Sand Layer in the Gravel System = 4500 kg * 0.164 $mg.kg^{-1}$

= 738 mg

The TN amounts that were adsorbed by the sand layer in both of the wetlands of METU were in negligible amounts (0.00063 kg and 0.00074 kg). The TN-fixed by the slag samples were also not considered in the mass balance calculations of TN.

Generally, it was accepted that 5-10% of the removed TSS in the wetlands was due to the removal of particulate TN, which was captured in the organic matter of TSS and filtrated in the filter media (Sheldon Tarre, personal communication). Assuming 6% of TSS removed from the system was TN; and using the removed TSS data for slag and gravel systems as 46.32 kg and 36.94 kg (Table 4.32), respectively; the amount of TN filtrated in the slag and gravel systems was determined as around 2.78 kg (0.254 $g.m^{-2}.d^{-1}$) and 2.22 kg (0.203 $g.m^{-2}.d^{-1}$), respectively.

For TN, the magnitude of the unaccounted-for compartment in a balanced system could usually be considered as the quantity lost to the atmosphere through

denitrification (Breen, 1990). However, TN-desorption from the filter media, TN-release from the dead plant tissues, TN-uptake by biological assimilation, etc. could also be accepted as components of the unaccounted-for compartment. Similar to the calculations done for TP mass balance, it was estimated by taking the difference between the influent loading rate and the sum of all other measured compartments. In this regard, the TN mass balance for slag and gravel systems was calculated as follow:

$[Mass_{in}-Mass_{out}]$= [Plant TN Uptake] + [Filtration] ± [Unaccounted-for Components] Eqn (4.5)

For slag wetland system:

[36.06 kg -18.51 kg] = 153.49 kg + 2.78 kg ± [Unaccounted-for Components]

[Unaccounted-for Components] = – 139.13 kg

For gravel wetland system:

[36.06"kg - 20.86 kg] = 66.36 kg + 2.22 kg ± [Unaccounted-for Components]

[Unaccounted-for Components] = – 53.34 kg

According to the above-findings, the unaccounted-for compartment for the slag system was comparable higher that that of the gravel system. A negative sign observed for the unaccounted-for compartment indicated the importance of the TN-generation mechanisms (like TN-release from the dead plant tissues and dead microorganism cells, TN-desorption from the filter media) over TN-removal mechanisms (like denitrification, TN-uptake by microorganisms). The nitrification/denitrification coupling was most often listed as the predominant source of N removal from treatment wetlands (Watson et al., 1989; Kadlec and Knight, 1996).

However, denitrification has only rarely been directly measured in wetlands used for wastewater treatment (Brodrick et al., 1988). Other denitrification estimates were based either on indirect methods or direct measurements in non-treatment

wetlands (Gersberg et al., 1984). Brodrick et al. (1988) measured denitrification using acetylene-block analysis method in a natural wetland treating secondarily treated municipal wastewater. Van Oostrum and Russel (1994) reported 3.8 $g.m^{-2}.d^{-1}$ of nitrogen removed from the wastewater (at 20°C) due to denitrification. Based on total nitrogen reductions, not direct measurement of denitrification, Gersberg et al. (1984) reported a 25% of nitrogen due to denitrification for a wetland constructed to process pretreated municipal wastewater in California, USA.

For METU case, the rate of denitrification could be not determined without conducting the above-mentioned experiments and only considering at the magnitude of the unaccounted-for compartment. Thus, it was difficult to conclude which wetland system of METU had higher denitrification capacity. However, as the higher nitrification capacity of the slag system indicated that there were more oxygenated sites in the slag system, which might have suppressed the denitrification, it can be stated that the denitrification capacity of the gravel system was higher than the slag system. Nevertheless, a detailed further research should be conducted to have certain results.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Summary

In order to foster the practical development of the constructed wetlands for water quality enhancement in Turkey, 2 two-staged subsurface flow constructed wetlands (vertical flow: 30 m^2, horizontal flow: 15 m^2, a hybrid system: 45 m^2 and total area: 90 m^2) were implemented in summer 2001 on the campus of METU to treat pre-settled domestic wastewater. The main objective of the research was to quantify the effect of different fill mediums on the nutrient removal performance of the constructed wetlands operated identically in the prevailing climate of Ankara.

Isotherm tests to screen level of P-sorption capacity of fill media were conducted. While the initial P-concentrations of the solutions changed between 0-320 $mg.L^{-1}$, the adsorption capacities for pumice mined in İzmir Cumaovası and the blast furnace granulated slag provided from the KARDEMİR Iron and Steel Company, Karabük, Turkey, varied between 0-8,300 mg $P.kg^{-1}$ and 0-9,150 mg $P.kg^{-1}$, respectively. Slag retained phosphorus more efficiently compared to pumice, hence, it was chosen as a filter material with a total depth of 60 cm in one of the hybrid wetland system of METU. Whereas, other wetland included fill media of different sizes of sand and gravel.

During the implementation phase, in 2001 the wetlands were constructed that were planted with common reeds (*Phragmites australis)* at a density of 9 shoots per square meter. Since plants did not survive in the first year, thus, in the following year the wetland cells had to be replanted and the operation phase started. Plants adapted themselves to the wetlands successfully and developed healthy root zone.

During the operation phase (July 2002-July 2003), 2 vertical flow constructed wetlands (30 m^2 each, 60 cm depth) were operated identically at a flowrate of $3m^3.d^{-1}$ and a hydraulic loading rate of 0.1 $m.d^{-1}$, intermittently. The domestic wastewater applied to the constructed wetlands of METU had lower biodegradability when compared to that of the literature values (Metcalf and Eddy, 1991). Weak characteristics of the domestic wastewater have resulted in removal of organic pollutants, as well as the removal of nitrogen and phosphorus species from the influent wastewater of the constructed wetlands of METU. For the whole monitoring period, neither mosquito, nor odor problems were observed in the hybrid constructed wetland systems at METU.

First year monitoring revealed that both vertical flow wetland systems had statistically similar TSS, COD and TN removal performances. However, the slag filled wetland with thinner biofilm formation, more surface area for adsorption and more Ca, Al and Fe content, was significantly more efficient than the gravel system for removal of ammonium and phosphorus; and production of nitrate.

The effluents from the first-stage hybrid wetlands implemented at METU met the Turkish Discharge Standards for of TSS, COD. However, only the slag system could meet the standards for TP, whereas both of the vertical flow wetlands did not meet the effluent standards for TN. However, both of the systems had higher ammonification and nitrification capacities when compared to other wetland applications in other countries. The differences in the removal performances of the wetlands constructed at METU might have resulted from the physical structures and the chemical compositions of the fill mediums, as well as the differences of the aerobic and anaerobic environments within the wetland cells.

The areal removal rate constants of TSS, COD, TP, NH_4^+-N and TN for both of the gravel and slag systems were highly comparable to the literature values. Almost for all of the parameters, the removal rate constants of winter and spring period were

lower than that of the summer and autumn period indicating the temperature effect on the kinetic parameters.

At the end of a year operation period, plant and substrates samples were analyzed for determination of some compounds, nutrients and heavy metals. Reed in the slag system grew slightly faster than that of the plants in the gravel system with below-ground biomass of 1.884-3.685 kg dry matter.m^{-2} (July and November). They were in the range of 0.5-5.0 kg dry matter.m^{-2}, as given in the literature. The above-ground biomass ranged between 1.46 and 3.85 kg dry matter.m^{-2}, which was also comparable to the literature. In the literature (Gumbricht, 1993), TN and TP content of the reed plant tissues varied between 1.8-2.1% and 0.2-0.3% of the total dry-weight biomass, respectively. Even though TP content of the plants in constructed wetlands of METU were generally comparable to the literature values, TN content was lower. However, N-uptake capacities of both systems agreed well with the literature values (Obarska-Pempkowiak, 1997). P-uptake capacities of the reeds in both systems were higher than the values reviewed by Obarska-Pempkowiak (1997). This could be due to the denser plantation in wetlands of METU, which resulted in higher biomass per unit area, thus in higher P-uptake capacities.

Even though metals were found up to certain degrees in reed biomass of the wetlands of METU, any plant kills were observed at least during the monitoring period of one year. The plant biomass of the gravel system stored higher amounts of Na, K, Fe, Cu, Mn, Mg and Ca than that of the slag system. Reed plants harvested from the slag and gravel systems accumulated higher levels of Na, Fe, Mn, Mg, and Ca in their below-ground parts than in their above-ground parts, which were also shown in numerous studies from natural and constructed wetlands (Vymazal, 1995).

To fractionate the inorganic phosphorus forms retained by sand and slag layers of the wetlands of METU P-extraction experiments were conducted. Both slag and sand adsorbed phosphorus in the forms of TP and P available for plants to certain

degrees. For the slag samples, almost all the P results found in different laboratories were highly comparable to each other; however, they were questionable for sand samples. Due to its P-binding capacity with Ca at high pH, formation of calcium phosphates (HAp) was believed to be a major mechanism of phosphorus removal by the slag systems. Similarly, for the slag samples taken from the slag wetland system of METU, chemical fractionation showed that the loosely-bound P (49.22%) and Ca-P (43.10%) were predominant forms of P-mineral.

Different removal mechanisms were dominant in each of the vertical flow wetlands constructed at METU. Following a mass balance approach for a period of 12 months, the effect of the major removal mechanisms on TP and TN removal were determined. For the slag system, the TP adsorbed by the slag particles, plant uptake, filtration and unaccounted-for components were 26.77%, 19.92%, 27.68% and +25.64% of the stored TP mass, respectively. A positive sign indicated the importance of the P removal mechanisms over P-generation mechanisms constituting this compartment. For the gravel system, the compartments namely plant P uptake, filtration and unaccounted-for components accounted for 7.47%, 9.34% and -9.56% of the stored TP mass, respectively. The negative value of unaccounted-for component indicated that the P-generating mechanism (like desorption, release from the dead tissues and microorganisms, etc.) were more important than the prevailing P-removal mechanisms (like biological uptake by plants and microorganisms, adsorption to sand and gravel media, fixation to atmosphere as phosphine, etc.) in the gravel system.

For the slag system, N-uptake rate by the biomass of *Phragmites australis* (above and below-ground) over the entire 12 month study was 0.448 $g.m^{-2}.d^{-1}$ and for the gravel system it was 0.182 $g.m^{-2}.d^{-1}$. For both of the wetlands of METU, the TN above-ground plant biomass compartments were larger than the TN below-ground plant biomass compartments for both of the wetland beds. The TN amounts that were adsorbed by the sand layer in both of the wetlands of METU were in negligible amounts. The amount of TN filtrated in the slag and gravel systems was found as approximately 2.78 kg and 2.22 kg, respectively.

For TN, the magnitude of the unaccounted-for compartment in a balanced system could usually be considered as the quantity lost to the atmosphere through denitrification (Breen, 1990), TN-desorption from the filter media, TN-release from the dead plant tissues, TN-uptake by biological assimilation, etc (Vymazal et al., 1998). The unaccounted-for compartment for the slag system was comparable higher that that of the gravel system. The unaccounted-for compartment indicated for both of the systems the importance of the TN-generation mechanisms (like TN-release from the dead plant tissues and dead microorganism cells, TN-desorption from the filter media) over TN-removal mechanisms (like denitrification, TN-uptake by microorganisms). Higher nitrification capacity of the slag system indicated that there were more oxygenated sites in the slag system, which might have suppressed the denitrification. Hence, it was claimed that the denitrification capacity of the gravel system was higher than the slag system.

5.2. Conclusion

As being one of the leading studies for implementation of the pilot-scale constructed wetlands in Turkey, this study contributed to the understanding of how vertical subsurface flow constructed wetlands with different fill media functioned under the prevailing climate in Ankara. The use of blast furnace granulated slag as a wetland fill media in a field application on a long-term basis indicated that it can be used as a suitable filter media in subsurface flow constructed wetlands due to the its rather stable phosphorus sorption capacity and higher ammonium removal efficiency. This study depicted that the subsurface constructed wetlands can be operated at significantly high hydraulic loading rates (110 $mm.d^{-1}$) and still can meet the effluent standards. This study also revealed that properly designed and operated constructed wetlands have a great potential for secondary and tertiary wastewater treatment in Turkey, especially in rural areas.

5.3. Recommendations for Future Studies

According to the knowledge and experience acquired during this dissertation, the followings are recommended for the further constructed wetland studies:

1. Before implementing a full-scale constructed wetland for any purpose at any site, it is strongly recommended to start of with a pilot-scale constructed wetlands at that site. These pilot-scale wetlands should be operated under the same prevailing conditions that will be also valid for the full-scale application. Moreover, monitoring studies should be performed at least for one year.
2. The macrophytes that will be planted into the constructed wetlands should come from the natural flora of the local area, if possible. The use of exotic species in the constructed wetland applications, especially in surface flow wetlands, should be prevented.
3. Due to the limited budget of the project, at the bottom of the wetland cells of METU, cheaper nylon liner had to be used as a sealing material instead of using expensive geomembrane, concrete, clay, etc. To prevent any leakage from the bottom of the wetland cells to the groundwater or to the underlying soil layers, thicker impermeable layers should be preferred as a sealing material
4. While monitoring the influent and effluent water quality parameters, to monitor the concentrations of the pollutants in the different layers of the wetland filter media, as well as the dissolved oxygen, redox potential, pH could give a comprehensive understanding to understand the wetland removal processes.
5. To improve the understanding for the natural processes that are proceeding in the constructed wetlands, more detailed monitoring studies should be performed with an interdisciplinary team. To elucidate the importance of the removal processes, specific methodologies should be developed for the wetland compartments (air, plant, water, substrate, sediment, microorganisms, etc.) each of which might have a crucial role in the treatment performance of the constructed wetlands.

6. To distinguish between adsorbed and precipitated products in the filter media, X-ray fluorescence and scanning electron microscopy can be used, if available.
7. Figures generated from P-adsorption isotherm tests must be used with caution. They are not intended to be used for design purposes, as they represent adsorption properties from static test conditions, not from the field conditions.
8. While considering the cost of the constructed wetlands, the operation and maintenance cost should also be evaluated even though its value will be still very lower than that of the chemical treatment alternatives.
9. To understand the role of the plants, filter media, operating conditions, design configurations, climate, etc., various pilot-scale wetland experiments should be performed and monitored under varying conditions.

REFERENCES

Abwasser Technische Vereinigung (ATV), 1998. "Grundsatze für Bemessung, Bau und Betrieb von Pflanzenbeeten für kommunales Abwasser bei Ausbaugrössen bis 1000 Einwohnerwerte", Germany.

Abbona, F. and Franchini-Angela, M., 1995. "Crystallization of Hydroxyapatite from very Dilute Solutions". Neues Jahrbuch für Mineralogie Monatshefte Vol: 12, pg. 563-575.

Akca, L., Tuna, M., Sevimli, M.F., Bayhan, H., 1998. "Wastewater Treatment in Constructed Wetlands". *First International Workshop on Environmental Quality and Environmental Engineering in the Middle East Region,* Konya, Turkey.

Ayaz, Ç.S., and Saygın, Ö. (1996). "Hydroponic Tertiary Treatment", Water Research, Vol: 30(5), 1295-1298.

Allen, L.H., 1997. "Mechanics and Rates of Oxygen Transfer to and Through Submerged Rhizomes and Roots via Aerechyma". *Soil and Crop Science Society, Florida Proc.*, Vol: 56.

Ann, Y. Reddy, K.R., Delfino, J.J., 1999. "Influence of Chemical Amendments on Phosphorus Immobilization in Soils from a Constructed Wetland". *Ecological Enginering*, Vol: 14(1-2), pg. 157-167.

Armstrong, J. and Armstrong, W. 1990. "Pathways and Mechanisms of Oxygen Transport in *Phragmites australis*". In: *Constructed Wetlands in Water Pollution Control*, No 11, Pergamon Press, Oxford.

Armstrong, W., Armstrong, J., Beckett, P.M., and Justin, S.H.F.W., 1991. "Convective Gas-Flows in Wetland Plant Aeration". In: Plant Life Under Oxygen Deprivation".SPB Academic Publishing. The Hague, The Netherlands, pg. 283-302.

Ayaz, S.Ç. and Akça, L., 2000. "Treatment of Wastewater by Constructed Wetland in Small Settlements". *Water Science and Technology*, Vol: 41(1), pg. 69-72, Oxford.

Ayaz, S.Ç. and Akça, L., 2001. "Treatment of Wastewater by Natural Systems". *Environment International,* Vol: 26 (3), pg. 189-195.

Baker, M.J., Blowes, D.W., Ptacek, C.J., 1998. "Laboratory Development of Permeable Reactive Mixtures for the Removal of Phosphorus from Onsite Wastewater Disposal Systems". In On-Site Wastewater Systems: Protecting the Environment into the Next Millenium Conference Proceedings, Missiisauga, ON.

Baker, M.J., Blowes, D.W., Ptacek, C.J., 2000. "Development of a Reactive Mixture to Remove Phosphorus from On-site Wastewater Disposal Systems". In: *On-Site Wastewater Systems: Protecting the Environment into the Next Millenium Conference Proceedings*, Missiisauga, ON.

Bastian, R.K., Benforado, J., 1983. "Waste Treatment: Doing What Comes Naturally". *Technol. Rev.* 86(2):58.

Bastian, R.K. (ed), 1993. "Constructed Wetlands for Wastewater Treatment and Wildlife Habitat: 17 Case Studies". USEPA 832-R-93-005, Municipal Technology Branch, Washington.

Bastian, R.K., Hammer, D.A., 1993. "The Use of Constructed Wetlands for Wastewater Treatment and Recycling". *Constructed Wetlands for Water Quality Improvement*, CRC Press, Florida.

Bavor, H.J., Schulz, T.J., 1993. "Sustainable Suspended Solids and Nutrient Removal in Large-Scale, Solid-Matrix, Constructed Wetland Systems". In: Moshiri, G.A. (eds.), Constructed Wetlands for Water Quality Improvement, CRC Press, Boca Raton, Florida, pg. 219-25.

Bavor, H.J. and Mitchell, D.S. (ed), 1994. "Wetland Systems for Water Pollution Control". *Water Science and Technology*, Vol: 29(4), Oxford.

Bayley, M.L., Davison, L., Headley, T.R., 2003. "Nitrogen Removal from Domestic Wastewater Effluent Using Subsurface Flow Constructed Wetlands: Influence of Depth, Hydraulic Residence Time and Pre-Nitrification". *Water Science and Technology*, Vol: 48(5), pg. 175-182.

Benefield, L.D., Judkins, Jr., Weand, B.L., 1982. "Process Chemistry for Water an Wastewater Treatment" Prentice-Hall Inc, Englewood Cliffs, NJ.

Boyd, C.E., 1975. "Chemical Composition of Wetland Plants". In: Freshwater Wetlands: Ecological Processes and Management Potential (Ed. Good, R.E. et al.), pg. 155-167. Academic Press, New York.

Börner, T., 1992. "Einflussfaktoren für die Leistungsfahigkeit von Pflanzenklaranlagen". *Schriftenreihe WAR*, TH, Darmstadt, 58.

Börner, T., Von Felde, K., Gschlössl, E., Kunst, S., Wissing, F.W., 1998. "Germany". In: Vymazal, J., Brix, H., Cooper, P.F., Green, M.B., Haberl, R. (ed), *Constructed Wetlands for Wastewater Treatment in Europe*. Backhuys Publishers, Leiden.

Brady, N.C., 1990. *The Nature and Properties of Soils*. 10th Eddition, Macmillan Publishing Company, NY.

Breen, P.F., 1990. "A Mass Balance Method for Assessing the Potential of Artificial Wetlands for Wastewater Treatment". *Water Research,* Vol: 24(6), pg. 689-697.

Brenner, 2000. "Use of Constructed Wetlands for Acid Mine Drainage Abatement".In: *Proceedings of the IWA 7th International Conference on Wetland Systems for Water Pollution Control*, Lake Buena Vista, Florida.

Brix, H. and Schierup, H.-H., 1990. "Soil Oxygenation in Constructed Reed Beds: The Role of Macrophyte and Soil Atmosphere Interface Oxygen Transport". In Cooper, P.F., and Findlater, B.C. (eds.), *Constructed Wetlands in Water Pollution Control*, Pergamon Press, Oxford, UK, pg. 53-66.

Brix, H., 1990. "Gas Exchange through the Soil-Atmosphere Interface and through dead Culms of *Phragmites australis* in a Constructed Reed Bed receiving Domestic Sewage". *Water Resource*, Vol: 24.

Brix, H., 1993. "Wastewater Treatment in Constructed Wetlands: System Design, Removal Processes and Treatment Performance". In: Moshiri, G.A. (ed), *Constructed Wetlands for Water Quality Improvement*, CRC Press, Boca Raton, Florida.

Brix, H., 1994. "Constructed Wetlands for Municipal Wastewater Treatment in Europe". In: Mitsch, W.J. (Ed.), Global Wetlands; Old World and New. Elsevier, Amsterdam, pg. 325–334.

Brix, H., Sorrell, B.K., Schierup, H.-H., 1996. "Gas Fluxes achieved by in-situ convective flow in *Phragmites australis*". *Aquatic Botany*, Vol: 54, pg. 151-163.

Brix, H., 1997. "Do Macrophytes play a Role in Constructed Wetlands?". *Water Science and Technology*, Vol: 35(5), pg. 11-17.

Brix, H., 1998. "Denmark". In: Vymazal, J., Brix, H., Cooper, P.F., Green, M.B., Haberl, R. (ed), Constructed Wetlands for Wastewater Treatment in Europe, Backhuys Publishers, Leiden.

Brodrick, S.J., Cullen, P., Maher, W., 1988. "Denitrification in a Natural Wetland Receiving Secondary Treated Effluent." *Water Research*, Vol: 22(4), 431-439.

Brooks, A.S., Rozenwald, M.N., Geohring, L.D., Lion, L.W., Steenhuis, T.S., 2000. "Phosphorus Removal by Wollastonite: A Constructed Wetland Substrate". *Ecological Engineering*, Vol: 15, pg. 121-132, Elsevier Science.

Chang, S.C., Jackson, M.L., 1957. "Fractionation of Soil Phosphorus". *Soil Sci.* Vol: 84, 133-144.

Comin, F.A., Romero, J.A., Astorga, V. and Garcia, C., 1997. "Nitrogen Removal and Cycling in Restored Wetlands Used as Filters of Nutrients for Agricultural Runoff". *Water Science and Technology*, Vol: 35(5), Oxford.

Cooke, L.G. 1994. "Nutrient Transformatins in a Natural Wetland Receiving Sewage Effluent and the Implications for Waste Treatment". *Water Science and Technology*, Vol: 29(4), Oxford.

Cooper, P.F., Findlater, B.C., 1990. *Constructed Wetlands in Water Pollution Control.* Pergoman Press, New York.

Cooper, P. and Green, B., 1994. "Reed Bed Treatment Systems for Sewage Treatment in the U.K.-the First 10 Years Experience". In: *Proceedings of the 4th IAWQ Conference on Wetland Systems in WaterPoll. Control*, Guangzhou.

Cooper, P., Smith, M. and Maynard, H., 1996. "The Design and Performance of a Nitrifying Vertical Flow Reed Bed Treatment System". *Water Science and Technology*, Vol: 35(5), Oxford.

Cooper, P., 1999. "A Review of the Design and Performance of Vertical-flow and Hybrid Reed Bed Treatment Systems" . *Water Science and Technology*, Vol: 40 (3), Oxford.

Cooper, D.J. and Willoughby, N., 1999. "Dewatering of Sludge at Small Sewage Treatment Works using Reed Beds. In: 4th European Biosolids and Organic Residuals Conference, Wakefield, Yorkshire, 15-17 November 1999, Aqua-Enviro and C.I.W.E.M.

Crites, R.W., Reed, S.C., Middlebrooks, E.J., 1995. *Natural Systems for Waste Management and Treatment.* McGraw-Hill, Inc., Tokyo.

Crolla, A., Hurd, S., Weil, C., McBride, N., 2000. "Treatment of Municipal Wastewater in Rural Areas-The Alfred Pilot System (Phosphorus Adsorption)-Interim Report". College d'Alfred-Universite de Guelph. Alfred ON.

Crumpton, 2000. "Using Wetlands for Water Quality Improvement in Agricultural Watersheds; The Importance of a Watershed Scale Approach". In: *Proceedings of the IWA 7th International Conference on Wetland Systems for Water Pollution Control*, Lake Buena Vista, Florida.

Davies, T.H., Watson, J.T. and Jenkins D.B., 1990. "Treatability Assessment of Industrial Wastes By A Portable Wetland Unit". In: *Constructed Wetlands In Water Pollution Control.* WRc Swindon, Wiltshire, UK.

De Maesener, J.L., 1997. "Constructed Wetlands for Sludge Dewatering". *Water Science and Technology*, Vol: 35(5), 279-285, Oxford.

Denny, P., 1997. "Implementation of Constructed Wetlands in Developing Countries". *Water Science and Technology*, Vol: 35(5), Oxford.

Devai, I., Felfoldy, L., Wittner, I., 1988. "Detection of Phosphine: New Aspects of the Phosphorus Cycle in the Hydrosphere". *Nature*, Vol: 333, 343-345.

Diaz, O.A., Reddy, K.R., Moore, P.A., 1994. "Solubility of Inorganic Phosphorus in Stream Water as Influenced by pH and Ca Concentration". *Water Res.*, Vol: 28, pg. 1755-1763.

Dinges, R., 1982. *Natural Systems for Water Pollution Control*, Van Nostrand Reinhold, New York.

Dortch, M.S., 1996. "Removal of Solids, Nitrogen, and Phosphorus in the Cache River Wetland". *Wetlands*, Vol: 16(3), The Society of Wetland Scientists, Vicksburg.

Drizo, A., Frost, C.A., Grace, J., Smith K.A., 1999. "Physico-Chemical Screening of Phosphate-Removing Substrates for Use in Constructed Wetland Systems". *Water Research*, Vol: 33(7):3595-3602.

Dunhabin, J.S., Pokorny, J. and Bowmer, K.H., 1988. "Rhizosphere oxygenation by Typha domingensis Pers. in Miniature Artificial Wetland Filters used for Metal Removal from Wastewaters". *Aquatic Botany*, Vol: 29.

Edwards et al, 2000. "Reed Bed Dewatering of Agricultural Sludges and Slurries". In: *Proceedings of the IWA 7th International Conference on Wetland Systems for Water Pollution Control*, Lake Buena Vista, Florida.

Etnier, C., Guterstam, B., 1991. *Ecology Engineering for Wastewater Treatment.* Boksogen/Stensund Folk College, Sweden.

Farahbakhshazad, N. and Morrison, G.M., 2000. "Phosphorus Removal in a Vertical Upflow Constructed Wetland System". In: *Proceedings of the IWA 7th International Conference on Wetland Systems for Water Pollution Control*, Lake Buena Vista, Florida.

Faulkner, S.P., Richardson, C.J., 1989. "Physical and Chemical Characteristics of Freshwater Wetland Soils". In: Hammer, D.A., Freeman, R.J. (Eds.), Constructed Wetlands for Wastewater Treatment. Lewis Publishers, Chelsea, Michigan, pg. 41–72.

Faust, S.D., Aly, O.M., 1987. "Adsorption Processes for Water Treatment", Butterworth Publishers, Toronto, ON.

Fiala, K. "Underground Organs of *Phragmites communis*: Their Growth, Biomass and Net Production". *Folia Geobotica et Phytotaxonomica*, Vol: 11, pg. 225-259.

Froelich, P.N., 1988. "Kinetic Control of Dissolved Phosphate in Natural Rivers and Estuaries: A primer on the Phosphate Buffer Mechanism". *Limnol. Oceanogr.*, Vol: 33, pg. 649–668.

Frossard, E., Brossard, M., Hedley, M.J., Metherell, A., 1995. "Reactions Controlling the Cycling of P in Soils". In: *Phosphorus in the Global Environment-Transfers, Cycles and Management*, (Ed.) Tiessen, H., John Wiley and sons, W Sussex, 107-138.

Gale, P.M., Devai, L., Reddy, K.R. and Graetz, D.A., 1993. "Denitrification Potential of Soils from Constructed and Natural Wetlands". *Ecological Engineering*, Vol: 2.

Geary, P. M. and Moore, J. A., 1999. "Suitability of a Treatment Wetland for Dairy Wastewaters". *Water Science and Technology*, Vol: 40(3), Oxford.

Gersberg, R.M., Elkins, S.R., Goldman, C.R., 1984. "Use of Artificial Wetlands to Remove Nitrogen from Wastewater". *Journal of the Water Pollution Control Federation*, Vol: 56(2), 152-156.

Gersberg, R.M., Elkins, S.R., Lyons, S.R., Goldman, C.R., 1985. "Role of Aquatic Plants in Wastewater Treatment by Artificial Wetlands". *Water Res.*, Vol: 20, pg. 363-368.

Gopal, B., 1999. "Natural and Constructed Wetlands for Wastewater Treatment: Potentials and Problems". *Water Science and Technology*, Vol: 40(3), Oxford.

Goulet, R.R., Pick, F.R., Droste, R.L., 2001. "Test of the First-Order Removal Model for Metal Retention in a Young Constructed Wetland". *Ecological Engineering*, Vol: 17(4), pg. 357–371.

Green, M. Friedler, E., Ruskol, Y. and Safrai, I., 1997. "Investigation of alternative method for nitrification in constructed wetlands". *Water Science and Technology*, Vol: 35(5), Oxford.

Greenway, M., Woolley, A., 1999. "Constructed Wetlands in Queensland: Performance Efficiency and Nutrient Bioaccumulation. *Ecological Engineering*, Vol: 12, pg. 39–55.

Gries, C., Kappen, L., Lösch, R., 1990. "Mechanism of Flood Tolerrance in Reed, *Phragmites australis*." Trin ex. Steudel. *New Phytol.*, Vol: 114, pg. 589-593.

Grobbelaar, J.U. and House, W.A. 1995. "Phosphorus as a Limiting Resource in Inland Waters; Interactions with Nitrogen". In: In: *Phosphorus in the Global Environment-Transfers, Cycles and Management*, (Ed.) Tiessen, H., John Wiley and sons, W Sussex, 255-274.

Grüneberg, B., and Kern, J. 2001. "Phosphorus Retention Capacity of Iron-Ore and Blast Furnace Slag in Subsurface Flow Constructed Wetlands". *Water Science and Technology*, Vol: 44(11).

Gschlössl and Stuible, 2000. In: *Proceedings of the IWA 7th International Conference on Wetland Systems for Water Pollution Control*, Lake Buena Vista, Florida.

Gumbricht, T. 1993. "Nutrient Removal Processes in Freshwater Submersed Macrophyte Systems". *Ecological Engineering*, Vol: 2.

Haberl, R., Diebold, W. and Parsian, R. 1983. "Darstellung verschiedener Systeme der Abwasserreinigung mit Macrophyten". *Österreichische Wasserwirtschaft*, 35 (9/10).

Haberl, R. and Perfler, R., 1990. "Seven Years of Research Work and Experience with Wastewater Treatment by a Reed Bed System". In: *Constructed Wetlands in Water Pollution Control*, Pergamon Press, Oxford.

Haberl, R., Perfler, R., Mayer, H., 1995. "Constructed Wetlands in Europe". Water Science and Technology, Vol:32 (3), pg. 305-315, Oxford.

Haberl, R., Perfler, R., Laber, J., Grabher, D. 1998. "Austria". In: Vymazal, J., Brix, H., Cooper, P.F., Green, M.B., Haberl, R. (Eds.), Constructed Wetlands for Wastewater Treatment in Europe. Backhuys Publishers, Leiden.

Haberl, R., 1999. "Constructed Wetlands: A Chance to Solve Wastewater Problems in Developing Countries". *Water Science and Technology*, Vol: 40(3), Oxford.

Hammer, D.A., 1989. *Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural.* Lewis Publishers, Chelsea, MI.

Hammer, D.A., Rogers, P., 1980. "Treating Fish Rearing Pond Discharge Waters with Artificial Wetlands". Mimeo, Knoxville, TN.

Hartikainen, H., 1979. "Phosphorus and its Reactions in Terrestrial Soils and Lake Sediments". *J.Sci.Agric.Soc.Finl.* Vol: 51, 537-624.

Headley, T.R., Huett, D.O., Davison, L., 2003. "Seasonal Variations in Phosphorus Removal Processes within Reed Beds-Mass Balance Investigations". *Water Science and Technology*, Vol: 48(5), pg. 59-66.

Heliotis, F.D. and De Witt, C.B., 1983. "A Conceptual Model of Nutrient Cycling in Wetlands used for Wastewater Treatment: a Literature Analysis". *Wetlands,* 3, 134-152.

Herskowitz, J., Black, S., Lewandowsk, W., 1987. "Listowel Artificial Marsh Project". In: Reddy, K.R., Smith, W.H. (Eds.), Aquatic Plants for Water Treatment and Resource Recovery. Magnolia Publishers, Orlando FL, pg. 247–250.

Hieltjes, A.H.M., and Lijklema, L., 1980. "Fractionation of Inorganic Phosphates in Calcareous Sediments". J. Environ. Quality. Vol: 9 (3), pg. 405-407.

Higgins, 2000. "The Treatment of of Landfill Leachates in Engineered Wetlands". In: *Proceedings of the IWA 7th International Conference on Wetland Systems for Water Pollution Control*, Lake Buena Vista, Florida.

Hillbricht-Ilkowska, A., Ryzskowski, L., Sharply, A.N., 1995. "Phosphorus Transfers and Landscape Structure: Riparian Sites and Diversified Land Use Patterns". In: *Phosphorus in the Global Environment-Transfers, Cycles and Management*, Tiessen, H. (Eds.), John Wiley and Sons, W. Sussex, 201-228.

Hochheimer, J., Yates, C. and Cavacas, A., 1991. "Constructed Wetlands as a Nonpoint Source Control Practice". *Draft Report prepared for USEPA.*

Hocking, P.J., 1989. "Seasonal Dynamics, and Nutrient Accumulation and Cycling by *Phragmites australis* (Cav.) Trin. ex Stuedel in a Nutrient-enriched Swamp in Inland Australia: I. Whole Plants", *Australian Journal of Marine and Freshwater Research*, Vol: 40, pg. 421-444.

Howard Williams, C., 1985. "Cycling and Retention of Nitrogen and Phosphorus in Wetlands: A Theoretical and Applied Perspective". *Freshwater Biol.* 15, 391-431.

Husband, J.D., Martin C.D., Johnson, K.D., 2000. "A Review of Constructed Wetland Treatment Technologyfor Industrial Wastewater Treatment". In: *Proceedings of the IWA 7th International Conference on Wetland Systems for Water Pollution Control*, Lake Buena Vista, Florida.

Hylander, L., Johansson, L., Renman, G., Ridderstolpe, P., Siman, G., 1998. "Phosphorus Recycling from Wastewater by Filter Media used as Fertilisers". *Use of Municipal Organic Waste*, Nov. 23-25, *Agricultural Research Centre*, Joikoinen, Finland.

IWA Specialist Group on Use of Macrophytes in Water Pollution Control, 2000. Constructed *Wetlands for Pollution Control - Processes, Performance, Design and Operation, Scientific and Technical Report No:8.* Kadlec, R.H., Knight, R.L., Vzmayal, J,.Brix, H., Cooper, P., Haberl, R. (eds), International Water Association, London.

Johansson, L., 1996. "Use of Leca (Light Expanded Clay Aggregates) for the Removal of Phosphorus from Wastewater". *Water Science and Technology*, Vol: 35(5), pg. 87–94.

Johansson, L., 1997. "Use of Leca (Light Expanded Clay Aggregates) for the Removal of Phosphorus from Wastewater". *Water Science and Technology*, Vol: 35(5), 87–94.

Johansson, L. and Hylander, L., 1998. "Phosphorus Removal from Wastewater by Filter Media: Retention and Estimated Plant Availability of Sorbed Phosphorus". *Journal of Polish Academy of Science*, Vol: 458, 397-409.

Johansson, L., 1999 (a). "Blast Furnace Slag as Phosphorus Sorbent-Column Studies". *The Science of the Total Environment*, Vol: 229, 89-97.

Johansson, L., 1999 (b). "Industrial By-Products and Natural Substrata as Phosphorus Sorbents". *Environmental Technology*, Vol: 20, pg. 309-316.

Johansson, L. and Gustafsson, J.P., 2000. "Phosphate Removal from Wastewaters using Blast Furnace Slags and Opaka-Mechanisms". *Water Research* Vol: 34(1), 259-265.

Joko, L., 1984. "Phosphorus Removal from Wastewater by the Crystallization Method". *Water Science and Technology*, Vol: 17, 121-132.

Kacar, B., Kovancı, İ., 1982. "Bitki, Toprak ve Gübrelerde Kimyasal Fosfor Analizleri ve Sonuçlarının Değerlendirilmesi" Ege Üniversitesi Ziraat Fakültesi Yayınları Yayın No:354 İzmir.

Kadlec, R.H., 1985. "Aging Phenomena in Wastewater Wetlands". In: Godfrey, P.J., Kaynor, E.R., Pelczarski, Benforado, J. (Eds.), Ecological Considerations in Wetlands Treatment of Municipal Wastewaters. Van ostrand Reinhold, New York, pg. 338–347.

Kadlec, R.H. and Brix, H. (ed) 1995. "Wetland Systems for Water Pollution Control". *Water Science and Technology*, Vol: 32 (3), Oxford.

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

Kadlec, R.H., 1997. "An Autobiotic Wetland Phosphorus Model". *Ecological Engineering*, Vol: 8, pg. 145–172.

Kao, C.M. and Wu, M.J., 2000. In: *Proceedings of the IWA 7th International Conference on Wetland Systems for Water Pollution Control*, Lake Buena Vista, Florida.

Kent, D. M. (ed) 1994. *Applied Wetland Science and Technology*. CRC Press Inc., Boca Raton, Florida, USA.

Kim, B.J., 1997. "Evaluation of Sludge Dewatering Reed Beds: A Niche for Small Systems", *Water Science and Technology*, Vol: 35(6), pg. 21-28.

Kivaisi, A.K., 2001. "The Potential for Constructed Wetlands for Wastewater Treatment and Reuse in Developing Countries: A Review", *Ecological Engineering*, Vol: 16(4), pg. 545-560.

Knight, R.L. 1992. "Wetlands for Wastewater Treatment Date Base". Presented at: *Int. Conference Wetlands in Water Pollution*, Sydney, Australia.

Knight, R.L., PayneJr, V.W.E., Borer, R.E., ClarkeJr., R.A., Pries, J.H., 2000. "Constructed Wetlands for Livestock Wastewater Management". *Ecological Engineering*, Vol: 15(1-2), pg. 41-55.

Kraft, M., 1985. "Einsatzmöglichkeiten und Erfahrungen mit Pflanzenklaeranlagen". *Berichte aus Wassergütewirtschaft und Gesundheitsingenieurwesen*, TU, München.

Kreissl, J.F. and Brown, D.S. 2000. "Constructed Wetlands as Blue-Collar Treatment Systems". No:22, UK.

Kuo, J. 1999. "Mass Balance Concept and Reactor Design". *Practical Design Calculations for Groundwater and Soil Remediation,* Boca Raton: CRC Press LLC.

Küçük, Ö.S., Şengül, F., Kapdan, İ., 2003. "Treatment of Tannery Effluent by Constructed Wetland Systems: A Case Study". Chamber of Environmental Engineers, Fifth National Environmental Engineering Congress, 01-04 October 2003, Ankara, Turkey

Laber, J., Haberl, R., Perfler, R, Langergraber, G., 2000. "Influence of Substrate Clogging on the Treatment Capacity of a Vertical-Flow Constructed Wetland System". In: *Proceedings of the IWA 7th International Conference on Wetland Systems for Water Pollution Control*, Lake Buena Vista, Florida.

Langergraber, G., Haberl, R., Laber, J. and Pressl, A., 2003. "Evaluation of Substrate Clogging Processes in Vertical Flow Constructed Wetlands". *Water Science and Technology*, Vol: 48(5), pg. 25-34.

Lantzke, I.R., Mitchell, D.S., Heritage, A.D., Sharma, K.P., 1999. "A Model of Factors Controlling Orthophosphate Removal in Planted Vertical Flow Wetlands". *Ecological Engineering*, Vol: 12 (1-2), pg. 93–105.

Lee, C.C., Lin, S.D., 1999. *Handbook of Environmental Engineering Calculations,* Vol: I, McGraww-Hill, New York.

Lemos, L. and Antunes, P., 2000. "The Performance Evaluation, Through Modelling, of a Constructed Wetland Integrated in an Agro-Industrial Ecological Engineering System". In: *Proceedings of the IWA 7th International Conference on Wetland Systems for Water Pollution Control*, Lake Buena Vista, Florida.

Lienard, A., Esser, D., Deguin, A., Virloget, F., 1998. "Sludge Dewatering and Drying in Reed Beds: An Interesting Solution?". In: *Constructed Wetlands in Water Pollution Control*, P.F Cooper and B.C. Findlater (ed.), Pergamon Press, Oxford, pg. 257-267.

Lienard, A., Duchene, Ph., Gorini, D., 1995. "A Study of Activated Sludge Dewatering in Experimental Reed-Planted or Unplanted Sludge Drying Beds". *Water Science and Technology*, Vol: 32(3), 251-261.

Lienard, A., Coutin, C., Esser, D., 1998. "France". In: Vymazal, J., Brix, H., Cooper, P.F., Green, M.B., Haberl, R. (Eds.), *Constructed Wetlands for Wastewater Treatment in Europe*. Backhuys Publishers, Leiden.

Luederitz, V., Eckert, E., Lange-Weber, M., Lange, A., Gersberg, R., 2001. "Nutrient Removal Efficiency and Resource Economics of Vertical Flow and Horizontal Flow Constructed Wetlands". *Ecological Engineering*, Vol: 18(2), pg. 157-171.

Luker, M. and Montague, K., 1994. *Control of Pollution from Highway Discharges, Report 142*, CIRIA, London.

Lundager-Madsen, H. E., Christensson, F., Polyak, L. E., Suvorova, E. I., Kliya, M. O. and Chernov, A., 1995. "Calcium Phosphate Crystallization under Terrestrial and Microgravity Conditions". *Journal of Crystal Growth*, Vol:152, 191-202.

Maehlum, T., 1998. "Wetlands for Treatment of Landfill in Cold Climates". In: *Constructed Wetlands for the Treatment of Landfill Leachates*, Lewis Publishers, Boca Raton, Fl.

Maehlum, T., Stalnacke, P., 1999. "Removal Efficiency of Three Cold-Climate Constructed Wetlands Treating Domestic Wastewater: Effects of Temperature, Seasons, Loading Rates and Input Concentrations". *Water Science and Technology*, Vol: 40(3), pg. 273-281.

Mann, R.A., 1990. "Phosphorus Removal by Constructed Wetlands: Substratum Adsorption". In: Cooper, P.F., Findlater, B.C. (Eds.), *Constructed Wetlands in Water Pollution Control.* Pergamon Press, Oxford UK, pg. 97–406.

Mann, R.A., Bavor, H.J., 1993. "Phosphorus Removal in Constructed Wetlands Using Gravel and Industrial Waste Substrate". *Water Science and Technology*, Vol: 27, pg. 107-113.

Mann, R.A., 1997. "Phosphorus Adsorption and Desorption Characteristics of Constructed Wetland Gravel and Steelworks Byproducts". *Austr. J. Soil Res.* , Volume 35, pg. 375–384.

Martin, C.D. and Johnson, K.D., 1995. "The use of extended aeration and in-series surface-flow wetlands for landfill leachate treatment". *Water Science and Technology,* Vol: 32 (3), Oxford.

Martin, M., Johnson, K.D. and Moshiri, G.A., 1999. "Performance of A Constructed Wetland Leachate Treatment System at the Chunchula Landfill, Mobile County, Alabama". *Water Science and Technology*, Vol: 40(3), Oxford.

McDowell, H., Gregory, T. M. and Brown W. E. 1977. *J. Res. Natl. Bur. Std.* (US) 81A, 273.

Metcalf and Eddy, (Eds.), 1991. *Wastewater Engineering: Treatment, Disposal, and Reuse.* McGraw-Hill Series in Water Resources and Environmental Engineering. New York.

Mitsch, W.J., Cronk, J.K., 1992. "Creation and Restoration of Wetlands: Some Design Consideration for Ecological Engineering". *Adv. Soil Sci.*, Vol: 17, pg. 217–255.

Mitsch, W.J., and Gosselink, J.G., 1993. *Wetlands (Second Edition).* Van Nostrand Reinhold, New York, U.S.

Middlebrooks, J., 1987. "Research and Development Needs for Utilization of Aquatic Plants for Water Treatment and Resource Recovery".(Ed) Reddy, K.R. and Smith, W.H., pg. 1009-1011.

Moshiri, G.A., 1993. *Constructed Wetlands for Water Quality Improvement.* Lewis Publishers, CRC Press, Boca Raton, Florida, USA.

Naylor, S., Brisson, J., Labelle, M.A., Drizo, A., Comeau, Y., 2003. "Treatment of Fresh Fish Farm Effluent Using CWSS-The Role of Plants and Substrate". *Water Science and Technology*, Vol: 48(5), pg. 215-222.

Newbold, D.J., Elwood, J.W., O'Neil, R.V., Sheldon, A.L., 1983. "Phosphorus Dynamics in a Woodland Stream Ecosystem: A Study of Nutrient Spiraling. *Ecology,* Vol: 64, pg. 1249–1263.

Njau, K.N., Minja, R.J.A. and Katima, J.H.Y., 2003. "Pumice Soil: A Potential Wetland Substrate for Treatment of Domestic Wastewater". *Water Science and Technology*, Vol: 48(5), pg. 85-92.

Nichols, D.S., 1983. "Capacity of Natural Wetlands to Remove Nutrients from Wastewater". *Journal of the Water Pollution Control Federation*, Vol: 55(5), pg. 495-505.

Nielsen, S.M., 1990. "Sludge Dewatering and Mineralisation in Reed Bed Systems". In: *Constructed Wetlands in Water Pollution Control*, P.F Cooper and B.C. Findlater (ed.), Pergamon Press, Oxford, pg. 245-255.

Nielsen, S.M., 1995. "Biological Sludge Drying in Reed Bed Systems-Six Years of operating Experiences", *Water Science and Technology*, Vol: 32(3), pg. 447-457.

Nix, R., 1999. *An Introduction to Surface Chemistry.* Queen Mary and Westfield College, University of London. http://www.chem.qmw.ac.uk/surfacs /scc

Nur Onar, A., Balkaya, N., Akyuz, T., 1996. "Phosphate Removal by Adsorption". *Enve. Tech.*, Vol: 17, pg. 207-213.

Nuttall, P.M., Boon, A.G., Rowell, M.R., 1997. *Review of the Design and Management of Constructed Wetlands, Report 180.* Construction Industry Research and Information Association, London.

Obarska-Pempkowiak, H., 1997. "Seasonal Variations in the Efficiency of Nutrient Removal from Domestic Effluent in a Quasi-Natural Field of Reeds (*Phragmites australis*)". *Ecological Engineering for Wastewater Treatment.* (Ed. Etnier, C and Guterstam), Lewis Publisher, Boca Raton, pg. 207-216.

Obarska-Pempkowiak, H., 2000. "Retention of Selected Heavy Metals: Cd, Cu, Pb in a Hybrid Wetland System". In: *Proceedings of the IWA 7th International Conference on Wetland Systems for Water Pollution Control*, Lake Buena Vista, Florida
O'Hogain, S., 2003. "The Design, Operation and Performance of a Municipal Hybrid Reed Bed Treatment System". *Water Science and Technology*, Vol: 48(5), pg. 119-126.

Olsen, R.A., Clark, R.B., Bennett, J.H., 1981. "The Enhancement of Soil Fertility by Plant Roots". *American Scientists*, Vol: 69 (July-August), 1981, pg. 378-384.

Pant H.K., Reddy, K.R., Lemon E., 2001. "Phosphorus Retention Capacity of Root Bed Media of Subsurface Flow Constructed Wetlands". *Ecological Engineering*, Vol: 17(4), pg. 345–355.

Patrick, W.H., Wyatt, R., 1964. "Soil Nitrogen Loss as a Result of Alternate Submergence and Drying". *Soil Science Soc. Am. Proc.*, Vol: 28, pg. 647- 652.

Patten, B.C., 1990. "Introduction and Overview". In: Patten, B.C. (ed), *Wetlands and Shallow Continental Water Bodies,* Vol: 1, SBP Academic Publishing , The Hague.

Phytoremediation Inventory, Cost Action 837 View (2003). Edited by Tomas Vanek and Jean-Paul Schwitzguebel, Czech Republic.

Platzer, C. and Mauch, K., 1997. "Soil clogging in Vertical-Flow Reed Beds-Mechanisms, Parameters, Consequences, and.... Solutions?" *Water Science and Technology*, Vol: 35 (5), Oxford.

Platzer, C., 2000. "Development of Reed Bed systems-A European Perspective". In: *Proceedings of the IWA 7th International Conference on Wetland Systems for Water Pollution Control*, Lake Buena Vista, Florida.

Pontier, H., Williams, J.B., May, E., 2000. "Metals in Combined Conventional and Vegetated Road Runoff Control Systems". In: *Proceedings of the IWA 7th International Conference on Wetland Systems for Water Pollution Control*, Lake Buena Vista, Florida.

Prior and Whitehead, 2000. In: *Proceedings of the IWA 7th International Conference on Wetland Systems for Water Pollution Control*, Lake Buena Vista, Florida.

Reddy, K.R., Khaleel, R., Overcash, M.R., Westermann, P.W., 1979. *A Non-point Source Model for Land Areas Receiving Animal Wastes. I. Mineralization of Organic Nitrogen.* Trans. ASAE, 22, pg. 863-876.

Reddy, K.R., Patrick, W.H., Jr., 1984. "Nitrogen Transformations and Loss in Flooded Soils and Sediment". *CRC Crit. Rev. Environ. Control*, Vol: 13, 273-309.

Reddy, K.R., Smith, W.H., 1987. *Aquatic Plants for Water Treatment and Resource Recovery*, Magnolia Pub., Orlando, FL.

Reddy, K.R., Debusk, W.F., 1987. "Nutrient Storage Capabilities of Aquatic and Wetland Plants". In Reddy, K.R., and Smith, W.H. (eds.), Aquatic Plants for Water Treatment and Resource Recovery, Magnolia Publishing, Orlando, FL, pg. 337-357.

Reddy, K.R., D'Angelo, E.M. and DeBusk, T.A., 1989. "Oxygen Transport through Aquatic Macrophytes: The Role in Wastewater Treatment". *J. of Environmental Quality,* Vol: 19.

Reddy, K.R. and D'Angelo, E.M., 1994. "Soil Processes Regulating Water Quality in Wetlands". In: *Global Wetlands-Old World and New*, Elsevier Publ., New York.

Reddy, K.R and D'Angelo, E. M., 1997. "Biogeochemical Indicators to Evaluate Pollutant Removal Efficiency in Constructed Wetlands". *Water Science and Technology,* Vol: 35 (5), Oxford.

Reddy, K.R., O'Connor, G.A., Gale, P.M., 1998. "Phosphorus Desorption Capacities of Wetland Soils and Stream Sediments impacted by Dairy Effluent". *J. Enviro. Qual.* , Vol: 27, pg. 1–10.

Reddy, K.R., Kadlec, R.H., Flaig, E., Gale, P.M., 1999. "Phosphorus Retention in Streams and Wetlands: A Review". *Crit. Rev. Environmental Science and Technology*, Vol: 29, pg. 83–146.

Reed, S.C.; Middlebrooks, E.J., Crites, R.W., 1988. *Natural Systems for Waste Management.* McGraw-Hill Book Company, New York.

Reed, S., 1992. *Constructed Wetland Design: The First Generation.* Water Env. Res, Vol: 64(6.)

Reed, S.C., and Brown, D., 1995. "Subsurface Flow Wetlands-A Preformance Evaluation". *Water Env.Research*, Vol: 67.

Richardson, C.J., and Craft, C.B., 1993. "Effective Phosphorus Retention in Wetlands: Fact or Fiction? In: Constructed Wetlands for Water Quality Improvement, Moshiri, G.A. (eds), Lewis Publisher, Boca Raton, Florida, pg. 271-282.

Richardson, C.J., Tilton, D.L., Kadlec, J.A., Chamie, J.P.M. and Wentz, W.A., 1978. "Nutrient Dynamics of Northern Wetland Ecosystems" In: *Freshwater Wetlands: Ecological Processes and Management Potential,* Academic Press, New York.

Romero, J.A., Comin, F.A. and Garcia, C., 1999. "Restored Wetlands as Filters to Remove Nitrogen". *Chemosphere*, Vol: 39.

Ross, S.M., Kaye, K.J.(eds), 1994. *Toxic Metals in Soil-Plant Systems.* Wiley, Chichesters.

Roser, D.J. and Bavor, H.J., 1994. "SWAMP. A Computerized Decision Support System for Employing Wetlands in the Biological Removal of Nutrients and Other Water Pollutants". In: *Biological Nutrient Removal 2.* Albury, Australia.

Sakadevan, K., Bavor, H.J., 1998. "Phosphate Adsorption Characteristics of Soils, Slags and Zeolite to be used as Substrates in Constructed Wetland Systems''. *Water Resources,* Vol: 32 (2), 391-399.
Sakadevan, K., Huang Zheng, and Bavor, H. J., 1999. "Impact of Heavy Metals on Denitrification in Surface Wetland Sediments Receiving Wastewater". *Water Science and Technology,* Vol: 40 (3), Oxford.

Sather, J.H. and Smith, R.D., 1984. "An Overviewof Mafor Wetland Functions and Values". FWS/OBS84/18. Western Energy and Land Use Team, U.S. Fish and Wildlife Service, Washington.

Seidel, K., 1955. "Die Flechtbinse Scirpus lacustris, in Okologie, Morphologie und Entwicklung, ihre Stellung bei den Volkern und ihre wirtschaftliche Bedeutung". *Schweizerbartsche Verlagsbuchhdlg,* Stuttgart.

Seidel, K., 1961. "Zur Problematik der Keim-und Pflanzengewasser", *Verh. International Limnology,* 14:1035.

Seidel, K., 1976. "Macrophytes and Water Purification". *Biological Control of Water Pollution,* Pennsylvania University Press, Philadelphia.

Shrestha, R.R., Haberl, R., Laber, J., Manandahr, R., Mader, J., 2000. "Application of Constructed Wetlands for Wastewater Treatment in Nepal". In: *Proceedings of the IWA 7th International Conference on Wetland Systems for Water Pollution Control,* Lake Buena Vista, Florida.

Shutes, R.B.E, Rewitt, D.M., Scholes, L.N.L., Forshaw , M., Winter, B., 2000. "An Experimental Constructed Wetland System for the Treatment of Highway Runoff in the UK". "In: *Proceedings of the IWA 7th International Conference on Wetland Systems for Water Pollution Control,* Lake Buena Vista, Florida.

Sloey, W.E., Spangler, F.L, Fetter, C.W., 1978. "Management of Freshwater Wetlands for Nutrient Assimilation". In: Freshwater Wetlands: Ecological Processes and Management Potential (Ed.) Good, R.E., Academic Press, New York, pg. 321-340.

Sovik, A., Klove, B., 2002. "Phosphorus Retention Processes in a SSF Meso-Scale Constructed Wetland". In: Proceedings of the IWA 8th International Conference on Wetland Systems for Water Pollution Control, Arusha, Tanzania.

Sparks, D.L., 1995. *Environmental Soil Chemistry.* Academic Press, San Diego, 1995.

Standard Methods for the Examination of Water and Wastewater, 1999. AWWA, Washington, USA.

Steer, D., Fraser, L., Boddy, J., Seibert, B., 2002. "Efficiency of Small Constructed Wetlands for Subsurface Treatment of Single-Family Domestic Effluent". *Ecological Engineering*, Vol: 18, pg. 429–440.

Steinberg, S.L and Coonrod, H.S., 1994. "Oxidation of the Root Zone by Aquatic Plants growing in Gravwel Nutrient Solution". *J. of Environmental Quality*, Vol: 23.

Steven, C., 1998. "The Emergence of Treatment Wetlands". *Environ. Sci. and Tech.*, News, May.

Stober, J.T., O'Connor, J.T., Brazos, B.J., 1997. "Winter and spring Evaluations of a Wetland for Tertiary Wastewater Treatment". *Water Environment Research*, Vol: 69, pg. 961-968.

Stowell, R., Ludwig, R,. Colt, J., Tchobanoglous, G., 1981. "Concepts in Aquatic Treatment Design". *J.Env. Eng. Div.*, ASCE 107.

Stuanes, A., Nilsson, P., 1987. "Investigation of Soil Treatment Systems for Septic Tank Effluent". *Fate of Phosphorus*, VATTEN 43, pg. 45-53.

Syers, K., Harris, R.F., Armstrrong, D.E., 1973. "Phosphate Chemistry in Lake Sediments". *Journal of Environmental Quality*, 2:1-14.

Tan, K.H. (1993). *Principles of Soil Chemistry*. Marcel Dekker, Inc., pg. 254-254.

Tanner, C.C., Sukias, J.P.S., Upsdell, M.P., 1998. "Relationships between Loading Rates and Pollutant Removal during Maturation of Gravel-Bed Constructed Wetlands". *J. Environ. Qual.*, Vol: 27, pg. 448–458.

Tanner, C., D'Eugenio, J., McBride, G.B., Sukias, J.P.S., Thompson, K., 1999. "Effect of Water Fluctuation on Nitrogen Removal from Constructed Wetland Mesocosms". *Ecological Engineering*, Vol: 12 (1-2), pg. 67-92.

Tanner, C., 2001. "Plant as Ecosystem Engineers in Subsurface Flow Treatment Wetlands". *Water Science and Technology*, Vol: 44(11-12).

Tchobanoglous, G.T., Burton F.L. 1991. *Wastewater Engineering: Treatment, Disposal, Reuse*. METCALF and EDDY, McGraw –Hill, New York.

Unit Operations and Unit Processes Laboratory Manual, 1984. Association of Environmental Engineering Professors.

Van Dijk, J.C. and Braakensiek, H. 1984. "Phosphate Removal by Crystallization in a Fluidized Bed". *Water Science and Technology*, Vol:17, pg. 133-142.

van Oostrom, A.J. and Russell, J.M., 1994. "Denitrification in Constructed Wastewater Wetlands Receiving High Concentrations of Nitrate". *Water Science and Technology*, Vol: 29(4), pg. 7-14.

Vymazal, J., 1995. Algae and Nutrient Cycling in Wetlands. CRC Press/Lewis Publisher, Boca Raton, Florida.

Vymazal, J., Brix, H., Cooper, P.F., Green, M.B., Haberl, R. (ed), 1998. *Constructed Wetlands for Wastewater Treatment in Europe*. Backhuys Publishers, Leiden.
Vymazal, J., 2002. "The Use of Sub-Surface Constructed Wetlands for Wastewater Treatment in the Czech Republic: 10 Years Experience". *Ecological Engineering*, Vol: 18, pg. 633-646.

Watson, J.T., Reed, S.C., Kadlec, R.H., Knight, R.L., Whitehouse, A.E., 1989. "Performance Expactations and Loading Rates for Constructed Wetlands". In: Hammer, D.A. (ed), *Constructed Wetlands for Watewater Treatment*, Michigan.

Weber, A.S. and Tchobanoglous, G., 1986. "Prediction of Nitrification in Water Hyacinth Treatment Systems". *J. Water Pollt. Control Fed.*, Vol: 58: 376.

Williams, J.D.H., Syers, J.K., Harris, R.F., Armstrong, D.E., 1971. "Fractionation of Inorganic Phosphorus in Calcareous Lake Sediments". *Soil Sci.Soc.Am.Proc.*, Vol: 35, pg. 250-255.

Wynn, T.M., Liehr, S.K., 2001. "Development of a Constructed Subsurface Flow Wetland Simulation Model". *Ecological Engineering*, Vol: 16(4), pg. 519-536.

Wood, R.B., McAtamney, C.F., 1996. "Constructed Wetlands for Wastewater Treatment: The Use of Laterite in the Bed Medium in Phosphorus and Heavy Metal Removal". *Hydrobiologia*, Vol: 340, pg. 323–331.

Yamada, H., Kayama, M., Saito, K., Hara, M., 1986. "A Fundamental Research on Phosphate Removal by Using Slag". *Water Research,* Vol: 20(5), pg. 547-557.

Yıldız, C., Korkusuz, E.A., Arıkan, Y., Demirer, G.N., 2004. "Constructed Wetlands for Municipal Wastewater Treatment: A Study from Turkey". In: *Proceedings of the IWA 9th International Conference on Wetland Systems*, Avignon, France.

Zhu, T., Jenssen, P.D., Maehlum, T., Krogstad, T., 1997. "Phosphorous Sorption and Chemical Characteristics of Lightweight Aggregates (LWA)-Potential Filter Media in Treatment Wetlands", *Water Science and Technology*, Vol: 35(5), Oxford.

Zhu, T., Maehlum, T., Jenssen, P.D., Krogstad, T., 2002. "Fate of Phosphorus In A Light-Weight Aggregate Wastewater Treatment Wetlands". In: *Proceedings of the IWA 8th*

International Conference on Wetland Systems for Water Pollution Control, Arusha, Tanzania, pg. 556-566.

Zhu, T., Maehlum, T., Jenssen, P.D., Krogstad, T., 2003. "Phosphorus Sorption Characteristics of a Light-Weight Aggregate". *Water Science and Technology*, Vol: 48 (5), pg. 93-100.

Zurayk, R., Nimah, M., Geha, Y., Rizk, C., 1997. "Phosphorus Retention in the Soil Matrix of Constructed Wetlands". *Commun. Soil Sci. Plant Anal.*, Vol: 28, pg. 521–535.

APPENDIX A

A.1. CALIBRATION CURVES

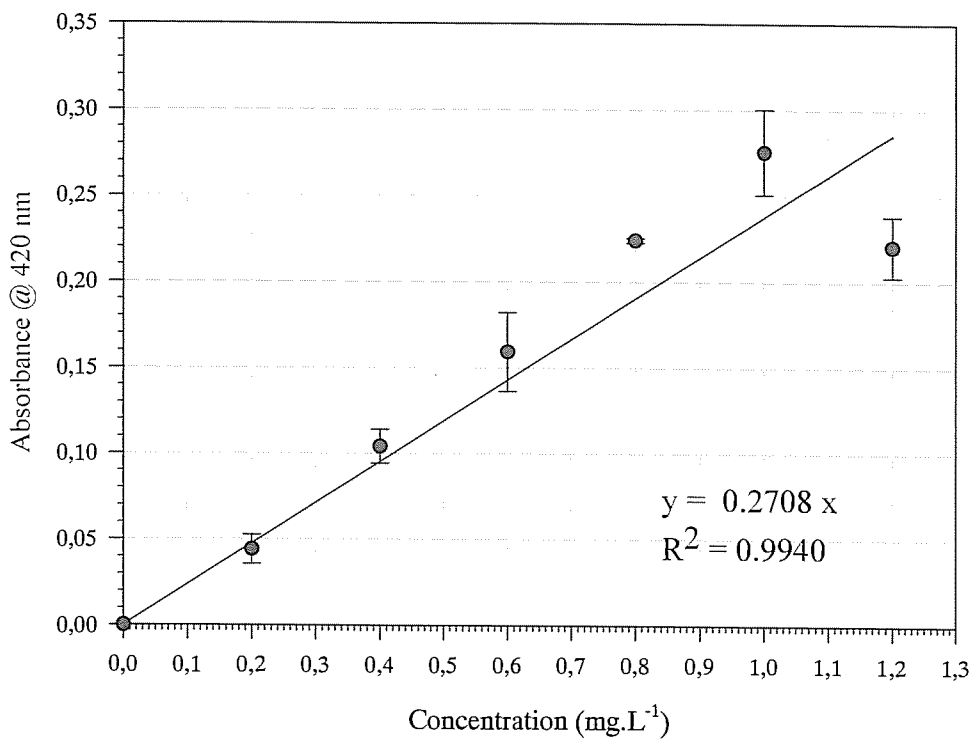

Figure A.1. NH_4^+-N Calibration Curve (27.07.2002)

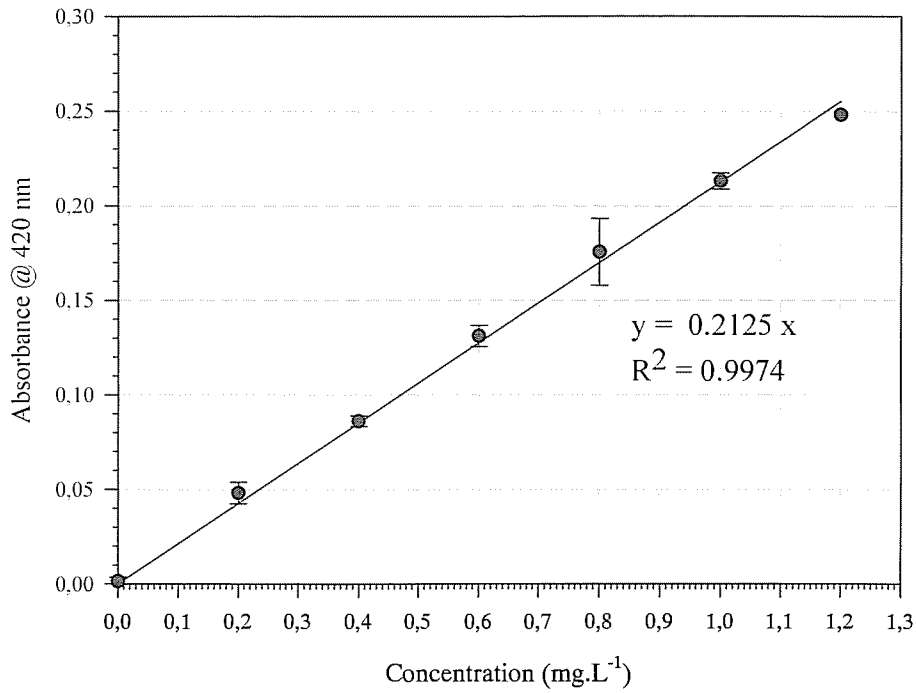

Figure A.2. NH_4^+-N Calibration Curve (07.01.2003)

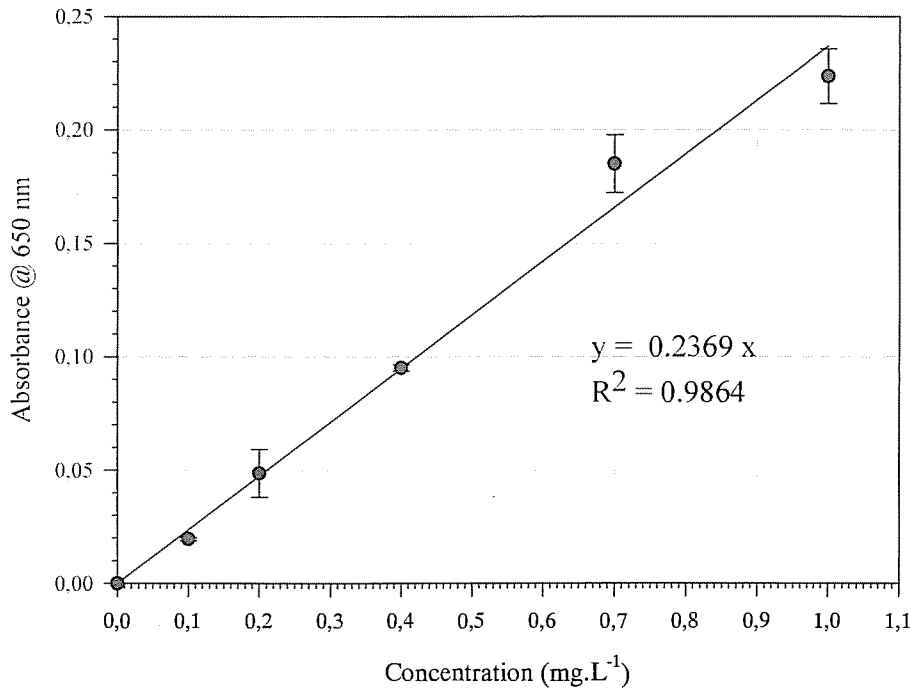

Figure A.3. NO_3^--N Calibration Curve (12.07.2002)

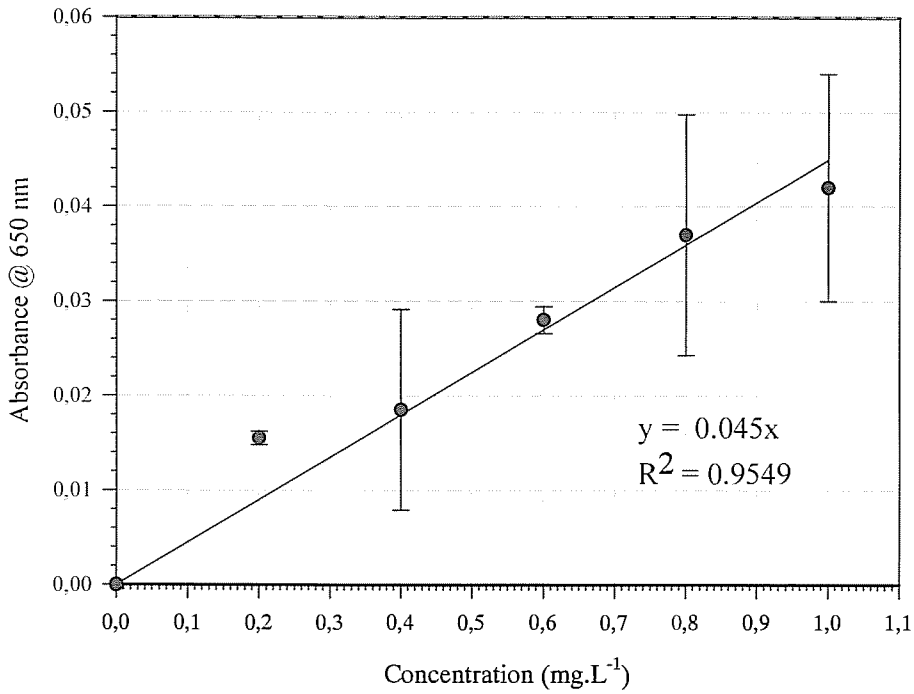

Figure A.4. NO_3^--N Calibration Curve (11.10.2002)

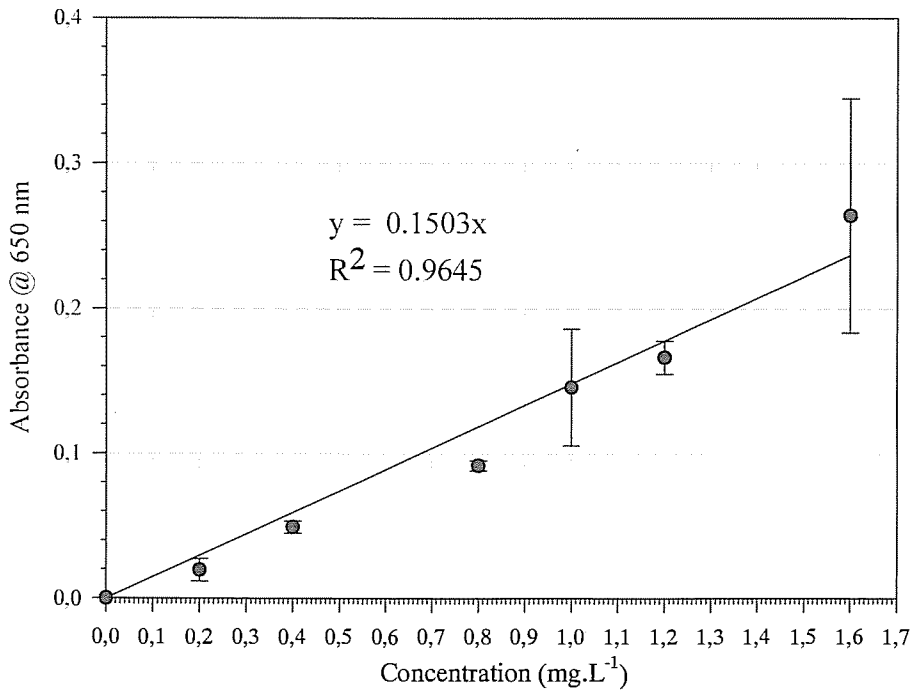

Figure A.5. TN Calibration Curve (11.10.2002)

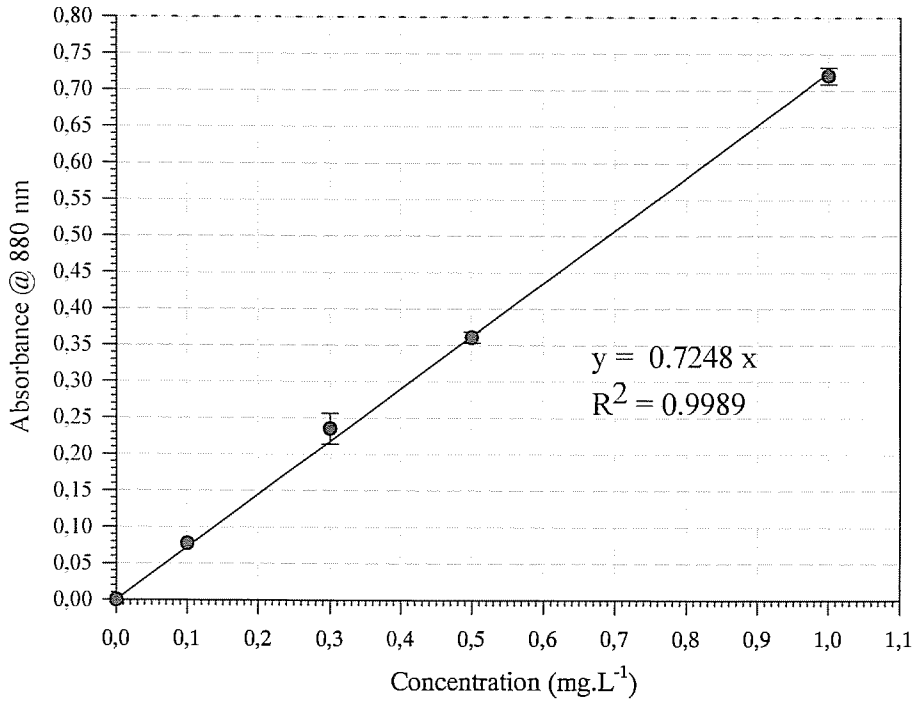

Figure A.6. PO_4^{+3}-P Calibration Curve (12.07.2002)

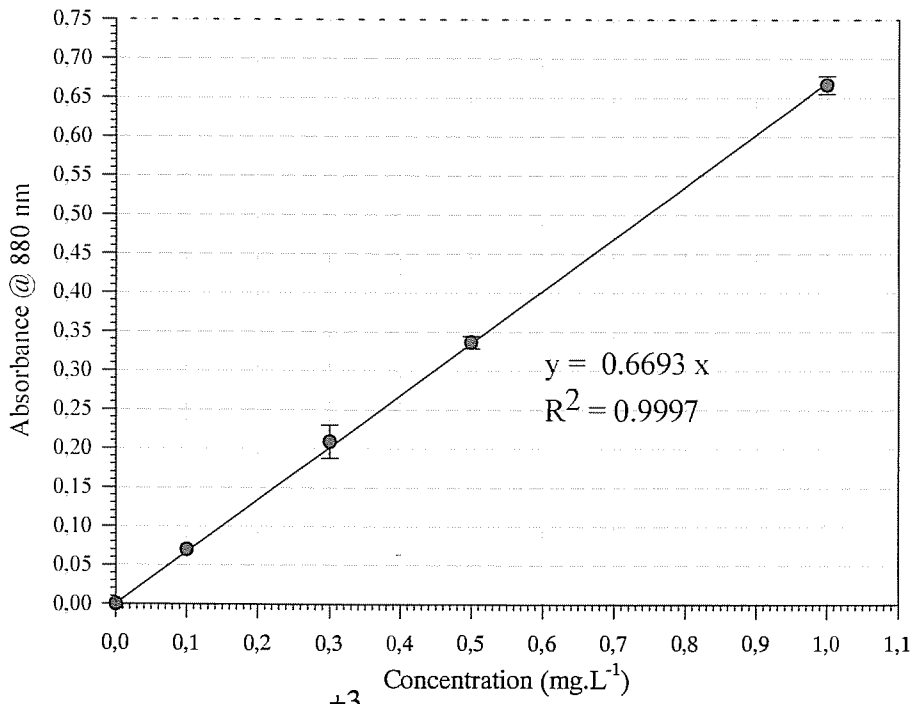

Figure A.7. PO_4^{+3}-P Calibration Curve (11.10.2002)

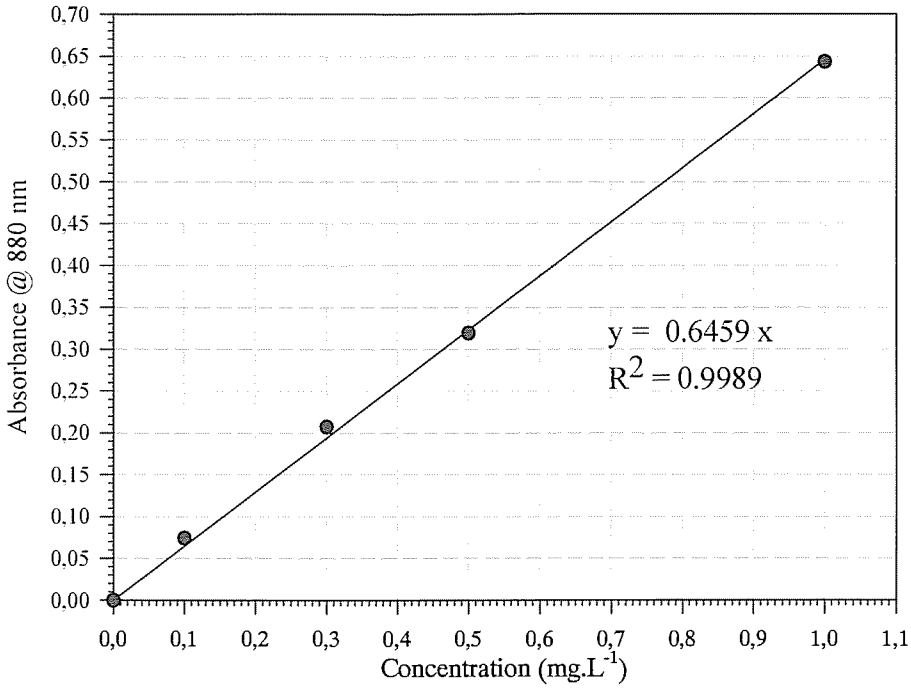

Figure A.8. PO_4^{+3}-P Calibration Curve (17.01.2003)

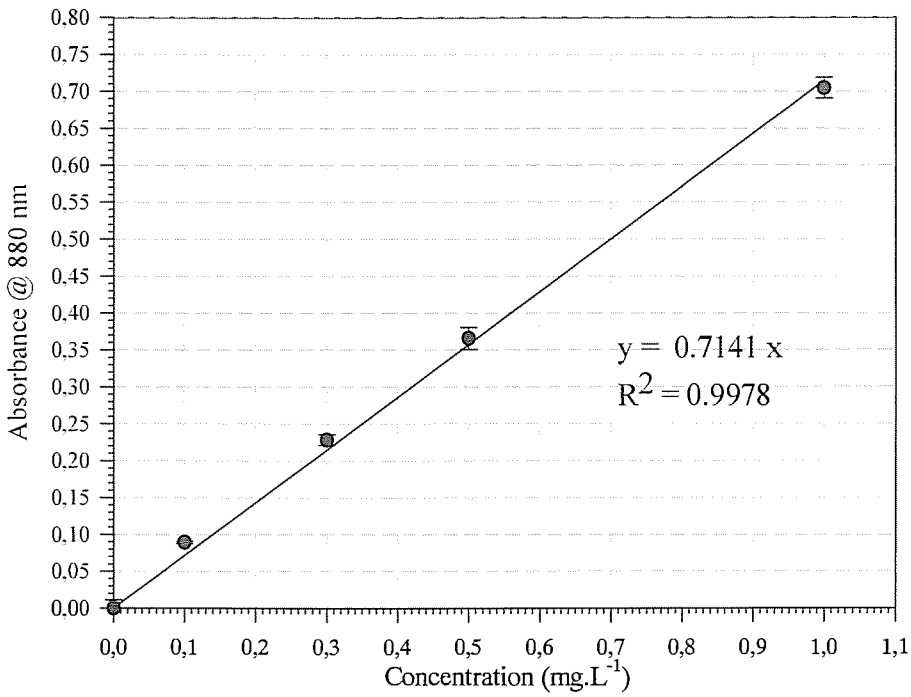

Figure A.9. PO_4^{+3}-P Calibration Curve (08.04.2003)

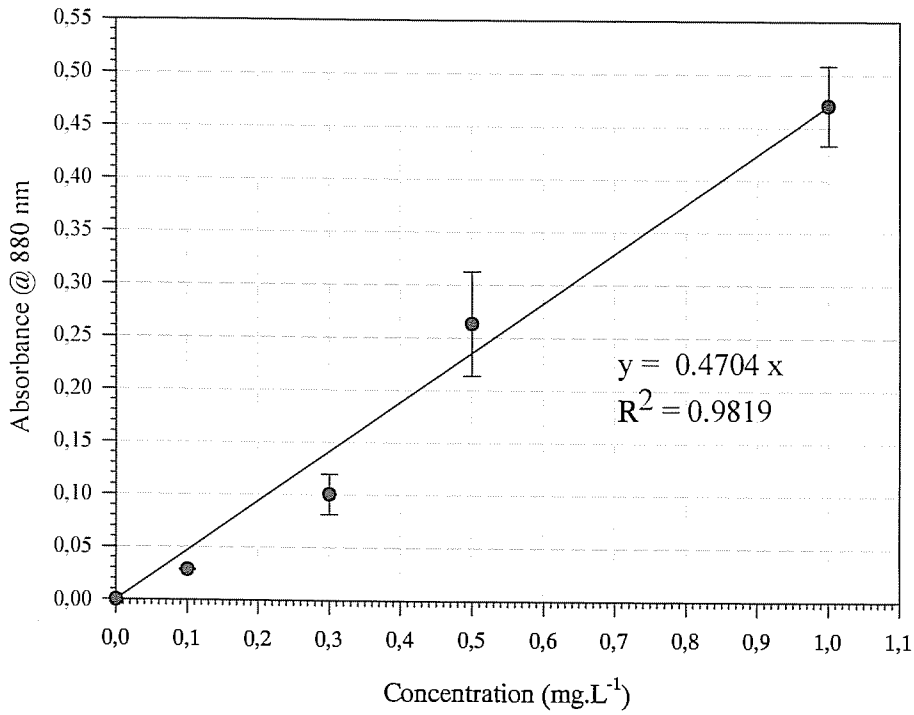

Figure A.10. TP Calibration Curve (12.07.2002)

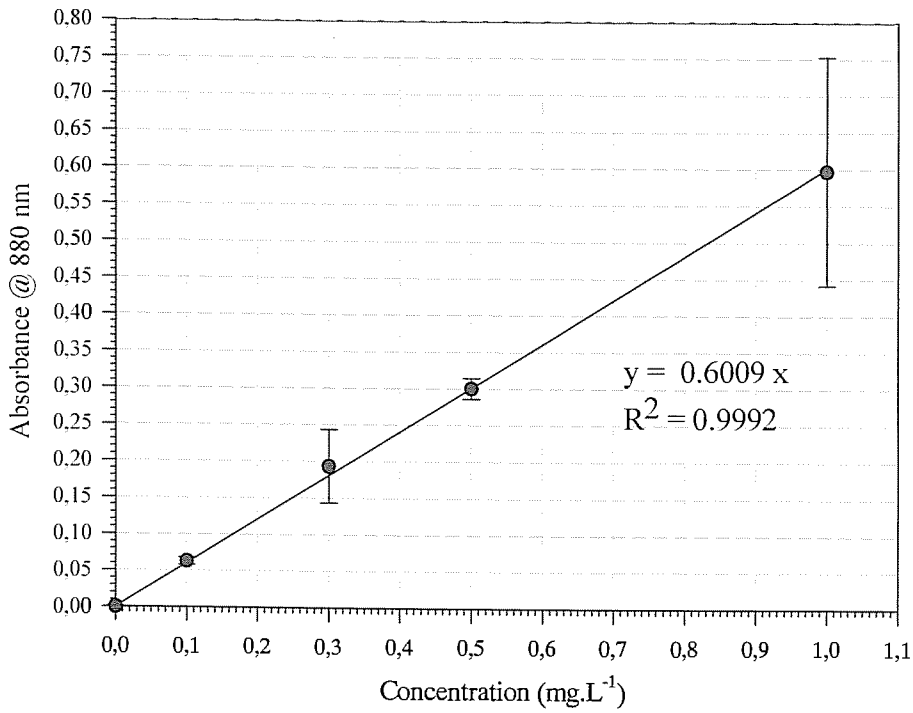

Figure A.11. TP Calibration Curve (11.10.2002)

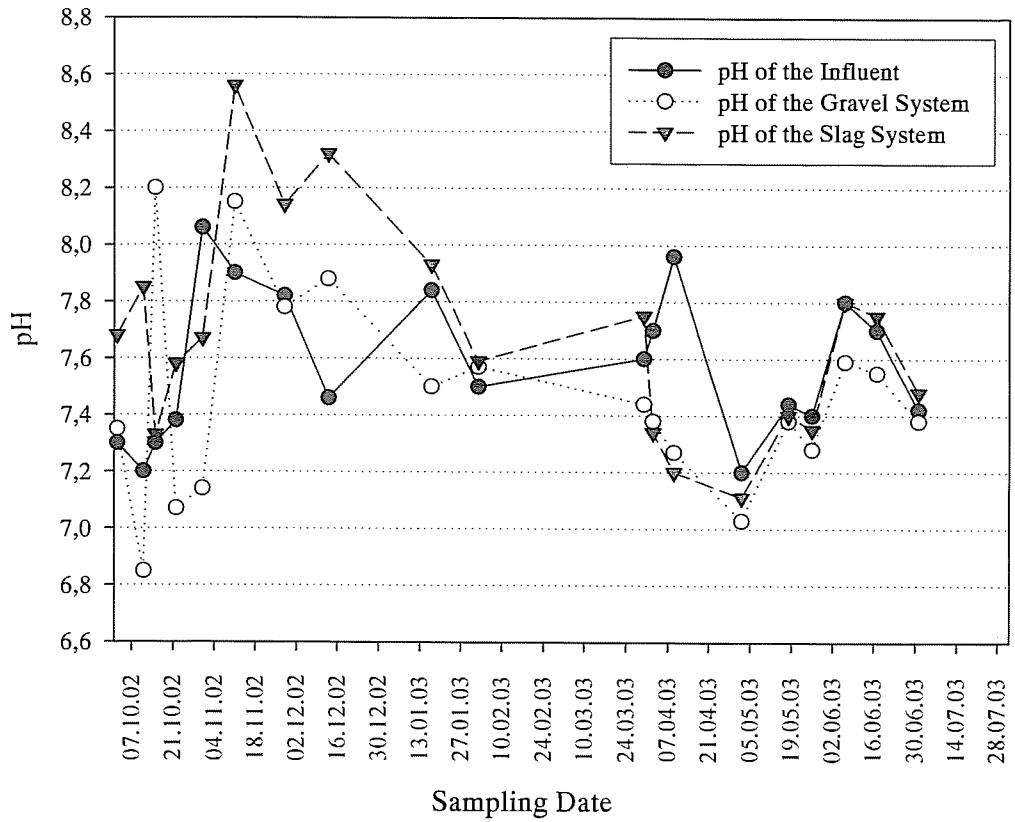

Figure A.12. Monitored pH values of the slag and gravel systems constructed at METU

Table A.1. Monitored pH values of the wetlands implemented at METU

pH	Influent (Primarily Treated DWW)	Effluent of the Slag System	Effluent of the Gravel System
Minimum	7.2	7.11	6.85
Maximum	8.06	8.56	8.2
Average	7.57	7.67	7.46
St Dev.	0.26	0.37	0.35

Sample size: 20

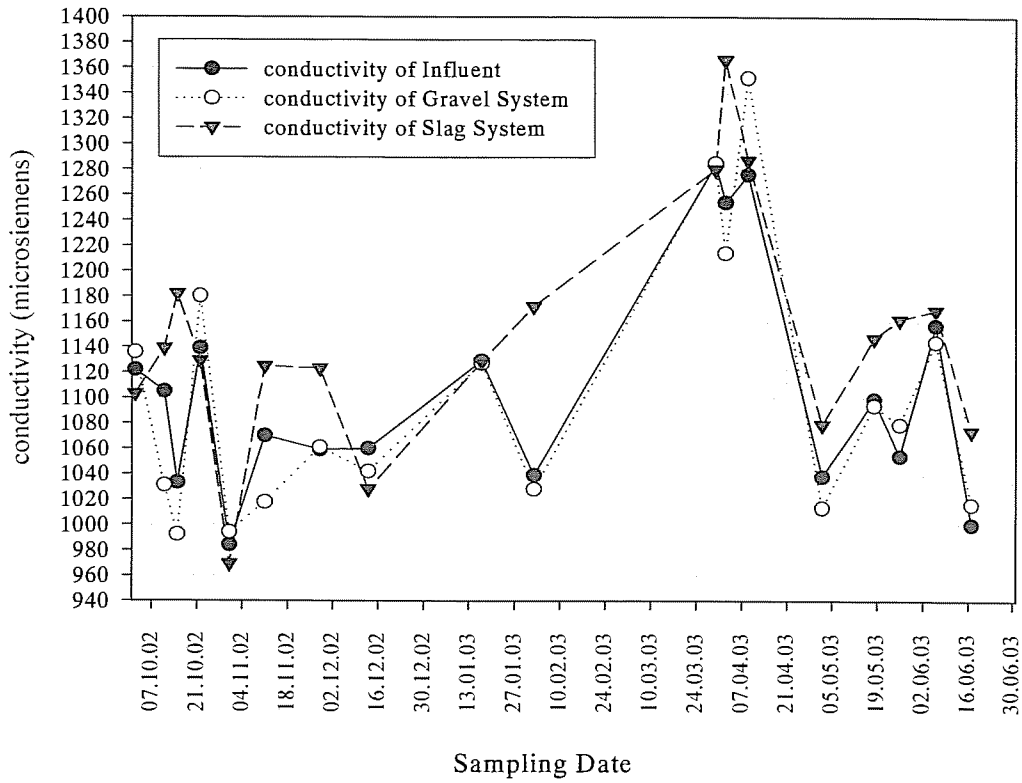

Figure A.13. Conductivity values (microsiemens) monitored in the slag and gravel systems constructed at METU

Table A.2. Monitored conductivity values of the wetlands constructed at METU

Conductivity (microsiemens)	Influent (Primarily Treated DWW)	Effluent of the Slag System	Effluent of the Gravel System
Minimum	1984	992	969
Maximum	1284	1352	1366
Average	1105.7	1100.3	1147.9
St Dev.	89.4	103.1	93.1

Sample size: 20

A.2. SIZING OF THE WETLANDS CONSTRUCTED AT METU

As explained in details in Section 2.11, combining the basic equation for a plug-flow model (Reed at al, 1988) with the water mass balance, an exponential relation between inlet and outlet concentrations can be described by the equation given by Kadlec and Knight (1996):

$$k = \frac{Q}{A} \ln \frac{(Ci - C^*)}{(Ce - C^*)} \qquad \text{Eqn (2.15)}$$

Solving the above-given equation for surface area of wetlands (A); assuming the background BOD_5 concentration is negligible, the equation turns to:

$$A = [Q/k]^* \ln [C_i/C_e]$$

where:

A = Surface area of the wetland (m^2),

Q = Input discharge to the wetland ($m^3.yr^{-1}$),

k = First-order areal rate constant ($m.yr^{-1}$),

C_i = Inlet concentration ($mg.L^{-1}$), and

C_e = Outlet concentration ($mg.L^{-1}$).

To be on safe side, the areal removal rate constant for BOD_5 was selected as 34 $m.yr^{-1}$ from Table 2.10. As found in the domestic wastewater characterization analyses (see Table 4.2), BOD_5 of the primarily treated domestic wastewater varied between 40-100 $mg.L^{-1}$. To be on the safe side, while sizing the wetlands, it was decided to consider the maximum BOD_5 value in the calculations as C_i. Even though the effluent standards for BOD_5 was determined as 50 $mg.L^{-1}$ in the Wastewater Treatment Plant Discharge Standards of Turkey (1991), a C_e value of 25 $mg.L^{-1}$ was chosen for calculations. Taking the amount of wastewater to be treated in one of the hybrid systems as 3 $m^3.d^{-1}$, the total surface area of the hybrid system (vertical flow + horizontal flow) was calculated as follows:

$A = [(365\ d.yr^{-1} * 3\ m^3.d^{-1})* \ln (100/25)] / (34\ m.yr^{-1})$

$A = 44.64\ m^2$

$A = 45\ m^2$

One of the vertical subsurface flow consructed wetlands was planned to have an surface area of 30 m^2; whereas the horizontal one would have an area of 15 m^2.

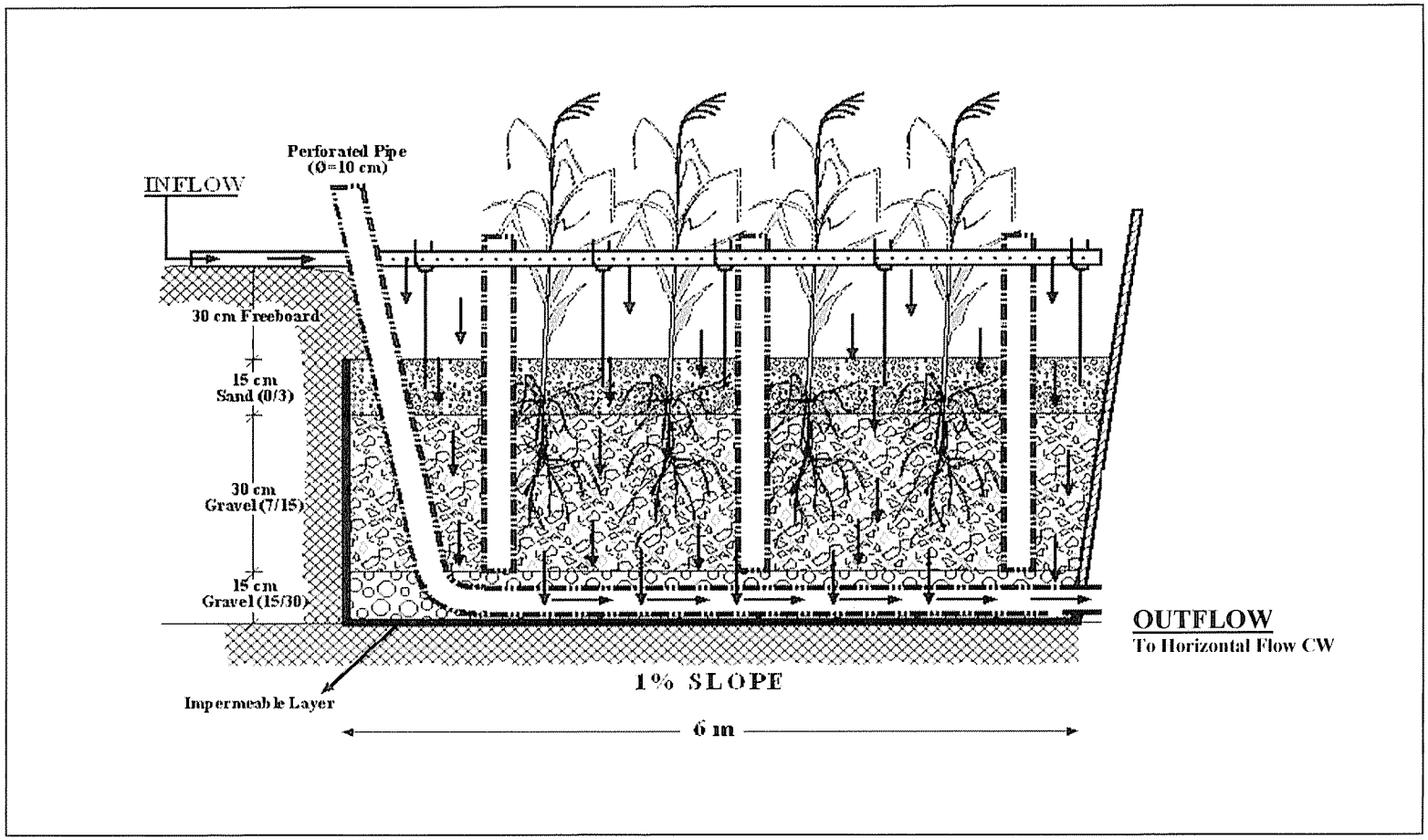

Figure A.14. Cross-section of the vertical flow subsurface constructed wetland filled with gravel

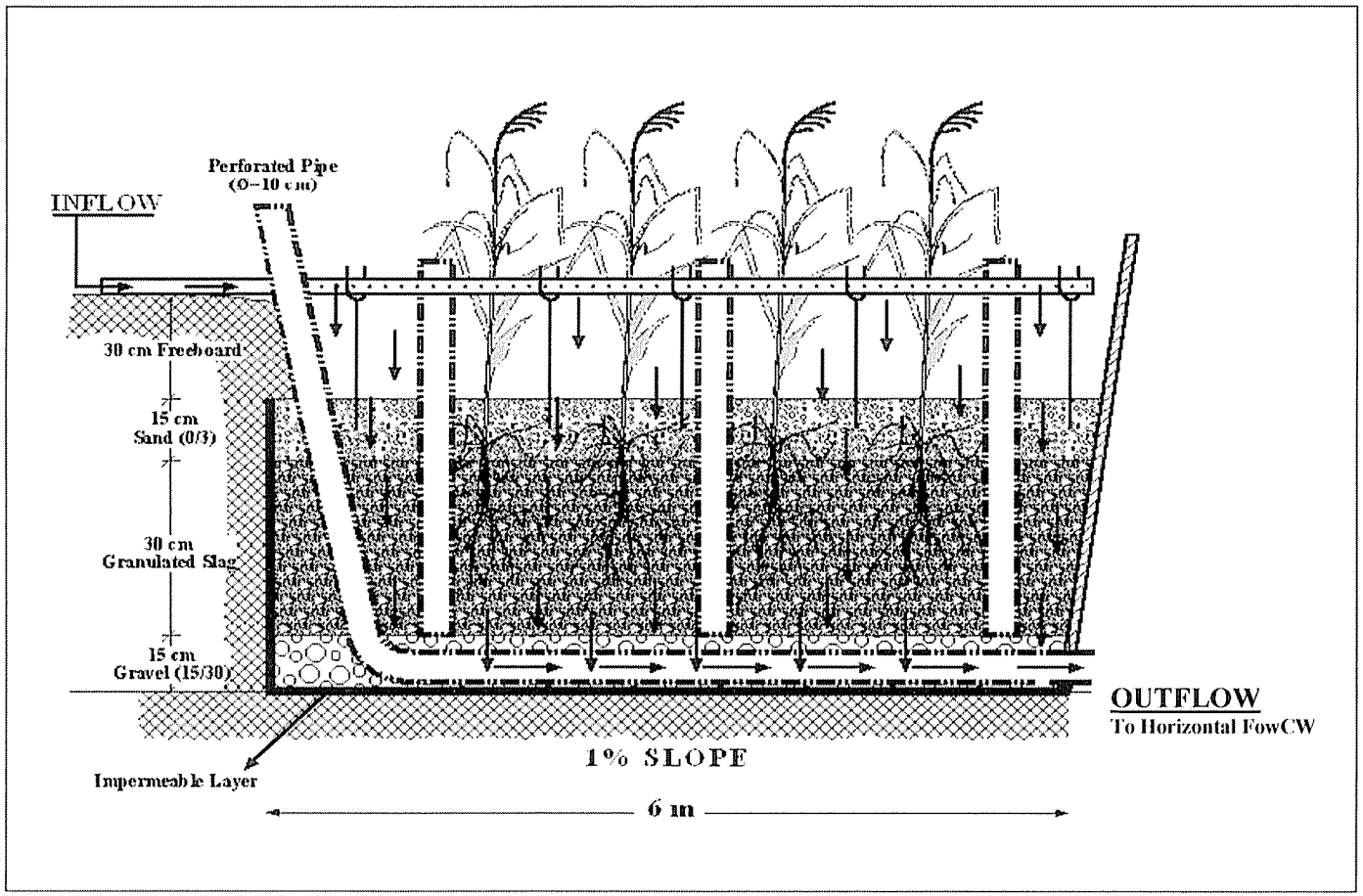

Figure A.15. Cross-section of the vertical flow subsurface constructed wetland filled with granulated slag

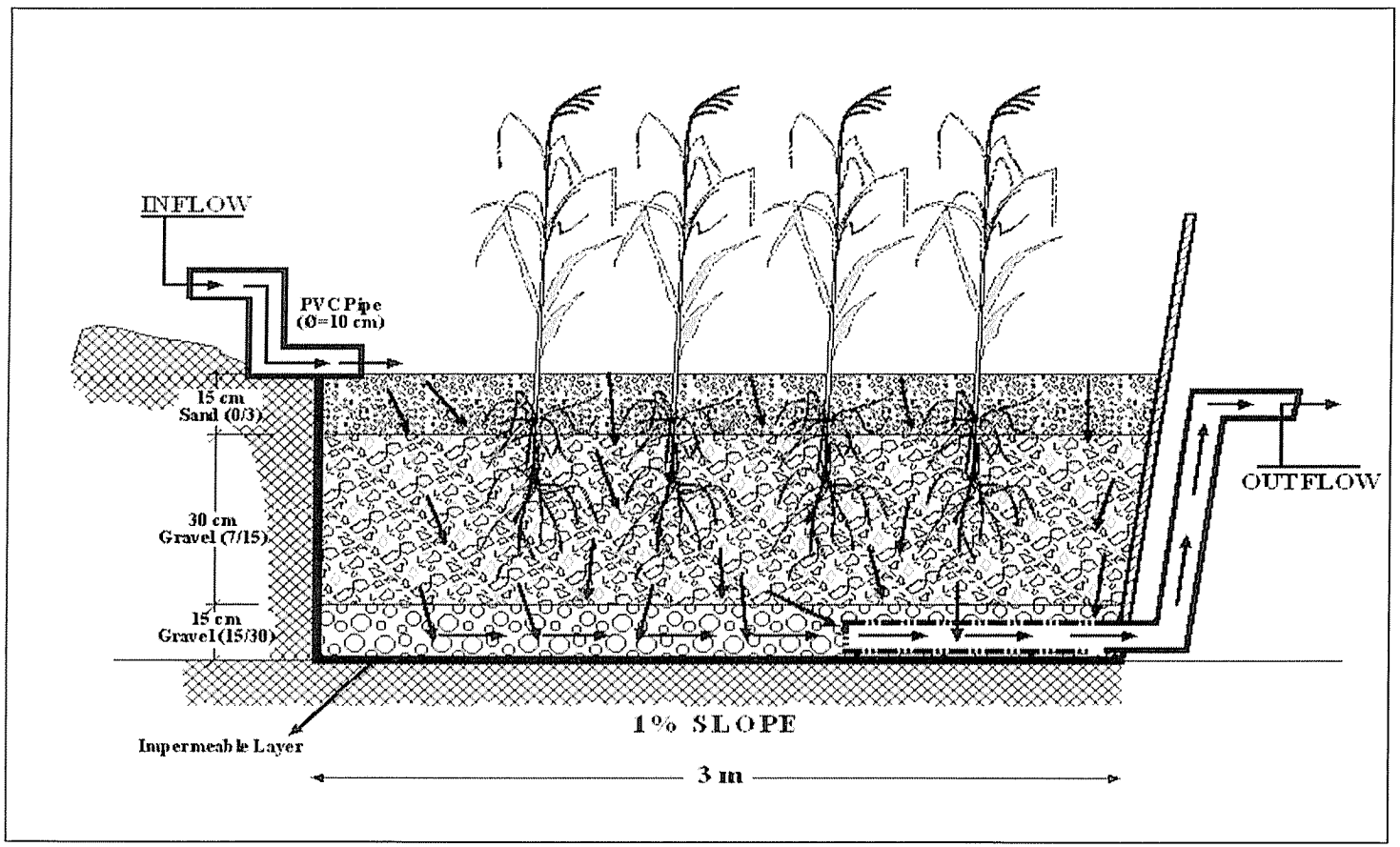

Figure A.16. Cross-section of the horizontal flow subsurface constructed wetland filled with gravel

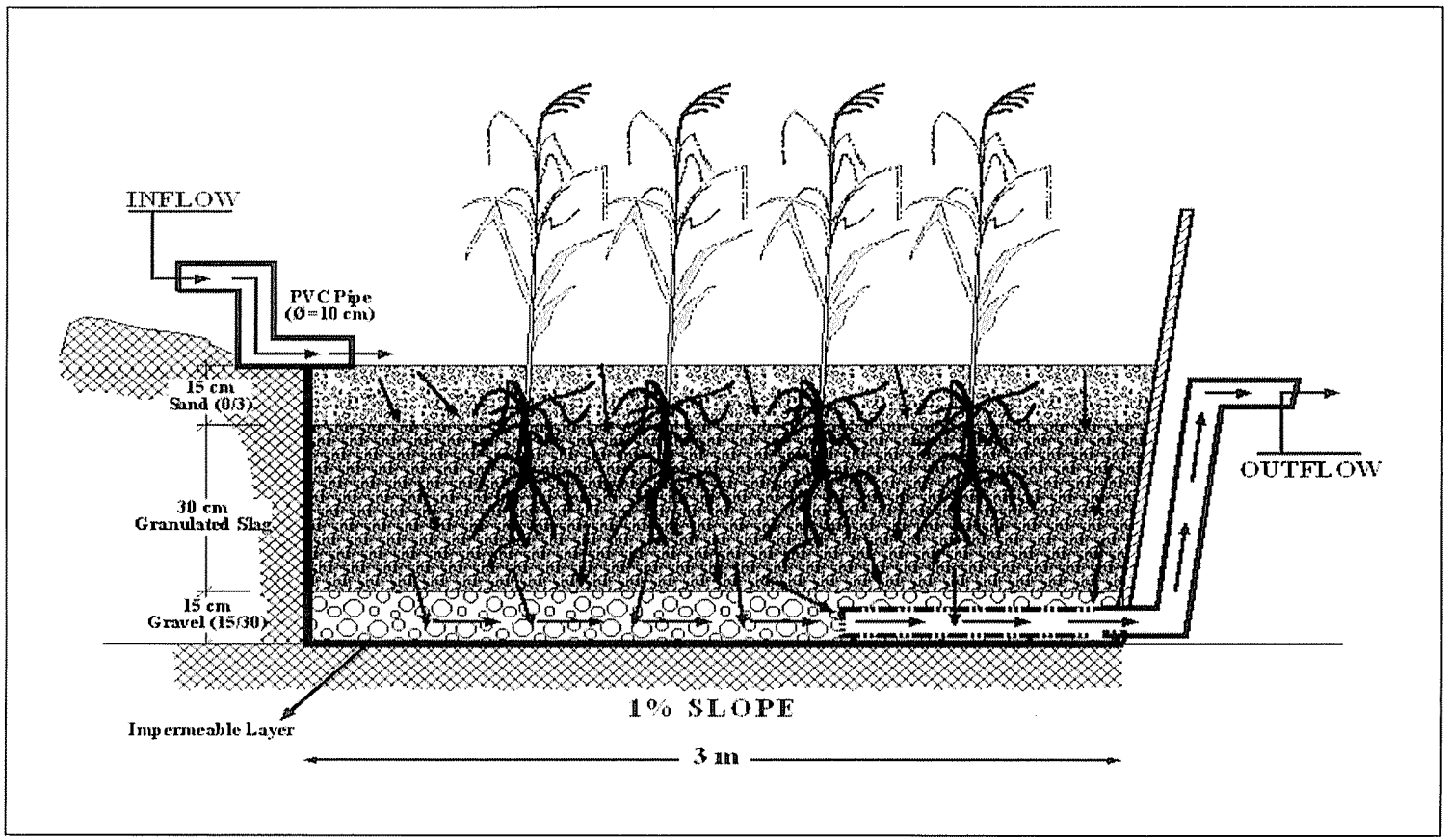

Figure A.17. Cross-section of the horizontal flow subsurface constructed wetland filled with granulated slag

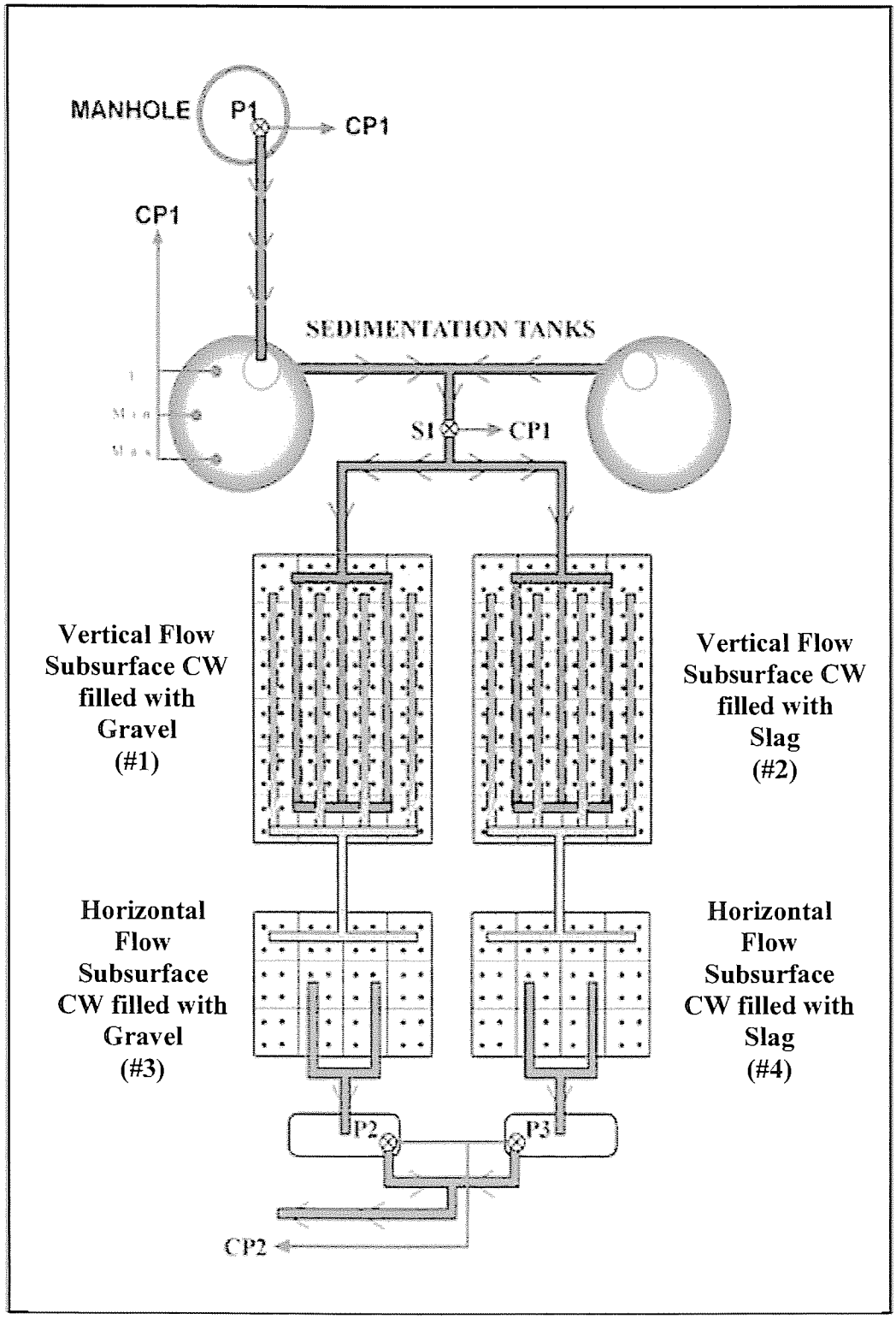

Figure A.18. Plan View of the Pilot-Scale Constructed Wetlands implemented at METU (where P1, P2 and P3 refer to the submersible pumps; CP1 and CP2 refer to the control panels; S1 to solenoid valve)

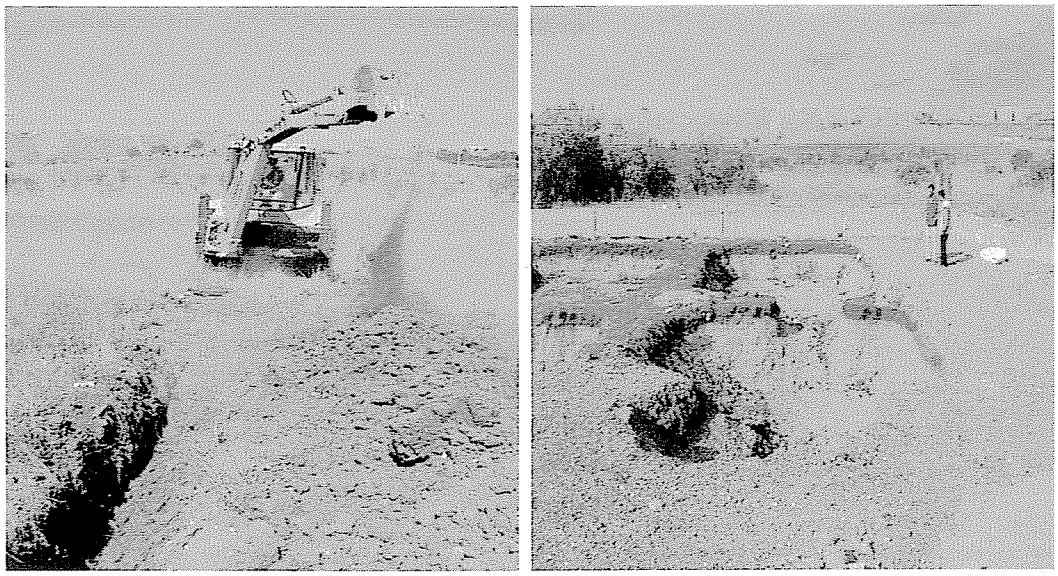

Figure A.19. Excavation phase of the constructed wetlands

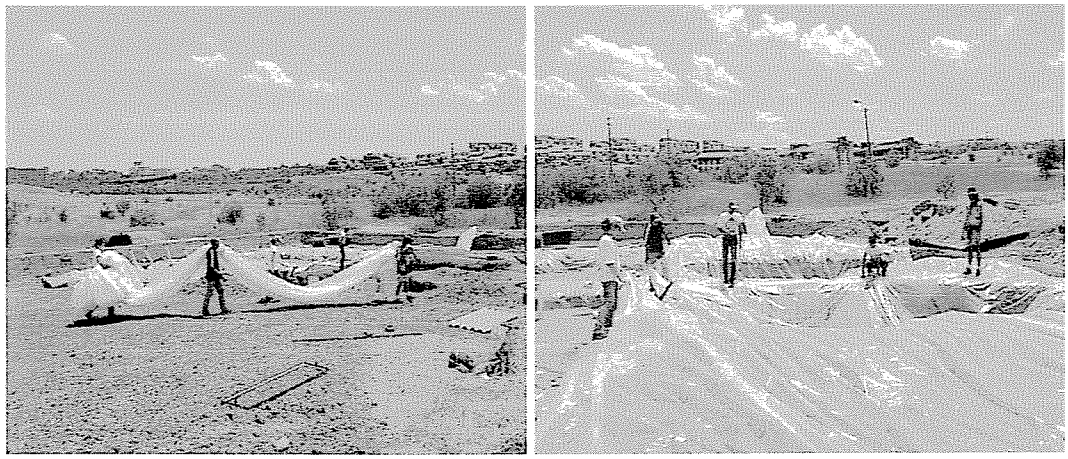

Figure A.20. Sealing of the constructed wetlands

Figure A.21. Placing the filter media into the wetland cells

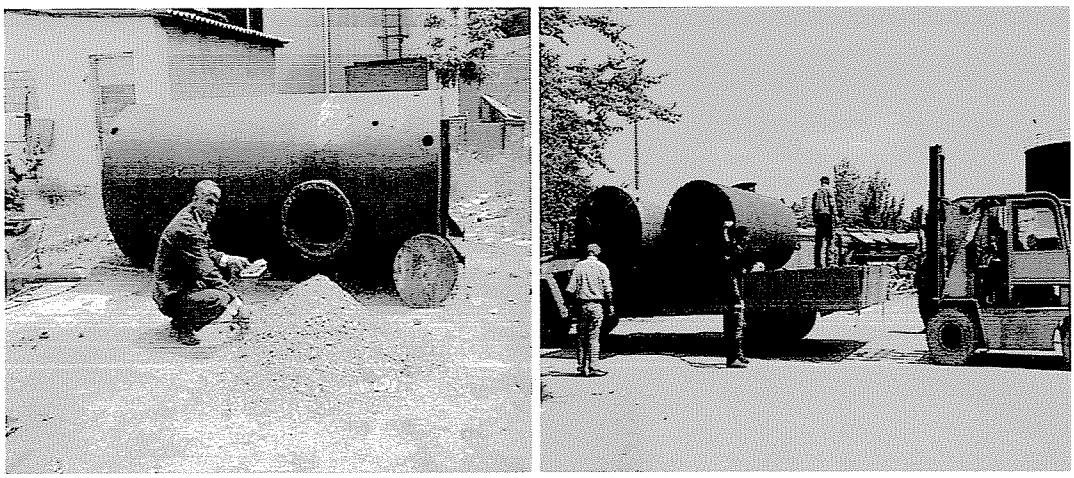

Figure A.22. Reuse of the old boilers of METU as sedimentation tanks

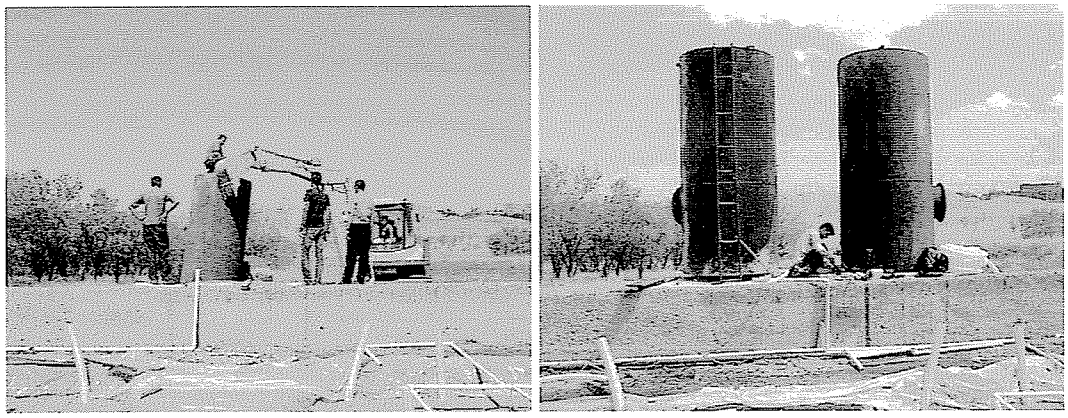

Figure A.23. Installation of the sedimentation tanks on the field

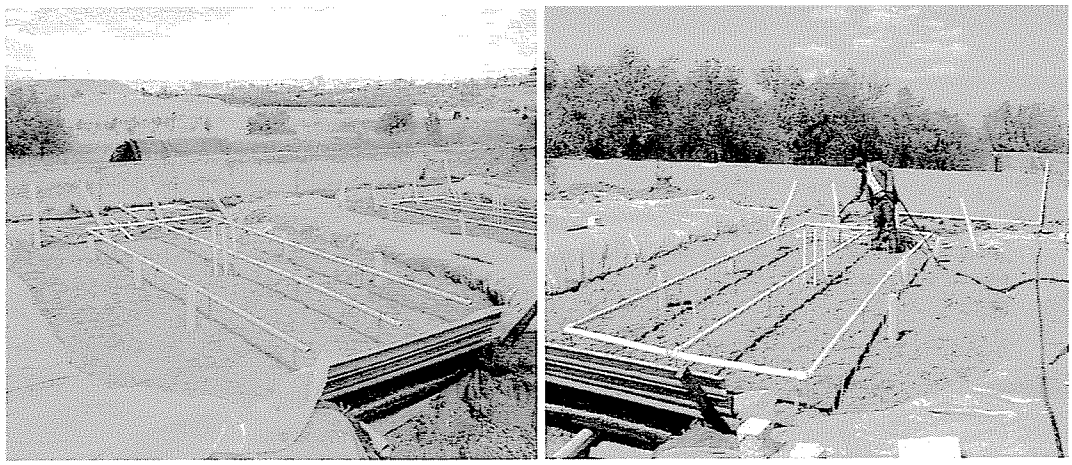

Figure A.24. Wastewater distribution pipes of vertical subsurface flow wetlands

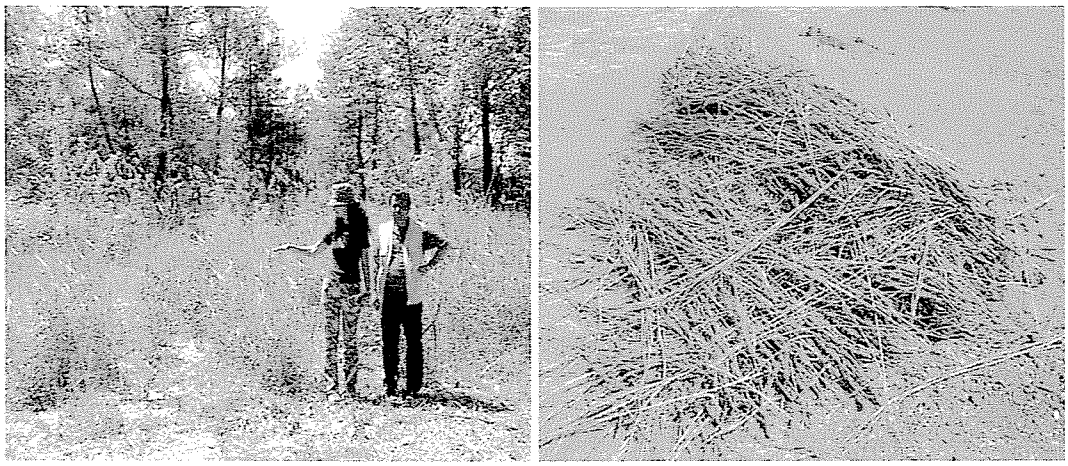

Figure A.25. Transfer of the reeds from the natural reed banks of METU in 2001

Figure A.26. Irrigation of the reeds planted in the wetlands

Figure A.27. Reed seedlings in the greenhouse (January 2002)

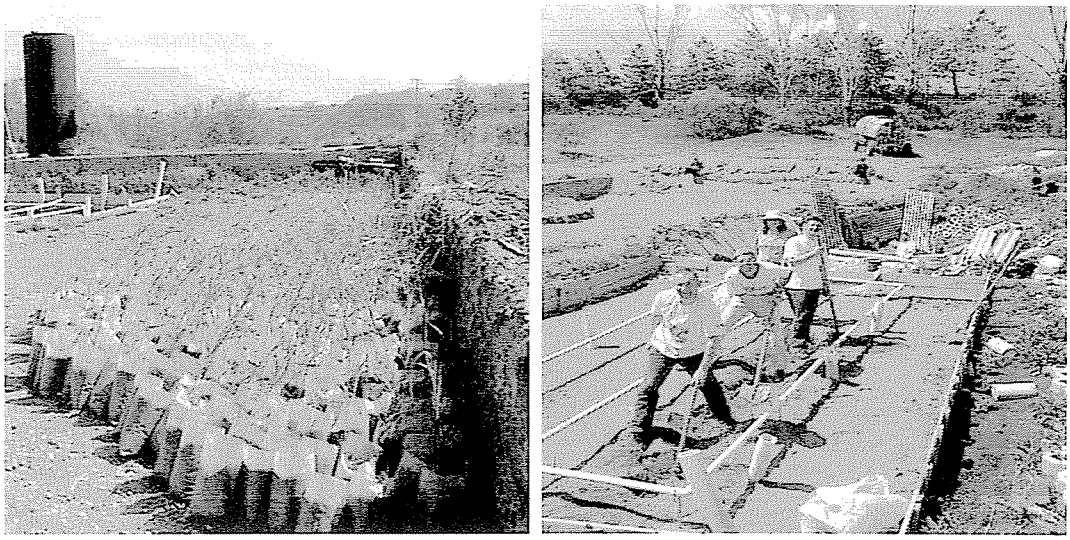

Figure A.28. Transfer and plantation of the reed seedlings in may 2002

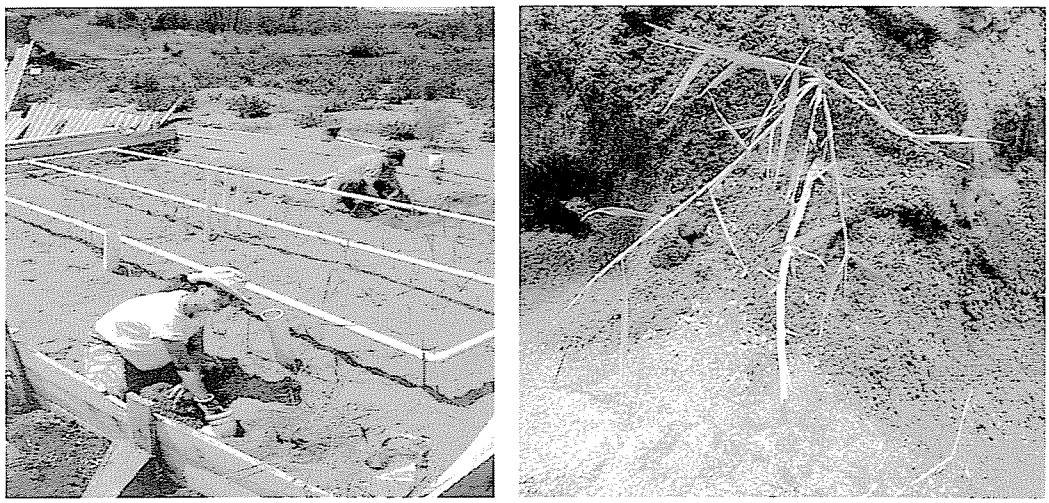

Figure A.29. Transplantation of reed seedlings into the wetland cells

Figure A.30. A general view from the constructed wetlands (June 2002)

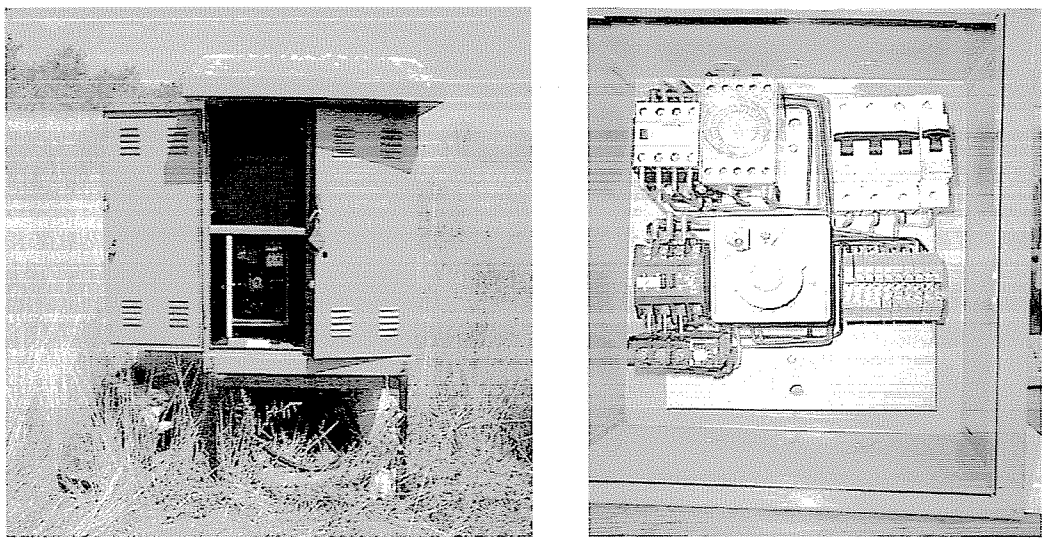

Figure A.31. The renewed control panel

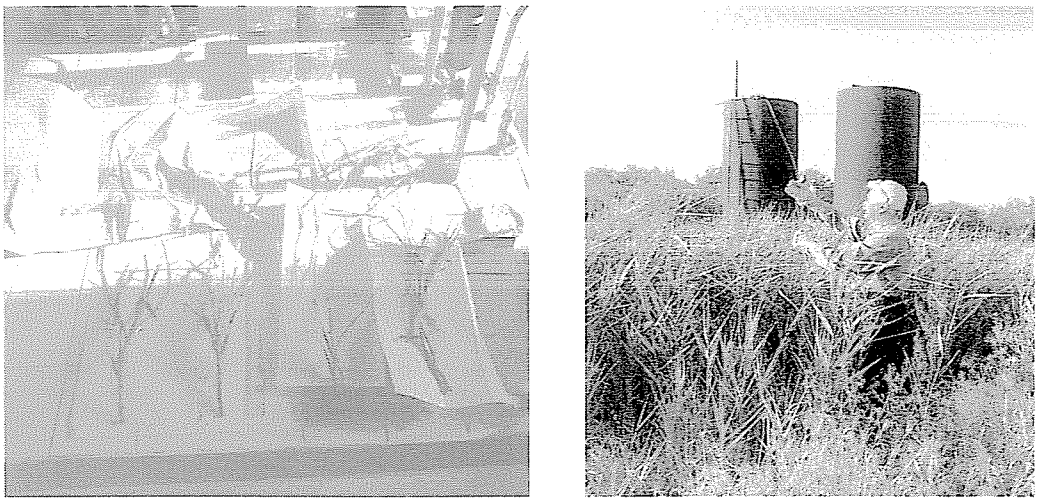

Figure A.32. Random measurements of the reed heights

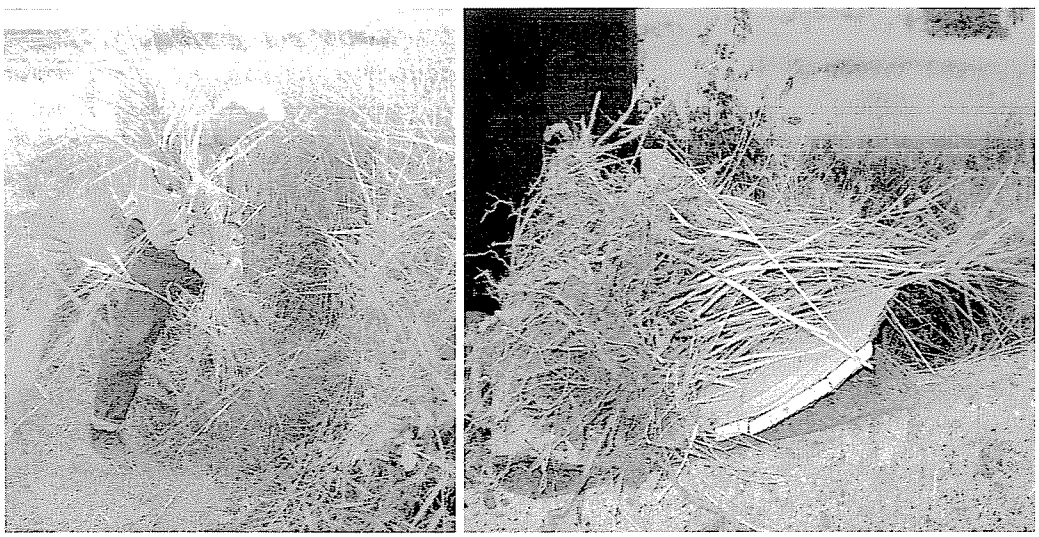

Figure A.33. Harvesting reed samples from the vertical flow wetland cells

Figure A.34. Dry-weight determination of above- and below-ground biomass

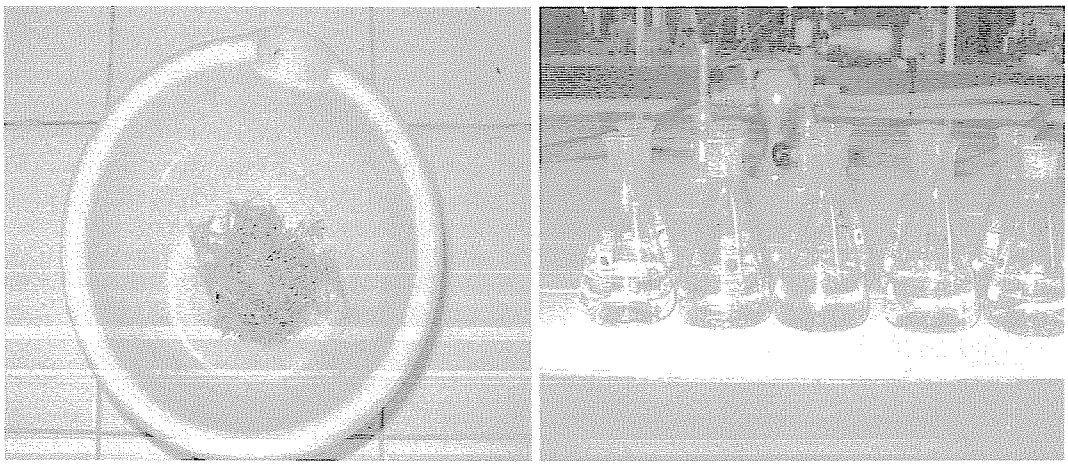
Figure A.35. Determination of the TN and TP content of the reed samples


Figure A.36. Sampling of the substrate samples from the vertical flow wetlands

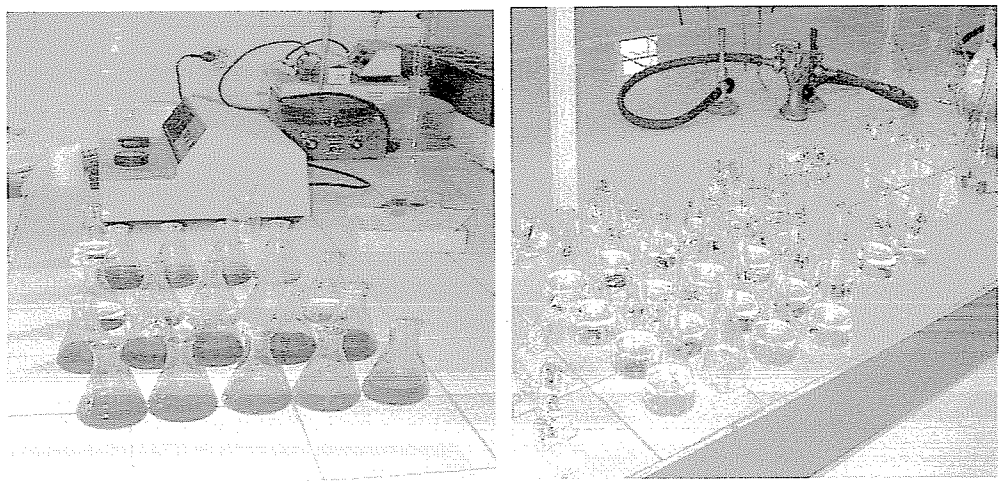

Figure A.37. Phosphorus extraction experiments conducted in the laboratory

APPENDIX B

B.1. RESULTS OF THE SORPTION STUDIES

Table B.1. Results of the Sorption Isoterms

Sample	PUMICE SAMPLES*		SLAG SAMPLES	
(C_i) (mg.L^{-1})	(C_f) mg.L^{-1}	q (mg P.kg^{-1} pumice)	(C_f) mg.L^{-1}	q (mg P.kg^{-1} slag)
0	0.81	0	0.03	0
4	-	-	0.69	103.42
8	-	-	2.11	183.96
9.14**	-	-	2.70	201.11
10	-	-	2.89	222.28
20	6.25	429.65	2.15	557.82
40	9.82	943.26	4.78	1100.57
80	16.40	1987.62	9.99	2187.77
160	36.63	3855.28	17.88	4441.01
320	55.06	8279.38***	27.10	9153.12

**For pumice samples, the sorption test was not conducted for the initial P-concentrations of 4, 8, 10 mg.L^{-1} and DWW.*

***Phosphorus Concentration of the Raw Domestic Wastewater taken from METU. In this sample, raw DWW used instead of P solution.*

$$q = \frac{(Ci - Cf) \times V}{M} \qquad \text{Eqn (3.1)}$$

where:

q = Amount of phosphorus adsorbed per unit of media (mg P.kg^{-1} sample)

Ci = Initial concentration of phosphorus (mg.L^{-1})

Cf = Final concentration of phosphorus (mg.L^{-1})

V = Volume of phosphate solution added to flask (0.250 L)

M = Mass of dry weight of the media (slag or pumice) (0.008 kg)

****Sample Calculation:*

q = (320-55.06)*0.250/0.008

q = 8279.38 mg P.kg^{-1} sample

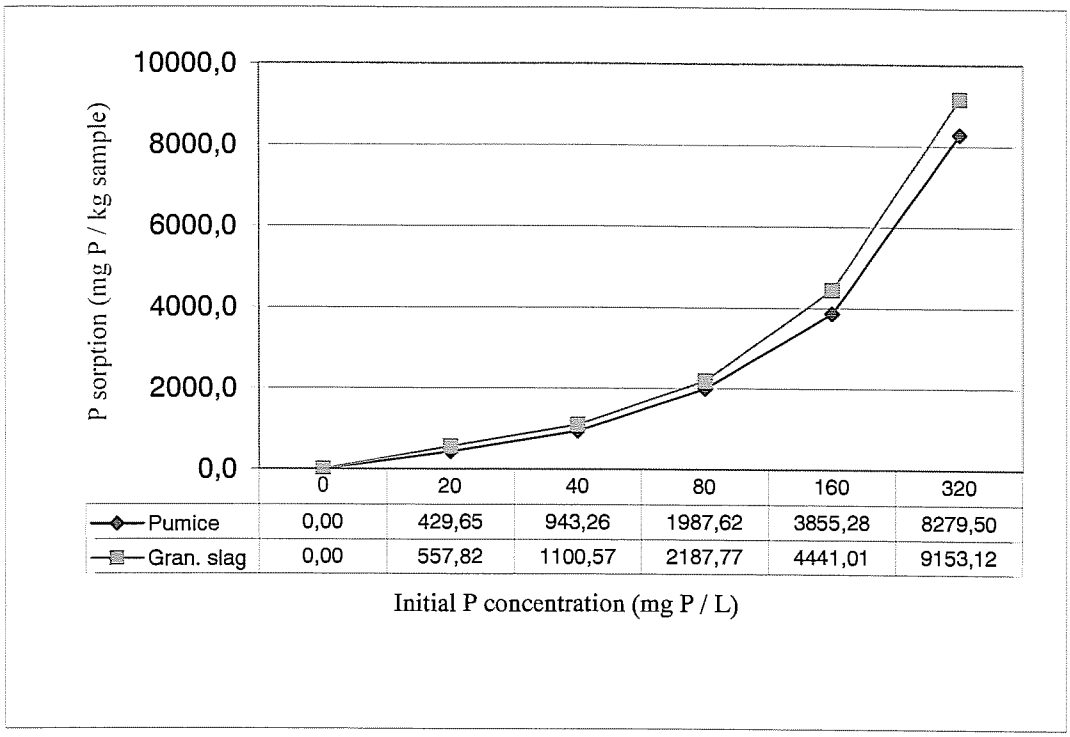

Figure B.1. Phosphorous-sorption capacity of pumice and granulated slag

B.2. RESULTS OF THE PARTICLE-SIZE DISTRIBUTION TESTS

Table B.2. Results of the Particle-Size Distribution Tests

Mesh Size of the Sieves (mm)	SLAG		SAND	
	Weight of Samples passing the Sieves (gram)	Cumulative Weight (%)	Weight of Samples passing the Sieves (gram)	Cumulative Weight (%)
0.149	4	0.45	15	2.3
0.297	29	3.25	55	8.5
0.59	232	25.98	160	24.8
1.19	587	65.73	295	45.7
2.38	817	91.49	445	69.0
4.76	872	97.65	600	93.0
9.5	893	100.00	645	100.0

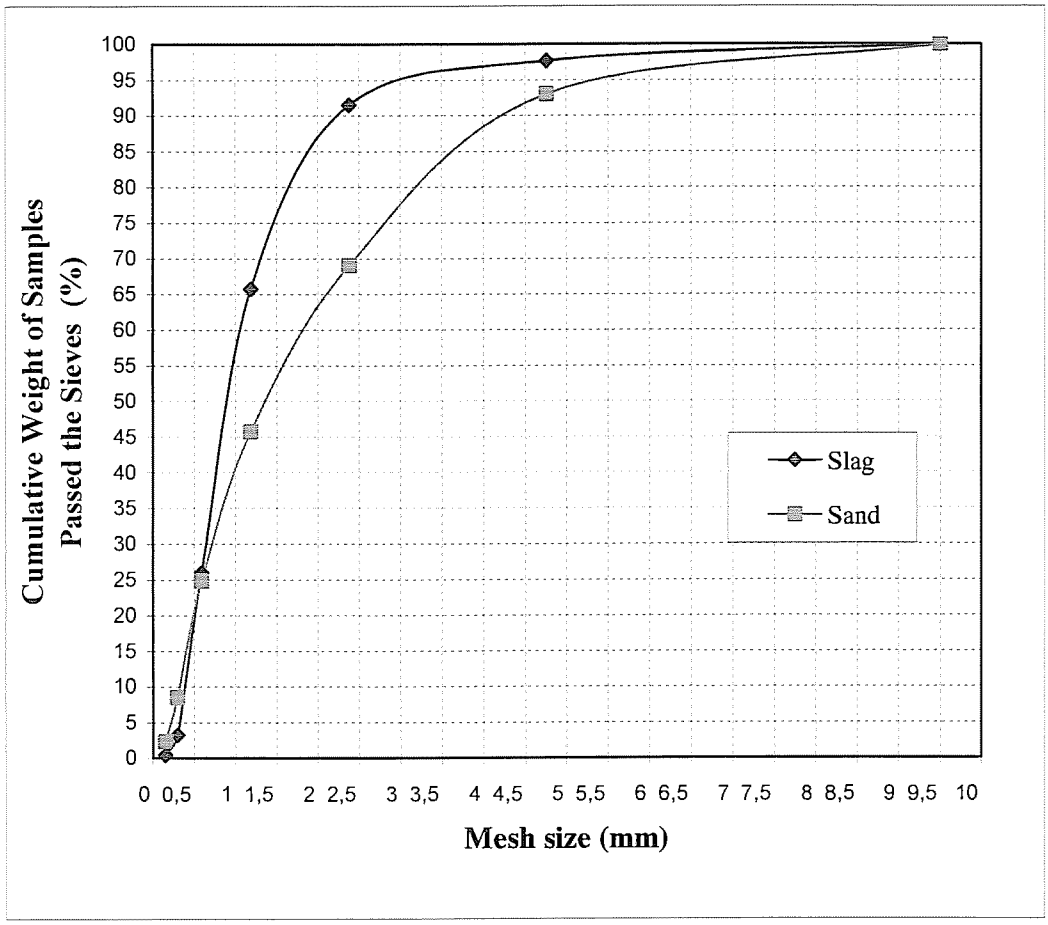

Figure B.2. Particle-size distribution of slag and sand

Table B.3. Physical characteristics of the slag and sand

Properties	Blast Furnace Granulated Slag		Sand	
	KARDEMİR	Literature*	This study	Literature**
Particle Density ($g.cm^{-3}$)	2.112	2.4–2.5	2.50	2.4-2.8
Bulk density ($g.cm^{-3}$)	1.067	1.38-1.61	1.50	1.2-1.8
Porosity (%)	50	40-55	42	35-50
Uniformity Coefficient	2.625	-	6.0	-

References: Johansson (1999)*; Vymazal et al., (1998)**.

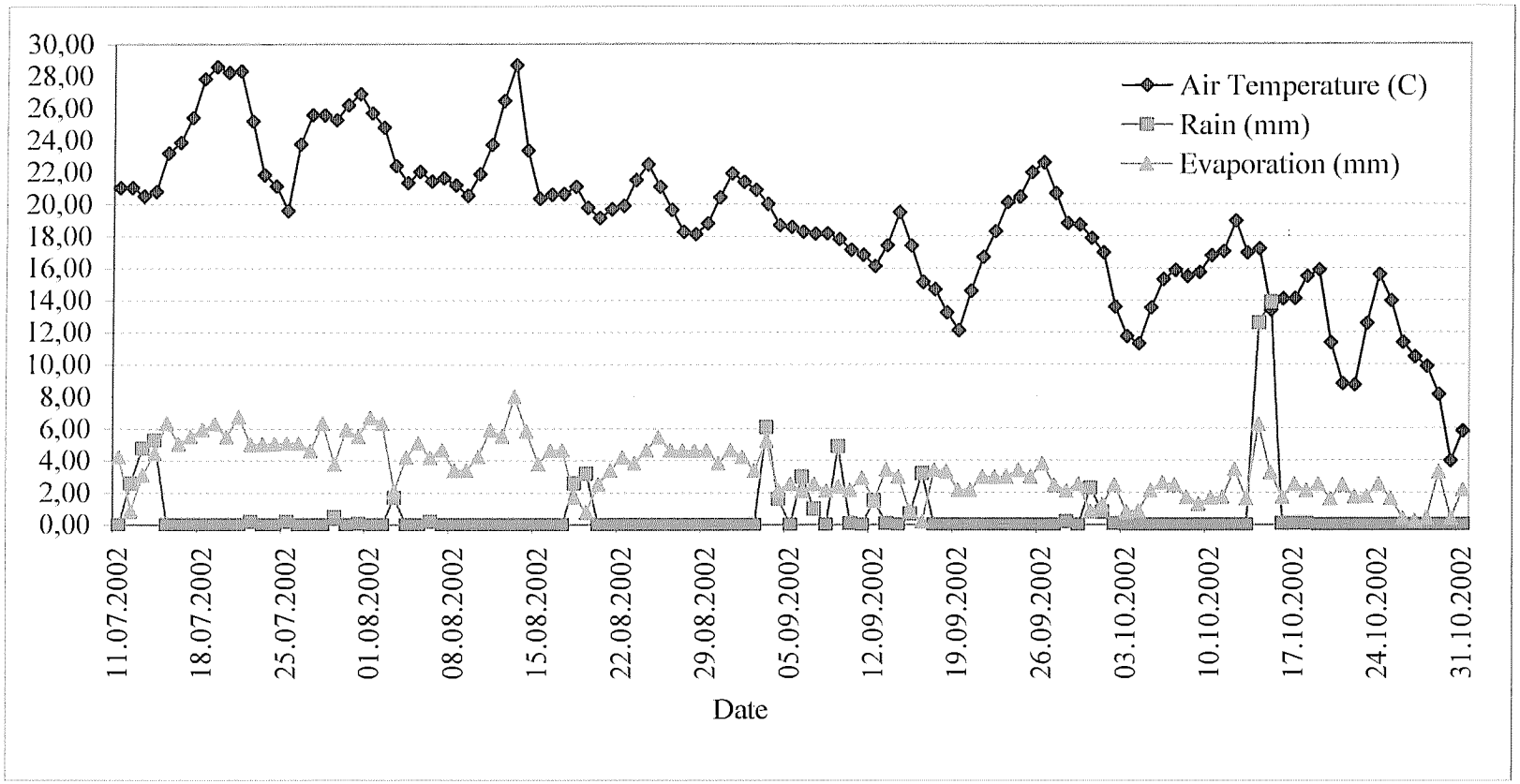

Figure B.3. Meteorological data for METU (July- October 2002)

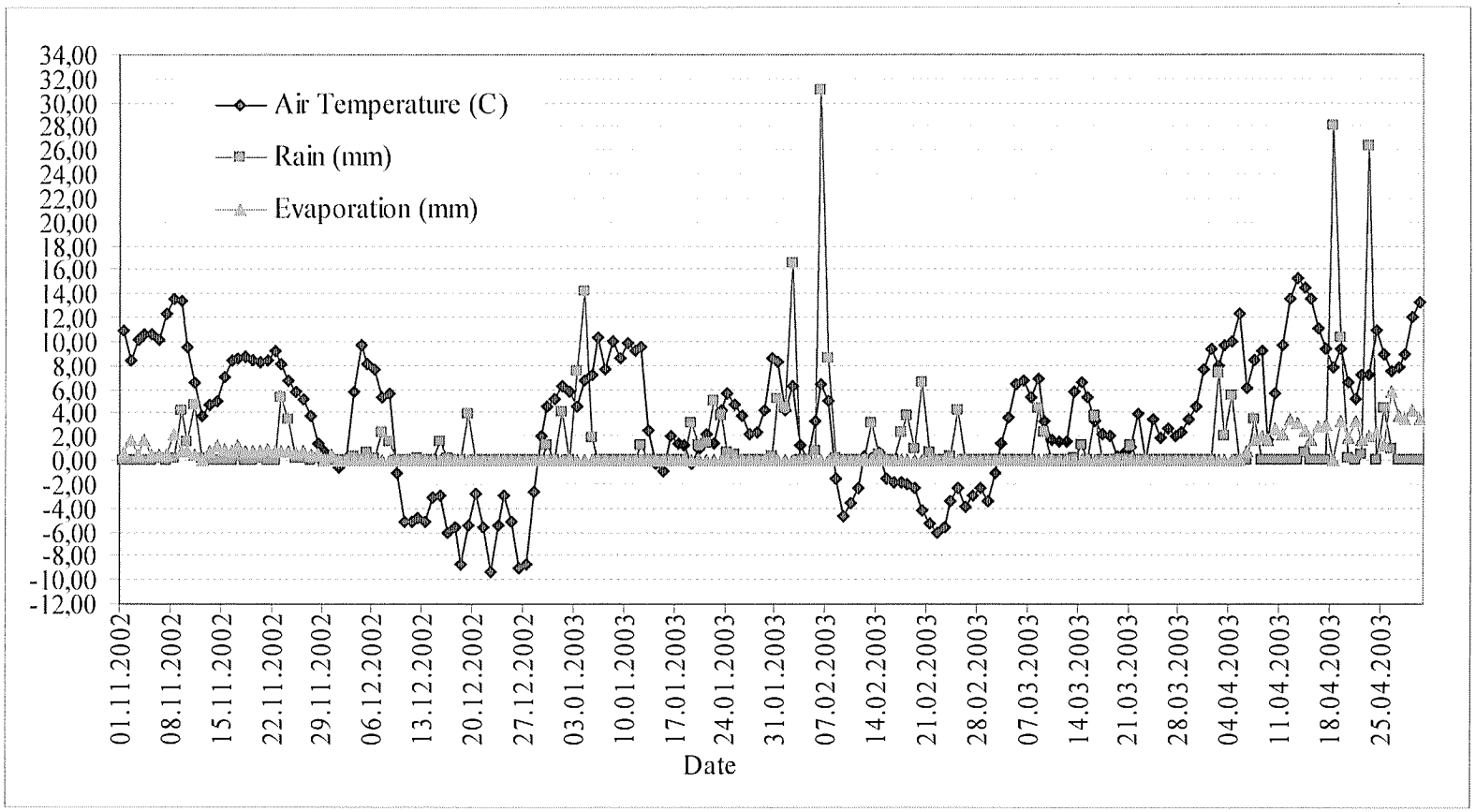

Figure B.4. Meteorological data for METU (November 2002-July 2003)

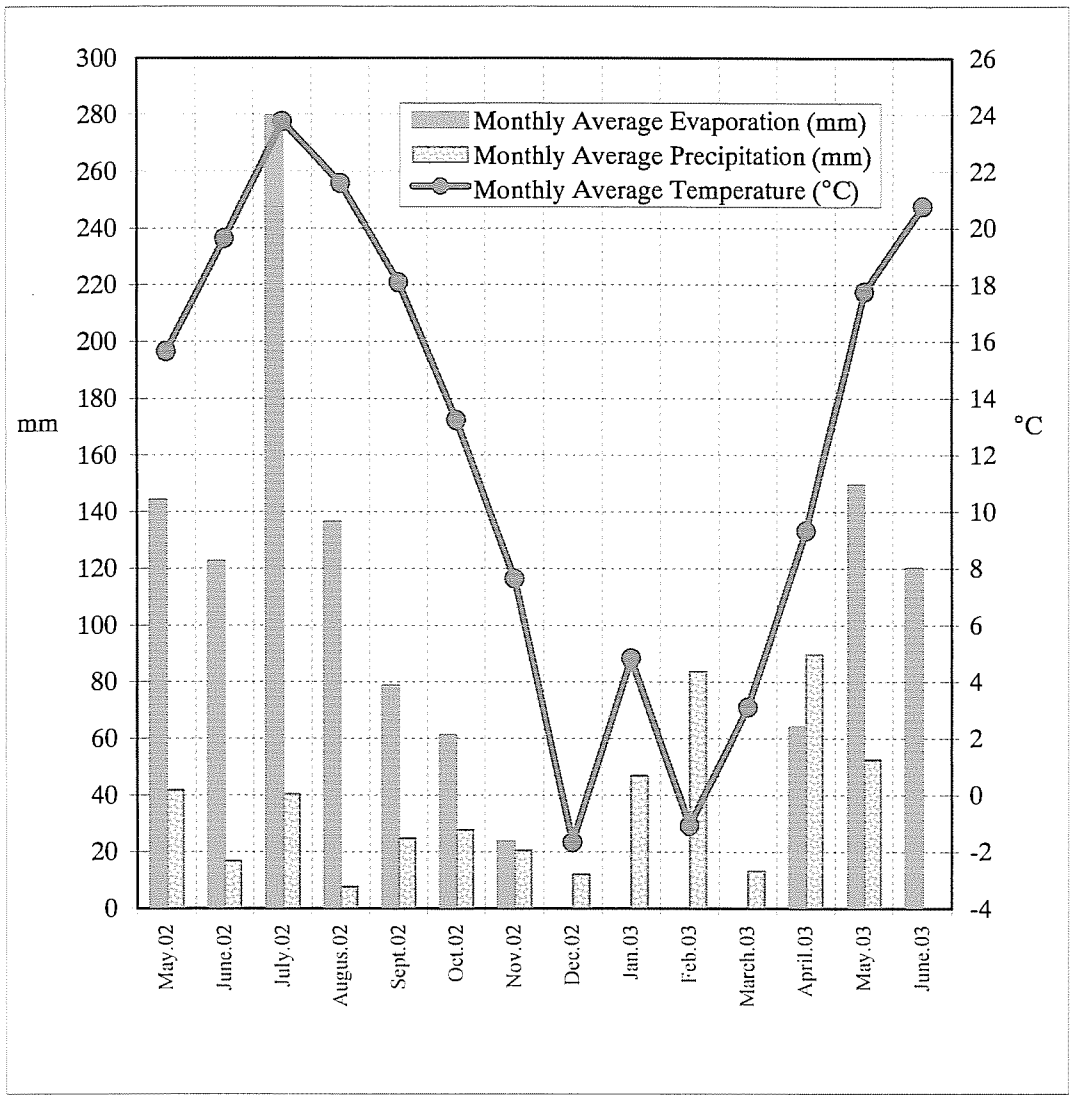

Figure B.5. Monthly average meteorological data (July 2002-July 2003)

B.3. WATER BUDGET OF THE CONSTRUCTED WETLANDS IMPLEMENTED AT METU

Table B.4. Water budget of the constructed wetlands implemented at METU

DATE	Rain (m^3)[b]	Evaporation (m^3)[a]	Q_{in} (m^3)[c]	Q_{out} (m^3)[d]	Correction Factors
15.06.2002	0	0.1407	3.00	2.859	0.953
26.06.2002	0.015	0.1755	3.00	2.840	0.947
12.07.2002	0.078	0.0258	3.00	3.052	1.017
16.07.2002	0.000	0.1518	3.00	2.848	0.949
25.07.2002	0.006	0.1536	3.00	2.852	0.951
06.08.2002	0.006	0.1257	3.00	2.880	0.960
12.08.2002	0.000	0.1659	3.00	2.834	0.945
20.08.2002	0.000	0.0762	3.00	2.924	0.975
28.08.2002	0.000	0.1389	3.00	2.861	0.954
03.09.2002	0.183	0.1572	3.00	3.026	1.009
11.09.2002	0.000	0.0876	3.00	2.912	0.971
02.10.2002	0.003	0.0744	3.00	2.929	0.976
11.10.2002	0.000	0.0516	3.00	2.948	0.983
15.10.2002	0.417	0.0975	3.00	3.320	1.107
22.10.2002	0.000	0.0522	3.00	2.948	0.983
31.10.2002	0.000	0.0648	3.00	2.935	0.978
11.11.2002	0.141	0.0150	3.00	3.126	1.042
28.11.2002	0.006	0.0129	3.00	2.993	0.998
13.12.2002	0.000	0.0000	3.00	3.000	1.000
17.01.2003	0.000	0.0000	3.00	3.000	1.000
02.02.2003	0.495	0.0000	3.00	3.495	1.165
30.03.2003	0.000	0.0000	3.00	3.000	1.000
02.04.2003	0.219	0.0000	3.00	3.219	1.073
09.04.2003	0.000	0.0495	3.00	2.951	0.984
17.04.2003	0.000	0.0894	3.00	2.911	0.970
02.05.2003	0.000	0.1410	3.00	2.859	0.953
18.05.2003	0.378	0.1530	3.00	3.225	1.075
26.05.2003	0.003	0.0990	3.00	2.904	0.968
06.06.2003	0.000	0.1290	3.00	2.871	0.957
17.06.2003	0.000	0.1770	3.00	2.823	0.941

a, b, d values have been found through calculations, whereas c values are measurements.

*For example: On the sampling date of 15.06.2002, the rain and evapotranspiration data were 0 mm and 4.69 mm, respectively. These values have been multiplied with the surface area of the wetlands (30 m^2 * 0.001 m/mm) so that 0 m^3 and 0.1407 m^3 have been found for rain and evapotranspiration, respectively. The difference of these values (-0.1407 m^3) was added to inflow value (3 m^3), where the outflow discharge value of the wetlands was obtained. Finally, the calculated outflow value (2.859 m^3) was divided by the measured inflow value (3 m^3), where the unitless correction factor of 0.953 was found.*

B.4. THE AREAL RATE CONSTANTS OF THE WATER QUALITY PARAMETERS FOR WINTER AND SUMMER PERIODS

Table B.5. The areal rate constants of the water quality parameters for winter and summer periods

Parameter	July 2002-November 2002		November 2002-July 2003	
TSS	**k slag (m/d)**	**k gravel (m/d)**	**k slag (m/d)**	**k gravel (m/d)**
AVG	0.118	0.138	0.125	0.086
MAX	0.187	0.256	0.230	0.151
MIN	0.018	0.029	0.077	0.048
MEDIAN	0.131	0.145	0.106	0.084
STDEV	0.046	0.070	0.048	0.038
COD	**k slag (m/d)**	**k gravel (m/d)**	**k slag (m/d)**	**k gravel (m/d)**
AVG	0.069	0.066	0.063	0.053
MAX	0.114	0.245	0.114	0.078
MIN	0.022	0.017	0.024	0.009
MEDIAN	0.065	0.047	0.058	0.060
STDEV	0.027	0.062	0.028	0.021
PO_4^{3-}-P	**k slag (m/d)**	**k gravel (m/d)**	**k slag (m/d)**	**k gravel (m/d)**
AVG	0.154	0.008	0.036	-0.001
MAX	0.252	0.018	0.066	0.018
MIN	0.037	-0.014	-0.029	-0.030
MEDIAN	0.161	0.010	0.046	-0.001
STDEV	0.064	0.009	0.028	0.014
TP	**k slag (m/d)**	**k gravel (m/d)**	**k slag (m/d)**	**k gravel (m/d)**
AVG	0.140	0.016	0.045	0.001
MAX	0.202	0.034	0.060	0.021
MIN	0.076	0.003	0.000	0.000
MEDIAN	0.155	0.017	0.046	0.002
STDEV	0.054	0.011	0.011	0.016
NH_4^+-N	**k slag (m/d)**	**k gravel (m/d)**	**k slag (m/d)**	**k gravel (m/d)**
AVG	0.287	0.109	0.223	0.078
MAX	0.493	0.136	0.372	0.164
MIN	0.085	0.081	0.077	0.030
MEDIAN	0.274	0.112	0.186	0.072
STDEV	0.156	0.023	0.097	0.039
TN	**k slag (m/d)**	**k gravel (m/d)**	**k slag (m/d)**	**k gravel (m/d)**
AVG	0.070	0.068	0.055	0.048
MAX	0.107	0.097	0.125	0.080
MIN	0.047	0.037	0.011	0.010
MEDIAN	0.051	0.066	0.051	0.047
STDEV	0.027	0.022	0.039	0.018

APPENDIX C

C.1. MASS BALANCE CALCULATIONS FOR THE CONSTRUCTED WETLANDS IMPLEMENTED AT METU

Sample Mass Balance Calculation (taken from Table C.1):

Sampling Date	TSS INFLOW ($mg.L^{-1}$)	$\lvert(C_2-C_1)\rvert$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	*Area below INFLOW ($day*(mg.L^{-1})$)	**Area below INFLOW (gram)
(T_i) 12.08.2002	(C_i) 52.00	22.00	8	3.00	390.00	1170.000
(T_{i+1}) 20.08.2002	(C_{i+1}) 30.00	10.00	(ΔT) 8	(Q) 3.00	(A_1) 328.00	(A_2) 984.000

* According to the trapezoidal rule, the area below the inflow concentration ($day*(mg.L^{-1})$) could be calculated as follows:

$A_1 = (C_i + C_{i+1})*(T_{i+1}-T_i)/2$

$A_1 = (C_i + C_{i+1})*(\Delta T)/2$

$A_1 = (52.0 + 30.0)*(8)/2$

$A_1 = 328.00\ d.mg.L^{-1}$

** The area below the inflow concentration (g) could be calculated as follows (since $1\ mg.L^{-1} = 1\ g.m^{-3}$):

$A_2 = A_1 * Q$

$A_2 = 328 * 3$

$A_2 = 984\ g$

Table C.1. Mass balance calculations for the TSS of the vertical flow wetland systems constructed at METU

Sampling Date	TSS INFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below INFLOW ($day*(mg.L^{-1})$)	Area below INFLOW (gram)
25.07.2002	25.14	0.86	12			
06.08.2002	26.00	26.00	6	3.00	312.17	951.515
12.08.2002	52.00	22.00	8	3.00	390.00	1170.000
20.08.2002	30.00	10.00	8	3.00	328.00	984.000
28.08.2002	40.00	12.00	6	3.00	360.00	1080.000
03.09.2002	28.00	32.00	8	3.00	204.00	612.000
11.09.2002	60.00	36.00	21	3.00	608.00	1824.000
02.10.2002	24.00	66.00	9	3.00	882.00	2646.000
11.10.2002	90.00	6.00	4	3.00	1107.00	3321.000
15.10.2002	96.00	44.00	7	3.00	396.00	1188.000
22.10.2002	140.00	92.00	9	3.00	1134.00	3402.000
31.10.2002	48.00	2.00	11	3.00	846.00	2538.000
11.11.2002	50.00	23.00	17	3.00	561.00	1683.000
28.11.2002	73.00	27.00	15	3.00	1436.50	4309.500
13.12.2002	100	36.00	35	3.00	2242.50	6727.500
17.01.2003	136.00	16.00	16	3.00	4830.00	14490.000
02.02.2003	120.00	48.30		3.00	2820.80	8462.400
30.03.2003	168.30	56.63	3	3.00	0.00	0.000
02.04.2003	111.67	15.33	7	3.00	465.95	1397.835
09.04.2003	127.00	18.50	8	3.00	813.16	2439.465
17.04.2003	108.50	4.80	15	3.00	980.40	2941.200
02.05.2003	113.30	72.20	16	3.00	652.50	1957.500
18.05.2003	41.10	4.45	8	3.00	1164.00	3492.000
26.05.2003	36.65	10.00	11	3.00	391.00	1173.000
06.06.2003	46.65	18.35	11	3.00	770.00	2310.000
17.06.2003	65.00	29.00	14	3.00	496.93	1490.775
01.07.2003	36.00	36.00	12	3.00	203.00	609.000
TOTAL			**285**			**73199.690**

Table C.2. Mass balance calculations for the TSS of the vertical flow slag system of METU

Sampling Date	TSS OUTFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below OUTFLOW ($day*(mg.L^{-1})$)	Area below OUTFLOW $Mass_{out}$ (gram)	Area below INFLOW $Mass_{in}$ (gram)	Removed Mass (IN-OUT) $Mass_{acc}$(gram)
25.07.2002	6.00	0.00	12					
06.08.2002	6.00	2.00	6	2.8524	72.00	205.373	951.515	746.142
12.08.2002	8.00	2.00	8	2.8803	54.00	155.536	1170.000	1014.464
20.08.2002	6.00	12.00	8	2.8341	56.00	158.710	984.000	825.290
28.08.2002	18.00	12.00	6	2.9238	192.00	561.370	1080.000	518.630
03.09.2002	6.00	20.00	8	2.8611	72.00	205.999	612.000	406.001
11.09.2002	26.00	6.00	21	3.0258	288.00	871.430	1824.000	952.570
02.10.2002	20.00	2.00	9	2.9124	483.00	1406.689	2646.000	1239.311
11.10.2002	22.00	18.00	4	2.9286	207.00	606.220	3321.000	2714.780
15.10.2002	40.00	2.00	7	2.9484	196.00	577.886	1188.000	610.114
22.10.2002	42.00	11.00	9	3.3195	301.00	999.170	3402.000	2402.831
31.10.2002	31.00	11.00	11	2.9478	328.50	968.352	2538.000	1569.648
11.11.2002	20.00	2.00	17	2.9352	280.50	823.324	1683.000	859.676
28.11.2002	22.00	8.00	15	3.126	391.00	1222.266	4309.500	3087.234
13.12.2002	30.00	20.00	35	2.9931	510.00	1526.481	6727.500	5201.019
17.01.2003	50.00	38.00	16	3	2100.00	6300.000	14490.000	8190.000
02.02.2003	12.00	46.34		3	496.00	1488.000	8462.400	6974.400
30.03.2003	58.34	13.34	3	3.495	0.00	0.000	0.000	0.000
02.04.2003	45.00	18.00	7	3	155.01	465.030	1397.835	932.805
09.04.2003	27.00	23.00	8	3.219	252.00	811.188	2439.465	1628.277
17.04.2003	50.00	26.70	15	2.9505	492.00	1451.646	2941.200	1489.554
02.05.2003	23.30	1.70	16	2.9106	549.75	1600.102	1957.500	357.398
18.05.2003	25.00	0.00	8	2.859	413.60	1182.482	3492.000	2309.518
26.05.2003	25.00	10.00	11	3.225	200.00	645.000	1173.000	528.000
06.06.2003	15.00	16.65	11	2.904	220.00	638.880	2310.000	1671.120
17.06.2003	31.65	27.65	14	2.871	439.73	1262.450	1490.775	228.325
01.07.2003	4.00	4.00	12	2.823	249.55	704.480	609.000	-95.480
TOTAL			**285**		**8998.64**	**26838.065**	**73199.690**	**46361.625**

Table C.3. Mass balance calculations for the TSS of the vertical flow gravel system of METU

Sampling Date	TSS OUTFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below OUTFLOW ($day*(mg.L^{-1})$)	Area below OUTFLOW $Mass_{out}$ (gram)	Area below INFLOW $Mass_{in}$ (gram)	Removed Mass (IN-OUT) $Mass_{acc}$(gram)
25.07.2002	4.00	0.00	12					
06.08.2002	4.00	0.00	6	2.8524	48.00	136.915	951.515	814.600
12.08.2002	4.00	0.00	8	2.8803	24.00	69.127	1170.000	1100.873
20.08.2002	4.00	26.00	8	2.8341	32.00	90.691	984.000	893.309
28.08.2002	30.00	26.00	6	2.9238	344.00	1005.787	1080.000	74.213
03.09.2002	4.00	16.00	8	2.8611	102.00	291.832	612.000	320.168
11.09.2002	20.00	16.00	21	3.0258	224.00	677.779	1824.000	1146.221
02.10.2002	4.00	30.00	9	2.9124	252.00	733.925	2646.000	1912.075
11.10.2002	34.00	22.00	4	2.9286	441.00	1291.513	3321.000	2029.487
15.10.2002	56.00	4.00	7	2.9484	268.00	790.171	1188.000	397.829
22.10.2002	60.00	27.00	9	3.3195	434.00	1440.663	3402.000	1961.337
31.10.2002	33.00	7.00	11	2.9478	418.50	1233.654	2538.000	1304.346
11.11.2002	26.00	19.00	17	2.9352	324.50	952.472	1683.000	730.528
28.11.2002	45.00	10.00	15	3.126	926.50	2896.239	4309.500	1413.261
13.12.2002	55.00	26.00	35	2.9931	900.00	2693.790	6727.500	4033.710
17.01.2003	81.00	39.00	16	3	3290.00	9870.000	14490.000	4620.000
02.02.2003	42.00	1.15		3	984.00	2952.000	8462.400	5510.400
30.03.2003	43.15	23.52	3	3.495	0.00	0.000	0.000	0.000
02.04.2003	66.67	11.67	7	3	235.29	705.870	1397.835	691.965
09.04.2003	55.00	8.50	8	3.219	425.85	1370.795	2439.465	1068.670
17.04.2003	46.50	21.49	15	2.9505	406.00	1197.903	2941.200	1743.297
02.05.2003	25.01	0.02	16	2.9106	536.33	1561.028	1957.500	396.472
18.05.2003	24.99	3.34	8	2.859	400.00	1143.600	3492.000	2348.400
26.05.2003	21.65	5.00	11	3.225	186.56	601.656	1173.000	571.344
06.06.2003	26.65	1.66	11	2.904	320.65	931.168	2310.000	1378.832
17.06.2003	24.99	8.99	14	2.871	284.02	815.421	1490.775	675.354
01.07.2003	16	16.00	12	2.823	286.93	810.003	609.000	-201.003
TOTAL			**285**		**12094.12**	**36264.004**	**73199.690**	**36935.686**

Table C.4. Mass balance calculations for the COD of the vertical flow wetland systems constructed at METU

Sampling Date	COD INFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below INFLOW ($day*(mg.L^{-1})$)	Area below INFLOW (gram)
25.07.2002	288.33	4.33	12			
06.08.2002	284.00	4.33	6	3.00	3434.00	10302.000
12.08.2002	288.33	140.33	8	3.00	1743.00	5229.000
20.08.2002	148.00	40.00	8	3.00	1745.33	5236.000
28.08.2002	108.00	84.00	6	3.00	1024.00	3072.000
03.09.2002	192.00	65.00	8	3.00	1404.00	4212.000
11.09.2002	257.00	50.33	21	3.00	2316.00	6948.000
02.10.2002	307.33	41.66	9	3.00	6982.40	20947.185
11.10.2002	265.67	7.83	4	3.00	2578.50	7735.500
15.10.2002	273.50	100.50	7	3.00	1109.66	3328.980
22.10.2002	173.00	33.50	9	3.00	1562.75	4688.250
31.10.2002	139.50	2.83	11	3.00	1406.25	4218.750
11.11.2002	142.33	54.00	17	3.00	1581.20	4743.585
28.11.2002	196.33	183.67	15	3.00	3796.61	11389.830
13.12.2002	380.00	17.50	35	3.00	7077.53	21232.575
17.01.2003	397.50	16.17	16	3.00	14218.75	42656.250
02.02.2003	381.33	31.33		3.00	6230.64	18691.920
30.03.2003	350.00	1.33	3	3.00	0.00	0.000
02.04.2003	348.67	3.67	7	3.00	1048.01	3144.015
09.04.2003	345.00	66.67	8	3.00	2427.85	7283.535
17.04.2003	411.67	180.42	15	3.00	3560.04	10680.120
02.05.2003	231.25	71.75	16	3.00	4821.90	14465.700
18.05.2003	303.00	126.67	8	3.00	5422.00	16266.000
26.05.2003	176.33	2.66	11	3.00	1917.32	5751.960
06.06.2003	173.67	80.67	11	3.00	1925.00	5775.000
17.06.2003	93.00	6.00	14	3.00	1466.69	4400.055
01.07.2003	87.00	87.00	12	3.00	1260.00	3780.000
TOTAL			**285**			**246178.210**

Table C.5. Mass balance calculations for the COD of the vertical flow slag system of METU

Sampling Date	COD OUTFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below OUTFLOW ($day*(mg.L^{-1})$)	Area below OUTFLOW $Mass_{out}$ (gram)	Area below INFLOW $Mass_{in}$ (gram)	Removed Mass (IN-OUT) $Mass_{acc}$(gram)
25.07.2002	145.03	13.10	12					
06.08.2002	158.13	8.06	6	2.8524	1976.10	5636.630	10302.000	4665.370
12.08.2002	166.19	47.69	8	2.8803	1021.30	2941.650	5229.000	2287.350
20.08.2002	118.50	84.00	8	2.8341	1138.75	3227.319	5236.000	2008.681
28.08.2002	34.50	46.50	6	2.9238	612.00	1789.366	3072.000	1282.634
03.09.2002	81.00	39.50	8	2.8611	625.50	1789.618	4212.000	2422.382
11.09.2002	120.50	44.17	21	3.0258	1122.00	3394.948	6948.000	3553.052
02.10.2002	164.67	29.67	9	2.9124	3921.86	11422.011	20947.185	9525.174
11.10.2002	135.00	23.00	4	2.9286	1348.52	3949.261	7735.500	3786.239
15.10.2002	158.00	79.50	7	2.9484	678.00	1999.015	3328.980	1329.965
22.10.2002	78.50	33.17	9	3.3195	827.75	2747.716	4688.250	1940.534
31.10.2002	45.33	16.34	11	2.9478	557.24	1642.617	4218.750	2576.133
11.11.2002	61.67	92.66	17	2.9352	768.24	2254.938	4743.585	2488.647
28.11.2002	154.33	5.00	15	3.126	3411.22	10663.474	11389.830	726.356
13.12.2002	149.33	63.42	35	2.9931	2277.45	6816.636	21232.575	14415.939
17.01.2003	212.75	25.75	16	3	8556.10	25668.300	42656.250	16987.950
02.02.2003	187.00	39.00		3	3198.00	9594.000	18691.920	9097.920
30.03.2003	226.00	4.67	3	3.495	0.00	0.000	0.000	0.000
02.04.2003	221.33	110.83	7	3	671.00	2012.985	3144.015	1131.030
09.04.2003	110.50	130.50	8	3.219	1161.41	3738.563	7283.535	3544.972
17.04.2003	241.00	78.50	15	2.9505	2450.00	7228.725	10680.120	3451.395
02.05.2003	162.50	62.83	16	2.9106	3026.25	8808.203	14465.700	5657.497
18.05.2003	99.67	27.00	8	2.859	2097.36	5996.352	16266.000	10269.648
26.05.2003	72.67	14.00	11	3.225	689.36	2223.186	5751.960	3528.774
06.06.2003	86.67	23.00	11	2.904	1030.37	2992.194	5775.000	2782.806
17.06.2003	63.67	9.67	14	2.871	826.87	2373.944	4400.055	2026.111
01.07.2003	54.00	54.00	12	2.823	823.69	2325.277	3780.000	1454.723
TOTAL			**285**		**44816.31**	**133236.926**	**246178.210**	**112941.284**

Table C.6. Mass balance calculations for the COD of the vertical flow gravel system of METU

Sampling Date	COD OUTFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below OUTFLOW ($day*(mg.L^{-1})$)	Area below OUTFLOW $Mass_{out}$ (gram)	Area below INFLOW $Mass_{in}$ (gram)	Removed Mass (IN-OUT) $Mass_{acc}$(gram)
25.07.2002	174.75	41.81	12					
06.08.2002	216.56	39.29	6	2.8524	2849.65	8128.348	10240.309	2111.961
12.08.2002	177.27	65.77	8	2.8803	1181.50	3403.078	5197.701	1794.623
20.08.2002	111.50	39.00	8	2.8341	1155.08	3273.607	3552.000	278.393
28.08.2002	72.50	50.50	6	2.9238	736.00	2151.917	2605.440	453.523
03.09.2002	123.00	2.50	8	2.8611	889.50	2544.948	3482.820	937.872
11.09.2002	125.50	77.50	21	3.0258	1014.00	3068.161	6168.120	3099.959
02.10.2002	203.00	122.00	9	2.9124	5076.75	14785.527	19388.880	4603.353
11.10.2002	81.00	67.00	4	2.9286	1278.00	3742.751	7180.920	3438.169
15.10.2002	148.00	43.50	7	2.9484	726.00	2140.538	3292.920	1152.382
22.10.2002	104.50	54.50	9	3.3195	883.75	2933.608	3653.475	719.867
31.10.2002	50.00	15.00	11	2.9478	695.25	2049.458	3814.425	1764.967
11.11.2002	65.00	114.00	17	2.9352	797.50	2340.822	4712.070	2371.248
28.11.2002	179.00	13.33	15	3.126	4012.00	12541.512	10051.335	-2490.177
13.12.2002	192.33	88.67	35	2.9931	2984.93	8934.179	17105.175	8170.996
17.01.2003	281.00	71.67	16	3	11386.73	34160.175	41801.025	7640.850
02.02.2003	209.33	21.67		3	3922.64	11767.920	18315.120	6547.200
30.03.2003	231.00	39.33	3	3.495	0.00	0.000	0.000	0.000
02.04.2003	191.67	15.17	7	3	634.01	1902.015	3144.105	1242.090
09.04.2003	176.50	35.83	8	3.219	1288.60	4147.987	7263.165	3115.178
17.04.2003	212.33	63.33	15	2.9505	1841.96	5434.703	9886.320	4451.617
02.05.2003	149.00	49.33	16	2.9106	2709.98	7887.653	10512.900	2625.247
18.05.2003	99.67	0.00	8	2.859	1989.36	5687.580	14645.040	8957.460
26.05.2003	99.67	22.66	11	3.225	797.36	2571.486	4282.440	1710.954
06.06.2003	122.33	74.33	11	2.904	1470.26	4269.635	5800.575	1530.940
17.06.2003	48.00	23.00	14	2.871	936.82	2689.596	3138.465	448.869
01.07.2003	25	25.00	12	2.823	511.00	1442.553	3742.410	2299.857
TOTAL			**285**		**51768.60**	**153999.758**	**246178.210**	**92178.452**

Table C.7. Mass balance calculations for the PO_4^{3-}-P of the vertical flow wetland systems constructed at METU

Sampling Date	PO_4^{3-}-P INFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below INFLOW ($day*(mg.L^{-1})$)	Area below INFLOW (gram)
25.07.2002	4.44	0.09	12			
06.08.2002	4.53	0.23	6	3.00	54.83	164.487
12.08.2002	4.29	0.11	8	3.00	26.45	79.346
20.08.2002	4.18	0.25	8	3.00	33.88	101.650
28.08.2002	3.93	0.55	6	3.00	32.44	97.320
03.09.2002	4.48	3.55	8	3.00	28.53	85.590
11.09.2002	8.03	1.61	21	3.00	78.44	235.320
02.10.2002	6.42	1.41	9	3.00	151.73	455.175
11.10.2002	5.01	0.68	4	3.00	51.44	154.305
15.10.2002	4.33	2.75	7	3.00	18.68	56.040
22.10.2002	7.08	4.11	9	3.00	59.19	177.555
31.10.2002	2.97	0.76	11	3.00	45.23	135.675
11.11.2002	3.73	0.60	17	3.00	45.21	135.630
28.11.2002	4.33	0.26	15	3.00	78.71	236.130
13.12.2002	4.07	0.15	35	3.00	63.00	189.000
17.01.2003	4.22	2.48	16	3.00	150.33	450.975
02.02.2003	6.70	0.15		3.00	127.04	381.120
30.03.2003	6.55	0.98	3	3.00	0.00	0.000
02.04.2003	5.57	0.35	7	3.00	18.18	54.540
09.04.2003	5.92	1.64	8	3.00	42.67	127.995
17.04.2003	7.56	5.31	15	3.00	67.04	201.120
02.05.2003	2.25	1.19	16	3.00	73.58	220.725
18.05.2003	3.44	0.23	8	3.00	64.56	193.680
26.05.2003	3.21	0.77	11	3.00	26.60	79.800
06.06.2003	3.98	0.80	11	3.00	48.02	144.045
17.06.2003	3.18	0.56	14	3.00	39.38	118.140
01.07.2003	2.62	2.62	12	3.00	40.60	121.800
TOTAL			**285**			**4397.163**

Table C.8. Mass balance calculations for the PO_4^{3-}-P of the vertical flow slag system of METU

Sampling Date	PO_4^{3-}-P OUTFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below OUTFLOW ($day*(mg.L^{-1})$)	Area below OUTFLOW $Mass_{out}$ (gram)	Area below INFLOW $Mass_{in}$ (gram)	Removed Mass (IN-OUT) $Mass_{acc}$(gram)
25.07.2002	0.36	0.27	12					
06.08.2002	0.63	0.09	6	2.8524	9.15	26.092	164.487	138.395
12.08.2002	0.54	0.07	8	2.8803	3.50	10.074	79.346	69.272
20.08.2002	0.61	0.18	8	2.8341	5.17	14.646	101.650	87.004
28.08.2002	0.43	0.30	6	2.9238	4.16	12.163	97.320	85.157
03.09.2002	0.73	1.62	8	2.8611	5.28	15.107	85.590	70.483
11.09.2002	2.35	0.79	21	3.0258	25.28	76.492	235.320	158.828
02.10.2002	1.56	0.45	9	2.9124	41.06	119.569	455.175	335.606
11.10.2002	2.01	0.67	4	2.9286	20.12	58.909	154.305	95.396
15.10.2002	1.34	1.54	7	2.9484	6.70	19.754	56.040	36.286
22.10.2002	2.88	0.83	9	3.3195	25.55	84.813	177.555	92.742
31.10.2002	2.05	0.16	11	2.9478	22.19	65.397	135.675	70.278
11.11.2002	2.21	0.02	17	2.9352	25.19	73.938	135.630	61.692
28.11.2002	2.23	0.74	15	3.126	38.08	119.038	236.130	117.092
13.12.2002	2.97	0.98	35	2.9931	50.10	149.954	189.000	39.046
17.01.2003	3.95	0.19	16	3	155.40	466.200	450.975	-15.225
02.02.2003	4.14	0.18		3	67.76	203.280	381.120	177.840
30.03.2003	3.96	0.35	3	3.495	0.00	0.000	0.000	0.000
02.04.2003	3.61	0.80	7	3	11.36	34.065	54.540	20.475
09.04.2003	4.41	0.21	8	3.219	33.67	108.384	127.995	19.611
17.04.2003	4.20	1.20	15	2.9505	34.44	101.615	201.120	99.505
02.05.2003	3.00	0.12	16	2.9106	54.00	157.172	220.725	63.553
18.05.2003	3.12	0.39	8	2.859	50.88	145.466	193.680	48.214
26.05.2003	2.73	0.06	11	3.225	23.40	75.465	79.800	4.335
06.06.2003	2.79	0.30	11	2.904	31.02	90.082	144.045	53.963
17.06.2003	2.49	0.07	14	2.871	29.04	83.374	118.140	34.766
01.07.2003	2.42	2.42	12	2.823	34.37	97.027	121.800	24.773
TOTAL			**285**		**806.84**	**2408.075**	**4397.163**	**1989.088**

Table C.9. Mass balance calculations for the PO_4^{3-}-P of the vertical flow gravel system of METU

Sampling Date	PO_4^{3-}-P OUTFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below OUTFLOW ($day*(mg.L^{-1})$)	Area below OUTFLOW $Mass_{out}$ (gram)	Area below INFLOW $Mass_{in}$ (gram)	Removed Mass (IN-OUT) $Mass_{acc}$(gram)
25.07.2002	3.76	0.17	12					
06.08.2002	3.93	0.03	6	2.8524	48.21	137.504	164.487	26.983
12.08.2002	3.90	0.20	8	2.8803	23.49	67.656	79.346	11.690
20.08.2002	3.70	0.03	8	2.8341	30.39	86.130	101.650	15.520
28.08.2002	3.67	0.73	6	2.9238	29.48	86.194	97.320	11.126
03.09.2002	4.40	2.29	8	2.8611	28.59	81.799	85.590	3.791
11.09.2002	6.69	1.17	21	3.0258	62.68	189.657	235.320	45.663
02.10.2002	5.52	0.96	9	2.9124	128.21	373.384	455.175	81.791
11.10.2002	4.56	0.23	4	2.9286	45.36	132.841	154.305	21.464
15.10.2002	4.33	2.22	7	2.9484	17.78	52.423	56.040	3.617
22.10.2002	6.55	3.12	9	3.3195	53.62	177.992	177.555	-0.437
31.10.2002	3.43	0.86	11	2.9478	44.91	132.386	135.675	3.289
11.11.2002	4.29	0.15	17	2.9352	51.92	152.396	135.630	-16.766
28.11.2002	4.14	0.16	15	3.126	71.66	223.994	236.130	12.136
13.12.2002	4.30	0.16	35	2.9931	65.70	196.647	189.000	-7.647
17.01.2003	4.46	2.47	16	3	158.90	476.700	450.975	-25.725
02.02.2003	6.93	1.44		3	130.64	391.920	381.120	-10.800
30.03.2003	5.49	0.45	3	3.495	0.00	0.000	0.000	0.000
02.04.2003	5.04	0.77	7	3	15.80	47.385	54.540	7.155
09.04.2003	5.81	1.00	8	3.219	43.37	139.592	127.995	-11.597
17.04.2003	6.81	3.78	15	2.9505	58.48	172.545	201.120	28.575
02.05.2003	3.03	1.36	16	2.9106	73.80	214.802	220.725	5.923
18.05.2003	4.39	0.70	8	2.859	81.12	231.922	193.680	-38.242
26.05.2003	3.69	0.06	11	3.225	32.32	104.232	79.800	-24.432
06.06.2003	3.63	0.14	11	2.904	40.26	116.915	144.045	27.130
17.06.2003	3.49	0.91	14	2.871	39.16	112.428	118.140	5.712
01.07.2003	2.58	2.58	12	2.823	42.49	119.949	121.800	1.851
TOTAL			**285**		**1418.32**	**4219.392**	**4397.163**	**177.771**

Table C.10. Mass balance calculations for the TP of the vertical flow wetland systems constructed at METU

Sampling Date	TP INFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below INFLOW ($day*(mg.L^{-1})$)	Area below INFLOW (gram)
25.07.2002	8.36	0.91	12			
06.08.2002	7.46	0.86	6	3.00	94.90	284.711
12.08.2002	6.60	0.00	8	3.00	42.17	126.501
20.08.2002	6.60	1.12	8	3.00	52.80	158.400
28.08.2002	5.48	2.98	6	3.00	48.32	144.960
03.09.2002	8.46	0.01	8	3.00	59.70	179.100
11.09.2002	8.45	0.86	21	3.00	67.64	202.920
02.10.2002	7.59	0.58	9	3.00	168.42	505.260
11.10.2002	7.01	1.82	4	3.00	65.70	197.100
15.10.2002	5.19	1.95	7	3.00	24.40	73.200
22.10.2002	7.14	3.55	9	3.00	56.81	170.415
31.10.2002	3.59	0.92	11	3.00	48.29	144.855
11.11.2002	4.51	1.51	17	3.00	54.67	164.010
28.11.2002	6.02	0.23	15	3.00	115.18	345.525
13.12.2002	6.25	1.21	35	3.00	95.48	286.425
17.01.2003	7.46	0.47	16	3.00	282.28	846.825
02.02.2003	7.93	1.16		3.00	130.64	391.920
30.03.2003	9.09	1.35	3	3.00	0.00	0.000
02.04.2003	7.74	1.73	7	3.00	25.25	75.735
09.04.2003	9.47	0.52	8	3.00	72.35	217.035
17.04.2003	8.95	4.74	15	3.00	73.68	221.040
02.05.2003	4.21	0.20	16	3.00	98.70	296.100
18.05.2003	4.01	0.04	8	3.00	65.76	197.280
26.05.2003	3.97	1.78	11	3.00	31.92	95.760
06.06.2003	5.75	0.00	11	3.00	73.04	219.120
17.06.2003	5.75	2.02	14	3.00	63.25	189.750
01.07.2003	3.73	3.73	12	3.00	66.36	199.080
TOTAL			**285**			**5933.027**

Table C.11. Mass balance calculations for the TP of the vertical flow slag system of METU

Sampling Date	TP OUTFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below OUTFLOW ($day*(mg.L^{-1})$)	Area below OUTFLOW $Mass_{out}$ (gram)	Area below INFLOW $Mass_{in}$ (gram)	Removed Mass (IN-OUT) $Mass_{acc}$(gram)
25.07.2002	1.11	0.02	12					
06.08.2002	1.12	0.03	6	2.8524	13.60	38.804	284.711	245.907
12.08.2002	1.09	0.02	8	2.8803	6.66	19.174	126.501	107.327
20.08.2002	1.07	0.25	8	2.8341	8.66	24.540	158.400	133.860
28.08.2002	0.82	0.56	6	2.9238	7.56	22.104	144.960	122.856
03.09.2002	1.38	1.15	8	2.8611	9.96	28.497	179.100	150.603
11.09.2002	2.53	0.47	21	3.0258	24.84	75.161	202.920	127.759
02.10.2002	2.06	0.60	9	2.9124	48.20	140.363	505.260	364.897
11.10.2002	2.66	0.58	4	2.9286	26.64	78.018	197.100	119.082
15.10.2002	2.08	1.26	7	2.9484	9.48	27.951	73.200	45.249
22.10.2002	3.34	1.02	9	3.3195	27.79	92.249	170.415	78.166
31.10.2002	2.32	1.02	11	2.9478	25.47	75.080	144.855	69.775
11.11.2002	3.34	0.32	17	2.9352	42.35	124.306	164.010	39.704
28.11.2002	3.66	0.23	15	3.126	64.94	203.002	345.525	142.523
13.12.2002	3.43	1.06	35	2.9931	53.18	159.158	286.425	127.267
17.01.2003	4.49	0.05	16	3	175.70	527.100	846.825	319.725
02.02.2003	4.44	1.83		3	71.44	214.320	391.920	177.600
30.03.2003	6.27	0.55	3	3.495	0.00	0.000	0.000	0.000
02.04.2003	5.72	4.22	7	3	17.99	53.955	75.735	21.780
09.04.2003	9.94	4.92	8	3.219	84.35	271.523	217.035	-54.488
17.04.2003	5.02	2.16	15	2.9505	59.84	176.558	221.040	44.482
02.05.2003	2.86	0.75	16	2.9106	59.10	172.016	296.100	124.084
18.05.2003	3.61	0.12	8	2.859	63.76	182.290	197.280	14.990
26.05.2003	3.73	0.12	11	3.225	30.32	97.782	95.760	-2.022
06.06.2003	3.61	3.71	11	2.904	40.37	117.234	219.120	101.886
17.06.2003	7.32	3.93	14	2.871	100.93	289.756	189.750	-100.006
01.07.2003	3.39	3.39	12	2.823	74.97	211.640	199.080	-12.560
TOTAL			**285**		**1148.08**	**3422.581**	**5933.027**	**2510.446**

Table C.12. Mass balance calculations for the TP of the vertical flow gravel system of METU

Sampling Date	TP OUTFLOW ($mg.L^{-1}$)	$\lvert(C_2-C_1)\rvert$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below OUTFLOW (day*($mg.L^{-1}$))	Area below OUTFLOW $Mass_{out}$ (gram)	Area below INFLOW $Mass_{in}$ (gram)	Removed Mass (IN-OUT) $Mass_{acc}$(gram)
25.07.2002	6.30	0.26	12					
06.08.2002	6.04	0.49	6	2.8524	74.01	211.108	284.711	73.603
12.08.2002	5.54	0.41	8	2.8803	34.73	100.044	126.501	26.457
20.08.2002	5.13	0.19	8	2.8341	42.69	120.987	158.400	37.413
28.08.2002	5.32	2.15	6	2.9238	43.32	126.659	144.960	18.301
03.09.2002	7.47	0.26	8	2.8611	51.27	146.689	179.100	32.411
11.09.2002	7.21	1.04	21	3.0258	58.72	177.675	202.920	25.245
02.10.2002	6.17	1.19	9	2.9124	140.49	409.163	505.260	96.097
11.10.2002	4.98	0.28	4	2.9286	50.18	146.943	197.100	50.157
15.10.2002	4.70	1.86	7	2.9484	19.36	57.081	73.200	16.119
22.10.2002	6.56	2.77	9	3.3195	52.43	174.041	170.415	-3.626
31.10.2002	3.79	2.77	11	2.9478	46.58	137.294	144.855	7.561
11.11.2002	6.56	0.36	17	2.9352	87.40	256.522	164.010	-92.512
28.11.2002	6.20	0.80	15	3.126	108.46	339.046	345.525	6.479
13.12.2002	5.40	1.69	35	2.9931	87.00	260.400	286.425	26.025
17.01.2003	7.09	0.38	16	3	277.73	833.175	846.825	13.650
02.02.2003	7.47	0.11		3	122.56	367.680	391.920	24.240
30.03.2003	7.36	0.62	3	3.495	0.00	0.000	0.000	0.000
02.04.2003	6.74	0.48	7	3	21.15	63.450	75.735	12.285
09.04.2003	6.26	3.03	8	3.219	45.50	146.465	217.035	70.571
17.04.2003	9.29	5.01	15	2.9505	86.44	255.041	221.040	-34.001
02.05.2003	4.28	0.71	16	2.9106	101.78	296.226	296.100	-0.126
18.05.2003	4.99	0.31	8	2.859	85.52	244.502	197.280	-47.222
26.05.2003	4.68	0.03	11	3.225	38.68	124.743	95.760	-28.983
06.06.2003	4.65	0.55	11	2.904	51.32	149.019	219.120	70.101
17.06.2003	5.20	1.35	14	2.871	60.23	172.906	189.750	16.844
01.07.2003	3.85	3.85	12	2.823	63.35	178.837	199.080	20.243
TOTAL			**285**		**1850.87**	**5495.693**	**5933.027**	**437.333**

Table C.13. Mass balance calculations for the NH_4^+-N of the vertical flow wetland systems constructed at METU

Sampling Date	NH_4^+-N INFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below INFLOW ($day*(mg.L^{-1})$)	Area below INFLOW (gram)
25.07.2002	22.20	4.66	12			
06.08.2002	17.54	16.89	6	3.00	238.44	715.331
12.08.2002	34.44	18.65	8	3.00	257.29	771.880
20.08.2002	15.79	1.01	8	3.00	200.90	602.700
28.08.2002	16.80	8.03	6	3.00	138.44	415.320
03.09.2002	24.83	1.93	8	3.00	173.07	519.210
11.09.2002	22.90	11.63	21	3.00	190.92	572.760
02.10.2002	34.53	5.17	9	3.00	847.25	2541.735
11.10.2002	29.36	1.66	4	3.00	287.51	862.515
15.10.2002	31.02	10.34	7	3.00	127.40	382.200
22.10.2002	20.68	5.63	9	3.00	180.95	542.850
31.10.2002	15.05	9.88	11	3.00	160.79	482.355
11.11.2002	24.93	4.16	17	3.00	328.57	985.710
28.11.2002	20.77	0.09	15	3.00	388.45	1165.350
13.12.2002	20.68	17.44	35	3.00	310.88	932.625
17.01.2003	38.12	15.41	16	3.00	1639.40	4918.200
02.02.2003	22.71	1.76		3.00	486.64	1459.920
30.03.2003	24.47	1.65	3	3.00	0.00	0.000
02.04.2003	26.12	19.76	7	3.00	80.84	242.505
09.04.2003	45.88	2.94	8	3.00	390.32	1170.960
17.04.2003	48.82	29.41	15	3.00	402.32	1206.960
02.05.2003	19.41	9.53	16	3.00	511.73	1535.175
18.05.2003	28.94	5.29	8	3.00	539.28	1617.840
26.05.2003	23.65	9.29	11	3.00	210.36	631.080
06.06.2003	32.94	4.12	11	3.00	413.44	1240.305
17.06.2003	28.82	8.23	14	3.00	339.68	1019.040
01.07.2003	20.59	20.59	12	3.00	345.87	1037.610
TOTAL			**285**			**27572.135**

Table C.14. Mass balance calculations for the NH_4^+-N of the vertical flow slag system of METU

Sampling Date	NH_4^+-N OUTFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below OUTFLOW ($day*(mg.L^{-1})$)	Area below OUTFLOW $Mass_{out}$ (gram)	Area below INFLOW $Mass_{in}$ (gram)	Removed Mass (IN-OUT) $Mass_{nce}$(gram)
25.07.2002	2.99	2.47	12					
06.08.2002	0.52	3.91	6	2.8524	21.03	59.983	715.331	655.348
12.08.2002	4.43	3.41	8	2.8803	38.33	110.404	771.880	661.475
20.08.2002	1.02	1.02	8	2.8341	21.81	61.798	602.700	540.902
28.08.2002	0.00	0.18	6	2.9238	4.08	11.929	415.320	403.391
03.09.2002	0.18	9.61	8	2.8611	1.62	4.635	519.210	514.575
11.09.2002	9.79	1.30	21	3.0258	116.76	353.292	572.760	219.468
02.10.2002	8.49	1.38	9	2.9124	191.94	559.006	2541.735	1982.729
11.10.2002	7.11	1.66	4	2.9286	70.20	205.588	862.515	656.927
15.10.2002	5.45	1.48	7	2.9484	25.12	74.064	382.200	308.136
22.10.2002	3.97	2.68	9	3.3195	32.97	109.444	542.850	433.406
31.10.2002	1.29	2.13	11	2.9478	23.67	69.774	482.355	412.581
11.11.2002	3.42	2.77	17	2.9352	49.34	144.808	985.710	840.902
28.11.2002	0.65	0.00	15	3.126	34.60	108.144	1165.350	1057.206
13.12.2002	0.65	1.00	35	2.9931	9.75	29.183	932.625	903.442
17.01.2003	1.65	3.17	16	3	75.25	225.750	4918.200	4692.450
02.02.2003	4.82	1.30		3	102.48	307.440	1459.920	1152.480
30.03.2003	6.12	0.23	3	3.495	0.00	0.000	0.000	0.000
02.04.2003	6.35	14.83	7	3	19.40	58.185	242.505	184.320
09.04.2003	21.18	18.94	8	3.219	200.17	644.331	1170.960	526.629
17.04.2003	2.24	1.77	15	2.9505	93.68	276.403	1206.960	930.557
02.05.2003	0.47	0.82	16	2.9106	20.33	59.158	1535.175	1476.017
18.05.2003	1.29	1.29	8	2.859	27.20	77.765	1617.840	1540.075
26.05.2003	0.00	4.00	11	3.225	5.16	16.641	631.080	614.439
06.06.2003	4.00	3.53	11	2.904	66.00	191.664	1240.305	1048.641
17.06.2003	0.47	0.47	14	2.871	24.59	70.584	1019.040	948.456
01.07.2003	0.94	0.94	12	2.823	16.45	46.438	1037.610	991.172
TOTAL			**285**		**1291.89**	**3876.411**	**27572.135**	**23695.724**

Table C.15. Mass balance calculations for the NH_4^+-N of the vertical flow gravel system of METU

Sampling Date	NH_4^+-N OUTFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below OUTFLOW ($day*(mg.L^{-1})$)	Area below OUTFLOW $Mass_{out}$ (gram)	Area below INFLOW $Mass_{in}$ (gram)	Removed Mass (IN-OUT) $Mass_{acc}$(gram)
25.07.2002	3.22	3.57	12					
06.08.2002	6.79	2.16	6	2.8524	102.98	293.727	715.331	421.604
12.08.2002	8.95	4.89	8	2.8803	60.21	173.424	771.880	598.455
20.08.2002	4.06	3.42	8	2.8341	52.06	147.543	602.700	455.157
28.08.2002	7.48	3.23	6	2.9238	73.52	214.958	415.320	200.362
03.09.2002	10.71	3.69	8	2.8611	73.95	211.578	519.210	307.632
11.09.2002	7.02	4.24	21	3.0258	70.92	214.590	572.760	358.170
02.10.2002	11.26	0.46	9	2.9124	280.98	818.326	2541.735	1723.409
11.10.2002	10.80	4.80	4	2.9286	99.27	290.722	862.515	571.793
15.10.2002	15.60	7.85	7	2.9484	72.00	212.285	382.200	169.915
22.10.2002	7.75	1.48	9	3.3195	81.73	271.286	542.850	271.564
31.10.2002	9.23	3.14	11	2.9478	89.73	264.506	482.355	217.849
11.11.2002	6.09	6.56	17	2.9352	84.26	247.320	985.710	738.390
28.11.2002	12.65	0.19	15	3.126	270.81	846.552	1165.350	318.798
13.12.2002	12.46	10.13	35	2.9931	188.33	563.676	932.625	368.949
17.01.2003	22.59	13.30	16	3	967.93	2903.775	4918.200	2014.425
02.02.2003	9.29	8.83		3	255.04	765.120	1459.920	694.800
30.03.2003	18.12	0.23	3	3.495	0.00	0.000	0.000	0.000
02.04.2003	18.35	9.41	7	3	55.40	166.185	242.505	76.320
09.04.2003	8.94	13.88	8	3.219	95.52	307.463	1170.960	863.497
17.04.2003	22.82	14.47	15	2.9505	238.08	702.455	1206.960	504.505
02.05.2003	8.35	5.53	16	2.9106	233.78	680.426	1535.175	854.749
18.05.2003	13.88	1.76	8	2.859	266.32	761.409	1617.840	856.431
26.05.2003	12.12	6.47	11	3.225	104.00	335.400	631.080	295.680
06.06.2003	18.59	4.59	11	2.904	240.08	697.178	1240.305	543.127
17.06.2003	14.00	4.82	14	2.871	179.25	514.612	1019.040	504.428
01.07.2003	9.18	9.18	12	2.823	162.26	458.060	1037.610	579.550
TOTAL			**285**	**4398.37**	**13062.575**	**27572.135**	**14509.560**	**13062.575**

Table C.16. Mass balance calculations for the NO_3^--N of the vertical flow wetland systems constructed at METU

Sampling Date	NO_3^--N INFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below INFLOW ($day*(mg.L^{-1})$)	Area below INFLOW (gram)
25.07.2002	2.10	0.24	12			
06.08.2002	1.86	1.86	6	3.00	23.74	71.232
12.08.2002	0.00	0.00	8	3.00	5.57	16.716
20.08.2002	0.00	0.42	8	3.00	0.00	0.000
28.08.2002	0.42	0.42	6	3.00	5.04	15.120
03.09.2002	0.00	0.67	8	3.00	1.26	3.780
11.09.2002	0.67	0.23	21	3.00	8.04	24.120
02.10.2002	0.44	2.23	9	3.00	11.66	34.965
11.10.2002	2.67	0.23	4	3.00	34.07	102.195
15.10.2002	2.44	1.77	7	3.00	10.22	30.660
22.10.2002	0.67	0.11	9	3.00	10.89	32.655
31.10.2002	0.56	2.66	11	3.00	5.54	16.605
11.11.2002	3.22	2.22	17	3.00	50.05	150.150
28.11.2002	1	0.11	15	3.00	35.87	107.610
13.12.2002	1.11	0.11	35	3.00	17.48	52.425
17.01.2003	1.22	1.22	16	3.00	44.63	133.875
02.02.2003	0.00	0.00		3.00	9.76	29.280
30.03.2003	0.00	0.00	3	3.00	0.00	0.000
02.04.2003	0.00	4.89	7	3.00	0.00	0.000
09.04.2003	4.89	4.89	8	3.00	51.35	154.035
17.04.2003	0.00	6.33	15	3.00	19.56	58.680
02.05.2003	6.33	6.33	16	3.00	142.43	427.275
18.05.2003	1.26	38.26	8	3.00	70.80	212.400
26.05.2003	0.00	1.46	11	3.00	153.03	459.088
06.06.2003	6.44	6.44	11	3.00	78.89	236.669
17.06.2003	0.00	0.00	14	3.00	35.42	106.260
01.07.2003	2.22	2.22	12	3.00	31.08	93.240
TOTAL			**285**		**856.35**	**2569.035**

Table C.17. Mass balance calculations for the NO_3^--N of the vertical flow slag system of METU

Sampling Date	NO_3^--N OUTFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below OUTFLOW ($day*(mg.L^{-1})$)	Area below OUTFLOW $Mass_{out}$ (gram)	Area below INFLOW $Mass_{in}$ (gram)	Removed Mass (IN-OUT) $Mass_{acc}$(gram)
25.07.2002	1.15	9.10	12					
06.08.2002	10.26	1.14	6	2.8524	177.71	506.906	71.232	-435.674
12.08.2002	11.40	0.55	8	2.8803	71.80	206.813	16.716	-190.097
20.08.2002	11.95	1.52	8	2.8341	97.81	277.207	0.000	-277.207
28.08.2002	13.47	2.45	6	2.9238	113.84	332.845	15.120	-317.725
03.09.2002	11.02	2.46	8	2.8611	73.47	210.205	3.780	-206.425
11.09.2002	8.56	10.22	21	3.0258	78.32	236.981	24.120	-212.861
02.10.2002	18.78	0.56	9	2.9124	501.69	1461.122	34.965	-1426.157
11.10.2002	18.22	13.11	4	2.9286	166.50	487.612	102.195	-385.417
15.10.2002	31.33	11.55	7	2.9484	151.54	446.801	30.660	-416.141
22.10.2002	19.78	10.34	9	3.3195	178.89	593.809	32.655	-561.154
31.10.2002	9.44	12.89	11	2.9478	131.49	387.606	16.605	-371.001
11.11.2002	22.33	0.34	17	2.9352	316.53	929.064	150.150	-778.914
28.11.2002	22.67	12.34	15	3.126	388.28	1213.763	107.610	-1106.153
13.12.2002	10.33	2.23	35	2.9931	247.50	740.792	52.425	-688.367
17.01.2003	12.56	8.00	16	3	478.63	1435.875	133.875	-1302.000
02.02.2003	20.56	15.89		3	392.96	1178.880	29.280	-1149.600
30.03.2003	4.67	10.22	3	3.495	0.00	0.000	0.000	0.000
02.04.2003	14.89	9.33	7	3	60.00	180.000	0.000	-180.000
09.04.2003	24.22	7.11	8	3.219	202.20	650.866	154.035	-496.831
17.04.2003	31.33	21.11	15	2.9505	279.08	823.426	58.680	-764.746
02.05.2003	10.22	5.49	16	2.9106	311.63	907.016	427.275	-479.741
18.05.2003	15.71	5.46	8	2.859	295.28	844.206	212.400	-631.806
26.05.2003	21.17	17.21	11	3.225	191.20	616.620	459.088	-157.532
06.06.2003	3.96	5.06	11	2.904	138.22	401.376	236.669	-164.707
17.06.2003	9.02	1.00	14	2.871	127.05	364.761	106.260	-258.501
01.07.2003	10.02	10.02	12	2.823	147.28	415.771	93.240	-322.531
TOTAL			**285**		**5318.8**	**15850.321**	**2569.035**	**-13281.286**

Table C.18. Mass balance calculations for the NO_3^--N of the vertical flow gravel system of METU

Sampling Date	NO_3^--N OUTFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below OUTFLOW ($day*(mg.L^{-1})$)	Area below OUTFLOW $Mass_{out}$ (gram)	Area below INFLOW $Mass_{in}$ (gram)	Removed Mass (IN-OUT) $Mass_{acc}$(gram)
25.07.2002	1.58	4.59	12					
06.08.2002	6.16	5.66	6	2.8524	101.48	289.454	71.232	-218.222
12.08.2002	11.82	1.44	8	2.8803	87.89	253.136	16.716	-236.420
20.08.2002	10.38	4.36	8	2.8341	88.80	251.661	0.000	-251.661
28.08.2002	6.02	3.47	6	2.9238	65.60	191.801	15.120	-176.681
03.09.2002	2.55	1.89	8	2.8611	25.71	73.559	3.780	-69.779
11.09.2002	4.44	7.78	21	3.0258	43.08	130.351	24.120	-106.231
02.10.2002	12.22	2.55	9	2.9124	338.31	985.294	34.965	-950.329
11.10.2002	9.67	1.00	4	2.9286	98.51	288.482	102.195	-186.287
15.10.2002	10.67	0.45	7	2.9484	44.68	131.735	30.660	-101.075
22.10.2002	10.22	4.66	9	3.3195	73.12	242.705	32.655	-210.050
31.10.2002	5.56	3.22	11	2.9478	71.01	209.323	16.605	-192.718
11.11.2002	8.78	7.34	17	2.9352	114.29	335.464	150.150	-185.314
28.11.2002	1.44	7.23	15	3.126	86.87	271.556	107.610	-163.946
13.12.2002	8.67	3.67	35	2.9931	184.28	551.554	52.425	-499.129
17.01.2003	5.00	1.78	16	3	239.23	717.675	133.875	-583.800
02.02.2003	6.78	6.78		3	122.72	368.160	29.280	-338.880
30.03.2003	0.00	4.00	3	3.495	0.00	0.000	0.000	0.000
02.04.2003	4.00	28.44	7	3	18.00	54.000	0.000	-54.000
09.04.2003	32.44	16.44	8	3.219	326.62	1051.390	154.035	-897.355
17.04.2003	16.00	5.33	15	2.9505	193.76	571.689	58.680	-513.009
02.05.2003	10.67	2.81	16	2.9106	200.03	582.193	427.275	-154.918
18.05.2003	7.86	7.98	8	2.859	148.24	423.818	212.400	-211.418
26.05.2003	15.84	8.10	11	3.225	158.64	511.614	459.088	-52.526
06.06.2003	7.74	3.75	11	2.904	129.69	376.620	236.669	-139.950
17.06.2003	3.99	1.80	14	2.871	64.52	185.223	106.260	-78.963
01.07.2003	5.79	5.79	12	2.823	93.66	264.402	93.240	-171.162
TOTAL			**285**		**3118.70**	**9312.857**	**2569.035**	**-6743.822**

Table C.19. Mass balance calculations for the TN of the vertical flow wetland systems constructed at METU

Sampling Date	TN INFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below INFLOW ($day*(mg.L^{-1})$)	Area below INFLOW (gram)
25.07.2002		23.15	12			
06.08.2002	23.15	22.30	6	3.00	416.70	1250.100
12.08.2002	45.45	24.61	8	3.00	339.60	1018.800
20.08.2002	20.84	1.33	8	3.00	265.16	795.480
28.08.2002	22.17	10.60	6	3.00	182.68	548.040
03.09.2002	32.77	2.55	8	3.00	228.42	685.260
11.09.2002	30.22	15.35	21	3.00	251.96	755.880
02.10.2002	45.57	6.82	9	3.00	1118.15	3354.435
11.10.2002	38.75	2.19	4	3.00	379.44	1138.320
15.10.2002	40.94	13.65	7	3.00	168.14	504.420
22.10.2002	27.29	7.43	9	3.00	238.81	716.415
31.10.2002	19.86	13.04	11	3.00	212.18	636.525
11.11.2002	32.90	5.89	17	3.00	433.62	1300.860
28.11.2002	27.01	0.13	15	3.00	509.24	1527.705
13.12.2002	26.88	22.67	35	3.00	404.18	1212.525
17.01.2003	49.55	20.03	16	3.00	2130.98	6392.925
02.02.2003	29.52	2.29		3.00	632.56	1897.680
30.03.2003	31.81	2.15	3	3.00	0.00	0.000
02.04.2003	33.96	25.59	7	3.00	105.11	315.315
09.04.2003	59.55	1.27	8	3.00	506.42	1519.245
17.04.2003	58.28	26.71	15	3.00	471.32	1413.960
02.05.2003	31.57	6.05	16	3.00	673.88	2021.625
18.05.2003	37.62	6.88	8	3.00	650.32	1950.960
26.05.2003	30.74	12.08	11	3.00	273.44	820.320
06.06.2003	42.82	5.34	11	3.00	537.46	1612.380
17.06.2003	37.48	10.72	14	3.00	441.65	1324.950
01.07.2003	26.76	26.76	12	3.00	449.68	1349.040
TOTAL			**285**			**36063.165**

Table C.20. Mass balance calculations for the TN of the vertical flow slag system of METU

Sampling Date	TN OUTFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below OUTFLOW ($day*(mg.L^{-1})$)	Area below OUTFLOW $Mass_{out}$ (gram)	Area below INFLOW $Mass_{in}$ (gram)	Removed Mass (IN-OUT) $Mass_{ace}$(gram)
25.07.2002		10.77	12					
06.08.2002	10.77	5.06	6	2.8524	193.86	552.966	1250.100	697.134
12.08.2002	15.83	2.86	8	2.8803	110.16	317.294	1018.800	701.506
20.08.2002	12.97	0.50	8	2.8341	115.20	326.488	795.480	468.992
28.08.2002	13.47	2.27	6	2.9238	109.76	320.916	548.040	227.124
03.09.2002	11.20	7.15	8	2.8611	74.01	211.750	685.260	473.510
11.09.2002	18.35	8.92	21	3.0258	175.40	530.725	755.880	225.155
02.10.2002	27.27	1.94	9	2.9124	666.33	1940.619	3354.435	1413.816
11.10.2002	25.33	11.45	4	2.9286	236.70	693.200	1138.320	445.120
15.10.2002	36.78	13.03	7	2.9484	170.02	501.287	504.420	3.133
22.10.2002	23.75	13.02	9	3.3195	211.86	703.253	716.415	13.162
31.10.2002	10.73	15.02	11	2.9478	155.16	457.381	636.525	179.144
11.11.2002	25.75	2.44	17	2.9352	365.86	1073.872	1300.860	226.988
28.11.2002	23.31	12.39	15	3.126	417.01	1303.573	1527.705	224.132
13.12.2002	10.92	3.29	35	2.9931	256.73	768.404	1212.525	444.121
17.01.2003	14.21	11.17	16	3	554.93	1664.775	6392.925	4728.150
02.02.2003	25.38	14.59		3	495.44	1486.320	1897.680	411.360
30.03.2003	10.79	10.46	3	3.495	0.00	0.000	0.000	0.000
02.04.2003	21.25	11.92	7	3	79.44	238.320	315.315	76.995
09.04.2003	33.17	0.40	8	3.219	273.91	881.716	1519.245	637.529
17.04.2003	33.57	22.88	15	2.9505	270.16	797.107	1413.960	616.853
02.05.2003	10.69	6.32	16	2.9106	331.95	966.174	2021.625	1055.451
18.05.2003	17.01	4.16	8	2.859	322.72	922.656	1950.960	1028.304
26.05.2003	21.17	13.21	11	3.225	186.00	599.850	820.320	220.470
06.06.2003	7.96	1.53	11	2.904	160.22	465.264	1612.380	1147.116
17.06.2003	9.49	1.48	14	2.871	112.81	323.863	1324.950	1001.087
01.07.2003	10.97	10.97	12	2.823	163.94	462.803	1349.040	886.237
TOTAL			**285**		**6209.56**	**18510.577**	**36063.165**	**17552.588**

Table C.21. Mass balance calculations for the TN of the vertical flow gravel system of METU

Sampling Date	TN OUTFLOW ($mg.L^{-1}$)	$\|(C_2-C_1)\|$ ($mg.L^{-1}$)	Delta Time (day)	Discharge OUTFLOW ($m^3.d^{-1}$)	Area below OUTFLOW ($day*(mg.L^{-1})$)	Area below OUTFLOW $Mass_{out}$ (gram)	Area below INFLOW $Mass_{in}$ (gram)	Removed Mass (IN-OUT) $Mass_{acc}$(gram)
25.07.2002		12.96		2.8524				
06.08.2002	12.96	7.81	12	2.8803	233.28	665.408	1250.100	584.692
12.08.2002	20.77	6.33	6	2.8341	148.05	426.428	1018.800	592.372
20.08.2002	14.44	0.94	8	2.9238	140.84	399.155	795.480	396.325
28.08.2002	13.50	0.24	8	2.8611	111.76	326.764	548.040	221.276
03.09.2002	13.26	1.80	6	3.0258	80.28	229.689	685.260	455.571
11.09.2002	11.46	12.02	8	2.9124	98.88	299.191	755.880	456.689
02.10.2002	23.48	3.01	21	2.9286	619.29	1803.620	3354.435	1550.815
11.10.2002	20.47	5.80	9	2.9484	197.78	579.204	1138.320	559.116
15.10.2002	26.27	8.30	4	3.3195	116.68	344.019	504.420	160.401
22.10.2002	17.97	3.18	7	2.9478	154.84	513.991	716.415	202.424
31.10.2002	14.79	0.05	9	2.9352	147.42	434.565	636.525	201.960
11.11.2002	14.84	0.75	11	3.126	163.52	479.949	1300.860	820.911
28.11.2002	14.09	6.16	17	2.9931	245.91	768.699	1527.705	759.006
13.12.2002	20.25	7.34	15	3	349.95	1047.435	1212.525	165.090
17.01.2003	27.59	11.51	35	3	1094.10	3282.300	6392.925	3110.625
02.02.2003	16.08	2.04	16	3.495	349.36	1048.080	1897.680	849.600
30.03.2003	18.12	4.23		3	0.00	0.000	0.000	0.000
02.04.2003	22.35	31.28	3	3.219	73.40	220.185	315.315	95.130
09.04.2003	53.63	14.75	7	2.9505	484.89	1560.861	1519.245	-41.616
17.04.2003	38.88	19.85	8	2.9106	370.04	1091.803	1413.960	322.157
02.05.2003	19.03	2.71	15	2.859	434.33	1264.146	2021.625	757.479
18.05.2003	21.74	6.32	16	3.225	369.52	1056.458	1950.960	894.502
26.05.2003	28.06	1.72	8	2.904	249.76	805.476	820.320	14.844
06.06.2003	26.34	8.35	11	2.871	299.20	868.877	1612.380	743.503
17.06.2003	17.99	3.02	11	2.823	243.82	699.993	1324.950	624.957
01.07.2003	14.97	14.97	14	2.8524	230.72	651.323	1349.040	697.717
TOTAL			**285**		**7007.59**	**20867.619**	**36063.165**	**15195.546**

CURRICULUM VITAE

PERSONAL INFORMATION:

Surname, Name: KORKUSUZ, Elif Asuman
Nationality: Turkish (TC)
Date and Place of Birth: 11 November, 1973, Ankara
Phone: +90 312 235 06 21
Fax: +90 312 210 12 60
email: akelif@metu.edu.tr, asukork@yahoo.com

EDUCATION:

Degree	Institution	Year of Graduation
MS	METU Environmental Engineering	1999
BS	METU Environmental Engineering	1996
High School	Ankara Anadolu High School, Ankara	1991

WORK EXPERIENCE:

Year	Place	Enrollment
2004 - Present	The Turkish Foundation for Combating Soil Erosion, for Reforestration & Protection of Natural Habitats (TEMA), Ankara	Technical Counselor
2003-2004	Chamber of Environmental Engineers (ÇMO), Ankara	Technical Counselor
1998-2002	METU Graduate School of Natural and Applied Sciences	Research Assistant
1996-1997	PARMAS Industrial Researchers and Engineering Inc., Ankara	Environmental Engineer
1995 July	ÇEKOTEK Engineering Inc., Antalya	Intern Eng. Student
1994 July	Seka-Dalaman Paper and Pulp Industry, Muğla	Intern Eng. Student

FOREIGN LANGUAGES:

Advanced English, Advanced German.

CERTIFICATES:

October 2002-June 2003, "*Programme for Improvement of Young Entrepreneur*", METU KOSGEB Technology Development Center (TEKMER), Ankara.

PUBLICATIONS:

1) Korkusuz, E.A., Beklioğlu, M., Demirer, G.N., 2004. "Comparison of the Treatment Performances of Blast Furnace Slag-based and Gravel-based Vertical Flow Wetlands operated identically for Domestic Wastewater Treatment in Turkey", ***Ecological Engineering***, (accepted for publication).

2) Korkusuz, E.A., Beklioğlu, M., Demirer, G.N., 2004. "Treatment Efficiencies of the Vertical Flow Pilot-Scale Constructed Wetlands for Domestic Wastewater Treatment", ***Turkish Journal of Engineering and Environmental Sciences***, TUBITAK.

3) Korkusuz, E.A., Demirer G.N., Beklioğlu M., 2004. "Comparison of Gravel and Slag-based Vertical Flow Reed Bed Performance in Turkey". IWA 9th International Conference on Wetland Systems for Water Pollution Control, Avignon, France.

5) Korkusuz, E.A., Demirer G.N., Beklioğlu M., 2002. "First Pilot-Scale Constructed Wetland Implemented in Turkey for Domestic Wastewater Treatment.". IWA 8th International Conference on Wetland Systems for Water Pollution Control, Arusha, Tanzania, Africa.